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NANOTECHNOLOGIES

Principles, Applications, Implications and Hands-on Activities

A compendium for educators

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E-mail: RTD-PUBLICATIONS@ec.europa.eu

Contact: Matteo Bonazzi

European Commission
B-1049 Brussels

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NANOTECHNOLOGIES:

Principles, Applications, Implications and Hands-on Activities

A compendium for educators

Edited by the European Commission
Directorate-General for Research and Innovation
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Authors:
Luisa Filipponi and Duncan Sutherland

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EXECUTIVE SUMMARY

This publication has been developed within the context of the research developed by the European project NANOYOU, funded by the European Union's seventh framework programme (FP7, grant agreement n° 233433). It has been enriched by the authors with numerous and multifaceted inputs, reflections and insights on societal issues, also provided by the European project TimeforNano. (FP7, grant agreement n° 233481).

The outcomes from all these efforts have been integrated and edited into an overall and fully referenced book, showing how to address nanosciences and nanotechnologies concepts and applications.

It has been specifically developed to present in a single, balanced compendium, much of the relevant and valuable educational material that will help inform, motivate and inspire young people about nanotechnologies and their applications. Theory, application and experiments in nanosciences and nanotechnologies are organised in self-contained modules that offer increased flexibility throughout the development of the course. Moreover, a case study approach provides teachers with practical applications and examples to discuss in class.

The programme focuses on three application fields — information and communication technologies, energy and environment, and medicine — and also addresses the associated ethical, societal, legal and safety aspects to encourage further dialogue. Resources and training materials are available to educators, supported, also, by online tutor web portals where young people and educators can actively participate in virtual dialogues, experiments and games.

The lessons, discussions on applications and experiments presented in this book have been tested by teachers, professors and educators from about one thousand schools (50 pilot schools and 906 ancillary schools) in 20 European countries from 2010 to 2011, reaching about 40.000 students. This experience allowed for feedback and enriched this book with many comments and contributions, enabling to produce the final and inclusive version.

NOTE FROM THE EDITOR

The challenge of this book is to present in an understandable and attractive way nanosciences and nanotechnologies to the educational community.

The first version was written as part of the NANOYOU project with the aim of providing school teachers and educators of pupils aged 14-18 years with a comprehensive, yet easy to read and use, compendium on nanotechnologies that covers fundamental concepts of nanosciences and nanotechnologies, applications in three main application areas (medicine, environment and energy, information and communication technologies), and experiments that can be safely carried out by the teacher in school science laboratories. A key goal was to emphasize practical applications relevant to youngsters, and to include topics of ethics, legal and societal aspects associated with selected applications. The challenge was to provide school teachers and educators with a lasting tool they could use for their school teaching to integrate nanosciences and nanotechnologies concepts in their activities. As such, it should not be seen as a comprehensive scientific review (and for this reason some latest developments, in say graphene, are not included): it is rather a compendium that can be used by teachers, educators, or general readers interested in gaining some fundamental understand of nanotechnologies, their principles, applications but also implications, for individuals and society. After its first version, the book has been further reviewed, selecting and integrating diverse inputs, reflections and insights, also from other European projects: all these efforts have provided a very valuable and integrated view of the science, technology and applications of the nano disciplines, simultaneously offering innovative, inspiring and stimulating visions and understandings of the complexity and societal relevance they do represent.

In this light, the aim and domain of this book is to illustrate the essence of nanotechnology. To this end, the authors have succeeded in illustrating the new methods and materials, as well as explaining and discussing the theory, applications and scientific experimentations on nanosciences and nanotechnologies. In addition, the coverage of related ethics, legal, societal impact and safety complements the techno-scientific issues by raising awareness and stimulating debates on the benefits, challenges and risks for society that may be associated with the development of these and other emerging technologies.

We feel this work is particularly important: in fact, nanosciences and nanotechnologies are at the forefront of today's science and technology, engineering both matter and living systems at the scale of molecules and atoms. Their unique applications, products, markets and profitable revenue sources can bring new benefits and challenges to both society and economy, as they are becoming increasingly embedded in today's life. In fact, society at large needs to understand their pros and cons to make responsible choices about new products and processes: research, innovation and education constitute a living ecosystem, where education plays a key role.

Young Europeans might become increasingly attracted to boost their awareness and knowledge in these disciplines and their associated impacts: in fact, future scientists could need to become more conscious and equipped on the fundamentals, applications and prospects of nano disciplines to meet the new needs of research, economy and industry. This will entail the necessity to enrich the educational systems with innovative tools, methods and instruments to develop the new skills and understandings which are required to deliver responsible innovation.

In this light, developing and disseminating appropriate learning and teaching materials could contribute to shape a better informed ground for a more conscious, attentive and aware society, better equipped to make fully responsible choices on nanotechnologies' potential impacts, opportunities, benefits, uncertainties and drawbacks.

Nanotechnology is one of the very frontiers of science today. As a matter of fact, nanotechnology could affect us all, beyond nanoparticles, critical length scales and nanotools: so, European citizens should be able to see how all this science and technology could influence their lives ahead of the actual developments. Beyond any spontaneous enthusiasm or mistrust any such highly innovative scientific development may bring, the fact that nanotechnology is becoming more and more deeply embedded in today's life should warrant a meaningful, conscientious communication based on a continuous participation and exchange between stakeholders and citizens.

So, developing appropriate communication, dialogue and education actions is crucial. Out of this dialogue, desirable patterns could emerge. If the associated opportunities, risks and uncertainties were properly addressed, all of us would surely be far closer to reaching consensus on which decisions and choices to undertake. Every audience, be it young people, teachers, business, organisations or, more broadly, the general public, could be increasingly called on to become involved at all levels, enabling to promote good governance through inclusive policy debate. In this light, education is likely to be one key to communicate all this to young people.

This compendium aims to address this challenge: as a matter of fact, it stems from the EC project NANOYOU, and it has been enriched by the authors with numerous and multifaceted inputs, reflections and insights on societal issues, also provided by the European project TimeforNano. So it represents a valuable tool to support the educational communities on nanosciences and nanotechnologies. In fact, it provides educators and teachers with a selection of relevant, accurate and up-to-date theoretical and experimental materials to help them inform, motivate and inspire young people about nanosciences, nanotechnologies and their applications. The lessons, discussions on applications and experiments of this compendium have been tested from 2010 to 2011 by hundreds of teachers, professors and educators on tens of thousands students from about one thousand schools in 20 countries in Europe and beyond (Austria, Belgium, Cyprus, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Italy, Latvia, Lithuania, Portugal, Romania, Slovakia, Sweden, Spain, Turkey, UK).

The educational materials are organised in three self-contained modules to offer increased flexibility throughout the development of the course, addressing the fundamental concepts, the main application areas and selected hands-on experiments. Moreover, a case study approach provides educators and teachers with practical applications and examples to discuss in class. Background materials, literature reviews, specific case studies and ideas are presented to show educators how to address nanosciences and nanotechnologies concepts. Topics dealing with the ethical, societal and safety aspects of nanotechnologies are also included to help educators encouraging class debates, referenced with other European projects and relevant webpages.

Overall, this experience has been very well received by about a thousand of participating educational communities, which actively tested and enriched this book, enabling us to produce the inclusive, far-reaching and wide-ranging version you have in your hands: we are confident that the broadest possible panoply of readers could appreciate this effort.

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In nova fert animus mutatas dicere formas corpora.

My mind inclines me to speak of forms changed into new bodies.

(Publius Ovidius Naso,
Metamorphoseon - Proemium)

MODULE 1:
FUNDAMENTALS

Module addressing principles
and fundamental concepts

CHAPTER 1:

INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGIES

This introductory chapter defines nanoscience, nanotechnologies and nanomaterials. It illustrates in general terms what is 'special' about the 'nano-world' and why this new area of science and technology is exciting and worth bringing into the classroom.

Definition of nanoscience and nanotechnologies

The most common working definition of nanoscience is:

'Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale' ([1]).

Bulk materials (the 'big' pieces of materials we see around us) possess continuous (macroscopic) physical properties. The same applies to micron-sized materials (e.g. a grain of sand). But when particles assume nanoscale dimensions, the principles of classic physics are no longer capable of describing their behaviour (movement, energy, etc.): at these dimensions, the principles of quantum mechanics principles. **The same material (e.g. gold) at the nanoscale can have properties (e.g. optical, mechanical and electrical) which are very different from (and even opposite to!) the properties the material has at the macroscale (bulk)**. Nanotechnologies are defined thus:

'Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.'

In the next sections of this chapter we will discuss these definitions and their meaning, starting with what is meant by the 'nanometre scale'.

The nanometre scale

The nanometre scale is conventionally defined as 1 to 100 nm. One nanometre is one billionth of a metre (10^{-9} m). The size range is normally set to a minimum of 1 nm to avoid single atoms or very small groups of atoms being designated as nano-objects (**Figure 1**). **Therefore, nanoscience and nanotechnologies deal with clusters of atoms of 1 nm in at least one dimension**.

([1]) *Nanoscience and nanotechnologies: opportunities and uncertainties*, report by The Royal Society and The Royal Academy of Engineering 2004 (http://www.nanotec.org.uk/).

The upper limit is normally 100 nm, but this is a ‘fluid’ limit: often objects with greater dimensions (even 200 nm) are defined as nanomaterials.A valid question a student might ask is ‘Why 100 nm and not 150 nm?’, or even ‘Why not 1 to 1 000 nm?’ The reason why the ‘1 to 100 nm range’ is approximate is that the **definition itself focuses on the effect that the dimension has on a certain material — for example the insurgence of a quantum phenomenon — rather than at what exact dimension this effect arises**. Nanoscience is not just the science of the small, but the **science in which materials with small dimension show new physical phenomena**, collectively called quantum effects, which are size-dependent and dramatically different from the properties of macroscale materials.

Nanoscience is the study of materials that exhibit remarkable properties, functionality and phenomena due to the influence of small dimensions.

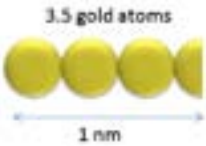

Figure 1: Three and a half gold atoms placed in a row equal 1 nm (assuming a covalent radius of 0.144 nm each)

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

What is a nanomaterial?

A nanomaterial is an object that has at least one dimension in the nanometre scale (approximately 1 to 100 nm). Nanomaterials are categorised according to their dimensions as shown in **Table 1**.

Table 1: Nanomaterials are categorised according to their dimensions

	Nanomaterial dimension	Example
	All three dimensions < 100 nm	Nanoparticles, quantum dots, nanoshells, nanorings, microcapsules
	Two dimensions < 100 nm	Nanotubes, fibres, nanowires
	One dimension < 100 nm	Thin films, layers and coatings

Nanomaterials can be of two types:

- ‘**non-intentionally-made nanomaterials**’, which refers to nano-sized particles or materials that belong naturally to the environment (e.g. proteins, viruses, nanoparticles produced during volcanic eruptions, etc.) or that are produced by human activity without intention (e.g. nanoparticles produced from diesel combustion);
- ‘**intentionally-made**’ nanomaterials, which refers to nanomaterials produced deliberately through a defined fabrication process.

The definition of nanotechnologies does not generally include ‘non-intentionally-made nanomaterials’ and is, therefore, limited to ‘intentionally-made nanomaterials’.

A very important concept to bring in to the classroom is ‘**the smallness of nano**’. Nanomaterials are larger than single atoms but smaller than bacteria and cells. It is useful to use a scale such as the one shown in **Figure 2** where students can visualise the relationship between bulk materials, for example a tennis ball, and nanomaterials.

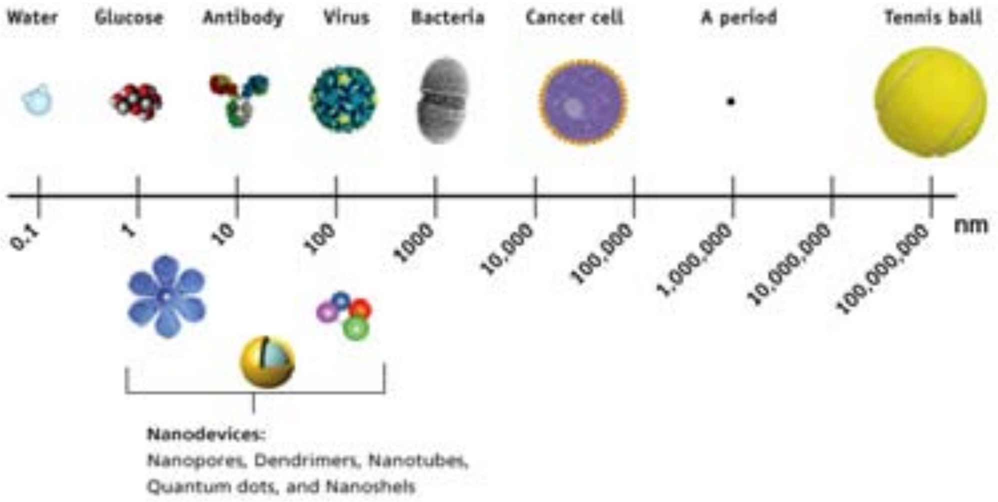

Figure 2: From macro-materials to atoms: nanomaterials and nanodevices that are of interest in nanotechnologies are at the lower end of the scale (1–100 nm)

Image: adapted from ‘A snapshot of nanotechnology’, National Cancer Institute

Some **good examples** to bring to the classroom:

- our **fingernails grow** at the rate of 1 nm per second;
- the **head of a pin** is about 1 000 000 nm in diameter;
- a **human hair** is about 80 000 nm in diameter;
- a **DNA molecule** is 1–2 nm wide;
- the **transistor** of a latest-generation Pentium Core Duo processor is 45 nm.

A simple activity for youngsters is to measure their height in nanometers! Details of the activity *How tall are you in nanometers?* can be found in the timefornano NanoKIT — Activity 1 (http://www.timefornano.eu/nanokit#ac01).

What makes 'nano' special

'Nano' means small, very small; But why is this special? There are various reasons why nanoscience and nanotechnologies are so promising in materials, engineering and related sciences. First, at the nanometre scale, the properties of matter, such as energy, change. This is a direct consequence of the small size of nanomaterials, physically explained as quantum effects. The consequence is that a material (e.g. a metal) when in a nano-sized form can assume properties which are very different from those when the same material is in a bulk form. For instance, bulk silver is non-toxic, whereas silver nanoparticles are capable of killing viruses upon contact. **Properties like electrical conductivity, colour, strength and weight change when the nanoscale level is reached: the same metal can become a semiconductor or an insulator at the nanoscale level.** The second exceptional property of nanomaterials is that they can be fabricated atom by atom by a process called **bottom-up**. The information for this fabrication process is embedded in the material building blocks so that these can self-assemble in the final product. These two fabrication methods are reviewed in **Module 1, Chapter 7: Fabrication methods**. Finally, nanomaterials have an **increased surface-to-volume ratio** compared to bulk materials. This has important consequences for all those processes that occur at the surface of a material, such as catalysis and detection. The properties that make nanomaterials 'special' are further discussed in **Module 1, Chapter 4: Fundamental 'nano-effects'**.

Nanoscience and nanotechnologies depend on the exceptional properties of matter at the nanoscale level. In this context, 'nano' doesn't only mean '1 000 times smaller than micro', and nanotechnologies are not just an extension of microtechnologies to a smaller scale. It is an entirely new paradigm that opens entirely new scientific opportunities.

The exceptional properties of matter at the nanoscale are the subject of **Module 1, Chapter 4: Fundamental 'nano-effects'**.

From nanoscience to nanotechnologies

Nanoscience is an 'interdisciplinary science', which means that it involves concepts of more than one discipline, such as chemistry, physics, etc. There are other disciplines that are inherently interdisciplinary, such as materials science (and engineering), which cover, at the same time, concepts of chemistry and physics. Nanoscience further expands the borders of material science by adding biology and biochemistry to the mix. Nanoscience is thus a 'horizontal-integrating interdisciplinary science that cuts across all vertical sciences and engineering disciplines' (2) (**Figure 3**).

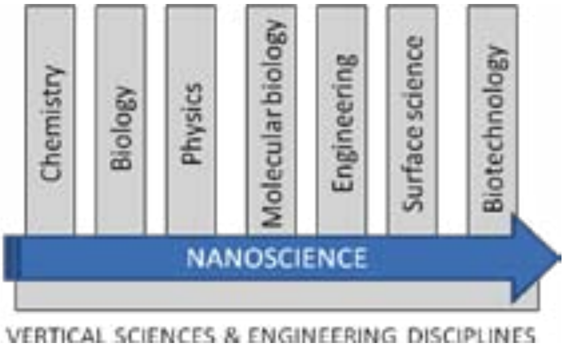

Figure 3: Nanoscience is a horizontal-integrating interdisciplinary science that cuts across all vertical sciences and engineering disciplines.

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

Nanoscience offers educators the possibility to bring intothe classroom the concept of 'interdisciplinary'. As will be discussed in the next chapters (**Chapters 2 and 3**), we have numerous examples of nanoscience in nature, as well as in historic artefacts. The educator, therefore, has an opportunity to truly show how nanoscience integrates not only scientific disciplines (chemistry, physics, biology, etc.) but also the humanities. Some practical ideas on how to exploit this opportunity are given throughout this book.

The application of nanoscience to 'practical' devices is called nanotechnologies. Nanotechnologies are based on the manipulation, control and integration of atoms and molecules to form materials, structures, components, devices and systems at the nanoscale. Nanotechnologies are the application of nanoscience especially to industrial and commercial objectives. All industrial sectors rely on materials and devices made of atoms and molecules thus, in principle, all materials can be improved with nanomaterials, and all industries can benefit from nanotechnologies. In reality, as with any new technology, the 'cost versus added benefit' relationship will determine the industrial sectors that will mostly benefit from nanotechnologies.

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(2) Hornyak, G. L. et al., Introduction to Nanoscience, CRC Press, 2008.

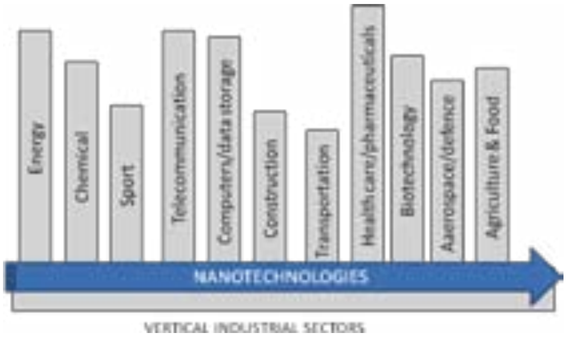

Figure 4: Nanotechnologies are horizontal-enabling convergent technologies which cross all vertical industrial sectors. The different heights of the industrial sectors in the graph are only indicative and are intended to emphasise the fact that the level of impact of nanotechnologies will be different in each industrial sector.

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

Thus, **nanotechnologies are horizontal-enabling convergent technologies** (**Figure 4**). They are 'horizontal' because they cut across numerous industrial sectors; they are 'enabling' since they provide the platform, the tools to realise certain products; and are 'convergent' because they bring together sectors of science that were previously separated.

One example is **DNA silicon chips**, which are an example of convergence between semiconductor science (inorganic chemistry) and biology, with applications in the medical industry.

Is it nanotechnology or nanotechnologies?

When the term was first used in 1959, it was used in the singular, 'nanotechnology'. In the last few years, the field has evolved steadily in terms of science and technology development. Scientists have also started to address the safety, ethical and societal impact of 'nanotechnology'. In doing so, it has become clear that this is not one technology, but that different nanotechnologies exist (which all share the common concept of using the properties of matter at the nanoscale). There has even been a call from a prominent scientist and expert in nanotechnologies to stop using the singular, and to use the plural, precisely to communicate the variety of materials and methods involved in nanotechnologies. Nowadays, the plural form is most used and it is the form that will be used in this Teachers Training Kit.

Bringing 'nano' into the classroom:
Why and how?

There are numerous reports that emphasise the need to 'revitalise' science teaching in school, particularly at the highschool (14+) level. It is also often recommended in those reports that inquiry-based science education (or problem-based learning) is encouraged, where teaching is conducted through an inductive (rather than deductive) method. This should be combined with numerous 'hands-on' activities to allow students to see science for themselves, and then learn and understand the theoretical explanation of what they see. Nanoscience and nanotechnologies offer such opportunities!

A cutting-edge science and technology

Nanoscience and nanotechnologies offer teachers a new instrument to **bring exciting science and technology into the classroom**. Nanotechnologies are now used in numerous devices with which young students are very familiar, such as computers, mobile phones and iPods. Nanoscience offers the possibility to improve numerous material properties and create new ones; in the future, we will have more and more products that incorporate some form of ‘nano’ — either a nanomaterial, or a nano-enabled technology. Bringing ‘nano’ into the classroom means bringing in the latest cutting-edge science and technology and talking about very exciting future scientific developments.

Hands-on nano!

One of the peculiarities of nanoscience is that numerous ‘nano-effects’ can be seen in our ‘macro world’. The best example is a gold colloid (gold nanoparticles of about 15 nm dispersed in water) which is red in colour. When some salt solution is added to the gold colloid, it turns blue! There are many ‘hands-on’ activities and demonstrations that can be used to show the properties of nanomaterials — effects that are visible! So even though the ‘nano-world’ is invisible, we can appreciate its effects in materials with which youngsters are very familiar, such as gold. In this Teachers Training Kit, these activities are described in an **Experiment Module** and throughout the main text as simple demonstrations that a teacher can perform in the classroom.

‘Nano’ in the context of ‘conventional’ scientific disciplines

One of the challenges a science teacher might face is how to insert nanoscience into conventional science curricula. Where does this ‘new’ science fit into the ‘conventional’ scientific disciplines — chemistry, physics or biology? The aim of this training kit is also to provide teachers with practical ideas on how to integrate nanoscience and nanotechnologies into their science curriculum.

Nanoscience is not new per se, it is a name we now give to a number of fields of research that share a common principle: the investigation of matter at a scale which is intermediate between ‘bulk’ matter, described by Newtonian physics, and atomic matter (i.e. atoms, electrons, etc.), described by quantum physics. Nanoscience works in this ‘size window’ (approximately 1 to 100 nm) where matter shows some remarkable properties. A number of scientific fieldswith very old origins are included in this window: for example, colloidal science (see also **Module 1, Chapter 3: History of nanotechnologies**. In a sense, **the study of atoms and molecules is the basis of most natural science disciplines**, such as chemistry, biochemistry and physics. Nanomaterials are not all new either: nanocrystals, nano-sized catalysts and magnetic nanoparticles have been studied for many years now, for a variety of applications. Some ‘nanotools’ are not that recent either: for instance, the Atomic Force Microscope (AFM) and the Scanning Tunnelling Microscope (STM) techniques were first introduced to the scientific community in the mid 1980s.

So the question is: **If it's not all new, why is it so special?** In recent years, researchers have been able to uncover the enormous potential of nanoscience and nanotechnologies thanks to a **new set of analytical and fabrication tools**. At the same time, in recent years, new nanomaterials have been intentionally fabricated or discovered, novel nanotools have been developed and old ones implemented, and novel properties of matter at the nanoscale level have been discovered.

All of this has allowed the **systematic investigation of nanomaterials and the realisation that the exceptional properties of matter at the nanoscale level can be used to build new materials, systems and devices with properties, capabilities and functions that could not be achieved if bulk materials were used**. This is where the novelty lies, and the reason for being excited about it! The exceptional properties of matter at the nanoscale have prompted scientists to 'reinvent' the way materials are engineered and produced, and are opening up exciting new opportunities in many different fields.

Nanoscience is thus a 'work-in-progress science'. A 'work' that finds its roots in disciplines, such as chemistry and physics, where much fundamental knowledge is well established, and that is progressing towards fields where new knowledge is currently being created and collected.

For these reasons, we prefer to describe **nanoscience as an evolution** of more traditional scientific disciplines. 'Nano' is not a revolution per se, but nanotechnologies might have some revolutionary implications for our society in terms of the applications or tools that they will enable.

Nanoscience in nature: a great starting point

Even though nanoscience is often perceived as a science of the future, it is actually the basis for all systems in our living and mineral world. We see hundreds of examples of nanoscience right in front of our eyes every day — from geckos that can walk upside down on a ceiling, apparently against gravity, to butterflies with iridescent colours, to fireflies that glow at night. **In nature, we encounter some outstanding solutions to complex problems in the form of fine nanostructures with which precise functions are associated**. In recent years, researchers have had access to new analytical tools to see and study those structures and related functions in depth. This has further stimulated research in the nanoscience area and has catalysed nanotechnologies. So, in a sense, natural nanoscience is the basis and inspiration for nanotechnologies.

Natural nanomaterials offer a great starting point to bring nanoscience into the classroom. Images from microscopes are a great resource, especially if used consequently in a 'zoom-in' fashion, starting from a macro object (e.g. a plant leaf) and showing how **zooming in** with subsequent magnifications reveals finer and finer structures. This becomes extremely effective if we start with familiar, natural objects such as plants (**Figure 5**) and animals. **Students will be fascinated to discover how many natural nanomaterials are around us**.

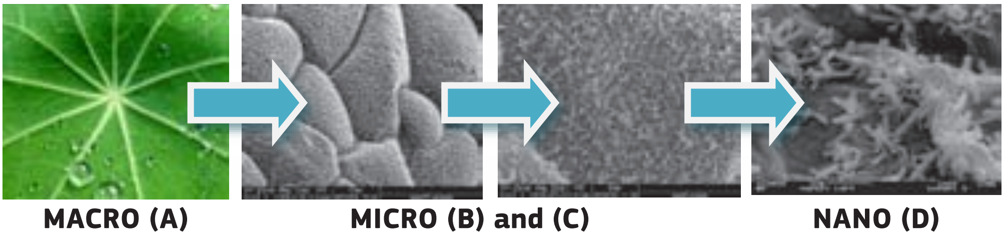

Figure 5: Close-up views at progressive magnification of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right)

Image: (A) A. Snyder, Exploratorium; (B, C) A. Marshall, Stanford University; (D) A. Otten and S. Herminghaus, Göttingen, Germany; all images are material of the NISE Network, reprinted under NISE Network Terms and Conditions

Teaching challenges

The definition of nanoscience naturally calls for the definition of a nanometre, which is a billionth of a metre. Although the are many examples that one can present of objects that have dimensions at this level, such as the width of DNA (2 nm), **mental visualisation of these objects is impossible**, and many studies have reported how young people, especially children, lack the mental capacity to actually imagine something this small because of lack of experience. Even for adults, *mental visualisation of objects with sub-micron dimensions is extremely difficult* (a result of the inherent resolution of our visual ability, which is 2 μm).

One concept that can easily be shown is the fact that even if we cannot see something, it doesn't mean is not there. A very simple way to show this is by performing progressive dilutions of a scented coloured liquid: at very high dilutions, although the colour can no longer be seen, we can still smell the scent. Details of this activity, *Dilution*, can be found in the *timefornano* NanoKIT — Activity 2 (http://www.timefornano.eu/nanokit#ac02).

However, as much as we can ask students to imagine something that is a thousand times smaller than their hair, we need to ask if they can really **understand the sense of the dimensionality** we are talking about. And, more importantly, if they can understand the difference between objects that are at the nanoscale level and objects that are even smaller, such as atoms. For some people, knowing that a rock is a million years old or a thousand million years old makes no difference: both dimensions are just ‘huge’ and are confused in a ‘time blur’. Similarly, the nanoscale and the atomic scale can be perceived as a ‘scale blur’, just too small to think of. Therefore, the challenge here is to introduce the nanoscale and the concept of nanoscience in a meaningful way, one that grasps the attention of the students but that also means something to them. In this sense, an enquiry-based approach (based on student questions) together with hands-on activities can help. For example, starting from a cube of a soft material and cutting it progressively until it can no longer be handled (which will not lead to a nanometre-sized cube, but will give a sense of smallness); or using **ratio examples**, such as how tall would a tower of single paper of sheets be, assuming each sheet is 1 nm. **Images from microscopes** are probably one of the best resources we have, especially if used consequently in a ‘zoom-in’ fashion, as described in the previous section. But, what is also important is showing the peculiarity of the nanometre scale, why objects at this level are ‘special’ and behave differently from their bulk counterparts. Examples should be given so that instead of trying to imagine a nanometre, students perceive what it means, for example, for a certain material to be 2 nm rather than 2 mm. Gold is a prime case, and the classic example is a gold wedding ring compared with multicoloured gold quantum dots (colloidal gold). Whatever the example or the methodology chosen to communicate, it is important to remember that young people will have great difficulty in conceiving nanoscale objects; so it is important not to ask them to visualise how small a nanometre is but rather that they appreciate what it means to be so small. NANOYOU has developed numerous tools (a memory game, puzzles and laboratory exercises) precisely to overcome those difficulties.

One aspect that is often overlooked (or assumed) when introducing nanoscience and nanotechnology is the actual nature of a ‘nano-object’ or ‘nanomaterial’. It is possible to mistakenly give the impression to the audience that these are free-standing objects or that these are aerosol-like particles that can float in a medium. Although some nanoparticles are airborne, most of the nanomaterials under research or used in commercial products are **integrated or attached to another substrate**. Furthermore, nanoscience does not just deal with nano-objects but also nanostructures within larger objects. For instance, a wire having the dimension of a hair (say, 2 μm) can be formed of molecules which are orderly arranged in nanowires.

Talking about the ‘bigger picture’

Nanotechnologies have progressed at a fast pace in the last few years, both in laboratories and in the commercialisation of numerous products. The promise of nanotechnologies is great in many applications and this has resulted in conspicuous investments both at research level and in industry. Other emerging technologies in the past were presented to the scientific community (and industry) as revolutionary, with enormous potential for commercialisation, most notably the genetic engineering of foodstuffs. Genetically modified organisms were expected to bring profit and advancement in the food and medical industries. Due to a number of issues (one of the most important being very poor communication between the scientific community and the popular media), GMOs were not received favourably by the consumer community, and the result has actually been the opposite. In many countries, these products have been banned or strongly regulated. Numerous ethical questions were also raised on ‘who’ would benefit from these products, and what implications they might have for people’s long-term health, as well as the life cycle of animal and plants. The GMO case is a clear example of an emerging technology that did not go through a careful **Ethical, Legal and Social Aspects (ELSA) analysis**. It is also a clear example of an innovative technology that suffered a backlash from consumers to the point where research was stopped and entire research centres were closed. Consumers had a power that scientists (and even the media) did not realise until it was too late.

With nanotechnologies, there is a general determination to ‘do it differently’ at all levels. **Probably for the first time in the history of scientific innovation, researchers, regulators, non-governmental organisations (NGOs), consumer organisations, trade unions and industry are all involved in setting guidelines, action plans, protocols, codes of conduct, regulations, etc., to make sure that nanotechnologies realise their potentials while protecting the safety of consumers and the environment (in terms of pollution and impact on its life cycles), and are ethically sound**. Clearly, this is a massive effort and the work is complex and has only started. Throughout this Teachers Training Kit, we will indicate areas of nanotechnology applications that are raising ELSA issues, and the actions that are currently being taken to address them.

For the teacher, bringing ELSA issues into the classroom is an opportunity to talk about science, technology and innovation in a more complex, ‘three-dimensional’ fashion. It gives educators an opportunity to stimulate discussions in class about which innovations students think are valuable (and which are not), who will benefit from these, at what cost, etc. **It is a chance to think and talk about the ‘bigger picture’ of science and innovation and think about its implications not just for the single individual, but for society**.

Talking about ELSA and safety in the classroom

Questions of ethics, social impact, safety, etc., are rarely part of a secondary science curriculum. Depending on age and school curricula, some students might have undertaken some philosophy courses, others probably not: therefore, ELSA issues are probably a new concept for most. The question is then **how to introduce those concepts** without overloading pupils with information, and how to respond adequately to questions raised in class. Otherwise, the result might be a feeling that ELSA and safety questions are just too big to be even analysed.

The aim of NANOYOU is also to provide teachers with resources to encourage class discussion about ELSA topics related to nanotechnologies. To focus the discussion, teachers have access to a number of tools (**Table 2**).

Table 2: Tools available in this training kit

NANOYOU Tool	Description
NANOYOU Nano role-playing game (http://www.nanoyou.eu)	This is a role-playing game with various dilemma scenarios. For each dilemma, several 'roles' have been created: each student (or group of students) is given one specific role and a class debate is held on the dilemma. The dilemmas relate to specific applications of nanotechnologies; these dilemmas are discussed in **Module 2** of this Teachers Training Kit within the various application areas (**NANOYOU dilemma**, blue boxes).
NANOYOU NT Virtual dilemmas (computerised animations) (http://www.nanoyou.eu)	These are computerised animations where students enter a virtual world and are confronted by various dilemmas relating to nanotechnology applications.
ELSA Topics in the **NANOYOU** Teachers Training Kit in Nanotechnologies	In this kit, teachers will find ELSA boxes throughout the chapters of **Module 2** (**ELSA Topic**, red boxes).
NANOYOU Video competition	Youngsters aged 18+ have produced some videos on the topic of Nanoelectronics and societal impact. All videos can be found in the **NANOYOU Project YouTube channel** (http://www.youtube.com/user/NANOYOUproject). Videos are cited throughout the document.
OTHER RESOURCES	**Description**
PlayDecide for TIME for Nano — Senior	This game is a variant of the game Decide (http://www.playdecide.eu). This version was made especially for the *timefornano* NanoKIT. Decide is a discussion game for young people in which the ethical and social issues arising from nanotechnologies are discussed. It works best when played by four to eight people and it takes about an hour and a half to play (http://www.timefornano.eu/nanokit).
PlayDecide for TIME for Nano — Junior	This is a **simplified version** for younger players. On the back of the cards, there are pictures that can be used to tell a story where nanotechnologies are involved. The players are free to choose as many cards as they wish and put them in a line so as to tell a story as in a comic book. They can tell their story to their friends or write it down (http://www.timefornano.eu/nanokit).

***timefornano* Videos**	A **video contest among youngsters** was also run by *timefornano*. Videos can be found in the *timefornano* **YouTube** channel (http://www.youtube.com/user/timefornano) or Vimeo channel (vimeo.com/channels/timefornano). Videos of the *timefornano* competition deal with some ELSA aspect of nanotechnologies and are useful to bring those topics into class … with fun and creativity!

In the next section, we provide an **overview of ELSA topics which relate to nanotechnologies** and an overview of the **safety of nanomaterials**. In each section, the **relevant NANOYOU tools** that have been developed to promote dialogue in class are highlighted.

When discussing ELSA and safety topics, it is useful to encourage students to reflect on **other innovative technologies** that they are familiar with and that have had important ELSA and safety implications. Some examples are provided in **Appendix A**.

Overview of ELSA issues in nanotechnologies

What follows is a short overview of crucial ELSA questions that are relevant to nanotechnologies. The list is not exhaustive and aims to give teachers an idea of the vastness and complexity of these issues. Most are open questions for which we don't provide answers —they are meant to spur debates in class with students.

Privacy

We live in a world where our movement is often controlled by hidden cameras. Miniaturisation has allowed these devices to be integrated into many objects, and nanotechnologies will most likely lead to even smaller devices allowing them to be integrated into textiles and other composite materials. Nowadays, consumer choices are tracked by Internet purchases and other indirect means, but 'smart' labels currently under development use a built-in tracking system called Radio Frequency Identification (RFID). These labels do already exist, but are fairly large, for instance, in e-passports (see **Module 2, Chapter 4: Information and Communication Technologies** for more information). The vision in the future is to miniaturise them to a point that every commercial object will contain a 'smart' label, and be able to communicate its position. This would ensure, for example, in the case of food packages, the product integrity, transport conditions, etc. RFID technology could be the ultimate solution to theft and fraud. Opponents warn that such devices could be used as 'spychips', even integrated into humans, and which could be used by governments, leading to an increased loss of civil liberties. If, for instance, food companies were to use this type of chip on the products we consume, they would have access to an incredible amount of private information.

Another vision of the ICT industry is the concept of **ambient intelligence**: computation and communication always available and ready to serve the user in an intelligent way (i.e. satisfying certain requirements). The vision is to have electronic devices that work as a gateway between the user and the environment. This will require **ubiquitous sensing and computing**: devices must be highly miniaturised, integrated in the environment, in soft materials like textiles, autonomous, robust, and require low power consumption. Nanotechnologies have the *conceptual* capacity to realise this vision. The time frame from 'vision' to reality could be decades but, if this was to come true, we would live in a world where we are even more interconnected, never 'alone', scrutinised. Clearly, this would add numerous benefits to our current life but would also threaten our personal privacy even more.

NANOYOU ROLE-PLAYING GAME and VIRTUAL DIALOGUE TOPIC	DILEMMA	MORE INFO ...
GPS Jacket	Should we buy a jacket with built-in GPS?	Module 2, Chapter 4: Information and Communication Technologies
Internet for everything	Do we want to live in a world where everything is connected, monitored, observed and open to scrutiny?	Module 2, Chapter 4: Information and Communication Technologies

More information, including videos, on the issue of Privacy implications of nanotechnology is available on the *timefornano* project page (http://www.timefornano.eu/privacy).

Justice

Who should benefit from nanotechnologies? Are nanotechnologies going to further increase the economic and social divide between 'north' and 'south' in the world? This is referred to as the '**nanodivide**'. Will medical diagnostic devices, or therapies, developed with nanotechnologies, be available for anyone, and distributed through the public health system, or will they be so expensive that only a limited sector of the population will have access to them?

NANOYOU PPT Teachers can find a PowerPoint presentation, **Benefits and risks for developed and developing countries**, which covers aspects of justice, the 'nanodivide', and the responsible development of nanotechnologies under the 'About' section of the NANOYOU website (http://www.nanoyou.eu).

The questions of justice related to nanotechnologies are not unique, but rather relevant to many technology advancements. The history of drug development, and the associate generation of patents behind commercialised drugs, is definitely filled with questions of justice. Nanotechnologies are enabling technologies with applications in many sectors, which promise to improve the quality of life of individuals in numerous ways. For this reason, the questions of justice are even more important and vast.

More information, including videos, on the issue of **Divide** (Justice) implications of nanotechnology is available on the *timefornano* project page (http://www.timefornano.eu/divide).

Early diagnostics

Diagnostic nanosensors allow the early detection of various diseases, such as cancer, at the very onset of the symptoms, before the disease is perceived by the patient (see **Module 2, Chapter 1: Medicine and healthcare**. Early detection means a higher chance of successfully treating and overcoming the disease. On the other hand, some worry that this will give doctors access to a large amount of personal information. The question is: Where is this information going to be stored, and who will have access to it? Furthermore, what if those devices are used not as a diagnostic tool but as a mean to assess a person's medical condition by other entities, such as insurance companies or job agencies? Clearly, these devices open questions of **privacy data use and possible misuse**.

Some early diagnostic devices already exist, such as genetic screening devices. Nanotechnology is directly involved in the development of more powerful and precise genetic screening devices, which, at present, are only available for a small range of common diseases and are fairly imprecise. In genetic screening, the doctor gathers information on the genetic predisposition a patient has to a certain disease. Scientists already know that the evolution of a disease does not only depend on genetic predisposition but also on the diet followed by the patient, the lifestyle and the environment in which they live. So the question is: Does having **a predisposition to a disease make a person 'ill'**? When does 'illness' start? And even more: Do we want to know this kind of information?

NANOYOU ROLE-PLAYING GAME and VIRTUAL DIALOGUE TOPIC	DILEMMA	MORE INFO …
Nanosensors in medical diagnostics	Should nanosensors be used to diagnose medical conditions in the early stages when there are still no definite restrictions in place to protect patients' privacy?	Module 2, Chapter 1: Medicine and healthcare

More information, including videos, on the issue of **Health** implications of nanotechnology is available on the *timefornano* project page (http://www.timefornano.eu/health).

More than 'human'?

Humans have always tried to improve their health status and lifestyle: nowadays, there are numerous drugs and medical technologies that can treat conditions that only few decades ago were deadly. But, medical advancements have not just been limited to the treatment of disease: the reconstruction of injured body parts is now possible though innovative biomaterials and implants, and tissue engineering is opening up the possibility to recreate organs from cultures of stem cells. Nanotechnologies are already playing an important part in modern medical diagnosis and treatment technologies, and are opening new venues for future developments.

Many technologies we have today allow doctors to restore a loss sustained as a consequence of an injury or a congenital condition (e.g. vision or hearing impairment). Some would argue that this is already ‘unnatural’, in the sense that it gives humans a capacity that they would not otherwise have. If you think about it, even glasses provide people who have poor vision a capacity they would not have naturally. Today, we also have access to treatments that alter our natural appearance through plastic surgery. In the future, researchers think it might be possible to create implants that allow humans to have additional skills, such as being able to see in the dark, or have implants that can improve human brain capacities. Neuroprosthetics are another example. Bioengineers and medical engineers say that their role should be to compensate for a body’s deficit (as result of an accident or a disease), not to replacing any existing function. It should not lead to the enhancement of human capabilities. Nevertheless, nanotechnologies are making these developments more feasible and affordable, obliging researchers in the field, as well as regulators, ethicists and sociologists to reflect on the social, medical and ethical consequences of these devices (see **Module 2, Chapter 1: Medicine and healthcare**).

Nanotechnologies are involved in those medical advancements, as are genetic engineering and biotechnology. So the question becomes: Are these developments leading to treatments that surpass being ‘human’?

NANOYOU ROLE-PLAYING GAME and VIRTUAL DIALOGUE TOPIC	DILEMMA	MORE INFO ...
Want to be superhuman?	Is it acceptable to use processes developed for medical treatment to enhance the human body?	Module 2, Chapter 1: Medicine and healthcare
Improving human brain capacities	Is it ethically acceptable to use technologies developed for specific medical treatments for other purposes such as improving human capabilities?	Module 2, Chapter 1: Medicine and healthcare

More information, including videos, on the issue of Enhancement implications of nanotechnology is available on the *timefornano* project page (http://www.timefornano.eu/enhancements).

Nanotechnologies in consumer products

In 2006, the Project on Emerging Nanotechnology (Woodrow Wilson International Center for Scholars) started compiling a nanotechnology consumer products inventory with the intention of collecting, archiving and sharing information on consumer products which producers claim to be nano. About 200 products were identified in March 2006: after little more than one year, this number had more than doubled. At the time of writing (August 2010), the inventory has more than 1 100 products listed.

Products in this inventory are categorised on their (explicit) application, specifically: Appliances; Automotive; Goods for Children; Electronics and Computers; Food and Beverages; Health and Fitness; Home and Garden. Although the project aims at identifying true nano products, the inventory curators clearly state 'we have made no attempt to verify manufacturers' claims about the use of nanotechnology in these products, nor have we conducted any independent testing of the products'. Therefore, the inventory contains products that claim to be enabled by nanotechnologies, but this is not checked nor demonstrated. For this reason, one should be cautious when looking at this list, and should also remember the following.

1. There are a large number of nanocharacteristics that could be included in a consumer product, such as a coating (thin coatings and layers in the nanometre range, either applied to the material or formed on use) or a nanomaterial (e.g. nanotubes, nanoparticles). Furthermore, nanotechnology could be used to produce the consumable without being responsible for its final characteristics: in this case, nanotechnology is only the enabling technology for production.
2. Technical, detailed information regarding these consumer products is often limited due to corporate secrecy.

To date, the majority of products listed belong to the 'Health and Fitness' group, among which cosmetics and textiles represent the majority of products.

Among the materials claimed to be responsible for the nanolabel, silver is the most common material mentioned, followed by carbon (which includes fullerenes), zinc (including zinc oxide), silica, titanium (including titanium dioxide) and gold.

Safety of nanomaterials

The safety of nanomaterials has become a crucial question in the last few years, particularly as the number of consumer products containing them has been rising every year.

The fact that nanomaterials, by definition, are materials that have a size comparable to biomolecules (e.g. proteins, DNA) raises the question of their safety. Could nanomaterials interact with biomolecules in an adverse manner, triggering a toxic effect? Could nanomaterials pass protection barriers in cells? In nanomedicine, as we will see in **Module 2, Chapter 1: Medicine and healthcare**, nanomaterials are used precisely to target infected cells and deliver drug agents locally. They are designed to pass though cell membranes, for instance. The question of toxicity extends also to ecotoxicity: What happens when materials containing nanoparticles reach landfills and degrade? Will nanomaterials be dispersed in the environment? In what dose? Could this cause harm to ecosystems?

It would be incorrect to say that we know nothing about the toxicological properties of nanomaterials. In the last years, a wealth of information has been collected and reported by authoritative research groups. What it is not clear is how relevant these results are for humans, since tests have so far been conducted in animal models or *in vitro*. Another problem is that different testing methods are used in different laboratories, making it difficult to compare results. Research so far has mainly focused on two groups of materials: carbon-based nanomaterials (carbon nanotubes and fullerenes) and metal or metal-oxide nanoparticles (e.g. ultrafine titanium dioxide, TiO_2). Several studies seem to indicate that some forms of carbon nanotubes show pulmonary toxicity and that this depends on the production method and the length and surface properties of the carbon tubes. Similarly, TiO_2 has been reported to cause inflammation in the lungs when inhaled in high doses.

Scientists recognise that before a full assessment of nanomaterial toxicity can proceed, some fundamental issues need to be resolved.

- The need for a **definition of nanomaterial** is crucial. It is not just a matter of nomenclature; it is, more importantly, a matter of defining what 'cut size' should be considered in nanotoxicology. It is a common belief among toxicologists that the conventional scale 1–100 nm now used to define a nanomaterial in nanotoxicology is not exhaustive, as nanomaterials often aggregate or agglomerate in larger particles with dimensions ranging from hundreds of nanometres to microns.
- The **reference materials** must be defined. Scientists have reported how the same nanomaterial (e.g. nano-sized TiO_2) purchased from two different manufacturers can give strikingly different toxicological results when tested. In order to define reference materials, they need to be fully **characterised**, which means deciding what standard **measuring methods** to use (or, possibly, developing new ones, if the existing ones prove inadequate).
- It is important to test **materials pure and free from contaminations**. For instance, carbon nanotubes are commonly contaminated with iron due to their manufacturing process. Scientists report that the removal of the iron from the carbon nanotube moiety dramatically reduces the oxidant generation and the cytotoxicity (i.e. toxicity to cells) of the material. The hypothesis is that it is the nano metal oxide — rather than the carbon nanotube — that generates the reactive oxygen species 8, responsible for the toxic effect.
- The **medium** used to disperse the nanomaterial during the toxicological testing is crucial. It has been reported how fullerenes are best dispersed in calf serum, whereas they cannot be dispersed at all in water. Lack of dispersion can lead to false results or confused toxicological results: therefore, it is essential that dispersion media are defined for each nanomaterial to be tested.

Overall, the scientific community agrees that progress has been made in the toxicological evaluation of nanomaterials. There is still much research to be done, but some key matrices have been identified — for example that surface area is a more important parameter than mass when dealing with engineered nanoparticles, and some targets and common behaviours have been also identified. The question is now how to make a risk assessment framework from these data, how to convert scattered numbers collected in numerous laboratories around the world into a risk management strategy for the safe handling of nanomaterials.

Before a **risk management for nanotechnologies** can be developed and implemented, a fundamental question needs to be answered: **What is the real risk of nanotechnologies?** Presently, nanotechnology is an umbrella term that covers a very large number of materials, applications and instrumentations. There is a need to classify nanotechnology applications and nanomaterials. This also applies to the risk debate: the starting point for this debate is to identify the real safety concerns of nanomaterials. Presently, while there is, at times, hype in describing the benefits of nanotechnology, there is also hype in the associated risk debate. The starting point should be to identify **the safety concerns that are peculiar to nanotechnologies and to identify the key safety needs in specific areas of applications**. This will allow us to move from a rather uncoordinated and scattered toxicological assessment of nanomaterials to coordinated research and cooperation between different institutions. Precisely for this reason, it is now preferred to use the plural (nanotechnologies) rather than the singular (nanotechnology) in discussing these matters.

The second question to be answered is: **How are engineered nanoparticles (ENPs) different from non-intentionally-made nanoparticles** (also called nanopollutionor ultrafine particles)? Nanopollution is already a reality in many workplaces, from the welding industries to paint shops and bakeries.

Nanoparticles are produced by aeroplane and motor vehicle exhaust emissions, erosion of man-made materials (e.g. tyres), as well as by natural erosion and volcanic activity. **Humans are already exposed to nanopollution** in many ways and to different degrees. In the workplace, there are already some effective protective measures for workers exposed to ultrafine particles (filters, textiles, gloves). There is some evidence that established protective measures against ultrafine particles would also be effective against ENPs, should these be classified as hazardous. So the question becomes: **Are ENPs new hazardous materials and, if so, do these pose a risk for humans and/or the environment?** Is this risk different to 'nanopollution', and, if so, how and what should be done to deal with it? This is a complex question, one that will need time to be fully answered. Basically, at the moment, there is not enough data to provide an exhaustive answer and more research is needed (and being undertaken). But the risk associated with any material depends on the **exposure route and dose**, so research is also focusing on developing some measuring tools capable of detecting and distinguishing the presence of nanoparticles in the environment, regardless of their source.

Research into the potential toxic effects of nanomaterials is now a priority in most funding institutions and agencies, as it is clear that the success of nanotechnologies will also depend on how the issue of safety is handled.

As a priority, particular attention is given to silver, titanium dioxide and silica nanoparticles and carbon nanotubes, since it appears that these are the nanomaterials mostly used in consumer products. For more information on these nanomaterials, their properties and uses, see **Module 1, Chapter 5: Overview of nanomaterials**.

NANOYOU ROLE-PLAYING GAME and VIRTUAL DIALOGUE TOPIC	DILEMMA	MORE INFO ...
Antibacterial socks	Is it right to sell antibacterial socks containing silver nanoparticles while it is not known yet if these are entirely safe for the environment?	Module 2, Chapter 2: Environment
Nano toothbrush	Will the prolonged use of the toothbrush cause the degradation of its material and the accidental release of nanoparticles into saliva, and if this could have negative health effects?	Module 2, Chapter 2: Environment
Nanotechnology in food packaging	Should nanoparticles be used in our food or pharmaceutical packaging to detect freshness when we still do not know the full ramifications of the using them?	Module 2, Chapter 2: Environment

Boat coating	Nanoparticles in the coating could break down and pollute the ocean waters.	Module 2, Chapter 2: Environment
Pioneering cancer therapy with nanoparticles	Should gold-coated nanoparticles be used to treat patients' bodies before possible health risks have been explored?	Module 2, Chapter 1: Medicine and healthcare
Sunscreens with nanoparticles	Nanoparticles of TiO_2 contained in sunscreens could penetrate through the skin and produce detrimental health effects?	Module 1, Chapter 4: Fundamental 'nano-effects'; Module 1, Chapter 5: Overview of nanomaterials
Revolution for the light bulb	Quantum dots (QD) integrated in light-emitting devices (QD-LEDs) could be toxic or ecotoxic once these devices are disposed.	Module 2, Chapter 2: Energy
Nano-based solar cell	Nanomaterials inside photovoltaic cells could be toxic or ecotoxic once these devices are disposed of.	Module 2, Chapter 2: Energy

More information, including videos, on the issue of **Environmental** implications of nanotechnology is available on the *timefornano* project page (http://www.timefornano.eu/environment).

APPENDIX

In this Appendix, some ideas are provided for teachers to use to encourage students to reflect on **other innovative technologies** with whichthey are familiar and that have had important ELSA and safety implications.

- **Automotive transportation:** cars and motor vehicles have certainly improved our lives by giving us the opportunity to move freely, save time in travel, and explore new places. However, pollution produced by fuel combustion is, in part, responsible for the global environmental issues that we facing now. In addition, transportation has mostly benefited industrialised nations: poor countries lack the infrastructure (metalled roads) in most cases, and people cannot afford these commodities. In our society, we have become extremely dependent on cars, especially for short trips, when alternative transport solutions exist but are not so convenient and easy (public transport, bicycles). In recent years, there has been a general call from health advisors and environmental organisations to reconsider the way we use cars, and to favour other means of transportation that pollute less and render us physically more active.
- **Synthetic plastic:** about 100 years ago synthetic plastics like Nylon® where created. Plastics have revolutionised fabrication processes and enabled a massive production of affordable consumable goods. Nowadays, nearly all tools we use and have around us are made of plastic: laptops, iPods, packages, shoes, cars, etc. Being artificial, these polymers do not degrade naturally (as opposed to the biopolymers used in biodegradable plastics). The consequence is that they pose a tremendous challenge when it comes to disposal. Indeed, plastics are one of the most important pollution agents in the water and on land. The problem of plastic toxicity is widespread and also involves humans: research is now showing that numerous chemicals used in plastics are toxic to humans and possibly carcinogenic. Nevertheless, the world as we know it would not exist without plastics.
- The **Internet**: our society has been enormously changed with the advent of the Internet. This tool was invented to allow research centres around the world to communicate and exchange information easily. Today, the Internet is an unlimited source of information for everyone and, more recently, it has become a new form of social communication and networking. Imagine what would happen if the Internet were to shut down … This tool also plays an important role politically: bloggers in war areas are able to communicate what is *really* happening. Socially, the Internet is reshaping the way people communicate, some even say too much. Experts are concerned that youngsters use the Web as their primary communication channel, and that personal, face-to-face communication is progressively being lost. There are concerns that an abuse of this form of communication could deprive youngsters of personal encounters, considered essential for personality development.

CHAPTER 2:

NANOSCIENCE IN NATURE

This chapter introduces the concept of 'natural nanomaterials' and illustrates in some detail a few examples that can be introduced in the classroom.

What is a natural nanomaterial?

All materials can, in principle, be described at the nanoscale. In this text, by 'natural nanomaterials' we mean materials that belong to the natural world (animal and mineral), without human modification or processing, and that have **remarkable properties because of their inherent nanostructure**.

The chemical identity and properties of a substance depend upon its molecular structure. The nanostructure of a biological material is due to its supramolecular organisation — the arrangement of tens to hundreds of molecules into shapes and forms in the nanoscale range. The interaction of light, water and other materials with these nanostructures gives the natural materials some **remarkable properties which can be appreciated at the macroscale**.

Natural nanomaterials provide an **inspiring way of bringing nanoscience into the classroom**. Many natural materials, with which students will be very familiar, owe their properties to nanostructures in their composition. It can be really enlightening to discover that common, natural materials, such as feathers and spider silk, or materials that we use every day, such as paper and clay, have properties that depend not only on their chemistry but also on their nanostructure.

Overview of natural nanomaterials

We see hundreds of examples of nanoscience under our eyes daily, from geckos that walk upside down on a ceiling, apparently against gravity, to butterflies with iridescent colours, to fireflies that glow at night. In nature, we encounter some **outstanding solutions to complex problems in the form of fine nanostructures** with which precise functions are associated.

A short list of some natural nanomaterials follows: it is not exhaustive, but the interested teacher can find more information in the bibliography at the end of this module.

- **Nanoparticles from natural erosion and volcanic activity**: nanoparticles are part of our mineral world since they are naturally produced during erosion and volcanic explosions.
- **Minerals**, such as **clays**, are nanostructured: clays are a type of *layered silicate* characterised by a fine 2D crystal structure. Among clays, **mica** has been the most studied. Mica is made up of large sheets of silicate held together by relatively strong bonds. Smectic clays, such as montmorillonite, have relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as Li^+, Na^+, K^+ and Ca^{2+}. The presence of the cations is

necessary to compensate for the overall negative charge of the single layers. The layers are 20–200 nm in diameter laterally and form into aggregates called tactoids, which can be about 1 nm or more thick. Naturally occurring clays include montmorillonite (MMT) and hecrite. The fine nanostructure of clays determines their properties. When water is added, the clay swells, but the volume change is rather unusual — it is several times the original volume due to the 'opening' up of the layered structure by the water molecules that replace the cations. Clay swelling is a significant factor in soil stability and must be taken into account when building roads etc.

- **Natural colloids**, such as milk and blood (liquid colloids), fog (aerosol type), gelatin (gel type): in these materials, nanoparticles are dispersed in the medium (liquid or gas) but do not form a solution, rather a colloid. All these materials have the characteristic of scattering light and often their colour (as in the case of blood and milk) is due to the scattering of light by the nanoparticles that make them up.

EXPERIMENT A in the **NANOYOU Experiment Module** investigates natural colloids (milk and gelatin) and how their properties are connected to their nanostructure. A **gold colloid** is the subject of **EXPERIMENT C** in the **NANOYOU Experiment Module**.

- **Mineralised natural materials**, such as shells, corals and bones: many of these materials are formed by calcium carbonate crystals that self-assemble together with other natural materials, such as polymers, to form fascinating three-dimensional architectures. For instance, a **shell** is grown by a layer of cells that first lays down a coating of protein supported by a polysaccharide polymer like chitin. The proteins act like a nano-assembly mechanism to control the growth of carbon carbonate crystals. Around each crystal remains a honeycomb-like matrix of protein and chitin. This relatively 'flexible envelope' is fundamental for the mechanical properties of the shell and mitigates cracking. The size of each crystal is around 100 nm. The result is that the nacre of mollusc shells has extraordinary physical properties (strength, resistance to compression, etc.).
- **Materials like skin, claws, beaks, feathers, horns, hair**: these materials are made largely of very flexible proteins like keratin, elastin and collagen. Keratins have a large glycine and alanine content. This leads to β-sheets that can bond strongly one with another in an aligned fashion. Fibrous keratin molecules can twist around each other to form helical intermediate filaments. Similarly, collagen (not related to keratin in terms of primary structure) has a high percentage of glycine and forms flexible triple-helix structures. In addition to intra and inter-molecular bonds, keratins have numerous cysteins that can form stable disulphide bonds. The amount of cysteins in the protein determines the strength and rigidity of the material: keratin in human hair, for instance, contains about 14 % cysteins. Materials like nails, hooves and claws have a higher percentage of cysteins.
- **Paper and cotton**: both are made mainly of cellulose. The high strength, durability and absorbency of cotton are due to the nanoscale arrangement of the fibres.
- **Insect wings and opals**: the colours seen in opals and butterflies are directly related to their fine structure, which reveals packed nanostructures that act like a diffraction grid and induce iridescence. In the case of opals, this is due to packed silica spheres in the nanometre range, uniform in size and arranged in layers. Butterflies often owe the colour of their wings to pigments that absorb specific colours; in some species, such as the beautiful *Morpho rhetenor*, colours are due to the presence in the wings of nanostructures which are photonic crystals. This example is discussed in more detail in the next section of this chapter.

- **Spider silk**: silk is the material with the greatest known strength — about five times that of steel of the same weight. The extraordinary properties of spider silk are due to the proteins that make up the silk (mainly fibroin) and its supramolecular organisation which is at the nanoscale level.
- **Lotus leaves and similar** (nasturtium): the nanostructure of the leaves of these plants is responsible for their extraordinary surface properties and their ability to 'self-clean'. This example is discussed in more detail in the next section of this chapter.
- **Geckos' feet**: the structure of the gecko foot is an amazing example of the relationship between function and nanostructure. The ability of geckos to walk upside down, against gravity, even on wet or dirty surfaces, is intimately connected to the nanostructure of their feet. This example is also discussed in more detail in the next section of this chapter.

Learning from nature

Natural nanomaterials are of interest not only to understand (and appreciate) the amazing properties of biological materials but also to gather **inspiration for the design and engineering of new materials with advanced properties**.

The physical origins of the remarkable properties of many biological materials are due to complex, often **hierarchical structures** (3). They are characterised by a surprising level of adaptability and multifunctionality. These materials can provide a **model for designing radically improved artificial materials** for many applications, such as solar cells, fuel cells, textiles, drug delivery systems, etc.

What is even more inspiring is the notion that in nature, some very simple laws apply.

1. Nature runs on sunlight and uses only the energy it needs. Natural nanomaterials are extremely energy efficient!
2. Nature fits form to function and recycles everything — waste products are minimised in nature!
3. Nature rewards cooperation although it encourages diversity and local expertise.

The field of materials engineering devoted to trying to fabricate artificial materials that mimic natural ones is conventionally called **biomimetics**. Nanoscience is a fundamental component of biomimetics.

READ MORE

Natural nanomaterials are inspirational for the engineering of new materials with advanced functionalities. In **Module 1, Chapter 5: Overview of nanomaterials**, some examples are given. A short list of biomimetic materials inspired by natural ones follows.

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(3) Hierarchical structures are those structures that are synthesised at different levels of complexity by alternating growth conditions.

Biomimetic material …	… inspired from
Polymers	Substructure of nacre
Structural elements	Wood, ligaments and bone
Electrical conduction	Eels and nervous system
Photoemission	Deep-sea fish and glow-worms
Photonic crystals	Butterfly and bird wings
Hydrophobic surfaces	Lotus leaves and human skin
Adhesives	Geckos' feet
High tensile strength fibre	Spider silk
Artificial intelligence and computing	Human brain

Detailed description of some natural nanomaterials

Now, a few fascinating natural nanostructures are described in some detail and how their natural nanostructure is responsible for their properties (adhesiveness, strength, flexibility, colour, etc.) is explained.

Bone

Thinking about it, the unique properties of bone are a list of apparent contradictions: rigid, but flexible; lightweight, but solid enough to support tissue growth; mechanically strong, but porous. Bone can withstand weight without breaking. Its compressive strength is about twice its tensional strength. These outstanding properties are the result of bone's complex hierarchical structure and composition: bone material is made of a composite of collagen (mainly Type I collagen) fibrils reinforced with calcium phosphate particles (hydroxyapatite) ([4]).

From a mechanical point of view, many bones such as the femoral head can be described as a 'sandwich' structure with a dense external shell (cortical bone) and a spongy interior (cancellous bone). In cancellous bone, only about 20 % of the volume is filled with bone material, the rest is made of bone marrow. Cortical bone is made of **fibrils regularly arranged** (**Figure 1**).

The fibrils consist of an **assembly of collagen molecules 300 nm long and 1.5 nm thick** which are deposited by the osteoblasts (bone-forming cells) into the extracellular space and self-assembled into fibrils. Adjacent fibrils molecules are staggered along the axial direction by about D = 67 nm (**Figure 2**), generating a characteristic pattern of gap zones of length 35 nm and overlap zones of length 32 nm within the fibril.

([4]) Hydroxiapatite: $Ca_5(PO_4)_3OH$.

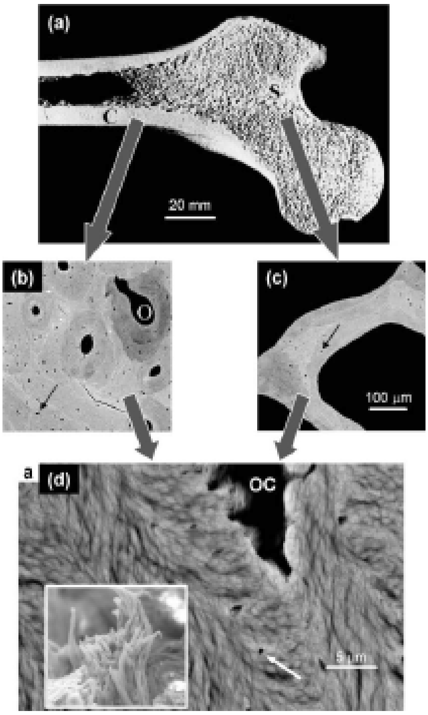

Figure 1: (a) Section through a femoral head showing the shell of cortical bone (C) and the spongious bone (S) inside; (b) enlargement of the cortical bone region revealing several osteons (O) corresponding to blood vessels surrounded by concentric layers of bone material; (c) picture of a single trabeculum from the spongious bone region; (d) further enlargement showing the lamellar and fibrillar material texture around an osteocyte lacuna (OC) as visible in scanning electron microscopy (white arrow). The lamellae are formed by bundles of mineralised collagen fibrils (insert).

Image: Fratzl et al., *Journal of Material Chemistry*, 2004, 14:2115–23, reprinted with the permission of the Royal Society of Chemistry

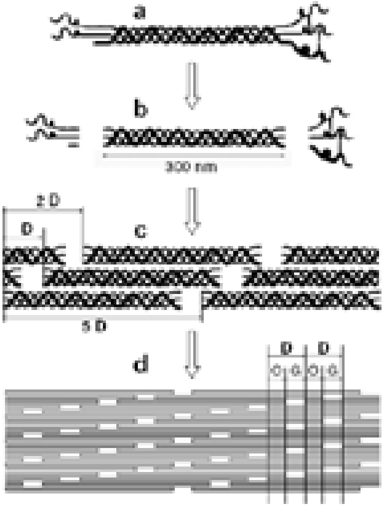

Figure 2: Self-assembly of collagen fibrils: (a) procollagen molecule after excretion from the cell; (b) collagen after cleavage of the propeptide ends; (c) parallel self-assembly with a staggering period of D; (d) periodic density variation along the fibril axis, resulting from the staggering. In the stripes labelled O, there is an overlap of all molecules. In the stripes labelled G (gap region), one molecule in five is missing and the density is accordingly less.

Image: Fratzl et al., *Progress in Materials Science*, 2007, 52(8):1263–334, reprinted with the permission of Elsevier

Collagen fibrils are filled and coated by tiny **mineral crystals of hydroxiapatite**. These are mainly flat plates mostly arranged parallel to each other and parallel to the fibril main axis. Crystals occur at regular intervals along the fibrils, with an approximate repeat distance of 67 nm. In mammalian species, bone mineral crystals have a thickness of 2–4 nm (**Figure 3**).

Figure 3: Sketch of the arrangement of mineral particles in collagen fibrils. Mineral particles are typically very thin objects (2–4 nm) and aligned with the collagen matrix.

Image: Fratzl et al., *Journal of Material Chemistry*, 2004, 14:2115–23, reprinted with the permission of the Royal Society of Chemistry

To summarise, bone is formed from a soft organic matrix (collagen) reinforced by an anisotropic stiff inorganic component (crystals of hydroxiapatite). These two components are assembled in a hierarchic structure which is organised at the nanoscale level. It is this nanoscale hierarchic organisation that allows bone to tolerate small microfractures that arise from normal activity and dissipate deformation energy without propagation of the crack. Hydroxiapatite is a rigid material which is not capable of dissipating much energy; therefore, collagen is believed to have a major role in the structural properties of bone (elastic and plastic deformation). **Figure 4** illustrates the **role of collagen** during bone deformation. Older bone, which is more mineralised and thus has a larger percentage of hydroxiapatite, is stiffer and breaks more easily.

READ MORE

Bone is a 'perfect' nanocomposite and is used as a model for **polymer composites reinforced with nanomaterials** such as carbon nanotubes. Polymer composites and their applications are covered in **Module 1, Chapter 5: Overview of nanomaterials**.

Lotus leaf

The lotus plant (*Nelumbo nucifera*) is a native Asian plant which has the distinct property of being able to maintain its leaves particularly clean even if its natural habitat is muddy. For this reason, this plant is considered sacred in some cultures and a sign of purity. The leaves of the lotus plant have the outstanding characteristic of totally repelling water because they are superhydrophobic (**Figure 5**). The consequence is that water droplets roll off the leaf surface and, in doing so, drag dirt away from it, as shown in **Figure 7**. This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt. The same effect is found in other leaves such as those of nasturtium (*Tropaeolum*) and some *Cannas*, and in some animals such as the water strider.

How is this 'Nano'?

The surface properties of the lotus leaf were first investigated by Wilhelm Barthlott. In 1997, he published an important paper where he described for the first time the 'Lotus effect' (a term that he later copyrighted) responsible for the self-cleaning properties of the lotus leaves. In his original paper, Barthlott showed that the self-cleaning properties of the lotus plant are produced by a **combination of**

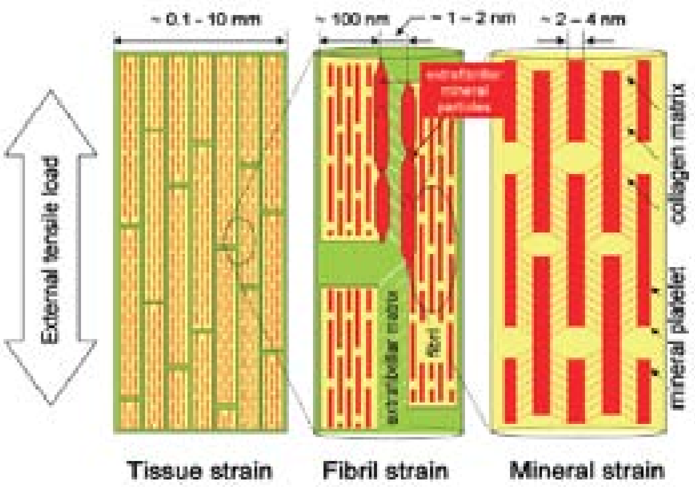

Figure 4: Schematic model for bone deformation in response to external tensile load at three levels in the structural hierarchy: at the tissue level (left), fibril array level (centre), and mineralised collagen fibrils (right). The stiff mineralised fibrils deform in tension and transfer the stress between adjacent fibrils by shearing in the thin layers of extra-fibrillar matrix (the white dotted lines in the centre plot show the direction of shear in the extra-fibrillar matrix). The fibrils are covered with extra-fibrillar mineral particles, shown only over a selected part of the fibrils (red hexagons) so as not to obscure the internal structure of the mineralised fibril. With each mineralised fibril, the stiff mineral platelets deform in tension and transfer the stress between adjacent platelets through shear in the interparticle collagen matrix (red dashed lines indicate shearing qualitatively and do not imply homogeneous deformation).

Image: Fratzl et al., *Progress in Materials Science*, 2007, 52(8), 1263–334, reprinted with the permission of Elsevier

Figure 5: Left to right: Lotus leaf; Tropaeolum (nasturtium) leaves; water droplet resting on the surface of a nasturtium leaf

Image: (left to right) iNANO, Aarhus University, Creative Commons ShareAlike 3.0; Wiki Commons, Creative Commons ShareAlike 3.0; A. Otten and S. Herminghaus, Göttingen, Germany, NISE Network, reprinted under NISE Network Terms and Conditions

the microstructure of the leaves and the epidermal cells on their rough surfaces, which are covered with wax crystals (**Figure 6**). These crystals provide a **water-repellent layer**, which is enhanced by the roughness of the surface, making it a superhydrophobic surface, with a contact angle of about 150°. The consequence is that water droplets on the surface tend to minimise the contact between the surface and the drop, forming a nearlyspherical droplet. **Figure 6** shows the progressive magnification of a nasturtium leaf. In the last image on the right, **nanocrystals a few tens of nanometres** in size are shown.

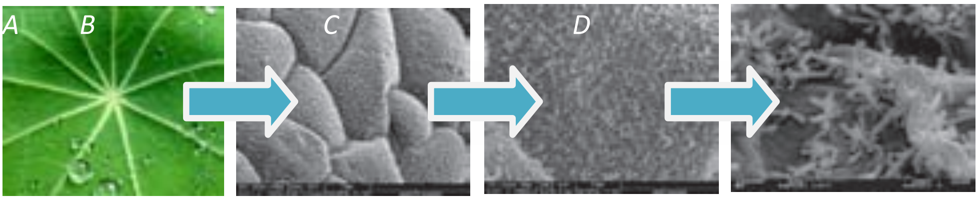

Figure 6: Close-up views at progressive magnifications of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right)

Image: (A) A. Snyder, Exploratorium; (B, C) A. Marshall, Stanford University; (D) A. Otten and S. Herminghaus, Göttingen, Germany; all images are material of the NISE Network, reprinted under NISE Network Terms and Conditions

The consequence is that water droplets roll off the leaf surface and, in doing so, drag dirt away from it, as shown in **Figure 7**. This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt.

Contaminants on the surface (generally larger than the cellular structure of the leaves) rest on the tips of the rough surface and when a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf (**Figure 8**).

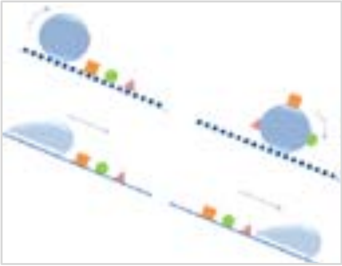

Figure 7: Diagram summarising the connection between roughening and self-cleaning: while on smooth surfaces, the particles are mainly redistributed by water (bottom); on rough surfaces, they adhere to the droplet surfaces and are removed from the leaves when the droplets roll off (right).

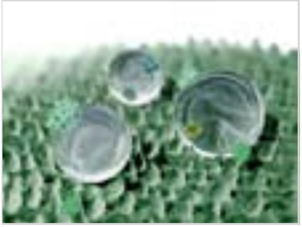

Figure 8: Graphical representation of water droplets on a lotus leaf

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The Lotus effect® has been an **inspiration for several innovative materials**, mainly involving self-cleaning properties to reduce the amount of cleaning needed, with an obvious environmental benefit. This also includes textiles and is discussed in **Module 2, Chapter 2: Environment**. The Lotus effect® is also used in new solarcell covers to increase their efficiency: this is explored in **Module 2, Chapter 3: Energy**.

EXPERIMENT

EXPERIMENT D in the **NANOYOU Experiment Module** investigates the Lotus effect® in real plants and in innovative materials such as Nano-Tex® fabric and nanoporous silicon.

A simple hands-on activity to show the superhydrophobic effect involves magic sand — a product that creates a superhydrophobic assembly in water. Details of the **Magic Sand** activity can be found in the *timefornano* NanoKIT — Activity 6 (http://www.timefornano.eu/nanokit#ac07).

Gecko

A gecko can cling to virtually any surface at any orientation; walk on smooth or rough surfaces, even upside down on a glass surface; and walk on a dirty or wet surface maintaining full contact and adhesion to it. As it walks, a gecko **does not secrete any sticky substance**, and its feet do not have any suction-like features (even at microscopic sizes). The reason for the gecko's amazing properties lies in the nanostructures that are present on its feet.

The gecko foot has a series of small ridges called scansors which contain numerous projections called setae. Each seta is about 100 μm long and has a diameter of about 5 μm. There are about half a million of these setae on the foot of a gecko. Each seta is further subdivided into about a thousand 200 nm-wide projections called spatulae (**Figure 9**). **As a result, the total surface area of the gecko's feet is enormous**. The gecko spatulae are very flexible, so they essentially mould themselves into the molecular structure of any surface. The result is a strong adhesion which is entirely due to van der Waals forces. A single seta can resist a force of 200 μN, or approximately 10 atmospheres of stress. **The gecko case is thus a very good example of the effect of large surface area on small forces.**

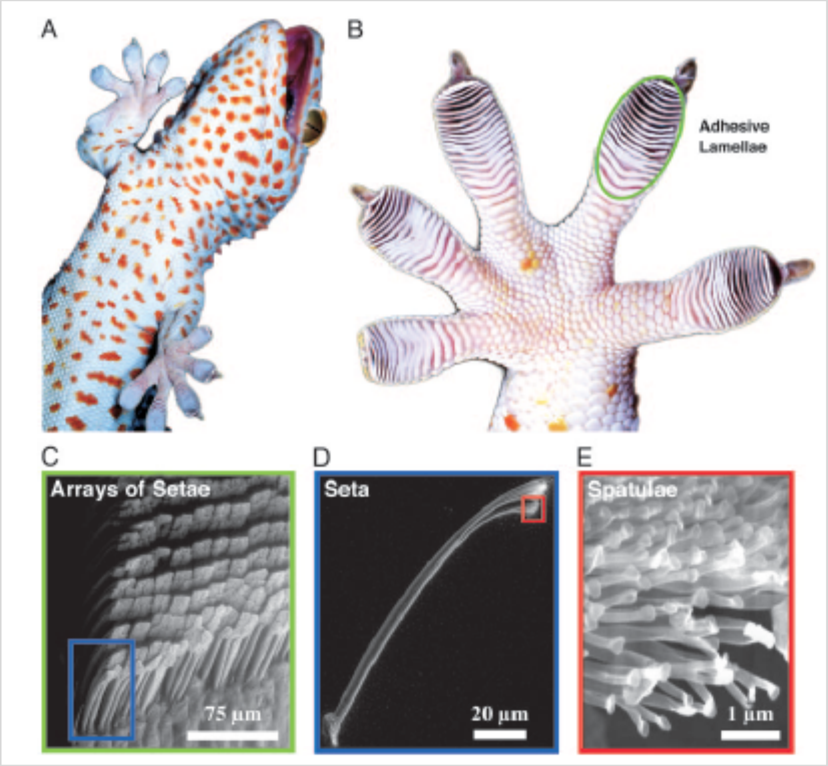

Figure 9: Structural hierarchy of the gecko adhesive system: (A) macrostructure: ventral view of a Tokay Gecko (*Gekko gecko*) climbing vertical glass; (B) mesostructure: ventral view of the foot, with adhesive lamellae (scansors) visible as overlapping pads (note the clean appearance of the adhesive surface); (C) microstructure: proximal portion of a single lamella, with individual setae in an array visible; (D and E) nanostructure: single seta with branched structure at upper right, terminating in hundreds of spatular tips.

Image: (A) Hansen et al., *Proceedings of the National Academy of Sciences*, 2005, 102(2), 386–9, reprinted with the permission of the National Academy of Science, USA, © 2005

Another very interesting property of geckos is that **their feet don't get dirty as they walk**, even if they walk on a surface covered with sand, dirt, water, etc. Their feet stay clean even on dirty surfaces and full adhesion is maintained. The phenomenon has been investigated and it was found that the feet remain clean because it is more energetically favourable for particles to be deposited on the surface than to remain adhering to the gecko spatulae. If a gecko walks over a dirty surface, it takes only few steps for its feet to be totally clean again, and adhesion is not compromised.

This self-cleaning property of the gecko foot is now being investigated with a view to designing new materials that stay clean and/or can self-clean, such as 'bio-rubbers'. This is discussed in **Module 1, Chapter 5: Overview of nanomaterials**.

Morpho rhetenor

The wings of butterflies often display extraordinary colours, a consequence of the wing surface and its interaction with light. The wings also exhibit iridescence: the shift in colour of an object when observed at different angles. The effect can easily be seen by observing a music CD.

Iridescence is a 'physical colour' and it results from the interaction of light with the physical structure of the surface. To interact with visible light, those structures must be nano-sized (the visible spectrum corresponds to wavelengths between 380 and 750 nm). The interaction of light with this nano-rough surface can lead to **constructive or destructive interference**. The colour, intensity and angles of iridescence depend on the thickness and refractive index of the substrate, and on the incident angle and frequency of the incident light.

In materials like opals, natural iridescence is observed, due to packed silica spheres in the nanometre range, uniform in size and arranged in layers. This provides appropriate conditions for interference.

In the case of butterflies and moths, the iridescence is produced in a peculiar way. Scientists have studied the structure of the wings of *Morpho rhetenor* in detail and have found that these are formed by rows of **scales** arranged like tiles on a roof. Each scale is about 70 x 200 μm and has a smaller structure on its surface, a very intricate and highly ordered nanometre organisation of ridges. Each ridge is about 800 μm wide. The spaces between them form a **natural photonic crystal** that can generate constructive and destructive interference. The SEM analysis of the cross-section of the ridges on the wings shows and an even more intricate structure that looks like fir trees (last image in **Figure 10**).

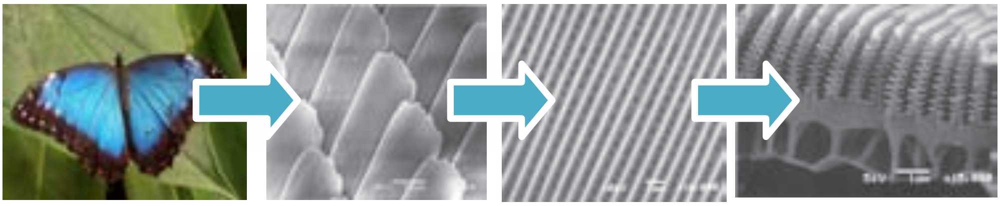

Figure 10: Close-up views at progressive magnifications of Morpho rhetenor showing the scales, which magnified show photonic crystal structures, which in turn show a cross-section displaying setae that look like fir trees

Image: (far left): Wiki Commons, Creative Commons Attribution ShareAlike 3.0; (all other images): S. Yoshioka, Osaka University, NISE Network, reprinted under NISE Network Terms and Conditions

These are called setae, are about 400 nm long, and are responsible for producing **constructive interference in the blue wavelengths** which generate the strong blue colour (**Figure 11**).

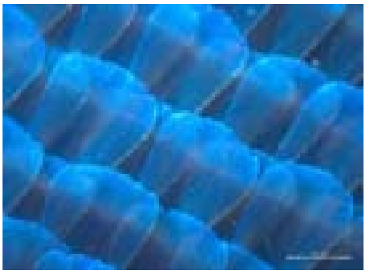

Figure 11: The blue colour of the wings is due to the constructive interference of light generated by the photonic crystal in the wings structure

Image: F. Nijhout, Duke University, NISE Network, reprinted under NISE Network Terms and Conditions

A photonic crystal is a periodic nanostructure that can modify the passage of light. The refractive indices of the materials that make up the crystal, and the presence of cavities or other defects determine which frequencies of light can propagate well.

READ MORE

In **computing**, propagation of light (rather than electrons) is being investigated as an alternative to current integrated circuits. Photonics and photonic crystals in particular are described **Module 2, Chapter 4: Information and Communication Technologies**.

CHAPTER 3:

HISTORY OF NANOTECHNOLOGIES

This chapter provides some historical background to nanotechnologies. A very valid question that students might bring up in class, and that we attempt to answer, is ‘When was nanotechnology invented?’ As discussed in Chapter 1, nanotechnologies are an evolution of other materials engineering disciplines (e.g. thin-film technology). The term is really an ‘umbrella’ term that covers disciplines that have very old historic roots. What is even more fascinating is that now scientists have the tools to study ancient artefacts, they have found that, in many cases, these were made using nanoparticles! **Nanotechnologies are around us in nature** (Chapter 2) **and in history**!

Feynman’s speech

The concept of nanotechnology is attributed to Nobel Prize winner Richard Feynman who gave a very famous, visionary speech in 1959 (published in 1960) during one of his lectures, saying: “The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom”. At the time, Feynman’s words were received as pure science fiction. Today, we have instruments (see the following section) that allow precisely what Feynman had predicted: creating structures by moving atoms individually.

Scanning tunnelling microscope

The development of nanotechnologies has been enabled by the invention of two analytic tools that have revolutionised the imaging (and manipulation) of surfaces at the nanoscale. These are the Scanning Tunnelling Microscope (STM) and the Atomic Force Microscope (AFM). The STM and the AFM are capable of imaging surfaces with **atomic resolution**.

READ MORE

The operation principle of the STM and AFM and their use for surface imaging and surface manipulation are described in **Module 1, Chapter 6: Characterisation methods**.

Both instruments were invented by Binning and his co-workers at IBM Zürich. Binning, Rohrer and Ruska (all at IBM Zürich) were awarded the **Nobel Prize in Physics in 1986** for the invention of these amazing tools, which, practically, **opened the doors of the nano-world to scientists**. With the advent of the STM, scientists were given the tool not only to image surfaces with atomic resolution, but also to move individual atoms. The STM is the first step in realising Feynman’s vision of atom-by-atom fabrication.

Coloured glass

Metal colloids (metal nanoparticles dispersed in a medium) are the best example of nanotechnology throughout ancient, medieval and modern times. In Chapter 4, it was seen how metal nanoparticles possess optical properties (i.e. different colours) that are related to surface plasmons. The size and shape of the metal nanoparticles influence their visible colours! There are numerous artefacts that have notable colour effects precisely because they are made with metal colloids.

- One of the most fascinating is a **piece of Roman glasswork**, the *Lycurgus cup*, dating from the fifth century. This magnificent cup, housed at the British Museum, depicts King Lycurgus dragged into the underworld by Ambrosia. When illuminated from the outside, the cup appears green. When illuminated from the inside, the cup appears ruby-red except for the King, who looks purple. The reason for this dichroism was unknown until detailed SEM analysis of the cup was performed in 1990. It was found that it was due to the presence of nano-sized particles of silver (66.2 %), gold (31.2 %) and copper (2.6 %), up to 100 nm in size, embedded in the glass. Light absorption and scattering by these nanoparticles determines the different colours.
- The beautiful **stained glass windows produced in medieval times**, and visible in numerous churches, are made of a composite of glass and nano-sized metal particles. The 'ruby-red' glasses often seen are a mixture of glass with ultrafine (nano-sized) gold powder. The 'purple of Cassius' is a colloidal mixture of gold nanoparticles and tin dioxide in glass.
- **Chinese art history** is also filled with examples of nanotechnology. For instance, the Chinese porcelain known as *famille rose* contains gold nanoparticles 20–60 nm in size.

Faraday's studies on gold colloids

If we look into the history of science, gold colloids have been the subject of research since the mid 19th century! It was actually **Michael Faraday who was the first to conduct systematic studies on the properties of metal colloids**, in particular gold. In 1857, during his lecture at the Royal Society of London, Faraday presented a purple-coloured slide, stating that it contained 'gold reduced in exceedingly fine particles, which becoming diffused, produce a ruby-red fluid … the various preparations of gold, whether ruby, green, violet or blue … consist of that substance in a metallic divided state'.

Faraday postulated correctly about the physical state of colloids; he also described how a **gold colloid would change colour (to blue) when salt is added**.

This effect is shown in **Experiment C** in the **NANOYOU Experiment Module**. Teachers have an opportunity to link this experiment with some concepts of science history.

In the early 20th century, Gustav Mie presented the **Mie theory**, a mathematical treatment (to which we still refer) of light scattering that describes the relationship between colloid-sized metals and the optical properties of solutions containing them.

Miniaturised electronics

Youngsters are surrounded by electronic devices — computers, mobile phones, portable electronic games, etc. It is really amusing to see their reaction when we show them pictures of the first mobile phones introduced in the 1980s! We (and, even more, they) take for granted the miniaturisation of electronic devices, and are used to expecting even more every year or so. The evolution of this miniaturisation has been brought about by the tremendous advances in the semiconductor industry and the ability to produce smaller and smaller integrated circuits (ICs). The 'core' of ICs is the transistor — every chip is made of numerous transistors that act like gates for the flow of electrons: they can be in the open or closed mode. Just to paint to picture, in 1965, 30 transistors populated a chip; in 1971, there were 2 000; and, today, there are about … 40 million! This exponential growth was actually predicted in 1965 by Gordon E. Moore (co-founder of Intel Corporation). Moore predicted that the 'complexity of integrated chips' would double every 18 months. At the time he was a visionary … but, indeed, Moore's law proved to be right. The data density of computer chips has increased in the last years at the predicted pace, doubling every 18 months.

TIP FOR TEACHERS: Ask your students to go home and collect information on old computers or laptops owned by their parents, friends or relatives. Ask them to record when they were purchased (approximate date of production), and what was the data storage capacity (hard disc capacity). Make an overall table with the information collected by all the class. Is Moore's law confirmed?

The history of integrated chips is, in a sense, the history of nanotechnology. The **first transistor invented in 1947** was a bulk, macro object (**Figure 1**). To keep up with the demand for miniaturisation, the dimensions of the transistor have been reduced considerably over the last 20 years. In 2002, the nano-size was reached and a single transistor was 90 nm. As of today (end of 2009), a single transistor in an Intel® Core™ 2 Quad processor is 45 nm.

Figure 1: Replica of the first bipolar transistor, this replica was photographed at the Nixdorf-Museum, Paderborn, Germany.

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

If they were to keep pace with Moore's law, transistors would have to be as small as 9 nm by 2016. This dimension is below the fabrication capabilities of the latest-generation tools used in the microelectronics industry. Moreover, at this dimension, electrons would be able to 'jump' the gate just with their own thermal energy. Numerous novel approaches are under investigation to realise workable transistors of this size. These include molecular electronics and quantum computing — both are examples of true nanotechnologies.

READ MORE

The fabrication techniques used in the microelectronics industry are reviewed in **this Module, Chapter 7: Fabrication methods**. The future evolution of computing and the impact of nanotechnologies are discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

The GMR effect

Numerous popular electronic products, such as the iPod, have components that use an effect called giant magnetoresistance (GMR). In simple terms, the electrical resistance of structures made of **very thin layers of magnetic and non-magnetic metals** can change by an unexpectedly large amount in the presence of an applied magnetic field. The effect was discovered independently by Albert Fert and Peter Grunberg in 1988 and, for its discovery, they shared the **2007 Nobel Prize in Physics**. When the prize was announced, the Swedish Academy of Science wrote: ‘GMR technology may also be regarded as one of the first major applications of the nanotechnology that is now so popular in a very diverse range of fields.’

READ MORE

The GMR effect is a true nano-effect! GMR is used in the latest-generation memory devices like the MRAM. The details of the GMR effect are described **in Module 2, Chapter 4: Information and Communication Technologies**.

Advanced materials

The **history of materials engineering** is full of examples of nanomaterials! Often, these were produced inadvertently and not characterised at the nanoscale as many of the analytic tools used today were not yet available. For instance, the process of **anodising** was first patented in the early 1930s. This represents one of the most important processes used in industry to protect aluminium from corrosion. It consists of depositing a thin protective oxide layer on the aluminium surface. The inventors of this technique were not aware that the **protective layer is actually a nanomaterial** — the anodic layer is composed of hexagonally close-packed channels with diameters ranging from 10 to 250 nm or greater.

Other familiar examples are: nanoparticles that are found in the rubber component of car tyres; titanium dioxide pigment found in some of the latest-generation sunscreens; components in computer chips; numerous synthetic molecules used in current drug compositions; thin, hard coatings used in industry.

There are many nanomaterials that have a long history: not all can be reviewed here, so the discussion will be limited to two examples.

Fullerenes and carbon nanotubes

In 1985, R. E. Smalley, H. W. Kroto and R. F. Curl discovered a new form of the element carbon: the *buckyball*, a molecule consisting of 60 atoms of carbon (C_{60}) assembled in a form similar to a football (**Figure 2**). The researchers were then able to develop a method to synthesise and characterise this new nanomaterial. The existence of C_{60} had actually been predicted by Eiji Osawa of Toyohashi University of Technology in a Japanese magazine in 1970. This new **allotrope of carbon** was officially named Buckminsterfullerene in honour of Buckminster Fuller, an architect famous for his geodesic dome design. Shortly after the discovery in 1985, various others fullerenes were discovered.

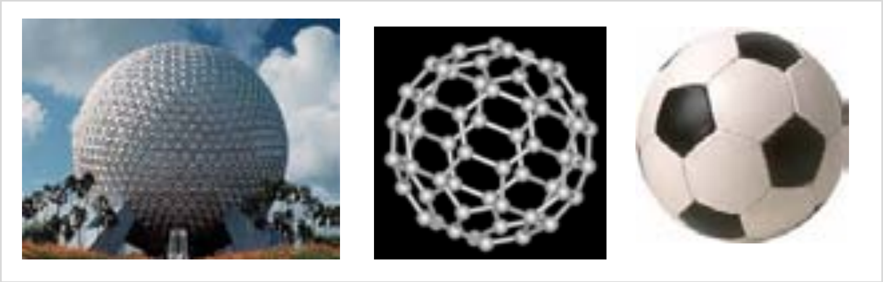

Figure 2: Left to right: a geodesic dome designed by architect Buckminster Fuller, the structure of C_{60} and a football.

Image: Wiki Commons Images, Creative Commons Attribution ShareAlike 3.0

In 1996, Kroto, Curl, and Smalley were awarded the **1996 Nobel Prize in Chemistry** for their roles in the discovery of this class of compounds.

READ MORE

The properties and applications of fullerenes and their parent nanomaterial carbon nanotubes are described in detail in **Module 1, Chapter 5: Overview of nanomaterials**.

Liquid crystals

Liquid crystals were first accidently discovered in 1888 by Friedrich Reinitzer, a botanical physiologist who was working in the Institute of Plant Physiology at the University of Prague. Reinitzer was conducting experiments on a cholesterol-based substance (cholesteryl benzoate) and trying to determine the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points. He found a first melting point at 145.5 °C, where the solid crystal melted into a cloudy liquid. This 'cloudy intermediate' existed up to 178.5 °C where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. At first, Reinitzer thought that this might be a sign of impurities in the material, but further purification did not show any changes in this behaviour. He concluded that the material had two melting points, but asked his colleague Otto Lehmann, a German physicist who was an expert in crystal optics, for help in understanding this unexpected behaviour. They isolated and analysed the ‘cloudy intermediate’ and reported seeing crystallites. Lehmann then conducted a systematic study of cholesteryl benzoate and other solids that displayed the double melting behaviour. He became convinced that the cloudy liquid had a unique kind of order. It could sustain flow like a liquid but under the microscope appeared like a solid. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids. Eventually, he realised that the cloudy liquid was a new state of matter and coined the name ‘liquid crystal,’ to emphasise that it was something between a liquid and a solid, sharing important properties of both. Not just a liquid, where molecules are randomly distributed, and not just a solid, where molecules are ordered in organised structures.

TIP FOR TEACHERS: The discovery of liquid crystals is a good example of how science often proceeds (i.e. with a discovery made by mistake that is then further investigated (rather than just dismissed as an error)). In fact, many major scientific discoveries were made this way. An educator may take this opportunity to illustrate to the class other scientific discoveries that were the result of an accidental discovery, followed by the studies of long-sighted scientists who pursued the scientific meaning of the ‘accident’ (another great example is the discovery of penicillin).

The scientific community challenged the conclusions of Reinitzer and Lehmann since, at that time, scientists knew only three states of matter: gas, liquid and solid. The general idea was that all matter normally had one melting point (where it turns from solid to liquid) and a boiling point (where it turns from liquid to gas).

Nevertheless, the work done by Lehmann was continued atthe beginning of the 20th century, but liquid crystals were treated by the scientific community as a pure scientific curiosity. Only later did scientists realise that these materials were indeed a fourth state of matter and could actually have commercial use. In 1969, Hans Kelker succeeded in synthesising a substance that had a nematic phase at room temperature, the N-(4-methoxybenzylidene)-4-butylaniline (MBBA) molecule. Later, other chemically stable substances (cyanobiphenyls) with low melting temperatures were synthesised: these materials opened the doors to the use of liquid crystals in practical applications such as displays. Since these discoveries, research on these materials has increased and in **1991 Pierre-Gilles de Gennes received the Nobel Prize in Physics** ‘for discovering that methods developed for studying order phenomena in simple systems can be generalised to more complex forms of matter, in particular to liquid crystals and polymer’.

Now it is known that the peculiar properties of a liquid crystal depend on how external factors, such as electric field or temperature, change its phase resulting in a rearrangement of its supramolecular nanostructure.

READ MORE

Nowadays, liquid crystals are used for many applications, mainly in the ICT sector, such as in mobile phone displays. Liquid crystals are described in detail in **Module 1, Chapter 5: Overview of nanomaterials** and their applications are discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

EXPERIMENT

In **EXPERIMENT B of the NANOYOU Experiment Module**, students prepare different types of liquid crystals that change phase with temperature and, as a consequence, change colour. Students can make a room thermometer with four different types of liquid crystals.

CHAPTER 4:

FUNDAMENTAL ‘NANO-EFFECTS’

Nanoscience is often referred to as ‘the science of small’. The question we address in this chapter is: Why does size matter? What is so special about nano-sized materials? How are their properties different from those of ‘conventional’ bulk materials? Here, a complete review of the topic, which would involve an in-depth review of quantum physics, cannot be provided, but some fundamental aspects of nanoscience that are essential to understanding the exceptional properties of nanomaterials are highlighted. Rather than focusing on the theory behind these effects, the focus is on **the implications that these effects have on the properties of materials**.

What happens at the nanoscale?

The macroscopic physical properties of a substance (melting point, boiling point, conductivity, etc.) are determined by studying a pure sample in quantities big enough to be measured under normal laboratory conditions. One mole of any material contains 6.022×10^{23} molecules; one mole of water, for instance, weights 18 g. Therefore, when the boiling point of one mole of water is determined, in reality the value which is obtained represents an average value based on the behaviour of billions and billions of molecules of water; we assume that the result should be true for any size of group of water molecules. This is not correct for many materials: as the size of the material is reduced, and the nanoscale level is reached, it is possible that the same material will display totally different properties (different melting point, conductivity, etc.). This is because matter at the nanoscale no longer follows Newtonian physics but rather quantum mechanics.

In other words, the properties of materials can be size-dependent. This might be a rather new concept to bring into the classroom as, conventionally, the properties of a substance (solid, liquid or gas) are related to the atoms and molecules that make up the substance and the way they are connected to one another (chemical bonds). Size is not normally mentioned as a key factor. Students will probably expect a piece of gold to be golden in colour however big or small it is. This is correct at the macro and micro-scale level: but at the nanoscale, things start to change dramatically due to quantum effects. In fact, gold can be used as a prime example: a colloid of gold nanoparticles is no longer ‘golden’ but ruby-red in colour (**Figure 1**).

Figure 1: The colour of gold depends on its size

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

TIP FOR TEACHERS: The concept that a material can have properties that are size-dependent can be illustrated through 'macro' analogies. For instance, a glass half-filled with water makes a different sound to a glass totally filled with water. In this analogy, the quantity (volume) of the water determines the sound that is emitted. Similarly, a guitar string under more or less tension will also make a different sound.

A different kind of small

Materials that belong to the 'nanoscale' are made of at least clusters of atoms and molecules, not just single atoms: for example, 3.5 atoms of gold or eight hydrogen atoms lined up in a row are one nanometre long. A glucose molecule is about 1 nm in size.

Nanomaterials represent a 'different kind of small' compared to other 'small' objects that a student might be familiar with. Nanomaterials are not as small as electrons or single atoms, and are bigger than other 'very small objects', such as a cell or bacterium, that a student can probably think of. Nanostructures are at the confluence of the smallest human-made objects (e.g. latest-generation transistors) and the largest molecules of living things (e.g. DNA, proteins). **Nanomaterials are intermediate in size between isolated atoms and molecules, and bulk materials. At this scale, matter shows exceptional properties.**

Thanks to their unique properties, nanomaterials offer two exciting possibilities:

- nanomaterials can be used to improve current materials or create new ones that have exceptional properties;
- as nanomaterials have dimensions in the range of the largest molecules found in the natural world, it is possible to integrate them and interact actively with them in a device.

The fabrication and utility of a range of nanomaterials are further discussed in **Module 1, Chapter 5: Overview of nanomaterials**.

Physics at the nanoscale

Nanomaterials are closer in size to single atoms and molecules than to bulk materials, and to explain their behaviour, it is necessary to use quantum mechanics. **Quantum mechanics** is a scientific model that was developed for describing the motion and energy of atoms and electrons. As quantum mechanics concepts are normally included in a secondary science (physics or chemistry) school curriculum, they are not described here in detail. Here, just a **brief summary** of the most salient quantum effects, together with other **physical properties that are relevant at the nanoscale** is provided.

- Due to the smallness of nanomaterials, their mass is extremely small and gravitational forces become negligible. Instead, **electromagnetic forces** are dominant in determining the behaviour of atoms and molecules.
- **Wave-corpuscle duality of matter**: for objects of very small mass, such as the electron, wavelike nature has a more pronounced effect. Thus, electrons exhibit wave behaviour and their position is represented by a wave (probability) function.
- One of the consequences is a phenomenon called **tunnelling**. Classic physics states that a body can pass a barrier (potential barrier) only if it has enough energy to 'jump' over it. Therefore, if the object has lower energy than that needed to jump over the energy barrier (the 'obstacle'), in classic physics, the probability of finding the object on the other side of the barrier is zero. In quantum physics, a particle with energy less than that required to jump the barrier has a **finite probability** of being found on the other side of the barrier. Figuratively, one can imagine that the particle passes into a 'virtual tunnel' through the barrier (**Figure 2**). It should be noted that in order to have a tunnel effect, the 'thickness' of the barrier (i.e. energy potential) must be comparable to the wavelength of the particle and, therefore, this effect is observed only at nanometre level. So, in simple terms, electron (or quantum) tunnelling is attained when a particle (an electron) with lower kinetic energy is able to exist on the other side of an energy barrier with higher potential energy, thus defying a fundamental law of classic mechanics. **Tunnelling is the penetration of an electron into an energy region that is classically forbidden**.

  Tunnelling is a fundamental quantum effect and it is the basis of a very important instrument for imaging nanostructured surfaces called the **Scanning Tunnelling Microscope (STM)**. The same instrument can be used as a nanofabrication tool (movement of single atoms). The operation principle and capabilities of the STM are discussed in **Module 1, Chapter 6: Characterisation methods**.

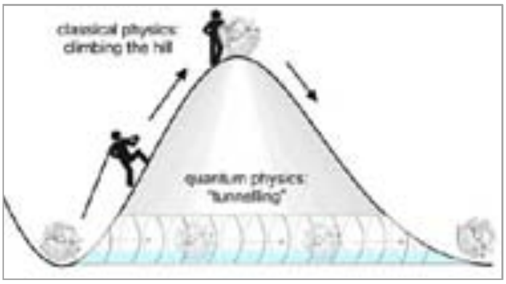

Figure 2: Schematic representation of tunneling

Image: ©Max Planck Institute for Quantum Optics

- **Quantum confinement**: in a nanomaterial, such as a metal, electrons are confined in space rather than free to move in the bulk of the material.
- **Quantisation of energy**: electrons can only exist at **discrete energy levels**. Quantum dots are nanomaterials that display the effect of quantisation of energy.
- **Random molecular motion**: molecules move due to their kinetic energy (assuming the sample is above absolute zero). This is called random molecular motion and is always present. At the macroscale, this motion is very small compared to the sizes of the objects and thus is not influential on how the object moves. At the nanoscale, however, these motions can be of the same scale as the size of the particles and thus have an important influence on how they behave. One example of a random kinetic motion is Brownian motion.

- **Increased surface-to-volume ratio**: one of the distinguishing properties of nanomaterials is that they have an increased surface area. This characteristic is described in more depth in the next section.

Chemistry at the nanoscale

It has already been stated that a nanomaterial is formed of at least a cluster of atoms, often a cluster of molecules. It follows that **all types of bonding that are important in chemistry are also important in nanoscience**. They are generally classified as:

- **intramolecular bonding** (chemical interactions): these are bondings that involve changes in the chemical structure of the molecules and include ionic, covalent and metallic bonds;
- **intermolecular bonding** (physical interaction): these are bondings that do not involve changes in the chemical structure of the molecules and include ion-ion and ion-dipole interactions; van der Waals interactions; hydrogen bonds; hydrophobic interactions; repulsive forces (such as steric repulsions).

It is assumed that the description of chemical and physical bonds is part of the secondary science school curriculum, so here some chemical and physical interactions that often used to describe the properties of nanomaterials are highlighted.

Nanomaterials often arise from a number of molecules held together or large molecules that assume specific three-dimensional structures through intermolecular bonding (**macromolecules**). Therefore, nanoscience also deals with **supramolecular chemistry** (i.e. the chemistry that deals with interactions among molecules), which is just a sub-area of the general field called ‘chemistry’. In these macromolecules, intermolecular bonding often plays a crucial role.

- Intermolecular bondings, such as **hydrogen bonding** and van der Waals bonding are weak interactions but in a large number they can have a total energy that can be quite significant. Consider, for instance, the structure of DNA (which has a cross-section of 2 nm): the two helixes are held together by numerous hydrogen bonds. This point becomes particularly relevant in nanoscience, where materials can have very large surface areas and, consequently, small forces can be applied to very large areas.

HANDS-ON ACTIVITY a very simple demonstration to show how small forces become important on large surfaces is to take two big books made of thin paper (such as a phonebook or Yellow Pages) and gradually lay one page of the first book over a page of the second book alternately. When only a few pages are overlapped, it is very easy to take the two books apart: you just need to pull. As the number of interconnected pages increases, it becomes harder to pull the two books apart. After a certain number of pages, it is no longer possible to separate the two books by hand! The interaction between the pages is due to weak forces (electrostatic and van der Waals). When the surface area is big, these weak forces result in a very strong interaction!

- Intermolecular bondings often hold macromolecules (such as proteins) together in specific three-dimensional structures with which **precise biological functions** are associated. Disruption of these interactions in a protein irreversibly affects its 3D structure (quaternary structure) and leads to a total loss of function (*protein denaturation*).
- One type of intermolecular bonding particularly significant in nanoscience is the **hydrophobic effect**. This is a process basically driven by entropy and which has a major role in biological materials. In simple terms, it is the property by which non-polar molecules (e.g. oil) tend to form aggregates of like molecules in water.

TIP FOR TEACHERS: Students will be familiar with the hydrophobic effect. A simple example is oil drops in water.

Molecules as devices

In nanoscience, macromolecules are often considered as ‘devices’ that, for instance, can trap or release a specific ion under certain environmental conditions (pH etc.). A biological example of such a macromolecule is ferritin. Therefore, in nanoscience and nanotechnologies, where molecules can themselves be devices, **bonds may also be device components**. One area of study is, for example, the use of molecules as **molecular switches, actuators and electronic wires**. This is further discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

Unique material properties

at the nanoscale

Surface properties

Regardless of whether we consider a bulk material or a nanoscale material, **its physical and chemical properties depend on many of its surface properties**. Surfaces perform numerous functions: they keep things in or out; they allow the flow of a material or energy across an interface; they can initiate or terminate a chemical reaction, as in the case of catalysts. The branch of science that deals with the chemical, physical and biological properties of surfaces is called **surface science**. In this context, the term **interface**, rather than surface, is often used, to emphasise the fact that it is a boundary between two phases: the material and the surrounding environment (liquid, solid or gas).

If a bulk material is subdivided into an ensemble of individual nanomaterials, the total volume remains the same, but the **collective surface area is greatly increased**. This is shown schematically in **Figure 3**.

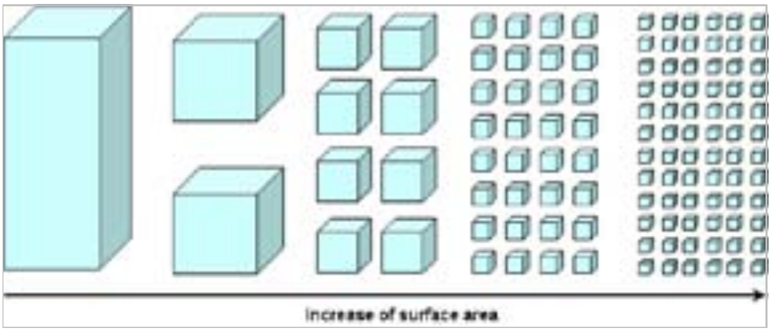

Figure 3: Schematic drawing showing how surface to volume increases as size is decreased (image not to scale)

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

The consequence is that the surface-to-volume ratio of the material — compared to that of the parent bulk material — is increased.

TIP FOR TEACHERS: A very simple example to mention in class is granular sugar and caster sugar. Caster sugar is finer, stickier (more surface absorption) and dissolves faster in water.

How would the total surface area increase if a cube of 1 m^3 were progressively cut into smaller and smaller cubes, until it is composed of 1 nm^3 cubes? **Table 1** summarises the results.

Size of cube side	Number of cubes	Collective surface area
1 m	1	6 m^2
0.1 m	1 000	60 m^2
0.01 m = 1 cm	10^6 = 1 million	600 m^2
0.001 m = 1 mm	10^9 = 1 billion	6 000 m^2
10^{-9} m = 1 nm	10^{27}	6 x 10^9 = 6 000 km^2

USEFUL VIDEO No 1 CUTTING CHEESE — a simple and fun video to watch that shows the increase in surface area as a material is cut into progressively smaller cubes can be watched online (http://community.acs.org/nanotation/NanoTubePlayer/tabid/131/VideoId/101/Small-Can-Be-Big-A-French-Cheesy-Perspective.aspx).

The importance of surface atoms

In surface science, the chemical groups that are at the material interface determine its properties. Properties like catalytic reactivity, electrical resistivity, adhesion, gas storage and chemical reactivity depend on the nature of the interface. **Nanomaterials have a significant proportion of atoms existing at the surface**. This has a profound effect on reactions that occur at the surface such as such as **catalysis** reactions, **detection reactions**, and reactions that, to be initiated, require the physical adsorption of certain species at the material's surface.

USEFUL VIDEO 2 MENTOS IN DIET COKE® — this video shows the effect of putting a mint Mentos into a bottle of Diet Coke®. The effect is linked to the surface roughness of the Mentos and to the chemistry of its coating. Even if this effect is not necessarily a 'nano-effect', the video illustrates the connection between surface properties and physical behaviour. The effect only occurs with a mint Mentos and not using a glazed (fruit) Mentos, a sign that the effect is due to surface chemistry/topography (http://dsc.discovery.com/videos/mythbusters-diet-coke-and-mentos.html).

The fact that in a nanomaterial a larger fraction of the atoms is at the surface influences some physical properties such as the **melting point**. Given the same material, its melting point will be lower if it is nano-sized. Surface atoms are more easily removed than bulk atoms, so the total energy needed to overcome the intermolecular forces that hold the atom 'fixed' is less, thus the melting point is lower.

Shape also matters

Given the same volume, **the extent of the surface area depends on the shape** of the material. A simple example is a sphere and a cube having the same volume. The cube has a larger surface area than the sphere. For this reason, in nanoscience, not only the size of a nanomaterial is important, but also its shape. **Figure 4** illustrates this concept. In the section on catalysis, an example is given of a nanomaterial whose properties are determined not only by size but also by shape.

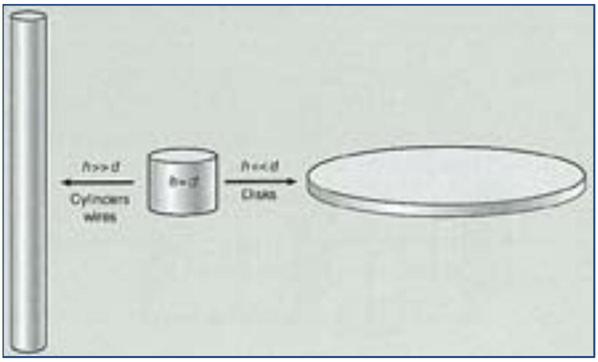

Figure 4: The ratio between the height (h) and the diameter (d) determines whether a shape is like a wire or a disc: shape influences surface area.

Surface energy

Atoms and molecules that exist at the surface or at an interface are different from the same atoms or molecules that exist in the interior of a material. This is true for any material. Atoms and molecules at the interface have enhanced reactivity and a greater tendency to agglomerate: **surface atoms and molecules are unstable**, they have **high surface energy**.

TIP FOR TEACHERS: A simple example to use in class to demonstrate the concept of 'high surface energy' is to coat some ping pong balls with Velcro (putting the two sides on different balls). If you place the balls in a plastic bag and shake, the balls will stick together. If normal balls are used, no attachment occurs.

As mentioned in the previous section, nanomaterials have a very large fraction of their atoms and molecules on their surface. On the other hand, a fundamental chemical principle is that 'systems of high energy will strive to attain a state of lower energy, by whatever means possible'. So how is it possible to have nanomaterials? Nanomaterials are abundant in nature (proteins, DNA, etc.). **Nanomaterials are inherently unstable**, therefore there are various methods that nanomaterials adopt to **minimise their inherent high surface energy**.

One of the ways of reducing the surface energy innanoparticles is **agglomeration**. Surface energy is an additive quantity. The surface of 10 identical nanoparticles is equal to the sum of the surface energy of each individual nanoparticle. If these were to agglomerate, and become one large particle, the overall surface energy would be reduced. The concept is illustrated in **Figure 5**. If a generic surface energy value γ is associated with each lateral surface of cube A, than its total surface energy is 6γ. The same applies to cube B. Therefore, the total surface energy of both cubes, A and B, separated, is 2 x 6γ = 12γ. The total surface energy of the parallelepiped C, on the other hand, is 10γ.

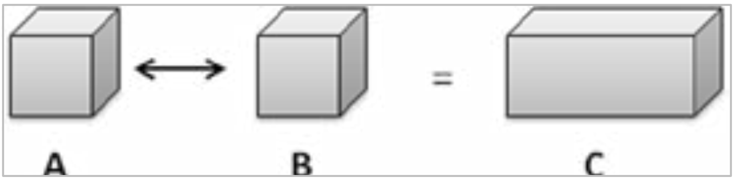

Figure 5: The surface energy of two separate cubes is higher than the surface energy of the two cubes agglomerated.

Nanoparticles have a strong intrinsic tendency to agglomerate. To avoid this, surfactants can be used. This also explains why when nanoparticles are used in research and industry they are often immobilised on a solid support or mixed within a matrix. Even in commercial products that claim to contain nanoparticles (such as sunscreens) microscope images show that they are actually present in the form of agglomerates of > 100 nm dimensions.

Reactions where surface properties are very important

In this last section, two reactions are briefly reviewed: catalysis and detection, where the surface properties of the material are particularly important, and what nanoscience can do to improve their outcome is highlighted.

Catalysis

A catalyst is a substance that increases a chemical reaction rate without being consumed or chemically altered. Nature's catalysts are called enzymes and are able to assemble specific endproducts, always finding pathways by which reactions take place with minimum energy consumption. Man-made catalysts are not so energy efficient: they are often made of metal particles fixed on an oxide surface, working on a hot reactant stream (to reduce the phenomenon, 'catalyst poisoning', which occurs when species dispersed in the atmosphere, such as CO, occupy the active sites of the catalysts is used). One of the most important properties of a catalyst is its **active surface** where the reaction takes place. The 'active surface' increases when the size of the catalysts is decreased: the smaller the catalyst particles, the greater the surface-to-volume ratio (**Figure 5**). The higher the catalysts' active surface, the greater the surface reactivity. Research has shown that the **spatial organisation of the active sites in a catalyst is also important**. Both properties (nanoparticle size and molecular structure/distribution) can be controlled using nanotechnology. Hence, this technology has great potential to expand catalyst design with benefits for the chemical, petroleum, automotive, pharmaceutical and food industries. **The use of nanoparticles that have catalytic properties allows a drastic reduction in the amount of material used, with resulting economic and environmental benefits.**

Catalysis and its importance in environmental and energy applications are discussed in **Module 2, Chapter 2: Environment** and **Chapter 3: Energy**. **Figure 6** illustrates the effect of nanostructuring on a catalyst surface.

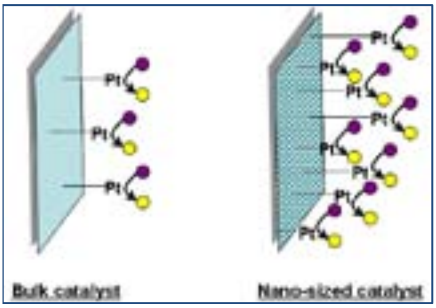

Figure 6: Schematic representation of the increased active surface of a nano-sized catalyst (right) compared to a bulk catalyst

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

A good example of how nanoscience can impact the development of catalytic materials is that of gold. Bulk gold is a noble metal: it is stable, non-toxic, and resistant to oxidation and chemical attack. For these reasons, it is widely used in jewellery. On the other hand, **nanoscale gold particles can catalyse chemical reactions**. It has been found that finely dispersed gold nanoparticles on oxide supports are catalytically very active. In many cases, the catalytic activity and selectivity of dispersed gold nanoparticles exceed those of the commonly used transition metal catalysts such as platinum, rhodium and palladium. This is an exciting result because metals like platinum and palladium (commonly used in catalysis such as car catalytic converters) are toxic and are also very rare metals, hence very expensive.

Detection

The detection of a specific chemical or biological compound within a mixture represents the basis for the operation of numerous devices, such as chemical sensors, biosensors and microarrays. These devices will be described in more detail in **Module 2, Chapter 1: Medicine and healthcare**. As with catalysis, a detection reaction occurs at the material interface. The rate, specificity and accuracy of this reaction can be improved using nanomaterials rather than bulk materials in the detection area. The higher surface-to-volume ratio of nanomaterials increases the surface area available for detection with a positive effect on the rate and on the limit of detection of the reaction. In addition, nanomaterials can be designed to have specific surface properties (chemical or biochemical), tailored at a molecular level. This way, the active sites on the material surface can act as 'locks' to detect specific molecules (the 'keys'). **Figure 7** illustrates this concept. Scaling down using nanomaterials allows **more detection sites to be packed into the same device**, thus allowing the detection of multiple analytes.

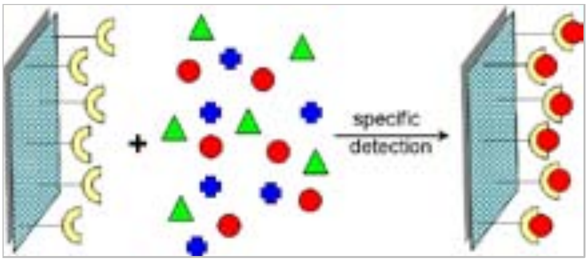

Figure 7: Schematic representation showing the specific detection of an analyte within a mixture by 'receptor' sites in a nanomaterial

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

This scaling-down capability, together with the high specificity of the detection sites obtainable using nanomaterials, will allow the fabrication of super-small '**multiplex detection devices**' (i.e. devices that can test and detect more than one analyte at the time).

Electrical properties

There are three categories of materials based on their electrical properties: (a) conductors; (b) semiconductors; and (c) insulators. The energy separation between the valence band and the conduction band is called E_g (band gap). The ability to fill the conduction band with electrons and the energy of the band gap determine whether a material is a conductor, a semiconductor or an insulator. In conducting materials like metals, the valence band and the conducting band overlap, so the value of E_g is small: thermal energy is enough to stimulate electrons to move to the conduction band. In semiconductors, the band gap is a few electron volts. If an applied voltage exceeds the band gap energy, electrons jump from the valence band to the conduction band, thereby forming **electron-hole pairs** called **excitons**. Insulators have large bandgaps that require an enormous amount of voltage to overcome the threshold. This is why these materials do not conduct electricity (**Figure 8**).

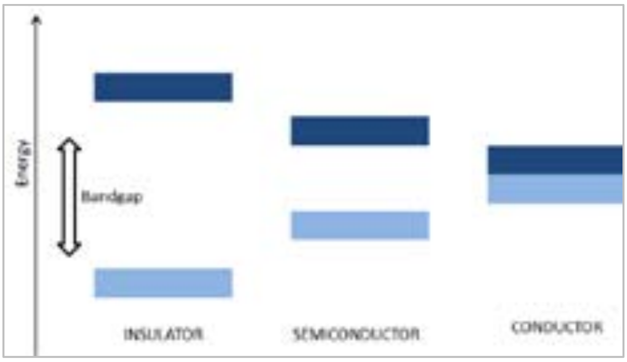

Figure 8: Schematic illustration of the valence and conduction bands in materials based on their electrical properties: insulator, semiconductor and conductor

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

Quantum confinement and its effect on material electrical properties

Quantum confinement causes the energy of the band gap to increase as illustrated in **Figure 9**. Furthermore, at very small dimensions when the energy levels are quantified, the band overlap present in metals disappears and is actually transformed into a band gap. **This explains why some metals become semiconductors as their size is decreased**.

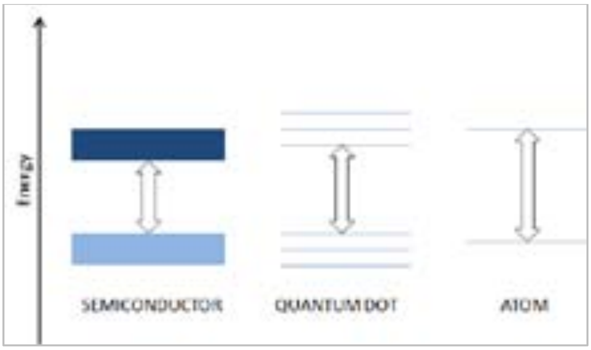

Figure 9: The image compares the energy of the band gap (arrow) in a bulk semiconductor, a quantum dot and an atom. As more energy states are lost due to the shrinking size, the energy band gap increases.

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

The increase in band gap energy due to quantum confinement means that more energy will be needed in order to be absorbed by the band gap of the material. Higher energy means shorter wavelength (blue shift). The same applies to the wavelength of the fluorescent light emitted from the nano-sized material, which will be higher, so the same blue shift will occur. Thus, a **method of tuning the optical absorption and emission properties of a nano-sized semiconductor** over a range of wavelengths **by controlling its crystallite size** is provided. The optical properties of nano-sized metals and semiconductors (quantum dots) are described in the section of this chapter on optical properties.

Nanomaterials with exceptional electrical properties

Some nanomaterials exhibit electrical properties that are absolutely exceptional. Their electrical properties are related to their unique structure. Two of these are **fullerenes and carbon nanotubes**. For instance, carbon nanotubes can be conductors or semiconductors depending on their nanostructure. These materials are discussed in **Module 1, Chapter 5: Overview of nanomaterials**. Another example is that of **supercapacitors** — materials in which there is effectively no resistance and which do not obey Ohm's law.

Optical properties

Some nanomaterials display very different optical properties, such as colour and transparency, compared to bulk materials. In this section, the reason for this behaviour is discussed and some examples provided. Before going into detail, some fundamentals are reviewed.

Interaction of light with matter

The 'colour' of a material is a function of the interaction between the light and the object. If a material absorbs light of certain wavelengths, an observer will not see these colours in the reflected light. Only reflected wavelengths reach our eyes and this makes an object appear a certain colour. For example, leaves appear green because chlorophyll, which is a pigment, absorbs the blue and red colours of the spectrum and reflects the green.

In general light (I) incident on a material can be transmitted (T), absorbed (A) or reflected (R):

$$I = T+A+R$$

As the size of the materials is reduced, **scattering (S) of light** can also contribute to its colour (or transparency). A short summary of each process follows.

- **Reflection (R)** occurs when lightstrikes a smooth surface and the incident wave is directed back into the original medium. The reflected wave has same geometrical structure as the incident wave.
- **Absorption (A)** is a process that involves energy transformation. The energy levels of a substance determine the wavelengths of light that can be absorbed. It is a molecular phenomenon, dependent on the chemical identity and structure of the substance (not on the size of the molecules or clusters), and involves electronic transitions, vibrations and rotations. Chromophores and fluorephores are examples of organic materials that have specific electronic transitions.
- **Transmission (T)** is the ability of light to pass through a material: it is complementary to absorption. Transmission of light is what is left after reflection, scattering and absorption have occurred.
- **Scattering (S)** is the phenomenon that occurs when radiation hits a structure with dimensions comparable to the incident wavelength. Therefore, it is a physical process that *depends on cluster size*, the refractive index of the cluster and the refractive index of the suspension medium. It is a physical interaction only — no energy transformations occur during scattering (as opposed to absorption), energy is simply redirected in many directions. The wavelength of

> the incoming light and that of the outgoing light are the same. After the light hits the clusters in the colloid and is redirected once, it can encounter another cluster and be redirected again. This phenomenon is called **multiple scattering**. At the 'macro' level, the overall effect can be that light is sent back the way it came (back scattering) or moves forward in the same direction it was moving initially (front scattering). **Maximum scattering occurs for wavelengths twice as large as the cluster size**. Therefore, if the cluster is about 200 nm, maximum scattering is observed at 400 nm, which lies within the range of the visible spectrum.

The formula indicated above still holds if scattering occurs. Scattering simply contributes to the 'reflection' (back scattering) and 'transmission' (front scattering) parts of the equation. Light that has been absorbed cannot be scattered.

Colour generation from nanoparticles and nanostructures

Nanomaterials in general can have peculiar optical properties as a result of the way light interacts with their fine nanostructure. An overview follows.

Colour due to …	Example of nanomaterial
Interference: The colour is based on the constructive interference of light wavelengths as they interact with the nanomaterial.	Butterfly wings (photonic crystals) — this example is described in **Module 1, Chapter 2: Nanoscience in nature** Liquid crystals (e.g. soap) — the colours of liquid crystals are explained in detail in **Module 3, Experiment B**
Scattering: Colours arise because different particle sizes scatter different wavelengths.	Colloids (milk)
Surface plasmons: This is a peculiar effect found in metal nanoparticles (see the next section) responsible for the vivid colours of metal colloids.	Metal colloids (nano-gold)
Quantum fluorescence: The quantum confinement in nano-sized semiconductors leads to discrete energy levels from which energy can be emitted (fluorescence) after it has been absorbed by the semiconductor.	Semiconductor quantum dots (QDs)

Colour in metal colloids (surface plasmons)

One of the distinguishing properties of **metal nanoparticles** in general is their optical properties, which are different from those of their bulk counterpart. This is due to an effect called **localised surface plasmon resonance**. In simple terms, when light hits a metal surface (of any size) some of the light wave propagates along the metal surface giving rise to a surface plasmon — a group of surface conduction electrons that propagate in a direction parallel to the metal/dielectric (or metal/vacuum) interface. When a plasmon is generated in a conventional bulk metal, electrons can move freely in the material and no effect is registered. In the case of nanoparticles, the **surface plasmon is localised in space**, so it oscillates back and forth in a synchronised way in a small space, and the effect is called Localised Surface Plasmon Resonance (LSPR). When the frequency of this oscillation is the same as the frequency of the light that it generated it (i.e. the incident light), the plasmon is said to be in resonance with the incident light.

LSPR energy is **sensitive to the dielectric function of the material and the surroundings, and to the shape and size of the nanoparticle**. This means that if a ligand, such a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes. Similarly, the LSPR effect is sensitive to other variations such as the distance between the nanoparticles, which can be changed by the presence of surfactants or ions. The LSPR effect has been observed not only on metal nanoparticles but also in nanorings, voids in metal films and other nanostructures (**Figure 10**).

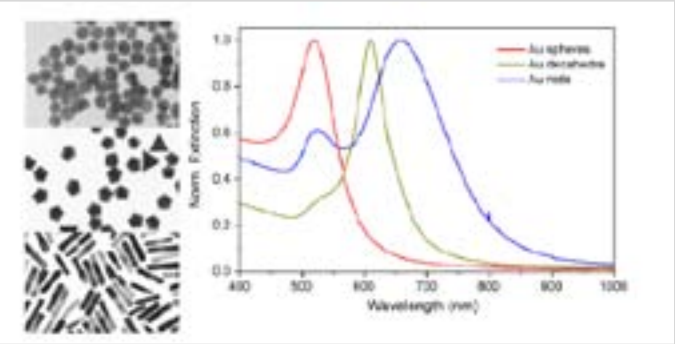

Figure 10: Transmission electron micrographs and UV-Visible spectra of gold nanoparticle colloids with various geometries: (top) spheres, (middle) decahedra and (bottom) rods

Image: Borja Sepúlveda et al., 'LSPR-based Nanobiosensors', *Nano Today*, 2009, 4(3), 244–251, reprinted with the permission of Elsevier

One of the consequences of the LSPR effect in metal nanoparticles is that they have **very strong visible absorption** due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold or silver can display **colours which are not found in their bulk form**, such as red, purple or orange, depending on the shape, size and surrounding media of thenanoparticles. An example has already been illustrated in **Figure 1**, which shows that a colloid of gold nanoparticles about 15 nm in size is ruby-red! The properties of metal nanoparticles make them useful in **sensing**.

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The applications of metal nanoparticles are discussed in **Module 1, Chapter 5: Overview of nanomaterials** and **Module 2, Chapter 4: Medicine and healthcare**.

Colour in semiconducting nanocrystals (quantum dots)

As already mentioned, nano-sized semiconductors have quantised energy states; therefore, the conduction and the valence bands split and become discrete. Charge transfer occurs between these discrete levels, so only wavelengths of a certain dimension are absorbed: as a consequence, emission is monochromatic. Quantum confinement causes the energy of the band gap to increase: therefore, more energy is needed in order to be absorbed by the band gap of the material. Higher energy means shorter wavelength (blue shift). The same applies to the wavelength of the fluorescent light emitted from the nano-sized material, which will be higher, so the same blue shift will occur. Tuning the size of the semiconductor nanocrystal is a means of tuning the band gap and, therefore, the wavelength absorbed/emitted by the crystal. As a result, **the same material (e.g. CdSe) emits different colours depending on its size** (**Figure 11**).

Figure 11: Ten distinguishable emission colours of ZnS-capped CdSe QDs excited with a near-UV lamp

Image: *Nature Biotechnology*, 2001, 19:631–5, reprinted with the permission of Macmillan Publishers Ltd, © 2001

QDs are currently used as an **alternative to conventional dyes** in fluorescence microscopy and in other methods where dyes are used (e.g. dye-sensitised solar cells). QDs are also being studied as alternative light-emitting sources.

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The applications of semiconducting nanoparticles (quantum dots) are discussed in **Module 1, Chapter 5: Overview of nanomaterials** and **Module 2, Chapter 3: Energy** and **Module 2, Chapter 4: Information and Communication Technologies**.

From white to transparent materials

The scattering of visible light is responsible for the **white appearance of high-protection sunscreens**. Students will be familiar with these thick, white paste-like sunscreens that are often used on children and on adults with sensitive skin. These sunscreens contain **ZnO and TiO_2 clusters of about 200 nm**. Visible light interacts with these clusters and all of its wavelengths are scattered. The combination of the visible spectrum is white: therefore, the sunscreen appears white (as illustrated in the curve shown in **Figure 12**).

If the **dimensions of the cluster are reduced**, **for instance from 200 to 100 nm**, maximum scattering occurs around 200 nm and the curve is shifted towards shorter wavelengths, which are no longer in the visible spectrum: the effect is that the same material (e.g. ZnO), now in smaller size (100 nm), no longer appears white but transparent (**Figure 12**).

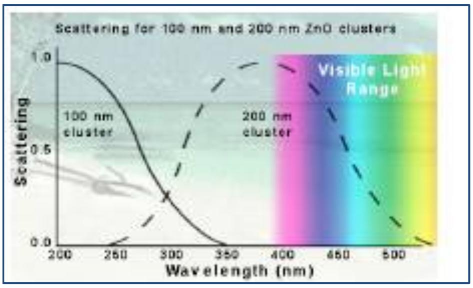

Figure 12: Scattering curves for 100 nm and 200 nm ZnO clusters

Image: reprinted from the NanoSense Curriculum Series 'Clear Sunscreen', © SRI International, 2005–08, Creative Commons Attribution ShareAlike 3.0

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The different light scattering of bulk and nano-sized ZnO and TiO_2 is exploited in the latest-generation sunscreens which appear transparent rather than white. This and other applications, including coatings for solar panels, are discussed in **this module, Chapter 5: Overview of nanomaterials**.

Magnetic properties

The magnetic properties of a magnet are described by its magnetisation curve. In general terms, the magnetisation curve of a ferromagnetic material is a plot of the total magnetisation of the sample versus the applied DC field with strength H, as illustrated in **Figure 13**.

Initially, as H increases, M increases until a saturation point Ms is reached. When H is decreased from the saturation point, M does not decrease to the same value it had before: rather, it is higher on the curve of the decreasing field. This is called **hysteresis**. When the applied field H is returned to zero, the magnet still has a magnetisation, referred to as **remnant magnetisation** M_r. In order to remove the remnant magnetisation, a field H_c has to be applied in the direction opposite to the field applied the first time. This field is called the **coercive field**.

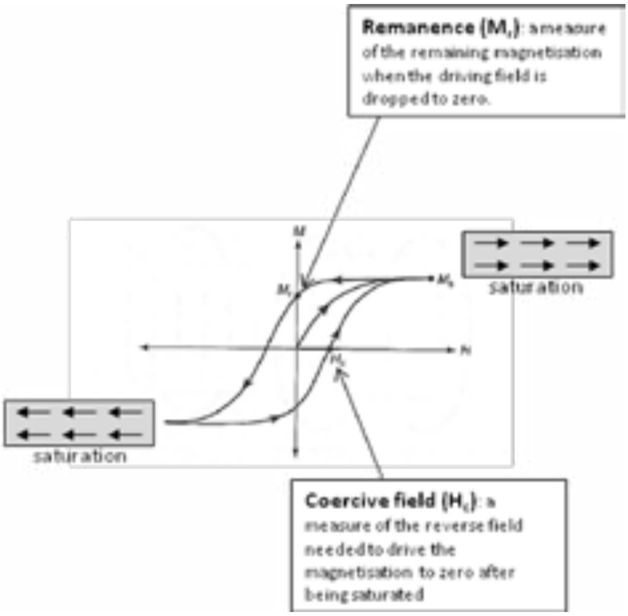

Figure 13: Magnetisation hysteresis loop showing the coercive field H_c, the remnant magnetisation M_r, and the saturation point M_s

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

The diverse **applications of magnets** require the magnetisation curves to have different properties. In general, for **soft magnetic materials** (e.g. those used in transformers and rotating electrical machinery), which are subject to rapidly alternating AC magnetic fields (so that they repeat the magnetisation curve many times), small or zero coercive fields are required to minimise the energy loss (in the form of heating) during operation. In the case of **permanent magnets** (hard magnets) used as part of high-field systems, large coercive fields are required and large hysteresis loops are sought, as well as high saturation magnetisations.

Nanostructuring of bulk magnetic materials can be used to design the magnetisation curve of the material, leading to soft or hard magnets with improved properties.

In general, the magnetic behaviour of a material depends on the structure of the material and on its temperature. In order to ‘feel’ a magnetic field, a material must have a non-zero net spin (transition metals). The typical size of expected magnetic domains is around 1 μm. When the size of a magnet is reduced, the number of surface atoms becomes an important fraction of the total number of atoms, surface effects become important, and quantum effects start to prevail. When the size of these domains reaches the nanoscale, these materials show **new properties due to quantum confinement**, for example the **giant magnetoresistance effect** (GMR). This is a fundamental nano-effect which is now being used in modern data storage devices. The effect of nanostructuring on magnetic materials in discussed in detail in **this module, Chapter 5: Overview of nanomaterials**.

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The GMR effect and its application to the data storage devices are discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

Mechanical properties

Some nanomaterials have **inherent exceptional mechanical properties** which are connected to their structure. One such material is **carbon nanotubes**: these are extremely small tubes having the same honeycomb structure of graphite, but with different properties compared to graphite. They can be single-walled or multi-walled, as illustrated in **Figure 14**. Carbon nanotubes are 100 times stronger than steel but six times lighter!! The different structures, properties and potential applications of carbon nanotubes are reviewed in the next chapter of **this module, Chapter 5: Overview of nanomaterials**.

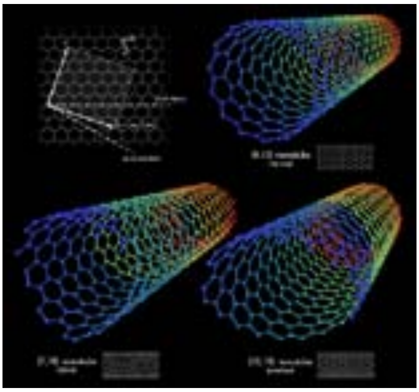

Figure 14: Types of carbon nanotubes

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Improving existing materials

Nanomaterials can also be used to **improve the mechanical properties of existing materials**. In this case, nanocomposites are formed.

One example is **nanocrystalline materials**, which are polycrystalline (i.e. made of many crystals which are identical but connected without orientation) and defined as materials with grain sizes from a few nanometres up to 100 nm. In contrast, the grain size in industrial metallic materials is about 10 000 nm or greater. These materials generally show improved mechanical properties (toughness, hardness, etc.).

Why is this so? A polycrystalline material (illustrated in **Figure 15**) has large pockets of regularity (crystals) in a ‘sea’ of atoms that are not ordered (amorphous region).

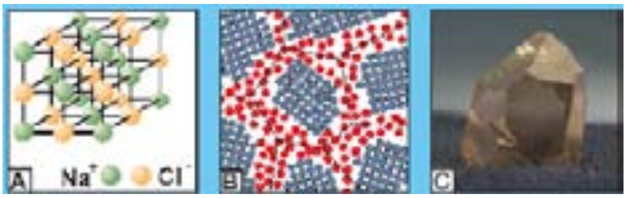

Figure 15: (A) structure of NaCl, where the vast majority of sodium and chlorine atoms are organised at a fixed distance from each other and always alternately (example of a single crystal); (B) structure of a polycrystalline material such as iron — large pockets of regularity are seen in a 'sea' of atoms that are not ordered (the blue atoms are organised in tiny single crystals, whereas the 'sea' consists of the red atoms where there is no crystal lattice); (C) SiO_2 crystal (quartz) which has the typical fracture surface of single crystals

Image: reprinted from 'Nanoteknologi– 12 historier om den nyeste danske nanoforskning', © iNANO, Aarhus University

Within the crystalline structures, there can be defects (cracks or dislocations). If subjected to mechanical stress, the polycrystalline materials can fracture because these defects allow the crack to propagate. To impede the movement of cracks and dislocations tiny particles (nanoparticles) of another material can be added in the lattice. Nanocrystalline materials can have vastly improved mechanical, magnetic, electrical, and catalytic properties and greater corrosion resistance compared to conventional materials with large grains.

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What can these materials be used for? Nanocrystalline materials are already used in the form of hard coatings to protect tools in industry, such as **cutting tools**, where they are making a great impact in improving tool performance and lifespan. **Nanoparticles added to a ceramic**, such as alumina, also increases its mechanical properties, and the same applies to the addition of **nanomaterials (such as carbon nanotubes) to polymers**. The possibility of using nanomaterials for improving the mechanical properties of materials involves both inorganic and organic (polymeric) composites. Both these types of **nanocomposites** are discussed in detail in **this module, Chapter 5: Overview of nanomaterials**. These materials have a very broad spectrum of utility, ranging from improved metals to improved plastics.

CHAPTER 5:

OVERVIEW OF NANOMATERIALS

Nanoscience will impact the design and fabrication of new materials with innovative properties and functions. Contributions to this field are very widespread, and include enhancing the properties of plastics, ceramics, coatings, composites, fibres and many more. Nanoscience also introduces an entirely new concept in material design, the bottom-up approach of material self-assembly, which is directly inspired from how organic and inorganic materials are created in nature. As a matter of fact, as shown in the first section, nature is a great source of inspiration to materials engineers, since many natural nanomaterials perform extraordinary functions as a result of their inner nanostructure.

This chapter provides an overview of nanomaterials, their properties and functions. The application areas of the cited nanomaterials are also mentioned. The second module of this Teachers Training Kit is devoted to applications of nanotechnologies.

The question: **What is a'nanostructured material'?** must be considered before discussing examples of various functional nanomaterials. Nanostructured materials are solids or semi-solids (e.g. hydrogels, liquid crystals) characterised by a *nano-sized inner structure*. They vary differ from crystalline, microstructured and amorphous solids because of the scale order. In crystalline solids, the atoms are neatly arranged in a grid where the distance between neighbouring atoms is well defined, and this order extends to macroscopic dimensions. In contrast, microstructured materials show structural variation only on a micron scale, whereas amorphous materials exhibit short-range order only. In nanostructured materials, the spatial order is at the nanoscale, which lies between the microscopic and the atomic scale.

The size of the nanostructures and the scale order within them in the solid impacts the properties of a material. Nanostructured materials differ from conventional polycrystalline materials in the size of the structural units of which they are composed. They can exhibit properties that are drastically different from those of conventional materials, and this is often a direct consequence of *the large fraction of grain boundaries* (i.e. the space between the nanostructures) in the bulk material. **This means that in a nanostructured material there is a large proportion of surface atoms** (i.e. atoms that are located at or near a surface). Due to the large surface area, bulk properties become governed by surface properties. This surface — also called an **interface** — can form a border with the embedding matrix, a nanoparticle, air or vacuum in the case of a pore or defect.

Examples of nanostructured materials are nanoporous, nanocrystalline, nanocomposite and hybrid materials: **nanoporous** materials have nano-sized pores; a **nanocrystalline** material consists of many nano-sized crystalline domains; a **nanocomposite** material contains two or more phase-separated components with morphology of spheres, cylinders or networks with nano-sized dimensions (further divided into **inorganic and polymer nanocomposites**); and **hybrid materials** are made of a combination of organic and inorganic components interconnected at a molecular level (e.g. block copolymers). The materials within this chapter were categorised based on the function they serve, and for this reason, throughout the text, they are often cross-referenced: a nanocoating can be a nanocomposite but, because of its specific function, is described in a separate group.

One of the distinguishing features of **nanostructured materials is that they can have properties that differ significantly from those displayed in bulk**. This means that scientists have the opportunity to design new materials with specific functions by exploiting the intrinsic properties of nanomaterials. As a result, **coatings, plastics and metals with new properties can be made to fulfil specific functions**. As discussed in this chapter, numerous new materials are being developed with exciting properties. Although much research is still needed in this field, numerous commercial realities already exist and exciting new materials should be expected in the future. These materials have numerous applications that extend from the medical sector (e.g. antibacterial coatings) to improved cutting tools.

Biomimetic nanomaterials

The first class of engineered nanomaterials to be reviewed is biomimetic materials. As mentioned in **Module 1, Chapter 2: Nanoscience in nature**, **nature is the best nanotechnology platform**. Over thousands of years of evolution, nature has developed an enormous array of materials, ranging from feathers to shells, wood, bone and many more that have intricate hierarchical structures at the nano, micron and macro levels which confer specific properties on the material, such as strength, lightweight, permeability, colour. Natural materials provide an amazing platform and inspire materials engineers to fabricate advanced materials that possess specific functions. As a matter of fact, numerous 'macro' materials we use today were developed after inspiration from natural materials. One example is Velcro, which was developed in 1948 by a Swiss engineer named George de Mistral who was inspired by the mechanism that enables *cockleburs* to cling to dog hair and fabric. Nanostructures in natural materials often play a crucial role, inspiring scientists to mimic them starting from a molecular level (molecular biomimetics). This is also called biomimetic nanotechnology. Now, some examples of these biomimetic nanomaterials are provided.

Gecko-inspired adhesive (or bio-rubber)

In **Chapter 2**, the adhesive properties of the gecko foot were discussed and, specifically, how these are not related to a glue in the foot, but rather to van der Waals and capillary forces exerted by millions of nanostructures (called setae) that make up the foot. This allows the animal to walk upside down, against gravity and on many different surfaces, including those which are wet. Moreover, a gecko can walk on a dirty surface without losing adherence, since its feet are also self-cleaning. A truly amazing material! Scientists have been inspired by this animal to design and fabricate adhesives for numerous applications. For instance, a group of researchers at the University of California, Berkeley, has developed adhesive gecko-foot-like surfaces for use in climbing robots. The adhesive is made of patches of microfibre arrays with 42 million polypropylene microfibre per square centimetre. The patches can support up to 9 N cm^{-2}: a 2 cm^2 patch can support a load of 400 g. This result is very close to the loads supported by a gecko, which are about 10 N cm^{-2}. This gecko-like adhesive is very similar in functionality to the natural gecko foot, but not as good—yet. Researchers still have to make it topography-independent (capable of attaching to any surface) and self-cleaning. At another university, a biomimetic gecko tape has been produced using polymer surfaces covered with carbon nanotube hairs, which can stick and unstick on a variety of surfaces, including Teflon®.

Other gecko-inspired nanomaterials are under development for medical applications, which will be covered in **Module 2, Chapter 1: Medicine and healthcare**.

Self-healing adhesives

Diatoms are a type of algae with nanostructured amorphous silica surfaces. Some diatom species have evolved strong self-healing underwater adhesives. Some are free-floating, others have adhesive properties in water: for instance, diatoms in the Antarctic seas can attach to ice. Others secrete viscous mucilage which binds colonies together while protecting the silica shells from wear as they rub against each other. Molluscs are another species that have **adhesive properties under water**. Both diatoms and molluscs have strong underwater glues that can also resist stress and self-heal if necessary. For these reasons, they serve as a biomimetic model for self-healing materials. Researchers have studied these natural adhesives and found that their self-healing properties are due to the properties of the proteins contained in them. These proteins have 'sacrificial' bonds that allow the molecule to be reversibly stretched by breaking and re-bonding. This sacrificial bond behaviour has been observed in many other materials, such as wool. The detailed analysis of these natural materials is inspiring new nano-adhesives with self-healing properties.

Biomimetic membranes, capsules and bioreactors

The bilipid membrane has served as a biomimetic model for decades. A simple example is liposomes (lipid vesicles) which are easily formed by shaking oil vigorously in water. Planar-supported bilayers are also inspired by the lipid membrane and are formed by simply 'dipping' a suitable substrate inside an organic aqueous phase.

Inside the cell, there are numerous self-assembled structures that encapsulate specific biomolecules and release them as a consequence of molecular signalling. These structures are inspiring a wide range of **nanocapsules for application in drug delivery**. In some cases, bacteria or viruses are used as templates for fabricating these nanocapsules. These nanomaterials are described in more detail in **Module 2, Chapter 1: Medicine and healthcare**.

Biomimetic energy nanomaterials

Many challenges that we are now facing in the energy area (improvements needed in solar panels, hydrogen fuel cells, rechargeable batteries, etc.) can be solved through the use of nano-engineered materials. Some of these materials have been developed following direct inspiration from nature, such as the new types of solar photovoltaic cells, which try to imitate the natural nanomachinery of photosynthesis. Another interesting example is that of using battery electrodes with self-assembling nanostructures grown by genetic engineered viruses.

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Both examples will be described in more detail in **Module 2, Chapter 3; Energy**.

NANOYOU GAME Nature-inspired nanomaterials are used in one of the NANOYOU jigsaw puzzle games (http://nanoyou.eu/en/play-nano.html) — students must match the nanomaterial to its application, connecting it to a specific need.

Self-assembled nanomaterials

The concept of self-assembly derives from the observation that, in natural biological processes, molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of the membrane cell from phospholipids. In self-assembly, *sub-units spontaneously organise and aggregate into stable, well-defined structures through non-covalent interaction*. This process is guided by information that is coded into the characteristics of the sub-units and the final structure is reached by equilibrating to the form of the lowest free energy. An external factor, such as a change in temperature or a change in pH, can disrupt this organisation. For instance, a protein self-assembles into a specific structure but, if exposed to conditions such as high heat or high acidity, it can denature, which means that its structure is damaged, and the protein unfolds. This means that the protein loses its function as its structure is damaged. So, in nature, self-organised structures have specific functions.

Molecules in nature change conformation and move from one self-organised structure into another as they bind to certain ions or atoms. Many examples are available, such as haemoglobin (which captures and releases an iron ion), or the potassium-sodium pump, chlorophyll, etc.

The use of self-assembly to create new materials is a **bottom-up approach to nanofabrication**, and is thus an essential tool in nanotechnology (see **Module 1, Chapter 7: Fabrication methods**). Instead of carving nanostructures out of larger materials (which is the typical top-down approach, such as micromachining and microlithography, used to fabricate integrated electronic circuits), nanostructures are created from the bottom, from atomic building blocks that self-assemble into larger structures. In the laboratory, scientists can make use of this self-organisation of matter as a way of programming the building of novel structures with specific functions. Examples of self-assembled nanomaterials include dendrimers, DNA nanostructures, cyclodextrins, self-assembled monolayers (SAMs), liquid crystals.

Self-assembled monolayers (SAMs)

Some organic molecules, when exposed from solution or vapour to a suitable substrate, self-assemble to produce homogeneous, densely packed layers of monomolecular thickness. These organic molecules have long chains with two different end groups. The monolayer is formed when one of the two end groups of the organic molecule reacts with a particular surface forming a chemical bond. The surface properties of the substrate are then defined by the exposed functional groups of the monolayer. For example, alkyl-silane or alkane thiol molecules exposed to a silica or metal surface assemble into organised layers. SAM-forming materials may be physisorbed layers, such as Langmuir-Blodgett films, or chemisorbed layers, such as organosilanes bonded to silica or organothiols bonded to gold. Films of mixed SAMs with tailored surface properties can be fabricated by mixing two (or more) precursor molecules and photosensitive SAM layers can be produced by molecularly engineering the precursor to include a photoreactive species. Whitesides and his co-workers from Harvard University have introduced the use of mixed SAMs of **alkanethiols on gold surfaces** to control protein and cell adhesion. SAMs of alkanethiol on gold are formed when a gold surface is exposed to a solution or to the vapour of an alkanethiol. The sulphur atoms of the alkanethiols coordinate with the gold surface, while the alkyl chains are closely pack and tilted to 30° from the surface normal. The terminal end group of a ω-substituted alkanethiol determines the surface properties of the monolayer.

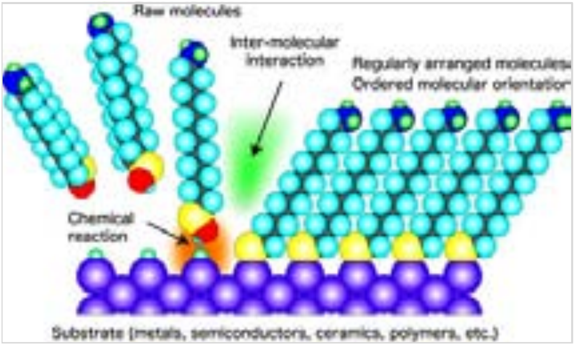

Figure 1: Schematic representation depicting the formation of a self-assembled monolayer on a surface

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Surfaces with micron and nanopatterns of SAMs are interesting since they allow the creation of **metallic** '**hybrid**' circuits where biomolecules can be selectively attached (and released) to patterns of gold. Different methods exist for creating micro and nanopatterns of SAMs, such as microcontact printing (µCP), nanocontact printing (nCP), conventional lithography and Dip Pen Nanolithography®. The details of these fabrication methods are discussed in **Module 1, Chapter 7: Fabrication methods**.

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SAMs are extremely useful in **thin-film technology** since they provide a simple, versatile and relatively inexpensive way of producing **coatings with specific functionalities**. Thin coatings are used in many applications, for example to control surface wetting and adhesion properties; to provide chemical resistance or specific biocompatibility; to confer antibacterial properties; and for sensors (see also: **Nanocoatings** in this chapter and **Module 2, Chapter 2: Environment**). SAMs are particularly interesting for developing DNA and protein micro and nanoarrays for medical screening (see **Module 2, Chapter 1: Medicine and healthcare**) and for future electronic components in computer chips and other ICT developments (see **Module 2, Chapter 4: Information and Communication Technologies**.

Liquid crystals

A liquid crystal is a fourth state of matter: it has properties between those of a conventional liquid and those of a solid crystal. Like a liquid, it flows, and, like a crystal, it can display long-range molecular order (**Figure 2**). In terms of classifications, liquid crystals (together with polymers and colloids), are often classified as 'soft matter' (**Figure 3**) and treated under the branch of physical chemistry of condensed matter.

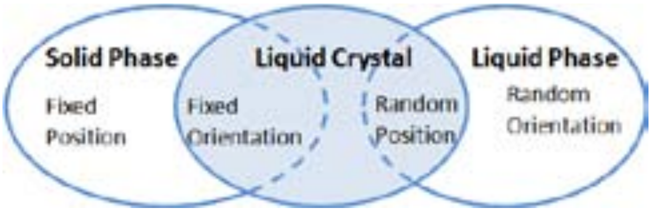

Figure 2: The liquid crystal phase is in between a solid and a liquid phase

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

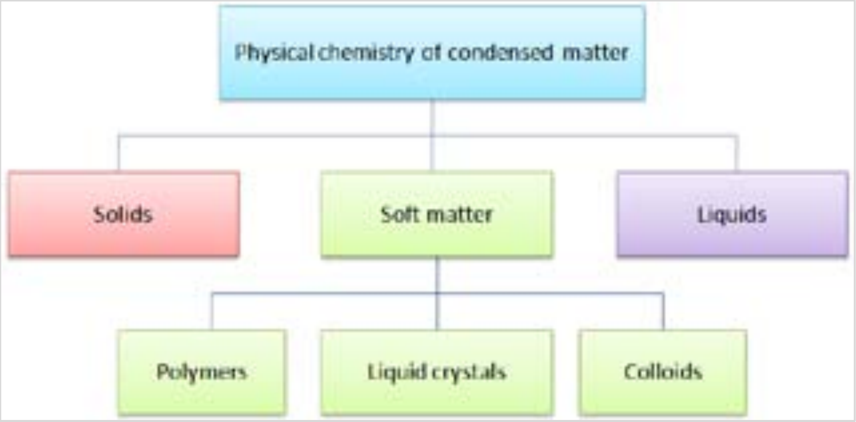

Figure 3: Diagram showing where the branch of 'liquid crystals' fits into the classification of physical chemistry of condensed matter

A fascinating and characteristic feature of liquid-crystalline systems is that they change their molecular and supermolecular organisation drastically as a result of very small external disturbances: the molecules in liquid crystal displays, for instance, are reoriented by relatively weak electrical fields. If a small amount of chiral molecules are dissolved in an achiral liquid-crystalline host phase, remarkable macroscopic chirality effects occur, ranging from helical superstructures to the appearance of ferroelectricity.

Liquid crystal self-assembly

Liquid crystals are partly ordered materials, somewhere between their solid and liquid phases. This means that liquid crystals combine the fluidity of ordinary liquids with the interesting electrical and optical properties of crystalline solids.

Molecules of liquid crystals are often shaped like rods or plates or some other form that encourages them to align collectively along a certain direction (**Figure 4**).

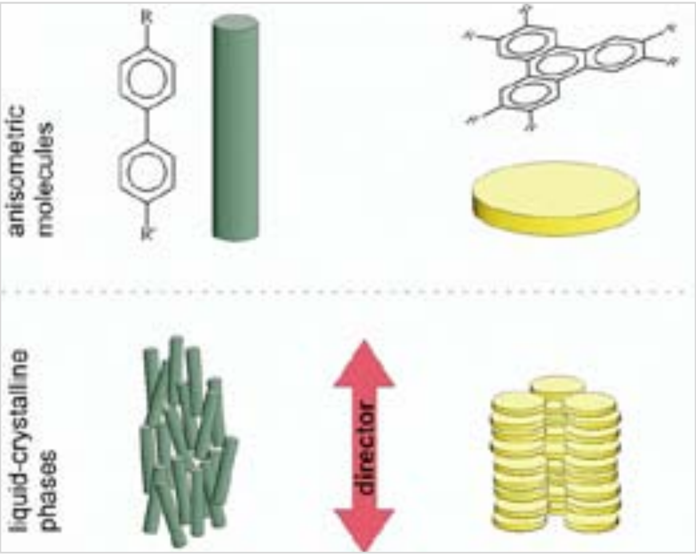

Figure 4: Example of the self-organisation of anisometric (i.e. with asymmetrical parts) molecules in liquid-crystalline phases

Left: Rod-like molecules form a nematic liquid, in which the longitudinal axes of the molecules are aligned parallel to a common preferred direction (director).

Right: Disc-like (discotic) molecules arrange to molecule-stacks (columns), in which the longitudinal axes are also aligned parallel to the director. As a result of their orientational order, liquid crystals exhibit anisotropic physical properties, just like crystals.

Image: http://www.ipc.uni-stuttgart.de/~giesselm/AG_Giesselmann/Forschung/Fluessigkristalle/Fluessigkristalle.html

Liquid crystals are **temperature sensitive** since they turn to solid if it is too cold and to liquid if it is too hot. This phenomenon can, for example, be observed on laptop screens when it is very hot or very cold.

Phases of liquid crystals and their properties

A liquid crystal is formed by the self-assembly of molecules into ordered structures, or phases. An external disturbance, such as a change in temperature or magnetic field, even very small, can induce the liquid crystal to assume a different phase. Different phases can be distinguished by their different optical properties (**Figure 5**).

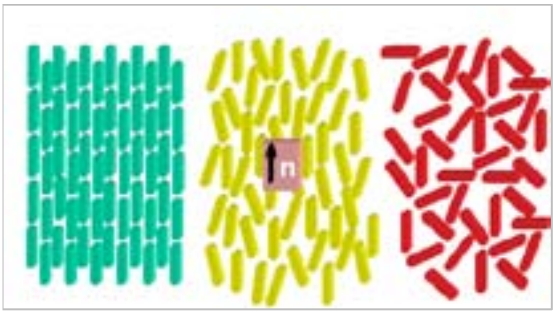

Figure 5: Schematic representation of molecules in a solid (left, molecules are well organised), in a liquid crystal (centre, molecules have a long range distance order) and in a liquid (right, molecules are not ordered)

Image: © IPSE Educational Resources, University of Wisconsin-Madison

Liquid crystals are divided into three groups:

- **thermotropic liquid crystals** consist of organic molecules, typically having coupled double bonds, and exhibit a phase transition as temperature is changed (**Figure 5, left**);
- **lyotropic liquid crystals** consist of organic molecules, typically amphiphilic (water-loving) and exhibit a phase transition as a function of both temperature and concentration of the liquid crystal molecules in a solvent (typically water) (**Figure 5, right,** and **Figure 6**);
- **metallotropic liquid crystals** are composed of both organic and inorganic molecules, and their liquid crystal transition depends not only on temperature and concentration but also on the organic-inorganic composition ratio.

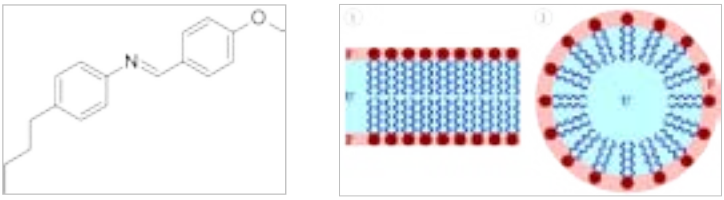

Figure 6: (left) Chemical structure of N (4-methoxybenzylidene)-4-butylaniline (MBBA); (right) structure of a lyotropic liquid crystal: (1) is a bilayer and (2) is a micelle (the red heads of the surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue).

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

Lyotropic liquid-crystalline phases are **abundant in living systems**, such as biological membranes, cell membranes, many proteins (such as the protein solution extruded by a spider to generate silk), as well as tobacco mosaic virus. Soap is another well-known material which is in fact a lyotropic liquid crystal. The thickness of the soap bubbles determines the colours of light they reflect.

Liquid crystal applications

The order of liquid crystals can be manipulated with mechanical, magnetic or electric forces. What is interesting is that this change of order can be obtained with very small variations of these forces. The properties of liquid crystals are useful in many applications. The colour of some liquid crystals depends on the orientation of its molecules, so any influence that disturbs this orientation (e.g. a difference in magnetic or electric field, temperature, or the presence of certain chemicals) can be detected with a colour change.

EXPERIMENT

EXPERIMENT B in the **NANOYOU Experiment Module** deals with synthesising and testing different temperature sensitive liquid crystals. In this experiment, students test how different liquid crystals are sensitive to different temperature ranges and build an liquid crystal thermometer.

READ MORE

The details of how a thermotropic liquid crystal works are described in the **background document** for **EXPERIMENT B** in the **NANOYOU Experiment Module**.

Liquid crystals are routinely used in **displays** for cell phones, cameras, laptop computers and other electronics. In these displays, an electric field changes the orientation of the molecules in the liquid crystal, and affects the polarisation of light passing through them. Because of their sensitivity to temperature, and the property of changing colour, they are also used in thermometers. In miniaturised sensors, liquid crystals can detect certain chemicals, electric fields and changes in temperature.

READ MORE

Liquid crystal displays (LCDs) are discussed in **Module 2, Chapter 4: information and Communication Technologies**.

In the future, liquid crystals might have very interesting applications. Recently, it has been found that the inclusion of specific molecules, often in the order of nanometres, in the liquid crystal can lead to inherent new electrical and optical properties. For example, liquid crystal materials have been modified to induce new photonic functions and for application in waveguides and optical storage (ICT application area). Another class of liquid crystals under development is photoconductive liquid crystals, which aim to use new materials in photovoltaic cells and light-emitting diodes (Energy application area). Another area of study is the modification of liquid crystals in such ways that allow them to be used in stimuli-responsive materials and as templates for nanoporous polymers (potential nanomedicine application area).

Nanostructured metals and alloys

This section covers metal nanoparticles — nanocrystalline materials consisting of a single metal or of alloys made of two or more metals and nanostructured metal surfaces.

Metal nanoparticles

Metal nanoparticles are a clear example of how the properties of matter can change at the nanometre scale. For instance, metal gold is notably yellow in colour and used for jewellery. As the noblest of all metals, gold is very stable (e.g. it does not react with oxygen or sulphur). However, if gold is shrunk to a nanoparticle, it changes colour, becoming **red if it is spherical** (**Figure 7**) and even **colourless if it is shaped in a ring**. Moreover, gold nanoparticles become very reactive and can be used as **new catalysts** (this is discussed in **Module 2, Chapter 2: Environment**).

Figure 7: Gold colloid is ruby-red, not golden!

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Plasmonic structures

Noble metal nanoparticles, meaning gold, silver, platinum and palladium nanoparticles, show localised surface plasmon-resonances (LSPR), an effect that was described in **Module 2, Chapter 4: Fundamental 'nano-effects'**. **The energy of the LSPR depends on the particle shape, size, composition, inter-particle spacing and dielectric environment**. The surface of the nanoparticles can be functionalised with numerous chemical and biochemical molecules enabling specific binding of organic molecules such as antibodies, making them useful in **sensors**.

For this reason, they are of special interest for optical detection and sensing in analytical chemistry and molecular biology. The refractive index can be used as the sensing parameter: changes in the local dielectric environment, induced by the sensing process, are used to detect the binding of molecules in the particle nano-environment. The change in aggregation between the nanoparticles as a result of analyte attachment affects the LSPR energy, so this effect can be used for highly miniaturised sensors. **Figure 8** schematically illustrates these two LSPR-based detection methods.

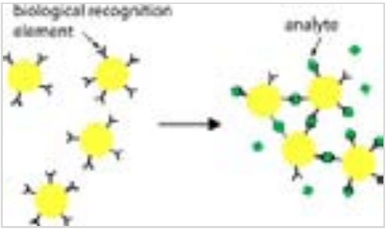

Figure 8: Top: LSPR sensor based on a change in refractive index induced by analyte attachment to a functionalised surface; bottom: LSPR sensor based on a change in nanoparticle aggregation induced by attachment to functionalised nanoparticles

Localised surface plasmons have been investigated in a range of nanoparticle shapes such as disks, triangles, spheres and stars. More complex structures have also been studied, such as holes in thin metal films, nanoshells and nanorings. Based on nanostructured metallic surfaces, a variety of optical applications are possible. An important feature of plasmonic structures is that they allow label-free detection, which is important in optical sensing. Currently, plasmonic components are being investigated with respect to future applications in cancer therapy, solar cells, waveguides, optical interconnection, camera LEDs, OLEDs and more.

The application of metal nanoparticles in medical diagnostics and targeted treatment is discussed in detail in **Module 2, Chapter 1: Medicine and healthcare**.

Reinforcements

Metal nanoparticles are used as **reinforcement in alloys for applications in lightweight construction** within the aerospace sector and, increasingly, the automotive sector. The method is used, for example, to harden steel. For instance, titanium nanoparticles are used as an alloy compound in steel, and the resulting material shows improved properties with respect to robustness, ductility, corrosion and temperature resistance. Particles of iron carbide are also precipitated in steel to make it harder. The nanoparticles block the movement of the dislocations in the crystalline material (this effect was described in detail in **Module 1, Chapter 4: Fundamental 'nano-effects'**) increasing the hardness. The trade-off between steel strength and ductility is an important issue, since modern construction requires high strength whereas safety and stress redistribution require high ductility. The presence of hard nanoparticles in the steel matrix could lead to a material with a combination of these properties, effectively matching high strength with exceptional ductility.

Environmental applications

Some forms of metal nanoparticles have important environment applications.

- **Zero-valent (Fe^0) iron nanoparticles** are under investigation for the remediation of contaminated groundwater and soil. Iron, when exposed to air, oxidises easily to rust; however, when it oxidises around contaminants such as trichloroethylene (TCE), carbon tetrachloride, dioxins, or PCBs, these organic molecules are broken down into simple, far less toxic carbon compounds. Iron nanoparticles are more effective than conventional 'iron powder', which is already used to clean up industrial wastes. Iron nanoparticles are 10 to 1 000 times more reactive than commonly used iron powders.
- **Silver nanoparticles** have a strong antibacterial capacity. They are used in numerous products to prevent or reduce the adherence of bacteria to surfaces.

Metal nanoparticles and their use in environment applications are covered in **Module 2, Chapter 2: Applications of nanotechnologies — Environment**.

Nanocrystalline metals

Nanocrystalline metals are classic metals and alloys that have an ultra-fine crystalline structure below 100 nm. They exhibit **extraordinary mechanical and physical properties** which make them interesting for many applications. Examples of nanocrystalline metal materials are aluminium, magnesium, and Al-Mg alloys which offer high strength and are lightweight. Other examples are titanium and Ti-Al alloys.

Some crystalline metals offer **exceptional magnetic properties**. An example is the Finemet® nanocrystalline soft magnetic alloys, which consist of melt-spun Fe-Si-B alloys containing small amounts of niobium and copper.

The application of nanomaterials in the field of magnetic materials is very important and promising, with applications in magnetic recording, giant magnetoresistance, magnetic refrigeration and magnetic sensing. These novel materials are composed of magnetic nanoparticles dispersed in a magnetic or non-magnetic matrix (particle-dispersed nanocomposites) or of stacked magnetic thin films (magnetic multilayer nanocomposites).

READ MORE

Applications of **nanostructured magnetic materials for memory storage** are discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

Ferrofluids

Ferrofluids are **colloidal mixtures composed of ferromagnetic or ferrimagnetic nanoparticles** (such as magnetite) suspended in a carrier fluid, usually an organic solvent or water. The ferromagnetic nanoparticles are coated with a surfactant to prevent agglomeration (due to van der Waals and magnetic forces). Although the name may suggest otherwise, ferrofluids do not display ferromagnetism, since they do not retain magnetisation in the absence of an externally applied field. Rather, they display bulk-like paramagnetism, and are often referred to as 'superparamagnetic' materials due to their large magnetic susceptibility. When a paramagnetic fluid is subjected to a sufficiently strong vertical magnetic field, the surface spontaneously forms a regular pattern of corrugations; this effect is known as the normal-field instability (**Figure 9**).

Figure 9: Ferrofluid with a magnet underneath

Image: G. F. Maxwell, Wiki Commons, GNU Free documentation licence

Students can see the fascinating properties of a ferrofluid through the **Ferrofluid** activity — Activity 5 in the *timefornano* NanoKIT (http://www.timefornano.eu/nanokit#ac06).

Ferrofluids have **numerous applications**: in mechanical engineering, particularly for vehicle suspension and breaking systems, due to their low-friction properties; in the ICT area, as liquid seals (ferrofluidic seals) around the spinning drive shafts in hard disks; and in the biomedical sector as drug carriers.

Ferrofluids are also fascinating to artists. An excellent video produced by two Japanese artists for the *timefornano* video competition is available online (http://www.youtube.com/user/timefornano#p/c/B69761C355310861/0/me5Zzm2TXh4), an example of 'Nano and Art'.

Shape-memory alloys

Most metals are very hard and take a lot of effort to deform, but once they have been moulded into shape, they will stay like that until another force changes them. Memory metals, or 'shape-memory alloys' (SMAs) are different. They can be 'programmed' to remember a specific shape and if the metal is bent or deformed, it quickly returns to its original configuration. This is because memory metal has **two distinct crystal structures at the nanoscale** and can be made to flip between them. Both are regular lattices. The so-called parent phase (or austenite phase) occurs when the metal is at higher temperatures (**Figure 10**). When shaped at high temperatures the metal will 'remember' this shape. As the metal cools, its crystal structure changes to the second (martensite) phase. Gentle heating of the metal makes it return to its original parent shape.

TIP FOR TEACHERS: An analogy can be made between thermotropic liquid crystals (LCs) and shape-memory alloys: in both materials there is a change in nanostructure as its temperature is changed, with a 'macroscopic' effect visible (i.e. a change in colour in the case of the liquid crystals, and a physical deformation in the shape-memory). The two materials differ dramatically in the type of nanostructure involved: a 'soft' structure in the case of the liquid cystals (see '**Liquid crystals**' in this chapter) and a crystalline structure in the case of the memory-alloy.

Glasses made of memory metal take advantage of the phenomenon 'pseudo elasticity'. In this instance, the metal is in its austenite phase at room temperature and the martensitic phase is brought about by applying a stress, rather than cooling. When the stress is removed, the metal reverts to its austenite phase and its associated shape. Nitinol is used in orthodontics for braces. Once the Nitinol is placed in the mouth, its temperature rises to ambient body temperature causing it to contract back to its original shape. This results in a constant force being applied to the teeth. Nitinol wires do not need retightening as often as they can contract as the teeth move, unlike conventional stainless steel wires.

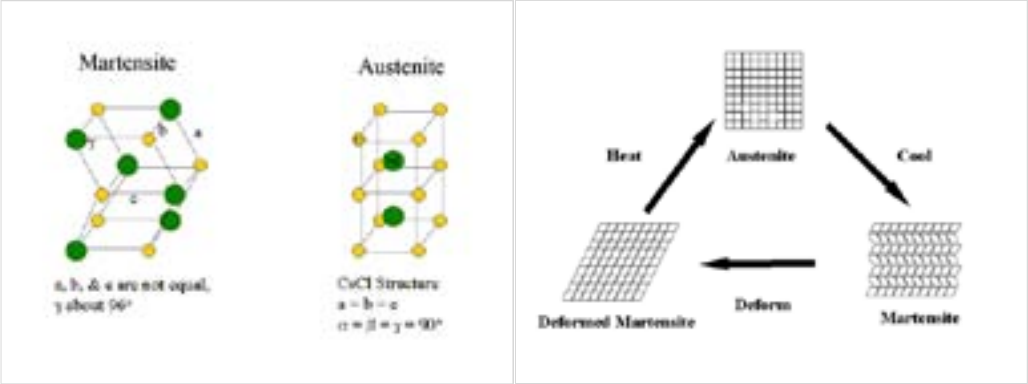

Figure 10: Left: Crystal structures of the two phases in a memory-shape alloy; right: schematic showing how the crystal lattice changes with temperature, 'remembering' its structure

Image: 'Memory Metal', Exploring the Nanoworld, University of Wisconsin-Madison (http://mrsec.wisc.edu/Edetc/background/memmetal/index.html), Creative Commons Nano-Commercial Attribution ShareAlike 3.0

Students can see the properties of a memory-shape alloy through the **Memory Metal** Activity — Activity 6 in the *timefornano* NanoKIT (http://www.timefornano.eu/nanokit#ac10.TXh4).

Polymers

A polymer is a large molecule made of a chain of individual basic units called monomers joined together in sequence. A copolymer is a macromolecule containing two or more types of monomers. When the polymer is a good conductor of electricity, it is referred to as conductive polymer (or organic metal). In this section, nanostructuring of polymers and the effect this can have on the properties of polymers are described. The focus is on copolymers since these are extremely useful in nanotechnologies.

Conductive polymers

Polymers that are good conductors of electricity are called conductive polymers and include polyacetylene, polyaniline, polypyrrole, polythiophene — many more have also been synthesised. These polymers are characterised by their alternating double-single chemical bonds, so they are π-conjugated. The π-conjugation of the carbon bonds along the oriented polymer chains provides a pathway for the flow of conduction electrons and is thus responsible for the **good electrical conduction properties of the material**. A detailed SEM analysis of conductive polymers has revealed that these are made of a a sequence of metallic nanoparticles about 10 nm in diameter. **The high conductivity of polymers such as polyacetylene and polyaniline is related to the nanostructure of the polymer**. Polyaniline and its analogues **change colour** when a suitable voltage is applied, or when reacting with specific chemicals (electrochromic and chemochromic). For this reason, they are promising for use in light-emitting diodes (LEDs). Other applications are the surface finish of printed-circuit boards, corrosion protection of metal surfaces, semi-transparent antistatic coatings for electronic products, polymeric batteries and electromagnetic shielding.

Block copolymers

A copolymer is a macromolecule containing two or more types of monomers and a block copolymer comprises these basic units or monomer types joined together in long individual sequences called blocks. An example is the diblock polymer (A)m(B)n, which is made of a linear sequence of m monomers of type A joined together to a linear sequence of n monomers of type B. A transition section joints the two blocks:

[end group]-[polyA]m-[transition member]-[polyB]n-[end group]

Often, block copolymers are made of a **hydrophilic (water-attractive) block, and a hydrophobic (water-repellent) block**. In general, macromolecules having hydrophilic and hydrophobic regions, such as lipids, **self-assemble in ordered structures when in water**: the hydrophobic region packs together, avoiding the water molecules, leaving the hydrophilic molecules to the exterior of the structure. In the same way, block copolymers made of hydrophilic and hydrophobic blocks when mixed in a selective solvent, such as water, can self-assemble into ordered architectures at the nanoscale level.

The geometry and degree of order of these structures depends on the concentration and the volume ratio between insoluble and soluble blocks. Depending on these parameters, the block copolymer can form **spherical micelles (nanospheres), cylindrical micelles and membranes**. Both cylindrical and spherical micelles consist of a non-soluble (hydrophobic) core surrounded by a soluble corona. Membranes are made up of two monolayers of block copolymer aligned to form a sandwich-like membrane: soluble block-insoluble block-soluble block. Molecules that, at low concentration, form spherical aggregates will assemble into cylindrical and eventually membrane-like structures as the concentration is increased (**Figure 11**).

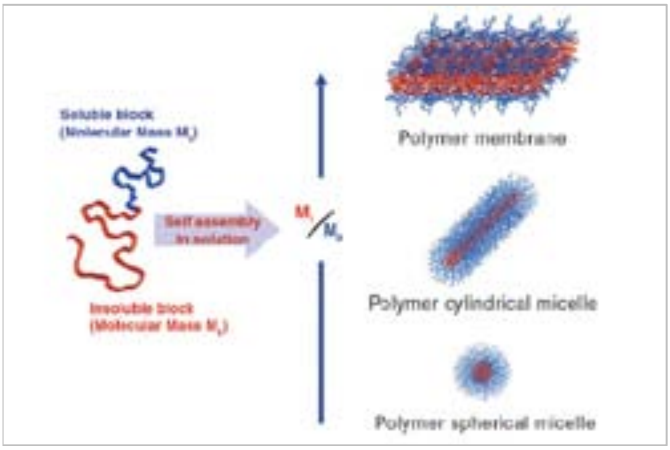

Figure 11: Different geometries formed by block copolymers in selective solvent conditions

Image: adapted from Smart et al., *Nano Today*, 2008, 3:3–4, 38–45, reprinted with the permission of Elsevier, © 2008

Among spherical micelles, if the lengths of the projections formed by the hydrophilic corona are short compared to the sphere diameter, the nanostructure is called a 'hairy nanosphere', whereas if the sphere is small and the projections long, it is called a 'star polymer' (**Figure 12**).

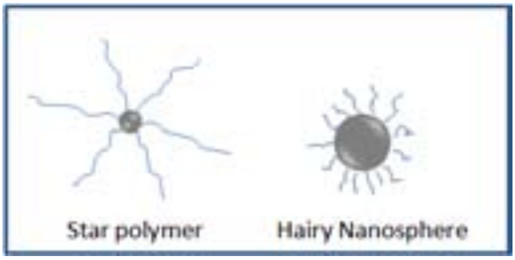

Figure 12: Sketch of a star polymer and a hairy polymer

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Responsive 'smart' polymers

Block copolymers form nanostructures that are **very sensitive to external fields**. For example, moderate electrical fields or shear stimulation can trigger macroscopic rearrangements in specific directions. This is a versatile property for making **materials that respond and change on demand**. The intrinsic macromolecular nature of these copolymers leads to very slow and kinetically controlled phase transitions. Thus, metastable or intermediate phases have longer lifetimes, which is desirable in applications that want to exploit the phase transition properties of these materials.

Biomedical applications

The ability of block copolymers to form nanoparticles and nanostructures in aqueous solutions makes them particularly useful for biomedical applications, such as therapeutics delivery, tissue engineering and medical imaging. In the field of **therapeutic delivery**, materials that can encapsulate and release drugs are needed. Hydrogels are very useful for the controlled release of drugs and block copolymer hydrogels are particularly advantageous for the possibility of conferring some stimuli-activated properties, such as temperature-sensitivity. Block copolymers form nanostructures with both hydrophilic and hydrophobic areas, so they can form vesicles that can encapsulate and carry both hydrophobic and hydrophilic therapeutic agents. Micelles formed using block copolymers have a hydrophilic corona that makes them more resistant to the interaction of proteins, in particular plasma proteins; therefore, these types of micelles exhibit long circulation times *in vivo*. Insoluble domains can also be engineered to exploit the sensitivity of specific hydrophobic polymers to external stimuli such as pH, oxidative species, temperature and hydrolytic degradation.

Block copolymers are also of interest for preparing **scaffolds in tissue engineering** — for instance, very long micelles that mimic the natural extracellular have recently been prepared exploiting the self-assembly properties of a peptide copolymer.

Nanoreactors

The ability to generate **compartmentalised volumes at the nanometre level** is one of the fundamental mechanisms used by cells in synthesising biomolecules and performing the biochemical processes necessary for their function. This motif is now reassembled using block copolymer micelles and vesicles as **nanoreactors**. This approach has been employed incarrying enzymatic reactions in nano-sized compartments.

It has been shown that this approach can also be extended into a non-aqueous solvent. For instance, a recent work reports block polymer nanostructures in ionic liquid and the ability of micelles to shuttle from an aqueous solvent to an ionic liquid as a function of temperature: this opens the way to using block copolymer technology in more sophisticated synthesis routes.

Artificial moving parts

Block copolymers structures can also be used to mimic the ability of biomolecules to convert chemical energy into mechanical energy, for instance by using a pH-sensitive block copolymer whose micelles swell according to pH variation. Thus, these materials are being investigated to create artificial muscles or moving nanostructures.

Other applications

The application of block copolymers is not limited to the biomedical field. They can be used in conjunction with other materials to form block copolymer nanocomposites. For instance, star polymers are used in industry to **improve metal strength**.

Finally, block copolymers can form nanoporous membranes for applications in **filtering systems and fuel cell technology**.

Polymeric nanofibres

Nanostructured fibrous materials, or **nanofibres**, are an important class of nanomaterials, now readily available due to recent developments in electrospinning and related fabrication technologies. In contrast to conventional woven fabrics, they have the typical structure illustrated in **Figure 13**.

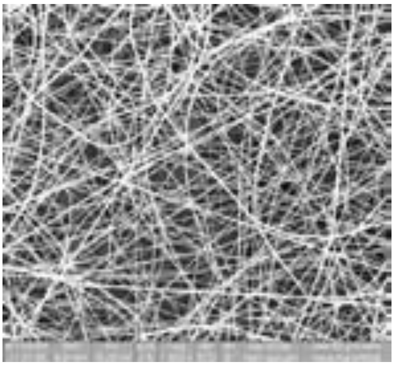

Figure 13: Typical sample of electrospun polystyrene

Image: T. Uyar, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, © 2008

Nanofibres have some unique properties: they are highly porous (i.e. they have a large interconnected void volume in the range of 50 % or even greater than 90 % and possess a very high surface-to-volume ratio). It is possible to increase the mechanical stability of nanofibrous structures by annealing the fabric so to join together the crossing points of those fibres. These properties make nanofibrous scaffolds useful for many biomedical and industrial applications.

In addition, researchers have succeeded in making **coaxial nanofibres composed on two different polymers** or composite coaxial fibres. Researchers are also trying to make **aligned nanofibres**. These types of materials, particularly if made of conducting polymers, could have important applications for electronic and medical devices.

Nanofibres have a **broad spectrum of applications** as schematised in **Figure 14**.

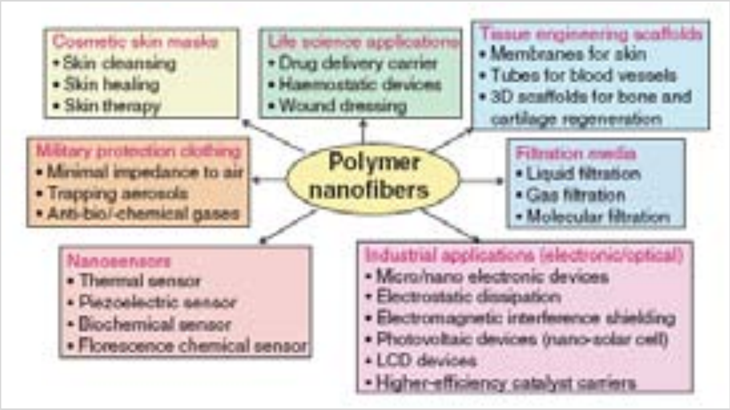

Figure 14: Overview of polymer nanofibre applications

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The two areas that have so far received most attention are the **medical field** (e.g. wound healing membranes) and **filtration applications**. These will be covered in **Module 2, Chapter 1: Medicine and healthcare** and **Module 2, Chapter 2: Environment**). Nanofibres are also being considered for composite material reinforcement. As nanofibres are a relatively recent type of nanomaterial, it is expected that many more applications will be explored in the future.

Semiconductors

Semiconductors, unlike metals, have a band gap. The band gap is between the valence band and the conduction band. In intrinsic semiconductors which possess no impurities (e.g. boron, germanium, indium, silicon), there are no electronic states in the band gap. The properties of semiconductors, in particular the band gap, are manipulated by the addition of dopants — impurities able to donate charge carriers in the form of electrons (n-type) or holes (p-type).

As with metals, the reduction in the size of the semiconductor triggers the insurgence of novel physical properties. The most evident example is that of quantum dots.

Quantum dots

Quantum dots are made of semiconductor materials, such as CdSe, ZnSe and CdTe, about 10 nm in size. As in the case of metal nanoparticles, electrons in quantum dots are localised in space.

A quantum dot (QD) has a discrete quantised energy spectrum, so it can absorb a specific wavelength and emit a **monochromatic colour**. Depending on their size, **QDs emit different colours**, as shown in **Figure 15**. The reason for this was explained in **Module 2, Chapter 4: Fundamental 'nano-effects'**: the width of the band gap is related to the size of the semiconductor, smaller sizes lead to a blue shift in the emission spectra.

Figure 15: Ten distinguishable emission colours of ZnS-capped CdSe quantum dots excited with a near-UV lamp: from left to right (blue to red), the emission maxima are located at 443, 473, 481, 500, 518, 543, 565, 587, 610, and 655 nm

Image: *Nature Biotechnology*, 2001, 19:631–35, reprinted with the permission of Macmillan Publishers Ltd, © 2001

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Quantum dots, like metal nanoparticles, hold great promise for nano-enhanced imaging which will bring progress to fields such as environmental monitoring, medical diagnostics and treatment. Quantum dots are also being investigated as novel light sources to improve LED technology and in solar cell technology. These applications of QDs in the energy and ICT sectors will be reviewed in **Module 2, Chapter 3: Energy** and **Module 2, Chapter 4: Information and Communication Technologies**.

Semiconducting oxides

Semiconducting oxides like TiO_2 and ZnO in bulk (macro) form are widely used in industry in many products. When they are in a nanoscale form, they display interesting physical properties that allow the design of new materials and the improvement of old. A short description of these properties follows.

Titanium dioxide

Titanium dioxide (TiO_2) is a mineral mainly found in two forms: rutile and anatase. Titanium dioxide is the most widely used white pigment because of its brightness (white colour) and very high refractive index (n = 2.4). It is used in paints, plastics, toothpastes, papers, inks, foods and medicines. In sunscreens with a physical blocker, titanium dioxide is used both because of its high refractive index and its resistance to discolouration under ultraviolet light. This is because TiO_2 is a UV filter: it absorbs UV light. Titanium dioxide, particularly in the anatase form, can be employed also as a photocatalyst under UV light. It oxidises water to create hydroxyl (OH) radicals and it can also oxidise oxygen or organic materials directly. For this reason, TiO_2 is added to confer sterilising, deodorising and antifouling properties to paints, cements, windows and tiles.

Titanium nanoparticles (30–50 nm, often referred to as **nano-TiO_2**) are at the centre of much attention due to their optical and catalytic properties: they retain the ability to absorb UV light but light scattering is dramatically reduced, so that TiO_2 goes from appearing white to transparent (a detailed explanation of this effect is given in **Module 1, Chapter 4: Fundamental 'nano-effects'**. **Nano-TiO_2** is thus suitable for transparent coatings, and for new-generation sunscreens, which are characterised by a high protective factor but transparent appearance. The catalytic properties of TiO_2 when nano-sized are also greatly enhanced by the large surface-to-volume ratio. This property is increasingly used for chemical catalysis applications such as photocatalytic purification of water and air to decompose organic pollutants (solar photocatalytic remediation). Thin films of TiO_2 are used on windows to confer self-cleaning properties on the glass (this application of nano-TiO_2 nanoparticles is reviewed in the section on nanocoatings).

ELSA and SAFETY TOPIC The use of nanoparticles in sunscreens is under much attention because some environmental organisations, such as Friends of the Earth Australia, have suggested that the nanoparticles used in these products can pass through the skin barrier and enter the bloodstream, causing unnecessary harm. To support this statement, they refer to research published on the toxicity of nano-titanium and nano-zinc oxide. These studies, though, often use amounts and exposure conditions (e.g. injection or inhalation) which are very different from what consumers of these sunscreens would be exposed to (cream rubbed on skin, amount and frequency of use, skin washed after some time, sun exposure, etc.). Manufactures claim that the nanoparticles used in the sunscreen formula are agglomerated: therefore, they have dimensions that don't allow for skin-penetration. Research seems to support this statement. Opponents reply that long-term studies must be performed before this can be demonstrated, and that skin types vary from person to person, not to mention cases of damaged skin, so generalisations are not possible yet (studies are mainly done *in vitro* using healthy skin). Overall, more research is called for by all stakeholders, including regulators, to establish the safety of these products.

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Another important application of nano-TiO_2 is in **organic solar cells**, such as the Grätzel solar cell, where nano-TiO_2 is used as acatalyst to promote light-induced electrical charge separation. The use of titanium dioxide in this type of solar cells is covered in more detail in **Module 2, Chapter 2: Environment**.

One limitation of using TiO_2 as a photocatalyst is that this material **only absorbs UV light**, which represents about 5 % of the solar spectrum. In this context, nanotechnology could bring an improvement in the form of nanoparticles with surfaces modified with organic or inorganic dyes to expand the photoresponse window of TiO_2 from UV to visible light.

NANOYOU DILEMMA The example of titanium dioxide in sunscreens is used in one of the NT Virtual Dialogue debates (http://www.nanoyou.eu/en/decide). In this dilemma, students consider the case of sunscreens with nanoparticles and reflect on their advantages and possible disadvantages.

Zinc dioxide

Zinc oxide (ZnO) has some similar properties to TiO_2 (i.e. its nanoparticles scatter light so it can be used for transparent UV filters, in creams or coatings). Like TiO_2, it is used for solar photocatalytic remediation but, compared to TiO_2, it has a weaker photocatalytic effect. Zinc oxide also suffers from the same limitation of absorbing only a fraction of the solar spectrum so research is underway to increase its photoresponse.

A peculiarity of ZnO is that it has a tendency to grow in **self-organised nanostructures**. By controlling crystal growth conditions, a variety of crystal shapes are possible. Researchers have been able to grow nanoscale wires, rods, rings, etc. (**Figure 16**). Zinc oxide nanocolumns are of particular interest since low-temperature photoluminescence measurements have revealed intense and detailed **ultraviolet light emission** near the optical band gap of ZnO at 3.37 eV. Thus, ZnO can act as an optical amplification medium and as a laser resonator.

Zinc oxide wires arrayed on a surface are also being investigated as piezoelectric elements for **miniaturised power sources**. This would allow the creation of flexible, portable power sources that could be included in textiles so that energy from body motion, light wind, air flow, etc., could be scavenged.

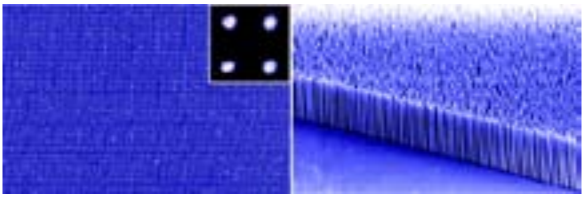

Figure 16: Patterned ZnO grown as vertical pillars in an arrayed format

Image: Xu et al., *Journal of the American Chemical Society*, 2008, 130:14958–14959, reprinted with the permission of the American Chemical Society, © 2008

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The use of ZnO for the development of miniaturised power sources is described in detail in **Module 2, Chapter 3: Energy**.

Indium tin oxide

Indium tin oxide (ITO) is a semiconducting material whose main feature is the **combination of electrical conductivity and optical transparency**. ITO is typically around 90 % indium(III)-oxide (In_2O_3) and 10 % tin(V)-oxide (SnO_2). It is widely used in its thin-film form as transparent electrodes in liquid crystal displays, touch screens, LEDs, thin-film solar cells, semiconducting sensors, etc. ITO is an **infrared absorber** and is currently used as a thermal insulation coating on window glass. Its anti-static properties make it additionally useful in applications such as the packaging and storage of electronic equipment. Since the material is very expensive, alternative materials, such as fluorescent tin oxides and aluminium zinc oxides are being considered. The use of ITO in 'smart coatings' is further discussed in the section on nanocoatings.

Photonic crystals

A photonic crystal consists of a lattice of periodic dielectric or metal-dielectric nanostructures that affects the propagation of electromagnetic waves. Essentially, photonic crystals contain regularly repeating internal regions of high and low dielectric constant. Photons (behaving as waves) propagate through this structure — or not — depending on their wavelength. The periodicity of the photonic crystal structure has to be of the same length-scale as half the wavelength of the electromagnetic waves (i.e. approximately 200 nm (blue) to 350 nm (red) for photonic crystals operating in the visible part of the spectrum). Such crystals have to be artificially fabricated by methods such as electron-beam lithography and X-ray lithography.

Photonic crystals exist in nature. For instance, in **Module 1, Chapter 2: Nanoscience in nature** it was shown how the beautiful blue wings of some butterflies owe their colour to their internal nanostructure, which is in fact a photonic crystal structure.

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Photonic crystals are receiving much attention at present because of their potential, in particular in the **optical communication industry**. Researchers are considering using **light and photonic crystals** (as an alternative to electrons travelling in wires) for the new-generation integrated circuits. Light can travel much faster in a dielectric medium than an electron in a wire, and it can carry a larger amount of information per second. Given the impact that semiconductor materials have had on every sector of society, photonic crystals could play an even greater role in the 21st century. Photonics and their impact in the ICT sector are analysed in **Module 2, Chapter 4: Information and Communication Technologies**.

Ceramic and glassy materials

Ceramic materials by definition are ionically bound; they are hard materials, both electrically and thermally very stable. Included in this category are, for example, Al_2O_3, Si_3N_4, MgO, SiO_2, Na_2O, CaO and ZrO_2. Ceramics are characterised by being **hard yet brittle**, therefore, in many cases, they are used as **composites** where they are mixed with other materials (e.g. metals) to increase their mechanical performance. Composite hard nanocoatings are particularly important for cutting tools (see the section on inorganic composites).

Ceramics exist both in a crystalline and non-crystalline form (e.g. the broad family of 'glass'). Nanostructures within the material have important consequences for their properties, as discussed in the next sections.

Porous alumina

Porous alumina membranes produced by anodic aluminium oxidation are characterised by having hexagonally close-packed channels with diameters ranging from 10 to 250 nm or greater. This material is often used as a **template** for the synthesis of other materials.

Zeolites

Zeolites are natural crystalline materials with pores having regular arrangements (**Figure 17**). They are also often used in the template synthesis of nanomaterial. They can also be used to prepare organised structures of a certain material to confer new optical properties on it. For instance, selenium can be incorporated into the channels of mordenite, a natural zeolite. The difference between a mordenite-selenium crystal and a natural selenium crystal is noteworthy: the optical absorption spectrum is considerably shifted to higher energies for the mordenite-selenium crystal.

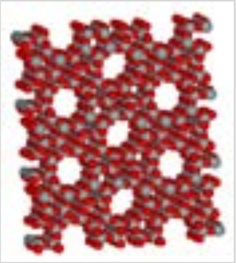

Figure 17: A schematic representation of a zeolite

Image: Wikimedia Commons, image for public domain

Aerogels

Silicon dioxide (SiO_2) is the main component of quartz. It is chemically robust and finds widespread applications. In commercial products, it appears as an additive in rubber products for vehicle tyres but it is also the component of new types of aerogels. Generally, an aerogel is considered as a solid with up to 95 % of the volume consisting of nanoscale pores. Aerogels are manufactured with a sol-gel technique and can be made of carbon, metal oxide, polymers or silicates.

Due to their **high porosity**, aerogels have an extremely high surface area and very low thermal conductivity. Thus they are suitable for **thermal insulation and as filter materials** (**Figure 18**). Another prominent property is their low specific weight, making them interesting for **lightweight construction**. Aerogels are also interesting for their optical properties, namely **high optical transparencies**. Silica aerogels are made of pores of about 10 nm arranged in distances between 10 and 100 nm. They are resistant and chemically inert to liquid metals, heat resistant up to 1 200 °C and non-toxic, thus they have also **biomedical applications**, such as substrates for cell growth and analysis. One of the problems of SiO_2 aerogels that needs to be addressed is that this material has to be expensively protected against humidity, since it is not water-resistant and suffers from a loss of stability and thermal conductivity once it gets wet.

Figure 18: The thermal insulating properties of a silica aerogel

Image: Wikimedia Commons, image for public domain

Carbon-based materials

In nature, there are some pure materials that have strikingly different properties even though they are made up of the same atoms. For instance, **graphite** and **diamond** (**Figure 19**): two very popular materials, one used conventionally in pencils and the other in jewellery. These two materials could not be more different: graphite is soft, light, flexible, and conducts electricity while diamond is extremely strong, hard and does not conduct electricity. Both materials are made of carbon atoms linked through strong bonds (covalent): in graphite, each carbon atom uses three out of its four electrons to form single bonds with its neighbours, forming a linear sheet, whereas, in diamond, each carbon atom uses all its four electrons to form four single bonds, resulting in a 3D structure. The different properties of graphite and diamond are a consequence of the different way the carbon atoms in the materials are bonded together.

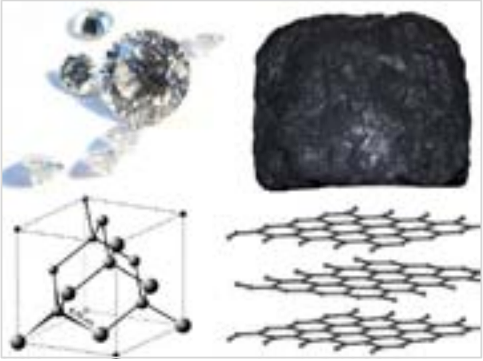

Figure 19: The two allotropes of carbon and their respective chemical structure: (left, top and bottom) diamond; (right, top and bottom) graphite

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

Graphite and diamond are two pure forms (**allotropes**) of carbon. In 1985, a new allotrope of carbon was discovered formed of 60 atoms of carbons linked together through single covalent bonds arranged in a highly symmetrical, closed shell that resembles a football. This material was officially named Buckminsterfullerene and is often referred to as buckyball, fullerene or simply C_60. Since its discovery, fullerenes with 70, 80 and even more carbon atoms have been discovered.

In the early 1990s, an incredible new carbon form was discovered: carbon nanotubes. These appear to be like graphite sheets rolled up with fullerene-type end caps, but have totally different properties compared to graphite. **Figure 20** shows different forms of carbon allotropes (images (d) and (h) are structures of C_60 and a nanotube, respectively).

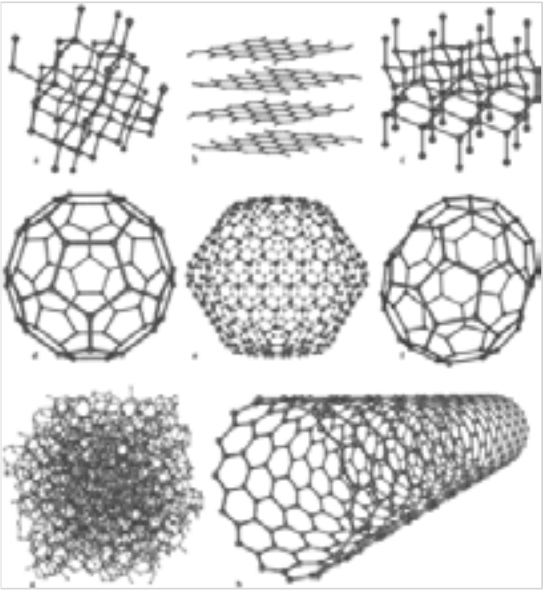

Figure 20: Eight allotropes of carbon: (a) diamond; (b) graphite; (c) lonsdaleite; (d) C_{60}; (e) C_{540}; (f) C_{70}; (g) amorphous carbon; and (h) a carbon nanotube

Image: Michael Ströc, GNU Free Documentation Licence

It is now known **that fullerenes and carbon nanotubes form naturally in common places like flames** (produced by burning methane, ethylene and benzene) and in soot. Scientists have now developed methods to synthesise these nanomaterials with control over their final properties.

Another exciting carbon-based nanomaterial is graphene which is the basic constituent of graphite (the material used in the lead of a pencil). Graphene is a layer of carbon atoms, just one-atom thick; although the thinnest material ever made, graphene is the strongest material ever measured, some 200 times stronger than steel and it is also the most conductive. This material was isolated in 2004 by Andre Geim and Konstantin Novoselov (University of Manchester) who used adhesive tape to repeatedly peel apart shavings of graphite until the pieces were just one atom thick. The scientists extensively investigated the amazing properties of graphene and were awarded the Nobel Prize in Physics in 2010 for their studies. Scientists believe in the future graphene could be used to make super-fast transistors and incorporated into plastics to make transparent electronics for flat panels and mobile phones.

Carbon nanotubes

Carbon nanotubes can appear as single-wall nanotubes (SWNTs), with a diameter of approximately 1.4 nm, or multi-wall nanotubes (MWNTs), consisting of 2–30 concentric tubes with an outer diameter of 30–50 nm. The structure of an SWNT can be conceptualised by wrapping a one-atom-thick layer of graphite sheet (grapheme) into a cylinder. To complete the nanotube, imagine adding two half fullerenes on each end of the nanotube.

Carbon nanotubes can range in length from a few tens of nanometres to several micrometres, and can have metallic properties (comparable to, or even better than, copper) or can be semiconductors (such as silicon in transistors), depending on their structure. These nanomaterials are truly amazing and have great potential in numerous fields as illustrated in **Figure 21**.

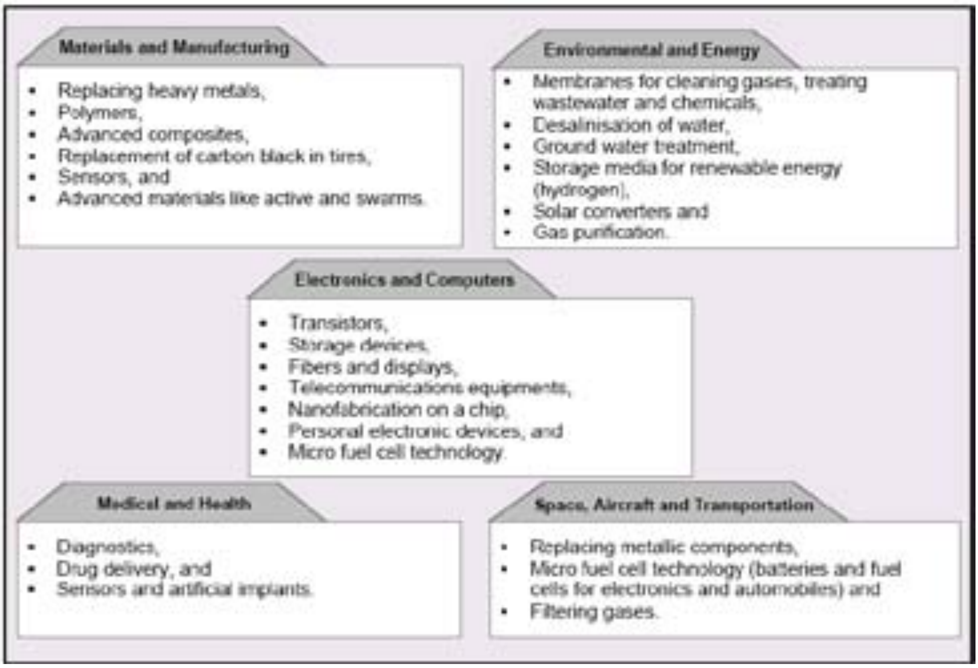

Figure 21: Overview of application areas of carbon nanotubes

Image: M. A. H. Hyder, Master Thesis, Technical University of Hamburg-Harburg, Germany, reprinted with the permission of the author, © M. A. H. Hyder, 2003

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The application of CNTs in the energy, environment, medicine and ICT sectors are covered in the respective chapters in **Module 2**.

Mechanical properties

The chemical bonding of nanotubes is composed entirely of sp^2 bonds (carbon double bonds) similar to those of graphite (whereas, in diamonds, all bonds are sp^3). This bonding structure, which is stronger than the sp^3 bonds found in diamonds, provides the molecules with their **unique strength**. Nanotubes naturally align themselves into 'ropes' held together by van der Waals forces.

Theoretical predictions say that carbon nanotubes are 100 times stronger than steel but only one sixth of its weight. Therefore, they are ideal in lightweight construction, for instance in the automotive and aviation industries. Carbon nanotubes are already used in some consumer products, such as tennis rackets to add strength (without compromising weight).

The mechanical properties of carbon nanotubes are summarised in **Table 1**. **Young's modulus** is a measure of how stiff, or elastic, a material is. The higher the value, the less a material deforms when a force is applied. **Tensile strength** describes the maximum force that can be applied per unit area before the material snaps or breaks. A third interesting measure of a material is its **density**, which gives an idea of how light it is. From **Table 1**, it can be seen that wood is very light but weak, whereas nanotubes are many times stronger than steel and yet much lighter.

Material	Young's Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm^3)
Single-wall nanotube	800	> 30	1.8
Multi-wall nanotube	800	> 30	2.6
Diamond	1 140	> 20	3.52
Graphite	8	0.2	2.25
Steel	208	0.4	7.8
Wood	16	0.008	0.6

Table 1: Properties of carbon alloptropes and other materials

Because of their mechanical properties, carbon nanotubes are very interesting as fillers in **polymeric and inorganic composites**.

Electrical and thermal properties

The electrical properties of a material are based on the movement of electrons and the spaces or 'holes' they leave behind. These properties are based on the chemical and physical structure of the material. In nanoscale materials, some interesting electrical properties appear. Carbon nanotubes are the best example of this effect at the nanoscale. If one considers 'building' a nanotube by rolling up a graphene sheet, the resulting nanotube can be conductive (and, indeed, very conductive!) or semiconductive with relatively large band gaps. The electrical properties of the nanotube depend on the way it was 'rolled up' (technically known as chirality). If it is rolled up so that its hexagons line up straight along the tube's axis, the nanotube acts as a metal (conductive). If it is rolled up on the diagonal, so the hexagons spiral along the axis, it acts as a semiconductor.

Why is this so? Graphene (that is, one layer of graphite) is not an insulator, but also neither a metal nor a semiconductor; it has electrical properties somewhere in between and is called a semi-metal. When rolled up, it leads to a structure that is either metallic or semiconducting. On the other hand, diamond has a tetrahedral structure (derived from the fact that carbons are hybridised sp^3 rather than sp^2 as in graphene) and is an insulator.

One interesting property found in single-walled carbon nanotubes (SWCNT) is that electric conductance within them is **ballistic** (which means that all electrons that go into one end of the conductor come out the other end without scattering, regardless of how far they need to travel).

Researchers are also investigating whether nanotubes can be **superconductors near room temperature**, meaning ballistic conductors that also exhibit a resistance of zero. A superconductor can transport an enormous amount of current flow at tiny voltages. At present, known superconductors work at very low temperatures. This field of research is very important since if a material were superconductive at room temperature, it would carry current with no resistance, with no energy lost as heat. This could lead to faster, lower-power electronics and the ability to carry electricity long distances with 100 % efficiency.

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Nanotubes as superconductors and their applications are further discussed in **Module 2, Chapter 3: Energy**.

In terms of thermal properties, carbon nanotubes **dissipate heat** better than any other known material and are **excellent thermal conductors**.

Chemical reactivity

Carbon nanotubes are very stable: they can withstand the attack of numerous chemicals and resist exposure to a large temperature range. However, their chemical structure can be changed by the addition of specific ligands with functional groups that allow interaction with different chemicals. This allows them to be used in **sensors**.

Applications

Carbon nanotubes are very promising materials for numerous applications (these will be described in more detail in **Module 2**). Applications include: nanomedicine (drug delivery), environment (chemical sensors), energy (supercapacitors, hydrogen storage materials, solar cells), ICT (integrated circuits, electronic paper), advanced materials for construction, transport, sports equipment and more.

ELSA and SAFETY TOPIC Carbon nanotubes are an extraordinary material which could improve numerous current materials, particularly some plastic composites, and be used in electronics and sensing. The range of application is fairly broad so the question of their safety is important. Carbon nanotubes are formed as nanometer-thin, long fibres, so the memory quickly goes back to asbestos, their claimed exceptional properties, but also their late-found toxicity (they cause cancer). Some recent research does suggest that carbon nanotubes, inhaled in large amounts, can be significantly toxic. As with other nanomaterials, though, the question of safety is more complex: carbon nanotubes are used as composites, embedded with polymers or other materials, so consumers would not be directly exposed to them (with the exception of workers in the industry). But what happens when the product is disposed of and the material degrades? Is waste containing carbon nanotubes safe? Should this waste be treated differently and undergo special treatment? There is intense research to find answers to these questions, but time is needed. Opponents advocate that until these answers are not found, products containing carbon nanotubes should not be placed on the market, and workers should treat these as hazard materials and wear the stringiest protection measures.

NANOYOU GAME Carbon nanotubes composites are used in one of the NANOYOU jigsaw puzzle games (http://nanoyou.eu/en/play-nano.html) — students must match the nanomaterial to its application, connecting it to a specific need.

Scientists have now developed methods to control the synthesis of carbon nanotubes to obtain regular structures with specific properties. To date, though, the synthesis methods lead to moderate amount of CNTs and mostly very limited length (of the order of millimetres). Often, these processes lead to CNTs which are not totally pure (traces of the catalyst used in the synthesis are present in the product) and this has been associated with toxicity issues of CNTs.

The cost associated with the production of carbon nanotubes is extremely high. In the future, this cost must be considerably reduced to allow large-scale production and use of CNTs.

The structure of fullerenes resembles that of a football and youngsters can familiarise themselves with this structure in a fun way using the **Make your own buckyball** activity — Activity 4 in the *timefornano* NanoKIT (http://www.timefornano.eu/nanokit#ac04).

Composites

The idea behind nanocomposites is to use building blocks with dimensions in the nanometre range to design and create new materials with unprecedented flexibility and improvements in their physical properties. This concept is exemplified in many naturally occurring materials, such as **bone**, which is a hierarchical nanocomposite built from ceramic tablets and organic binders (see **Module 1, Chapter 2: Nanoscience in nature**). When designing the nanocomposite, scientists can choose constituents with different structures and composition and, hence, properties, so that materials built from them can be **multifunctional**.

As a general definition, a nanocomposite is a conventional material reinforced by nanoscale particles or nanostructures which are dispersed throughout the bulk material. The base material itself generally consists of non-nanoscale matrices. Nanocomposites typically consist of an inorganic (host) solid containing an organic component or vice versa or two (or more) inorganic/organic phases in some combinatorial form. At least one component must be nano-sized. In general, **nanocomposite materials can demonstrate different mechanical, electrical, optical, electrochemical, catalytic and structural properties which are different from those of the individual components**. Apart from the properties of the individual components, **interfaces** in a nanocomposite play an important role in determining the overall properties of the material. Due to the high surface area of nanostructures, nanocomposites present many interfaces between the intermixed phases and, often, the special properties of the nanocomposite are a consequence of the interaction of its phases at interfaces. In comparison, the interfaces in conventional composites constitute a much smaller volume fraction of the bulk material.

In this chapter, nanocomposites are subdivided in two main groups: inorganic nanocomposites, which are characterised by an inorganic matrix (e.g. ceramic) reinforced by nanoscale particles or nanostructures of inorganic (e.g. metal) or organic (e.g. carbon-based) nature; and polymer nanocomposites, which are characterised by an organic matrix (e.g. polymer) reinforced by nanoscale particles or nanostructures by inorganic (e.g. clay) or organic nature.

Inorganic nanocomposites

High-performance ceramics are sought in many applications, such as highly efficient gas turbines, aerospace materials, cars, etc. The field of ceramics that focuses on improving their mechanical properties is referred to as **structural ceramics**.

Nanocomposite technology is also applicable to **functional ceramics** such as ferroelectric, piezoelectric, varistor and ion-conducting materials. In this case, the properties of these nanocomposites relate to the dynamic behaviour of ionic and electronic species in electro-ceramic materials. Among these materials,in this document, the review is limited to **nanocomposite with enhanced magnetic properties**.

Structural nanocomposites

Presently, even the best processed ceramics pose many unsolved problems such as poor resistance to creep, fatigue and thermal shock; degradation of mechanical properties at high temperatures; and low fracture toughness and strength. To solve these problems, one approach has been to incorporate a second phase such as particulates, platelets, whiskers or fibres in the micron-size range at the matrix grain boundaries. However, the results obtained with these methods have been generally disappointing. Recently, the concept of nanocomposites has been considered, where **nanometre-size second-phase dispersions** are inserted into ceramic matrices. Large improvements in both the fracture toughness and the strength of a ceramic can often be achieved with nanometre-range particles embedded in a matrix of larger grains at their grain boundaries. These can involve the incorporation of a **nano-ceramic in a bulk ceramic, a nano-metal in a ceramic, or a nano-ceramic in a metal**. Another possibility is the incorporation of a polymer in a ceramic. Without going into too much detail, the following are examples of inorganic **nanocomposites that have improved structural properties**.

- The incorporation of **fine SiC and Si_3N_4 nanoparticles in an alumina matrix** (Al_2O_3, a structural ceramic material) first demonstrated the concept of structural nanocomposites. The dispersion of these particles has been shown to improve the fracture toughness from 3 to 4.8 MPa m1/2 and the strength from 350 to 1 050 MPa at only 5 vol. % additions of SiC.
- One possibility for the fabrication of advanced structural ceramics is the dispersion of **metallic second-phase particles into ceramics** which improves their mechanical properties, such as fracture toughness, and influences other properties including magnetic and optical properties. Nanocomposites of this type are Al_2O_3/W or MgO/Fe. **Granular films** can also be made with a ceramic phase embedded with nano-size metal granules (such as Fe/Al_2O_3, Fe/SiO_2). Such films often show **unusual or enhanced transport, optical and magnetic properties**. The inclusion of nano-sized metals in a thin ceramic film can transform it **from an insulator to a conductive film**.
- Another possibility is to add fine, **rigid ceramic reinforcements to a ductile metal or alloy matrix** (metal matrix composites or MMCs). The reinforcement can be either in the form of particles (e.g. silicon carbide, aluminium oxide), fibres (e.g. silicon oxide, carbon) or a mixture of both (hybrid reinforcement). Materials produced by this method are particularly useful in the aerospace, automotive and aircraft industries. The advantage of MMCs is that they **combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus)**, leading to materials having greater strength to shear and compression and to higher working temperature capabilities. The properties of MMCs are controlled by the size and volume fraction of the reinforcements as well as by the nature of the matrix/reinforcement interface. The attention is now oriented towards the incorporation of **nanoparticles and nanotubes** for structural applications, since these materials exhibit even greater improvements in the physical, mechanical and tribological properties compared to MMCs with micron-size reinforcements.
- Nanoscale ceramic powders with **carbon nanotubes** provide another method for creating dense ceramic-matrix composites with enhanced mechanical properties. For instance, **hot pressed alumina with mixed carbon nanotubes results in lightweight composites with enhanced strength and fracture toughness compared to polycrystalline alumina**. The processing conditions greatly influence the properties of this material, though. In metal matrix composites (MMCs), the incorporation of carbon nanotubes is considered very promising since these materials have higher strength, stiffness and electrical conductivity compared to conventional metals.

Nanocomposites with enhanced magnetic properties

Materials with outstanding magnetic properties are in high demand as these are employed in nearly all important technical fields including electrical power, mechanical power, high-power electromotors, miniature motors, computer elements, magnetic high-density recording, telecommunications, navigation, aviation and space operations, medicine, sensor techniques, magnetic refrigeration, materials testing and household applications. Recent developments in the field of magnetic materials have involved materials with a nanocrystalline structure or, in the case of thin films, layers of nanometre thickness.

Nanostructuring of bulk magnetic materials leads to soft or hard magnets with improved properties. One example is the Finemet® **nanocrystalline soft magnetic alloys**, which consist of melt-spun Fe-Si-B alloys containing small amounts of niobium and copper. When annealing at temperatures above the crystallisation temperature, the Fe-Si-B-Nb-Cu amorphous phase transforms to a crystalline solid with grain size of about 10 nm. These alloys have excellent magnetic induction and large permeability, and a very small coercive field.

Nano-sized magnetic powders can have extreme properties and have no hysteresis at any temperature. These materials are called **superparamagnetic** and one example is nano-sized powders of a Ni-Fe-Co alloy.

Nanostructuring has also been studied in the context of **hard magnets** (permanent magnets). The strongest known magnets are made of neodymium (Nd), iron and boron (e.g. $Nd_2Fe_{14}B$). In these materials, it is has been found that the coercive field decreases significantly below approximately 40 nm and the remnant magnetisation increases. Another approach to improving the magnetisation curve of permanent magnets has been to fabricate nanocomposites made of hard magnetic phases, such as $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_3$, within soft magnetic matrices (e.g. soft phase of iron). The effect of the inclusion of a soft iron mixed in with a hard material is to increase the remnant field.

The **grain size of the material** also influences the magnetisation saturation point. For instance, the magnetisation of ferrite increases significantly below a grain size of 20 nm. Thus, **reducing the size of the grains in the magnet increases the energy product (which is the product of magnetisation and coercivity)**. The coercivity also increases with decreasing the grain sizes. In the case of nanocomposite magnetic films, this is true if the grains are isolated (no interaction), but when the grains are in contact and exchange interaction kicks in, the coercivity falls rapidly with grain size. The coercivity is thus highest at percolation, when the grains just start touching each other. This effect is important in the context of designing thin-film nanocomposites **(magnetic multilayer nanocomposites),** for instance for high magnetic density recording.

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Magnetic multilayer nanocomposites are becoming an essential component of the **new-generation data storage devices** like **magnetoresistive random access memory**(MRAM). This and other nanostructured devices made of nanomagnets with applications in the ICT sector are discussed in **Module 2, Chapter 4: Information and Communication Technologies**.

Polymer nanocomposites

Polymer composites are materials where a polymer is filled with an inorganic synthetic and/or natural compound in order to increase several properties, such as heat resistance or mechanical strength, or to decrease other properties, such as electrical conductivity or permeability for gases like oxygen or water vapour. Materials with synergistic properties are used to prepare composites with tailored characteristics; for instance, high-modulus but brittle carbon fibres are added to low-modulus polymers to create a stiff, lightweight polymer composite with some degree of toughness. Current polymer composites are really filled polymers, since these materials lack an intense interaction at the interface between the two mixed partners. Progress in this field has involved moving from macroscale fillers to micron-scale fillers, to even smaller fillers.

In recent years, scientists have started to explore a new approach to the production of polymer composites with the use of **nanoscale fillers**, in which the filler is below 100 nm in at least one dimension. Nanoscale fillers include: nanoparticles; nanotubes; and layered (also called 'plate-like') inorganic materials such as clays (**Figure 22**).

Figure 22: Schematic representation of nanoscale fillers

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Although **some nano-filled composites have been used for more than a century**, such as carbon-black and fumed-silica-filled polymers, researchers have only recently started to systematically produce and study these materials. The motivation has been the realisation of the exceptional combined properties that have been observed in some polymer nanocomposites. This, together with substantial development in the chemical processing of nanoparticles and in the *in situ* processing of nanocomposites, has led to unprecedented control over the morphology of these materials.

One of the most common reasons for adding fillers to polymers is to **improve their mechanical performance**. In traditional composites, this often compromises the ductility of the polymer and, in some cases, negatively impacts its strength because of stress concentration caused by the fillers. Well-dispersed nano-fillers, such as nanoparticles or nanotubes, can improve the modulus and the strength and maintain (or even improve) ductility because their small size does not create large stress concentration. For all nano-fillers, a key requirement is the homogeneous dispersion of the filler within the polymer matrix. As discussed in the following sections, this is a challenge in many cases, and a topic of intense research.

Although the scientific community has made remarkable progress in this field in the last years, **polymer nanocomposites have just started to be explored**, and many research questions still need to be addressed. What is clear so far is that the use of nanoscale fillers opens the way for the development of materials with exceptional properties. For instance, nanoparticles do not scatter light significantly, thus it is possible to make polymer composites with altered electrical or mechanical properties that remain **optically clear**. Nanoparticles are also of interest not just for their small size, but for their inherent unique properties. Carbon nanotubes, for instance, display the highest values so far seen of elastic modulus, as high as 1 TPa, and strengths that can be as high as 500 GPa. This could allow, for example, the fabrication of polymeric composites with exceptional strength and flexibility.

Another outstanding property that the use of nanoscale fillers confers on nanocomposites is an exceptionally **large interfacial area**. The increase of surface area below 100 nm is dramatic. The interface controls the degree of interaction between the filler and the polymer, and is thus responsible for the composite properties. Thus, the largest challenge in nanocomposite science is learning to control the interface.

Nanoscale fillers can potentially allow the creation of a vast range of different polymeric materials with advanced properties. In general, macroscopic reinforcement elements have the limitation of always containing imperfections, but as the reinforcements become smaller and smaller, structural perfection could be reached. The ideal reinforcements would have atomic or molecular dimensions and be intimately connected with the polymer. The use of nanoscale fillers, however, also introduces a series of **fabrication challenges**. Because of their small size and high surface area, nanoscale fillers such as nanoparticles have a strong tendency to agglomerate rather to disperse homogeneously in a matrix. This leads to particle-matrix mixtures with high viscosities, which can make the processing of those materials quite challenging. The result is that even the most exciting polymer nanocomposites have very low fractions of particle content, and relatively weak mechanical properties when compared tothose predicted in theory. Therefore, polymer nanocomposites are an exciting type of advanced materials that hold great promise in many application, but which are still mainly in a development stage. The intense research efforts in this area suggest, however, that these materials will become more readily accessible in the near future.

Nanoparticle-polymer nanocomposites

Nanoparticles are a type of nano-filler that offer the opportunity of developing polymers with new or advanced properties. As already discussed, the size of a nanoparticle affects its properties: for instance, gold nanoparticles have different optical absorption spectra depending on the particle size. One of the advantages of using nanoparticles in polymer composites is that the particle size and distribution can be tuned. Materials that cannot be grown easily as single crystals can be used at the nanoscale and dispersed in a polymer to take advantage of the single-crystal properties.

In general, nanoparticle-filled polymers display better mechanical properties, at least at low volume fractions and if well dispersed in the polymer. The reason is that nanoparticles are much smaller than the critical crack size for polymers and thus do not initiate failure. Thus, nanoparticles provide a way for simultaneously toughening and strengthening polymers. **Proper dispersion is critical**, however, in achieving this.

The size scale of nanoparticle-polymer composites ranges from hybrid nanocomposites, in which the polymer matrix and the filler are so intimately mixed that they are no longer truly distinct, to discrete particles in a continuous matrix. Hybrid nanocomposites often arise from the use of block copolymers, and this is discussed in the section on polymers in this chapter).

In terms of properties, the use of nanoparticles in filling polymers can influence not only the polymers' mechanical properties, but also the **polymers' mobility and relaxation behaviour**, which, in turn, are connected to the glass transition temperature of the polymer (Tg) (i.e. the temperature at which a polymer becomes brittle on cooling or soft on heating). In general, adding well-dispersed, exfoliated nano-filler increases the Tg of the polymer. Nanoparticle-filled polymers also show an **increase in the abrasion resistance** of the composite.

One of the most exciting prospects of using nanoparticles in polymer composites is to create composites with **combined functionalities**, such as electrically conducting composites with good wear properties that are optically clear: this is possible because nanoparticles do not scatter light.

Carbon nanotubes in polymer composites

Carbon nanotubes have very distinct properties compared to graphite, as summarised in **Table 1** in the section on mechanical properties. In the context of nanocomposites, **SWNTs are the most promising nanotube fillers**. Some properties are particularly interesting: in particular their **flexibility under mechanical stress**, behaviour under high temperature conditions and electrical properties. As with other applications that make use of carbon nanotubes, it has been observed that, in composites, the processing conditions ultimately affect the properties of the nanotubes and, as a consequence, the purity of the composite, as well as the purity of the nanotubes. Carbon nanotubes can also be doped, for example with nitrogen and boron, which changes their surface reactivity. For instance, nitrogen atoms inserted into the lattice of nanotubes makes them more dispersed in solution (carbon nanotubes are insoluble in water). Modified nanotubes present different electrical and optical properties and hence their use could lead to composites with novel properties.

It should be noted that the inclusion of carbon nanotubes in a polymer does not necessarily improve its mechanical properties. Although, in theory, the modulus of nanotubes is much higher than any graphite fibre, and hence the composite should have outstanding mechanical properties, it has been demonstrated that a number of variables influence this outcome. For SWNT composites, the SWNTs are in a bundle; until SWNTs are isolated from the bundles or the bundles are cross-linked, the modulus of composites made of these materials will be limited. For this reason, researchers are concentrating on developing processing methods that make it possible to obtain significant volume fractions of **exfoliated nanotubes**. As will be discussed later concerning clay-polymer nanocomposites, the structural arrangement of the nano-filler within the polymer is also important: if the nanotubes are not straight when placed in the composite, the modulus of the composite significantly decreases.

Apart from the mechanical enhancement of polymers, **nanotubes are also of interest for their electrical properties**. **Carbon nanotubes are inherently more conductive than graphite**. It has been found, for instance, that nanotube-PPV composites show a large increase in electrical conductivity, compared to simple PPV (poly(p-phenylene vinylene), of nearly eight orders of magnitude. Recently, an improvement of 4.5 orders of magnitude in the electrical conductivity of nanotube-PVA nanocomposites has been reported.

Finally, nanotube-polymer composites are promising in the context of **light-emitting devices**. These devices were developed after the discovery of electroluminescence from conjugated polymer materials (such as PPV). The practical advantages of polymer-based LEDs are their low cost, low operating voltage, ease of fabrication and flexibility. Small loadings of nanotubes in these polymer systems are used to tune the colour of emitted light from organic LEDs.

Polymer-clay nanocomposites

In the late 1980s, it was discovered that adding 5 % by weight of nano-sized clays to Nylon 6, a synthetic polymer, greatly increased its mechanical and thermal properties. Since then, polymer-clay nanocomposites have been widely studied and many commercial products are available. These hybrid materials are made of organic polymer matrices and clay fillers. **Clays are a type of layered silicates that are characterised by a fine 2D crystal structure**; among these, mica has been the most studied.

Mica is made up of large sheets of silicate held together by relatively strong bonds. Smectic clays, such as montmorillonite, have relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as Li^+, Na^+, K^+ and Ca^{2+}. The presence of the cations is necessary to compensate for the overall negative charge of the single layers. The layers are 20–200 nm in diameter laterally and come into aggregates called tactoids, which can be 1 nm or more thick. Naturally occurring clays include montmorillonite (MMT) and hecrite, and their synthetic equivalents are saponite and laponite respectively.

For these layered silicates to be useful as fillers in nanocomposites, **the layers must be separated, and the clay mixed thoroughly in the polymer matrix**. This is not trivial as silicate clays are inherently hydrophilic, whereas polymers tend to be hydrophobic. The solution is to exchange the cations that keep the layers in the silicate together with larger inorganic ions that can thus open the galleries between the layers (intercalation). When the silicate layers are completely separated, the material is said to be exfoliated. In the case of intercalation, extended polymer chains are present between clay layers, resulting in a multilayer structure with alternating polymer/clay phases at repeated distances of a few nanometres: in the exfoliated state, the silicate layers are totally separated and dispersed in a continuous polymer matrix.

As already mentioned, the fabrication of a **polymer-clay nanocomposite requires mixing two components that are intrinsically non-compatible**. Surfactants are ionic, and thus interact well with the clay, but not with the polymer. An ideal solution is the use of ‘macro-surfactants’ such as block copolymers combining hydrophilic and hydrophobic blocks that can interact with the clay and the polymer respectively. For instance, poly(ethylene oxide) (PEO) is an excellent intercalation material.

Although homogeneous dispersion of the filler in the polymer is an important parameter, another important aspect is the **packing (or alignment) of the filler in the polymer**. To understand this concept, it is useful to consider a natural nanocomposite, bone. The unique properties of bone are a list of apparent contradictions: rigid, but flexible; lightweight, but solid enough to support tissue; mechanically strong, but porous. In order to meet these different demands, bone has a hierarchical structure that extends from the nanoscale to the macroscopic length scale. *The hierarchical structure of bone is responsible for its load transfer ability* (see **Module 1, Chapter 2: Nanoscience in nature** for details on the structure of bone). Nanoparticle-filled polymer composites have mechanical properties that are actually disappointing compared to theoretical predictions, and this is due to the **difficulty in obtaining well-dispersed large volume fractions of the reinforcing nanomaterial and a lack of structural control**. Taking this into consideration, some scientists have recently reported the fabrication of ultra-strong and stiff layered polymer nanocomposites. In this work, bottom-up assembly of polymer-claynanocomposite allowed the preparation of a homogeneous, transparent material, where the clay nanosheets have planar orientation. It was found that the stiffness and tensile strength of these multilayer nanocomposites are one order of magnitude greater than those of analogous nanocomposites.

Nanoclays are also used as fillers in polymers to increase the **thermal stability of polymers**. This property was first demonstrated in the late 1960s for montmorillonite-PMMA composites. The dispersion of the clays is critical to increasing the thermal stability (that is, raising the degradation temperature) of the polymer.

In addition to thermal stability, the **flammability properties** of many polymer-clay nanocomposites are also improved. Combining traditional flame retardants with intercalated or, better, exfoliated clays can result in further improvements in flame retardancy.

Finally, polysaccharide-clay nanocomposites are a class of materials that are important especially to the **food industry**. These composites make use of naturally occurring polymers, such as starch, mixed with clay to make a biopolymer film with enhanced properties, in particular permeability to water vapour.

Nanocoatings

Nanocoatings are a type of nanocomposite. The layer thickness of a nanocoating is usually 1–100 nm. Nanocomposite films include multilayer thinfilms, in which the phases are separated along the thickness of the film, or granular films, in which the different phases are distributed within each plane of the film (**Figure 23**).

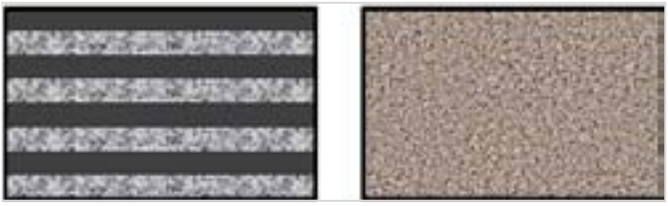

Figure 23: Schematic of possible structures for nanostructured coatings: left: multilayered microstructure (e.g. TiN/TiC) for nanocomposite coatings; right: homogeneous nanostructured coating (e.g. NiCoCrAlY alloy)

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Nanocoatings make it possible to **change the properties of some materials**, for example to change the transmission of visible and IR radiation in glass, or to **introduce new properties** such as 'self-cleaning' effects. Here, this first type of nanocoating will be discussed under the umbrella term 'responsive nanocoatings'.

Another important area of application of nanocoatings is **tribological coatings**. Tribology is the science and technology of interacting surfaces in relative motion. Tribological properties include friction, lubrication and wear. Tribological coatings are those coatings that are applied to the surface of a component in order to control its friction and wear. In this area, the term 'thin films' is often used as an alternative to nanocoatings — due to the fact that this is an area of innovation that has existed for many years and has now reached the nanoscale.

Tribological nanocoatings

Tribological coatings play a key role in the performance of the internal mechanical components of a vehicle, such as the engine and powertrain. They are also key elements in **cutting tools and machinery in general**. By reducing wear and friction, these coatings increase the lifetime of the working material while also reducing the dissipation of energy as heat, thus increasing the efficiency of the moving part. When applied to machinery and tools, tribological coatings can reduce (or eliminate) the need for lubricants, increase cutting speed, increase the rate of material removal, reduce maintenance costs or reduce processing cycle times.

Traditional materials used in coatings for tribological applications are carbides, cemented carbides, metal ceramic oxides, nitrides and carbon-based coatings. Since the microstructure controls many of the physical properties of the coating, having a nanoscaled microstructure may lead to significant improvements in the mechanical properties of the coating (e.g. hardness), the chemical properties (e.g. corrosion resistance) and the electrical properties. Thus, nanocomposite coatings are now being investigated as alternatives to the traditional approach of using specific alloying elements in single-phase coating materials to improve, for instance, properties such as hardness. One type of **nanocomposite coatings** is multilayered thin films made of different layers in the order of nanometres. These films are mostly used for their **enhanced hardness** and elastic moduli, which is higher in multilayered films than in homogeneous thin films of either component, and for their wear properties. Commercial multilayer coatings made with multilayer periods in the nanoscale range already exist, such as WC/C coatings used in the cutting tool industry. Other examples are films of alternating layers of TiN and NbN, or TiAlN/CrN multilayers, which are more efficient than TiAlN films.

Responsive nanocoatings

Responsive nanocoatings are those where the properties of the material in the coating **react to environmental conditions**, such as light or heat, either in a passive or an active way. These coatings allow the properties of some materials to change, such as glass, by conferring new or improved properties.

The use of glass is very common in modern buildings, since it allows the construction of transparent and seemingly lightweight structures. However, the relative high transmittance of visible and infrared (IR) light is a major disadvantage, since this leads to a large heat transfer which is particularly undesirable in summer. The problem is reversed in winter, when heat is dispersed through the glass. In order to address these problems, various types of **nanocoatings that modulate light transmission in glass** are under investigation and being commercialised. The aim is to reduce indoor heating in summer, so less air conditioning is required to keep the atmosphere cool, with consequent energy saving. One type of coating, referred to as 'low-e' (meaning 'low emissivity'), is based on a thin silver film, about 10 nm thick, surrounded by dielectric layers. Metallic layers have been widely used to increase the reflectivity of light (and reduce transmittance) for years, but they have the disadvantage of giving a mirror-like appearance. Silver loses its metallic appearance when scaled to a nano-film, thus eliminating this problem. Such a coating is commercialised by Von Ardenne.

'Low-e' coatings are a type of passive nanocoatings, since the properties of the layers are undisturbed during its operation. Another class of coatings used in glasses are those often described as dynamic or '**smart coatings**'. In this case, the environmental conditions, such as radiation intensity or temperature, induce a change in the properties of the coating (e.g. darkening of windows). When the effect is a change in the colour (including a change to transparency), they are called **chromogenic smart materials**. The change can be induced actively by pressing a button. This is the case of **electrochromic coatings** where applying a small voltage induces a change in transmittance and in the case of **gaschromic coatings** which change their transmittance in the presence of specific gases. Gaschromic glazing makes use of the properties of tungsten oxide thin films (WO_3) which go from colourless to blue in the presence of hydrogen with a suitable catalyst. Gaschromic windows follow a double pane model: on one pane a film of WO_3 is deposited with a thin layer of catalysts on top.

Hydrogen gas is fed into the gap producing colouration (windows colour with 1.1–10 % hydrogen, which is below the flammability concentration). To switch the colour of the window back, another gas is purged (oxygen). Smart coatings can also be passive in the sense of changing their optical properties due to a change of external temperature (**thermochromic**) or light incidence (**photochromic**). Another example of nanotechnology applied to smart coatings is the use of a family of wavelength-selective films for manufacturing 'heat mirrors'. One of these materials is indium tin oxide (ITO), an infrared absorber. A 300 nm ITO coating on glass provides more than 80 % transmission for the wavelengths predominant in sunlight. The transmission properties of the window can be varied by changing the thickness and material composition of the coating, so that a combination of materials could be used to produce smart windows that reflect solar energy in summer but transmit solar energy in winter.

Superhydrophilic coatings

Another example of functional nanocoatings is **photocatalytic coatings** (commercialised as 'self-cleaning' glass) which use the catalytic properties of titanium dioxide (TiO_2). When irradiated with UV light, the coating becomes **superhydrophilic**: therefore, rain water adheres to the glass providing 'self-cleaning'. Pilkington Activ™ Self-cleaning Glass is a commercial example of a glass with a photocatalytic coating that renders the material easier to clean. Details of this product are given in **Module 2, Chapter 2: Environment**.

Superhydrophilic coatings are also useful for rendering a surface **fog-resistant**. These coatings are produced using a solution or a colloid that reduces the surface tension of the material (e.g. glass). Substances that can be used as anti-fog agents include surfactants (e.g. soap), hydrogels, hydrophilic nanoparticles and colloids. The anti-fog agent creates a thin film that does not allow the formation of water droplets but rather 'forces' the water molecules to spread on the surface. This film reduces the surface tension of the liquid (the surface tension is the result of the cohesive forces between the molecules that are responsible for the formation of spherical droplets). In the case of water, its surface tension is very high (and, for this reason, liquid water tends to form droplets). The anti-fog agent creates a superhydrophilic surface (very low contact angle) so that water sprayed on the surface creates a thin layer instead of forming round droplets. The layer is so thin that it does not scatter light — meaning that it appears transparent to our eyes. This is explained by the fact that the water molecules are subjected to two different forces: inherent surface tension that tends to round off the droplets, and bonding to the anti-fog nanoparticles that flattens them. Bonding to the surface occurs through hydrogenbonds, weak forces that can become dominant when numerous. The result is a very thin layer of water on the surface: the layer is so thin that it does not scatter light, so that it appears transparent to our eyes and so we can see through it well. This type of technology helps prevent goggles used for skiing or swimming steaming up.

Superhydrophobic coatings

The opposite to superhydrophilc coatings are superhydrophobic coatings, which totally repel water. Droplets of water on these surfaces have very high contact angles and 'bead-up' forming nearly spherical droplets. **Superhydrophobic coatings** have surfaces that mimic the surface found in the lotus leaf and are being developed for many applications that require resistance to dirt and ease of cleaning. The details of the Lotus effect® are given in **Module 1, Chapter 2: Nanoscience in nature** while examples of applications of these coatings are given in **Module 2, Chapter 2: Environment**.

EXPERIMENT

EXPERIMENT D in the **NANOYOU Experiment Module** investigates the Lotus effect® in real plants and in innovative materials such as Nano-Tex® fabric and nanoporous silicon.

A simple hands-on activity to show the superhydrophobic effect involves **Magic Sand** — a product that creates a superhydrophobic assembly in water. Details of the Magic Sand activity can be found in the *timefornano* NanoKIT — Activity 6 (http://www.timefornano.eu/nanokit#ac07).

Superhydrophilic and superhydrophobic coatings are the opposite of the each other; however, they share a common feature: they influence water adhesion and, therefore, **influence surface cleaning**. Superhydrophilic coatings that use photocatalytic materials are often called 'easier to clean' in the sense that rain spreads on the surface and reduces the effort needed for cleaning. Superhydrophobic coatings are often defined as 'self-cleaning' since dirt cannot adhere easily to the surface and the motion of the water droplets on the surface 'mechanically' cleans it (i.e. by rolling on the surface and dragging the dirt away in doing so). It should be noted that, in both cases, water is needed to achieve the cleaning (i.e. in situations where rain is scarce, these surfaces will not be so effective).

CHAPTER 6:

CHARACTERISATION METHODS

'Seeing is believing' ... therefore, imaging of nanomaterials is an essential part of nanoscience and nanotechnologies. Imaging in nanoscience does not just mean 'to create an image', but to understand its meaning. Scientists nowadays have access to a variety of truly amazing instruments that allow them to see objects at the nanoscale. This was a dream for scientists until just a couple of decades ago, a dream that came true in the mid 1980s when a revolutionary instrument was invented, the scanning tunnelling microscope, and shortly after, the atomic force microscope. As a matter of fact, it was the invention of these instruments that truly opened the doors to the nano-world. Once scientists were able to see nanoscale objects, they started to be able to analyse them, understand their behaviour, and imagine ways of manipulating them.

This chapter summarises some of the methods used for imaging and characterisation of nanomaterials, meaning materials with at least one dimension atthe nanoscale level (1–100 nm). These include nanostructured surfaces, nanoparticles, nanoporous materials, etc. The aim of this chapter is to answer the question: How are nanomaterials imaged and characterised?

There are many methods available to image nanostructured materials (e.g. a nanostructured surface) and to characterise their physical and chemical properties. Here, only a short review and description of these methods is provided, but the interested teacher can find more resources at the end of the chapter.

In general, two fundamental types of characterisation methods exist: imaging by microscopy and analysis by spectroscopy. The methods employed have been developed specifically to meet the characterisation needs of nanomaterials.

Microscopy

An optical microscope uses visible light (i.e. electromagnetic radiation) and a system of lenses to magnify images of small samples. For this reason, it is also called a light microscope. Optical microscopes are the oldest and simplest of the microscopes. The resolution limit of an optical microscope is governed by the wavelength of visible light (5). Visible light is the part of the electromagnetic spectrum with wavelengths between 400 and 700 nm and the resolving power of an optical microscope is around 0.2 µm or 200 nm: thus, for two objects to be distinguishable, they need to be separated by at least 200 nm. Single objects smaller than this limit are not distinguishable: they are seen as 'fuzzy objects'. This is known as the 'diffraction limit' of visible light.

In order to overcome the limitations set by the diffraction limit of visible light, other microscopes have been designed which use other beams: rather than light, they use **electron beams** to illuminate

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(5) As a general rule of thumb, the resolution is about half the wavelength used in the measurement.

the sample. **Electron microscopes** have much greater resolving power than light microscopes that use electromagnetic radiation and can obtain much higher magnifications of up to two million times, while the best light microscopes are limited to magnifications of 2 000 times. Both electron and light microscopes have resolution limitations, imposed by the wavelength of the radiation used. The greater resolution and magnification of the electron microscope is because the wavelength of an electron (its de Broglie wavelength) is much smaller than that of a photon of visible light.

There are various types of electron microscopes, such as the **scanning electron microscope** (SEM) and or the **transmission electron microscope** (TEM). Conceptually, these microscopes are similar to an optical microscope in the sense that they use radiation to visualise a sample: photons in the case of an optical microscope, and electrons (i.e. particles) in the case of electron microscopes.

In 1981, a totally new concept of imaging was introduced by Binning and his co-workers from IBM. They used a small metal tip placed at a minute distance from a conducting surface: when the two are placed very close together, but not actually touching, a bias between the two can allow electrons to tunnel through the vacuum between them. This creates a tunnelling current (6), which can be measured and which is a function of the electron density on the surface. Electron density is the probability of finding an electron in a particular place: there is high electron density around the atoms and bonds in molecules.

This type of microscope is called the **Scanning Tunnelling Microscope** (STM). Variations in current as the probe passes over the surface are translated into an image. The STM can create detailed 3D images of a sample with atomic resolution. This means that the resolution is actually so high that it is possible to see and distinguish the individual atoms (0.2 nm = $2 * 10^{-10}$ m) on the surface. The invention of the STM earned Binning and his co-worker Heinrich Rohrer (at IBM Zürich) the **Nobel Prize in Physics in 1986**.

Scanning tunnelling microscope

The STM is a fundamental tool in nanoscience and nanotechnologies. It is used in both industrial and fundamental research to obtain atomic-scale images of metal and semiconducting surfaces (**Figure 1**). It provides a three-dimensional profile of the surface roughness, allowing the observation of surface defects and the determination of the size and conformation of molecules and aggregates.

Another astonishing property of the STM is that it can be used to manipulate (move!) individual atoms, trigger chemical reactions, as well as performing electronic spectroscopy.

Operational principle of the STM

STM is a **Scanning Probe Microscopy** (SPM) technique. SPM provides images of surfaces by scanning the surface line by line with a probe. Scanning works very similarly to the way the blind read Braille, line by line, by moving a finger over buds on the paper. In an STM, the probe is a very thin needle called the 'tip' that is so small that its point is just a few atoms across. The tip is made of a conducting material (e.g. metal, typically tungsten). The precise movement of the tip is controlled by a piezomotor.

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(6) For a definition and description of the tunnelling effect, see Chapter 4.

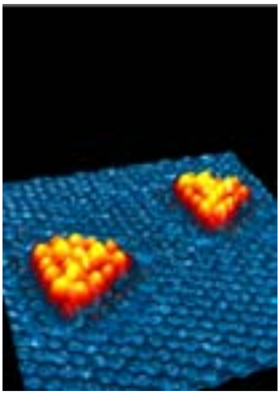


Figure 1: Nanocatalyst used for cleaning sulphur from crude oil: this STM image shows two molybdenum-disulfide nanoclusters consisting each of 15 Mo atoms and 42 S atoms.

Image: © iNANO

The tip of an STM is about 3 mm ($3 * 10^{-3}$ m) long and should be located very close to the surface to be scanned. In practice, the distance between the end of the tip and the surface must be less than 0.1 nm (10^{-10} m), without the tip actually hitting the surface. To visualise how small and precise this actually is, it corresponds to placing the 300 m tall Eiffel Tower ($3 * 10^{2}$ m) top down with a distance of 0.01 mm ($1 * 10^{-5}$ m) over a neighbourhood and scanning across it without actually touching it! (**Figure 2**). One of the fundamental elements of the STM is the tip of the probe that scans the surface, which must be sharpened to a very fine tip (**Figure 3**). The fabrication of sharper probes allows for better resolution of surface features. Ultimately, a probe tip sharpened to one atom would provide the best resolution.

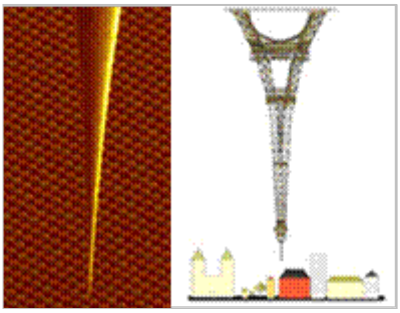


Figure 2: Left: 3 mm tip positioned 0.1 nm above the surface; right: macroscopic analogy: a 300 m high Eiffel Tower located 0.01 mm above the city

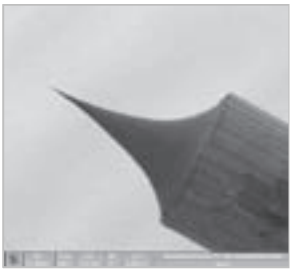


Figure 3: SEM image of a tungsten tip for STM imaging

Image: reprinted from http://www.mse.engin.umich.edu/research/highlights/electrochemical-etching-of-ultrasharp-tungsten-stm-tips

When a conducting tip is brought very near to a metallic or semiconducting surface, at a distance of about 0.1 nm, it can induce the formation of a tunnel current between the tip and the surface: a bias between the two atoms (tip and surface) can allow electrons to tunnel through the vacuum between them and induce the formation of a current. Variations in current as the probe passes over the surface are translated into an image (**Figure 4**).

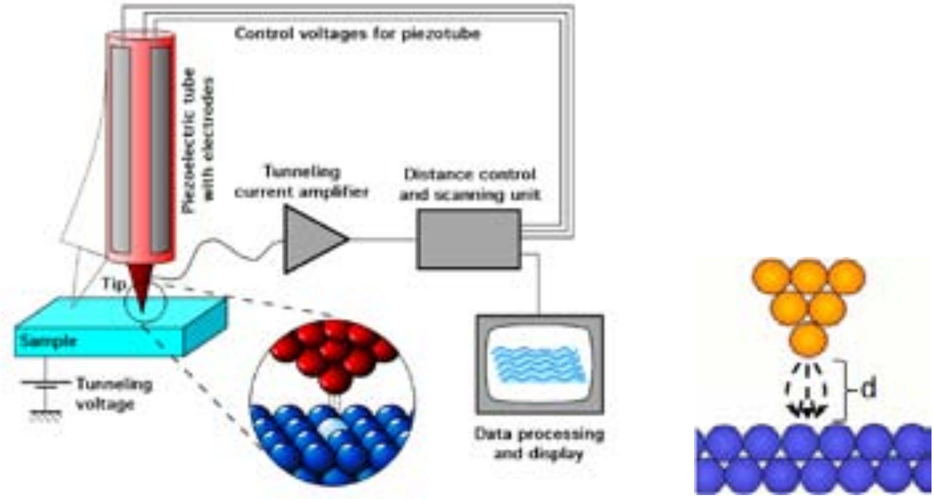


Figure 4: Schematic representation of STM scanning over a surface: (left) overview of an STM; (right) close-up of the tunnelling effect between the tip of the probe and the surface atoms. The intensity of the tunnel current depends on the distance d.

Image: Michael Schmid, TU Wien, Creative Commons Attribution ShareAlike 2.0

As the conducting tip of an STM scans over a conducting or semiconducting surface, a 'tunnel current' is formed, which arises from electrons jumping from the surface to the tip of the STM probe. The probability of this happening depends largely on the distance **d** between the surface and tip, thus the size of the current depends on this distance. Small changes in the distance between the probe tip and the substrate surface translate into large changes in tunnel current: atomic scale resolution by STM is possible in the x, y and z directions due to this phenomenon.

How are images created?

One way of using the STM to image the surface of the substrate is to keep the tunnel current constant, typically nanoamps (nA) (10^{-9} A) — by applying a constant tunnel current, the tip of the probe is kept at a specific distance above the surface. When the tip scans a surface, it will rise when it scans over an atom and drop when scanning between two atoms in the surface, as shown in **Figure 5**, where the STM tip moves from left to right.

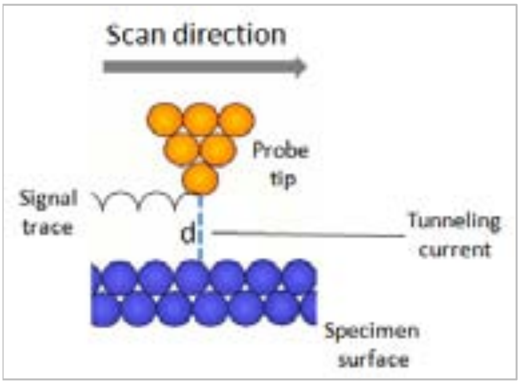


Figure 5: Schematic representation of the signal trace as a tip of an STM probe scans a surface

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

The movement of the tip can be transformed into a **coloured height map** of the surface. This map corresponds to an atlasmap, where each colour indicates a specific height, as in **Figure 6**.

Using the STM, surfaces can be scanned by moving the tip in steps of 0.1 nm (10^{-10} m), thus providing a very accurate representation of the surface. For the technique to work, it is necessary that, as the tip scans the surface, a tunnel flow is induced. **Thus, the surface must be conductive to some extent** (the substrate must be a conductor or semiconductor).

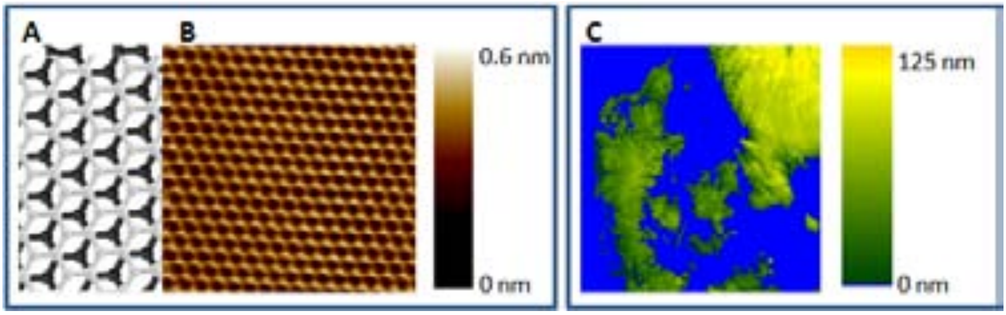


Figure 6: (A) model of two layers of graphite; (B) STM image of a graphite sheet (height scale on the right, note how the image fits the model); (C) relief map of Denmark (height scale on the right)

Image: E. Lykkegaard Poulsen, Aarhus University, Creative Commons ShareAlike 3.0

If it is necessary to scan a surface which in itself is **not electrically conductive**, it can be coated with a very thin layer of a conductive material such as gold. This does, however, imply that the STM is less suitable for some studies (e.g. to study biological molecules such as DNA (which is not conductive)). For these types of samples, other SPM techniques are more suitable, such as the **Atomic Force Microscope** (AFM). An AFM does not measure the tunnel current, but the forces between the tip and the surface and, therefore, does not require the surface to be conductive. The AFM was developed in 1985, also by Binning and co-workers at IBM Zürich. It was developed specifically to image materials that are insulating.

Atomic force microscope

The **Atomic Force Microscope** (AFM) was developed specifically to overcome the intrinsic limitations of the STM, which is not suitable for imaging surfaces coated with biological entities such as DNA or proteins. The AFM operates in air and not under a vacuum. Some versions of the instrument also allow operation in liquid, which is very advantageous when imaging biological samples that often need buffers to remain biologically active.

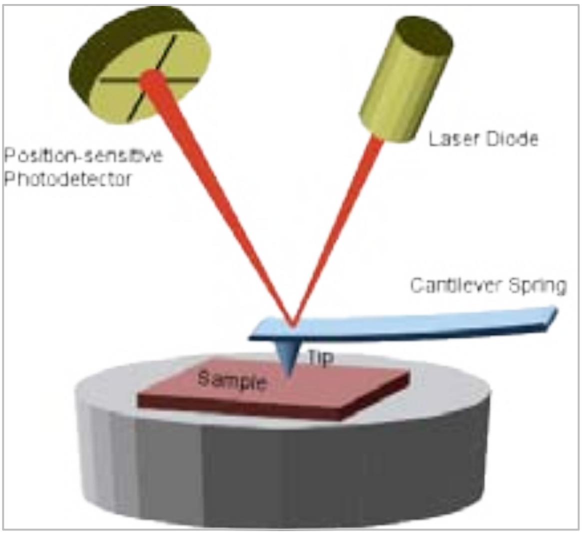


Figure 7: Operation principle of an AFM source

Image: http://www3.physik.uni-greifswald.de/method/afm/eafm.htm

The AFM measures the **interaction force** (attractive or repulsive) between the probe and the surface. The solid probe is located at the end of a very flexible cantilever; an optical system detects the deflection of a laser beam that bounces off the reflective back of the cantilever, thus reporting cantilever fluctuations, which are proportional to the applied force. The probe is continuously moved along the surface and the cantilever deflection is constantly monitored. A feedback loop continuously changes the height of the probe on the surface in order to keep the applied force constant. The vertical movement of the probe is recorded to create a **topographic map** of the surface under study.

The AFM probe tip is very sharp, with a radius of curvature in the range of tens of nanometres. If the surface under analysis is soft, the probe can penetrate it, with the risk of damaging it and degrading the spatial resolution of the resulting micrograph. To overcome this limitation, instruments working in dynamic modes have been developed. In these systems, the probe is not simply dragged on the surface but oscillated vertically with respect to the surface while it is scanned. These techniques (tapping mode and non-contact mode) significantly reduce the damage that can be caused by the probe and allow the imaging of soft, compressible samples, such as biomolecules and cells.

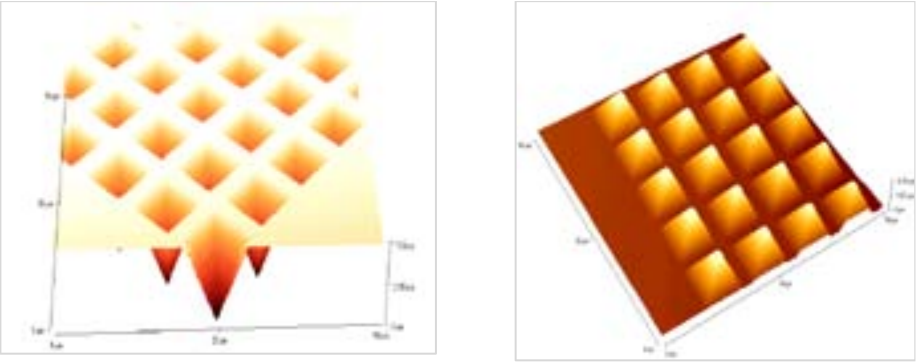


Figure 8: AFM image of an array of pyramidal wells (left) and pyramidal posts (right): the tips of the posts are about 100 nm wide

Image: L. Filipponi, PhD thesis, 'New micropatterning techniques for the spatial immobilisation of proteins', © L. Filipponi, 2006 Creative Commons Attribution ShareAlike 3.0

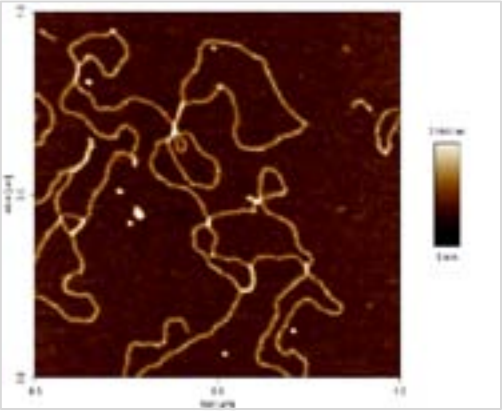


Figure 9: AFM image of DNA double strands on a mica surface

Image: JPK Instruments AG

On the other hand, the tip of an AFM can be used to **deliberately 'scratch' and remove some molecules from a surface** or to write with an '**ink**'. Both are 'writing' methods in the sense that they allow the creation of nanostructures on a surface with any geometry. This technique is called Dip Pen Nanolithography® (DPN®) and is discussed in **Chapter 7: Fabrication methods** since it is a fabrication method.

Spectroscopy methods

Spectroscopy is defined as the branch of science that is concerned with the investigation and measurement of spectra produced when matter interacts with or emits electromagnetic (EM) radiation. Depending on the wavelength of the electromagnetic used and the type of interaction with matter that occurs (absorption, scattering, etc.), different spectra are measured from which much information can be inferred.

Next, the spectroscopy methods that are most relevant in the characterisation of nanomaterials (particles and surfaces) are briefly reviewed.

X-ray methods

X-ray methods involve exciting a sample either with X-rays (creating more X-rays) or with electrons (creating X-rays). X-rays can be also generated by bombarding a sample with alpha particles. The energy of emitted X-rays is equal to the difference between the binding energies of the electrons involved in the transition. There are various methods that use X-rays: **X-ray fluorescence** (XRF), **X-ray diffraction** (XRD), etc. In the context of nanomaterials, the most important method is **small-angle X-ray scattering** (SAXS) analysis. Like XRD, this method is based on the principle of scattering of X-rays. Diffraction of X-rays is a result of scattering from atoms configured in regular arrays. In conventional XRD, only crystalline materials can be visualised, as it is necessary to have a periodicity in the structure in the long-range, which nanomaterials lack (owing to their size). XRD is used for bulk crystals. With SAXS, particle sizes of the order of 1–100 nm can be analysed. The method can be used to image powders in the dry state or suspended in a medium. The method can also be used to measure the nanoparticle size.

UV-visible plasmon absorption and emission

Metal nanoparticles, in particular gold and silver, are characterised by a plasmon resonance absorption that gives rise to intensely coloured solutions.

READ MORE

The **fundamentals of the plasmon resonance effect** are described in **Module 1, Chapter 4: Fundamental 'nano-effects'**.

The absorption band is due to electrons confined at the particle surface that collectively oscillate at a specific frequency, commonly referred to as the surface plasmon resonance frequency. As examples, the plasmon band of a 20 nm silver (Ag) particle is centred at 395 nm, resulting in a yellow solution, while a 20 nm gold (Au) particle absorbs at 520 nm resulting in a red solution. The **plasmon absorption effect** occurs for particles up to approximately 50 nm in diameter and scales with particle volume. Absorption can in be in the visible and UV area of the spectrum. Particles can be visualised by absorbance in solution at nanomolar and picomolar concentrations.

Plasmon resonance light scattering

In **larger metal nanoparticles** (> 30 nm) another effect, light scattering, is observed. When illuminated with white light, metal nanoparticles in the 50–120 nm diameter size range scatter light of a specific colour at the surface plasmon resonance frequency. This effect is called **plasmon resonance light scattering**. As in the case of plasmon absorbance, light scattering scales with particle volume, but the scattered light can be detected at much lower concentrations than absorbed light. For example, light scattered by a solution of 80 nm diameter gold particles is detectable down to 5 fM concentration (fM = 10^{-15} M). For this reason, metal nanoparticles are interesting materials for use in techniques that rely on labelling (such as microarray technology).

READ MORE

Metal nanoparticles are also described in **Module 1, Chapter 5: Overview of nanomaterials** and their application in the medical sector is described in **Module 2, Chapter 1: Medicine and healthcare**.

Surface-enhanced Raman scattering

Metal surfaces with nanometre scale roughness have the property of amplifying the Raman scattering signals of absorbed molecules. In simple terms, Raman scattering is the inelastic scattering of photons. Normally, when light is scattered from an atom or molecule, it has the same energy (frequency) and wavelength as the incident light (Rayleigh scattering). This is an elastic scattering. However, a small fraction of the scattered light (approximately 1 in 10 million photons) is scattered by excitation, with the scattered photons having energy (frequency) different to the frequency of the incident photons. Metal surfaces with nanoscale roughness increase the Raman scattering of molecules absorbed on them. This effect is due to chemical and electromagnetic factors, as well as increased surface area. The details of this effect will not be considered here: what is important is that the **surface-enhanced Raman scattering** (SERS) effect can induce a signal enhancement of up to 10^8 times. In one specific case, it has been possible to achieve a Raman enhancement effect of 10^{15} times! This means that the SERS effect makes it possible to push the detection limit of surface detection techniques. The SERS signal depends on the characteristics of the nano-substrate: the size, shape, orientation and composition of the surface nano-roughness. Advancements in SERS technology will allow detection at the attomole (10^{-18} mol) level, and single molecule detection.

Non-radiative and non-electron characterisation methods

There are numerous methods used to characterise nanomaterials which do not rely on the use of EM radiation. They include methods to determine particle size, surface area and porosity; thermodynamic methods (such as thermogravimetric analysis, TGA) to evaluate the temperature dependence of the nanomaterial (melting, etc.); and mass spectroscopy, to determine the chemical composition of the nanomaterial. An important surface method is the **quartz crystal microbalance** (QCM), which can measure mass changes as small as a few nanogrammes per square centimetre. This is sensitive enough to detect **monolayers** of deposited materials. It can be used to measure the amount of metal deposited on a surface after sputtering or evaporation, or to measure the amount of protein absorbed on a surface. Due to this great sensitivity, the QCM is used in the design of biosensors.

CHAPTER 7:

FABRICATION METHODS

This chapter summarises some of the methods used in the fabrication of nanomaterials, meaning materials with at least one dimension at the nanoscale level (1–100 nm). These include nanostructured surfaces, nanoparticles, nanoporous materials, etc. The aim of this chapter is to answer the questions: How are nanomaterials made? What fabrication tools are used in nanoscience and nanotechnologies?

Methods for fabricating nanomaterials can be generally subdivided into two groups: **top-down** methods, and **bottom-up** methods. In the first case, nanomaterials are derived from a bulk substrate and obtained by the progressive removal of material, until the desired nanomaterial is obtained. A simple way to illustrate a top-down method is to think of carving a statue out of a large block of marble. Printing methods also belong to this category. **Bottom-up** methods work in the opposite direction: the nanomaterial, such as a nanocoating, is obtained starting from the atomic or molecular precursors and gradually assembling it until the desired structure is formed. The method resembles building with Lego® bricks.

In both methods, two requisites are fundamental: control of the fabrication conditions (e.g. energy of the electron beam) and control of the environment conditions (presence of dust, contaminants, etc.). For these reasons, nanotechnologies use highly sophisticated fabrication tools that are mostly operated in a vacuum in clean-room laboratories.

Top-down

Numerous top-down fabrication methods used in nanotechnologies are derived from the fabrication methods used in the semiconductor industry to fabricate the various elements of computer chips (integrated circuits). These methods are collectively called **lithography** and use a light or electron beam to selectively remove micron-scale structures from a precursor material called **resist**. In recent years, there has been a tremendous push to reduce the size of electronic devices and integrate more functions into them, which has been possible thanks to the advances in lithographic fabrication methods. Nowadays, it is possible to obtain single features below 100 nm (the transistors in latest generation processors are about 45 nm). **Therefore, in the semiconductor industry, nanostructures are routinely fabricated**. Lithographic methods that are capable of producing nanoscale features are reviewed in the next section.

There are many more methods to fabricate nanostructures top-down; here, the discussion is limited to the most common methods.

Conventional lithography

Lithography includes a series of fabrication techniques that share the principle of **transferring an image from a mask to a receiving substrate**. A typical lithographic process consists of three successive steps: (i) coating a substrate (Si wafer or glass) with a sensitive polymer layer (called a resist);

(ii) exposing the resist to light, electrons or ion beams; (iii) developing the resist image with a suitable chemical (developer), which reveals a positive or negative image on the substrate depending on the type of resist used (i.e. positive tone or negative tone resist). In conventional micro-fabrication used in the semiconductor industry, the next step after lithography is pattern transfer from the resist to the underlying substrate. This is achieved through a number of transfer techniques, such as chemical etching and dry plasma etching.

Lithographic techniques can be broadly divided into two groups.

1. Methods that use a **physical mask**, where the resist is irradiated through the mask which is in contact or in proximity with the resist surface. These methods are collectively called mask lithography, among which photolithography is the most used.
2. Methods that use a **software mask**, where a scanning beam irradiates the surface of the resist sequentially, point by point, through a computer-controlled program where the mask pattern is defined. These methods are collectively called scanning lithography.

The main difference between mask and scanning lithography is speed: whereas mask lithography is a parallel, fast technique, scanning lithography is a slow, serial technique. Another important difference is resolution which, in general terms, is higher for scanning methods. The price paid for higher resolution is the use of more energetic radiation sources, which entails expensive equipment.

Photolithography

Photolithography uses light (UV, deep-UV, extreme-UV or X-ray) to expose a layer of **radiation-sensitive polymer** (photoresist) through a mask. The mask is a nearly optically flat glass (or quartz, depending on the light used) plate which contains the desired pattern: opaque areas (the pattern, made of an absorber metal) on a UV-transparent background. The image on the mask can be either replicated as it is, placing the mask in physical contact with the resist (contact mode photolithography) or reduced, usually by a factor of 5 or 10, and projected to the resist layer through an optical system (projection mode photolithography) (**Figure 1**).

The **resolution of contact mode lithography is typically 0.5–0.8 μm when UV light (360–460 nm) is used**. Higher resolutions cannot be achieved due to the inability to reduce the gap between the mask and the flat substrate below approximately 1 μm, even when elaborate vacuum systems are used to hold the two parts together. To produce patterns with higher resolution, projection photolithography or 'next-generation photolithography' techniques (i.e. extreme UV and X-ray photolithography) need to be employed. These technologies use very expensive equipment and, therefore, their use is limited to selected applications (such as photomask fabrication). The equipment needed is available only in specialised laboratories.

Scanning lithography

Energetic particles such as **electrons and ions can be used to pattern appropriate resist films** leading to features with nanometre resolution. When using electrons, the technology is called electron beam lithography (**e-beam**), whereas using ions, the technology is called **focused ion beam lithography**. Finally, a recently established technology uses nanometre scanning probes for patterning resist films and is therefore referred to as **Scanning Probe Lithography** (SPL). This technology has been extended to the deposition of a nanoquantity of material (Dip Pen Nanolithography® or DPN®).

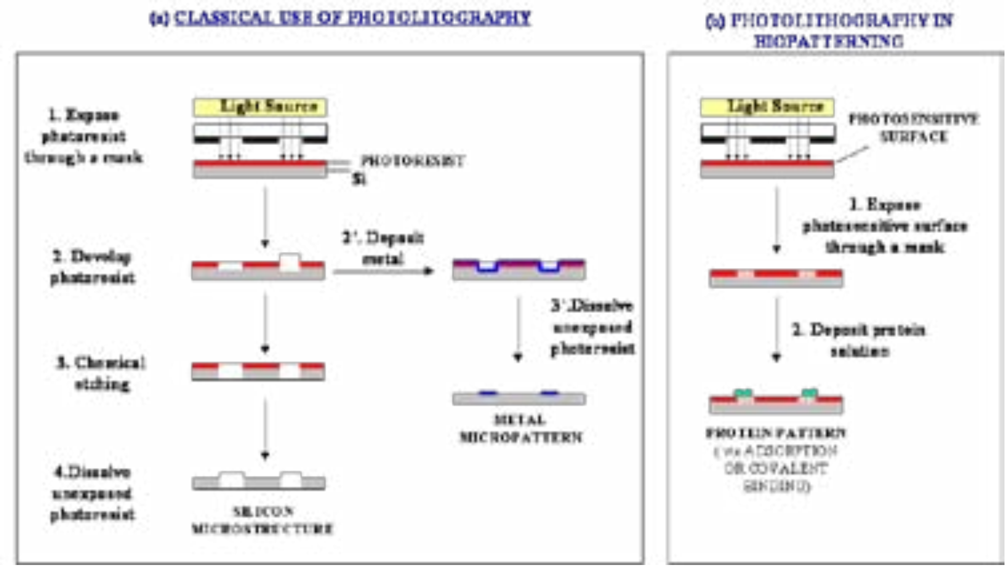


Figure 1: Conventional use of photolithography in the semiconductor industry for the fabrication of elements used in integrated circuits (e.g. computer chips). A photoresist is deposited on a silicon wafer, exposed to light through a mask, and the exposed area selectively removed with a developer. The resulting pattern can be used as a 'mask'for chemical etchingor as a pattern where a metal is selectively deposited.

Image: L. Filipponi, PhD thesis, 'New micropatterning techniques for the spatial immobilisation of proteins', © L. Filipponi, 2006, Creative Commons Attribution ShareAlike 3.0

E-beam lithography

In a typical e-beam lithography process, a tightly focused beam of electrons scans across the surface of an electron-sensitive resist film, such as poly(methyl methacrylate) (PMMA). The main advantage of e-beam lithography over photolithography is its high resolution: patterns with **features as small as 50 nm** can be routinely generated. The resolution of this technology is mainly determined by the scattering of the electrons in the resist film and the substrate. When using particles with a mass higher than electrons, however, this effect is largely reduced. Focused ion beam lithography works on the same principle of e-beam lithography, but ions such as H^+, He^{++}, Li^+ and Be^{++} are used. Both techniques provide a resolution much higher than photolithography but share a main disadvantage: both are serial techniques, very slow in process, so their use is mostly limited to producing photomasks in optical lithography.

Soft lithography

Soft lithography is the name for a number of techniques that fabricate and use a soft mould prepared by casting a liquid polymer precursor against a rigid master. These methods have been **developed specifically for making large-scale micro and nanostructures with equipment that is easier**

to operate compared to those used in 'conventional' lithography, cheaper and also available in biological laboratories. **Figure 2** shows the general principle of soft lithography.

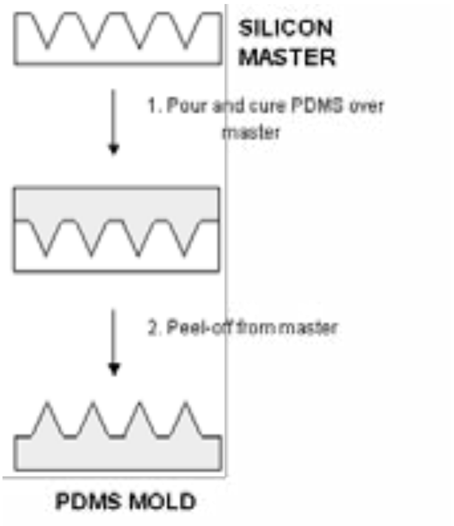


Figure 2: Overview of a soft lithography replication process. A silicon master is replicated with PDMS. The pre-polymer is poured (it is a very viscous liquid) over the master and cured at 65 °C for two hours (temperature and curing time can be adjusted). The polymer solidifies but remains very flexible. The PDMS mould is then peeled off from the master, and a negative copy obtained. AFM images of the master and the PDMS replica are shown in Figure 3.

Image: L. Filipponi, PhD thesis, 'New micropatterning techniques for the spatial immobilisation of proteins', © L. Filipponi, 2006, Creative Commons Attribution ShareAlike 3.0

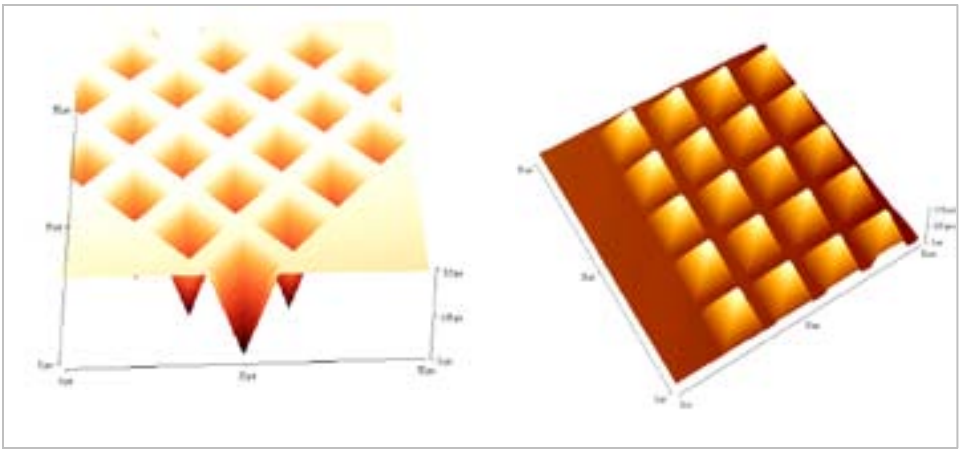


Figure 3: AFM image of an array of pyramidal wells in a silicon master (left) and pyramidal posts in a PDMS replica (right)

Image: L. Filipponi, PhD thesis, 'New micropatterning techniques for the spatial immobilisation of proteins', © L. Filipponi, 2006, Creative Commons Attribution ShareAlike 3.0

The resolution of soft lithography is mainly determined by van der Waals interactions, wetting and kinetic factors such as filling the capillaries on the surface of the master, but not by optical diffraction. This is an important advantage over 'conventional' lithographic techniques. The master is normally fabricated via a conventional lithographic method.

Various polymers (e.g. polyurethanes, epoxides and polyimides) can be used for moulding: most commonly, the elastomer poly(dimethylsiloxane) (PDMS) is used. PDMS is non-toxic so it can be used safely with biological materials, including live cells. This is a big advantage in devices that aim to integrate nanostructures with biological systems.

A PDMS mould is fabricated by pouring its liquid precursor over a lithographically-made master (e.g. a photoresist or silicon master), cured to induce cross-linking, and then peeled off. The stamp can then be used either for printing a desired material (the 'ink') from the stamp to a suitable surface (micro-contact printing, μCP) or, when in contact with a flat or curved surface, to define physical constraints where a liquid can be confined.

Nanocontact printing

Microcontact printing is useful for patterning features with lateral dimension of 500 nm or larger. One of the major challenges for μCP has been to achieve the capability to print with high resolution (i.e. with **lateral dimension lower than 100 nm**). This has recently been achieved by improving the stability of the PDMS, which, being soft and highly compressible, has a tendency to deform and collapse. One way to improve the stability of the patterns is to fix a stiff backplane to the stamp or to change the chemical formulation of the stamp itself, in order to obtain a harder polymer. With these modifications, it is now possible to print features as small as 50 nm. This printing method, which uses harder stamps, is called **nanocontact printing** (nCP).

Nano-imprint lithography

The concept of nano-imprint lithography is to use a hard master with a 3D nanostructure to mould another material, which assumes its reverse 3D structure. Imagine taking a Lego® block and pressing hard on a piece of Play-Doh. Since the master has a fine nano-structure, to be successful, the process must be done under pressure, a coating must first be placed on the master to avoid catastrophic adhesion to the mould, and the mould must be heated (above its Tg temperature) in order to be soft enough to completely enter the fine master nanostructure and be effectively replicated. The method is the equivalent of embossing at the nanoscale and requires specialised equipment.

Nanosphere lithography

In nanosphere lithography, an ensemble of nanospheres ordered on a surface is used as a mask (**Figure 4**). The nanospheres are dispersed in a liquid (i.e. a colloid) and a droplet placed on a surface and left to dry. Depending on the surface properties (e.g. charge) and media used in the colloid (e.g. presence of electrolytes) the nanosphere will self-assemble in an ordered pattern. In some conditions, a colloidal crystal is obtained: each nanoparticle is surrounded by six other nanospheres. This regular arrangement (which is a **2D colloidal crystal**) can be used to create ordered structures on surfaces.

TIP FOR TEACHERS: To illustrate this in class, take a number of spherical beads and pour them onto a shallow plate. The beads will self-organise in the same way.

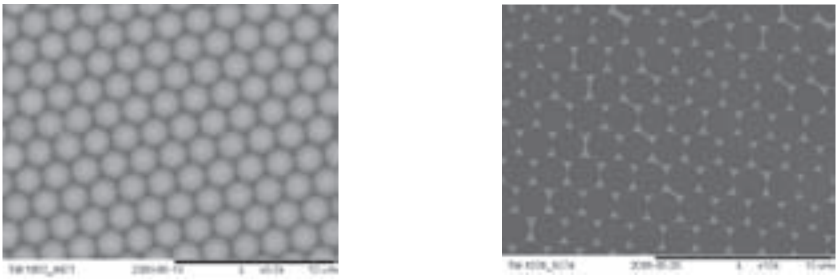


Figure 4: Nanosphere lithography: SEM images of a latex nanosphere mask (2 μm SiO_2 beads) (left) and triangular gold nanoprisms (right) obtained by evaporating gold over the colloidal mask (nanosphere lithography)

Image: R. Ogaki, iNANO, Aarhus University, © 2008

In the regular arrangement of nanospheres, there will be an empty space between them, which is regularly repeated over the entire surface. In the simplest method, this space is employed to create relatively flat nanopatterns on the surface. The nanosphere pattern is used as a mask, and a material (e.g. gold, silver) sputtered on top of it. Once the nanospheres are removed, a regular pattern of 'dots' is left, each shaped like a triangle but with concave sides.

The gold pattern (dots) can also act as growth sites, for example for the growth of carbon nanotubes or ZnO. **The result is a regular array of nanotubes or nanowires**, as shown in **Figure 5**.

Nanosphere lithography has now evolved into a method that allows the fabrication of very complex arrays of nanostructures, including **3D features with small holes in them**.

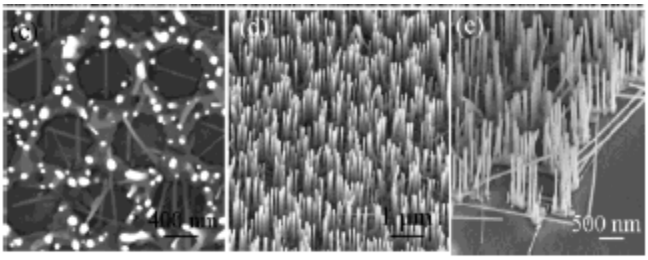


Figure 5: Top and 30° view of aligned ZnO nanorods, where the hexagonal pattern is apparent: (d) aligned ZnO nanorods at the edge of the growth pattern

Image: Wang et al., Nano Letters, 2004, 4(3):423–6, reprinted with the permission of the American Chemical Society, © 2004

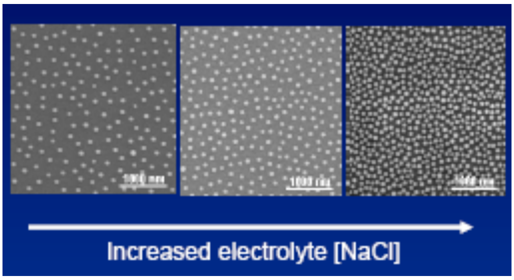
Colloidal lithography

Colloidal lithography shares the same principle of nanosphere lithography by using a colloid as a mask for the fabrication of nanostructures on surfaces (**Figure 6**). In this method, electrostatic forces are employed to obtain short-range ordered arrays of nanospheres on the surface.

The array can then be used to create a number of different nanostructures, through various processes such as etching, lift-off, etc.

Without going into details of the method, what is interesting to note is the **different types of nanostructures that can be formed: holes, cones, rings, 'sandwiches' made of different materials, etc**. (**Figure 7**).

If made of metals, these nanostructures present a localised surface plasmonic resonance effect (LSPR) which can be used for sensing. These materials are therefore under study for various **sensing applications** (e.g. for medical devices).



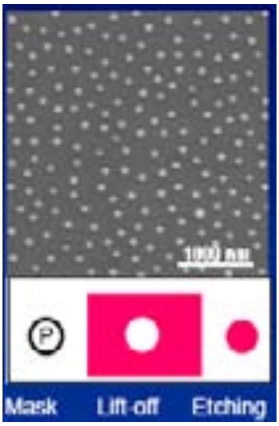


Figure 6: (left) effect of increasing the electrolyte concentration in the formation of the ordered array; (right) general principle of colloidal lithography

Images: D. Sutherland, iNANO, Aarhus University

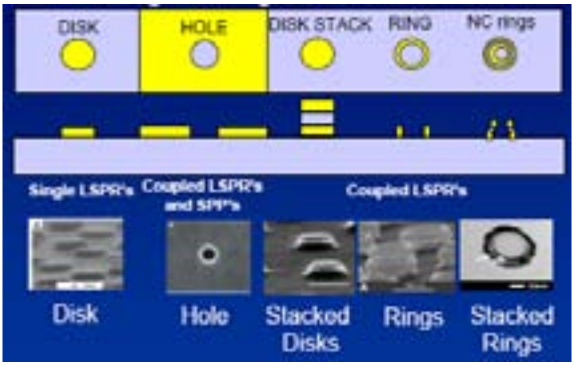
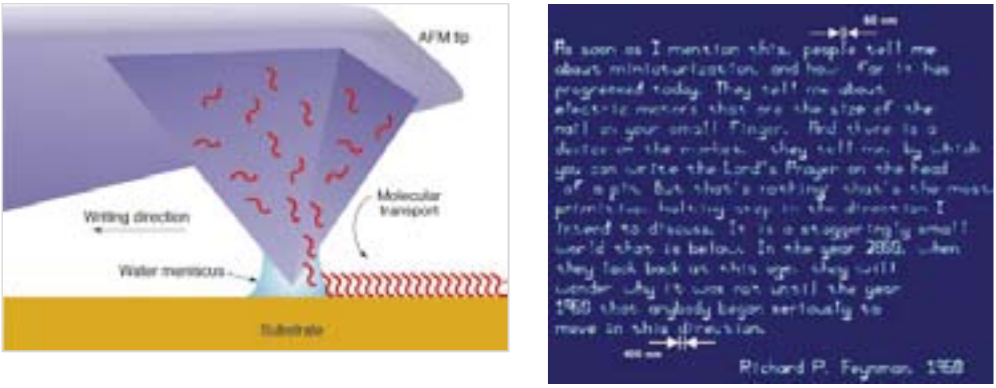


Figure 7: Summary of the various nanostructures that can be formed as regular arrays on surfaces

Image: D. Sutherland, iNANO, Aarhus University

Scanning probe lithography

Scanning probe microscopy (i.e. STM, AFM, etc.) uses small (< 50 nm) tips to image surfaces with atomic resolution (these methods are described in **Module 1, Chapter 6: Characterisation methods**). This ability suggests opportunities for their use in generating nanostructures and nanodevices. In this form, they are referred to as **Scanning Probe Lithography (SPL)**, which uses the tip of an AFM to selectively *remove* certain areas on a surface and **Dip Pen Nanolithography**® (DPN®), which, similarly, uses the AFM tip to *deposit* material on a surface with nanometre resolution (**Figure 8**).



As soon as I mention this, people tell me
about miniaturization, and how far it has
progressed today. They tell me about
electric motors that are the size of the
nail on your small finger. And there is a
device on the market, they tell me, by which
you can write the Lord's Prayer on the head
of a pin. But that's nothing; that's the most
primitive, halting step in the direction I
intend to discuss. It is a staggeringly small
world that is below. In the year 2000, when
they look back at this age, they will
wonder why it was not until the year
1960 that anybody began seriously to
move in this direction.

Richard P. Feynman, 1960

Figure 8: (left) The operation principle of DPN: the AFM tip is coated with a liquid containing the molecules to be deposited and as the tip scans the surface, the molecules are deposited through the water meniscus that forms between the tip and the surface; (right) part of the famous speech 'There is plenty of the room at the bottom' by Professor R. P. Feynman written with SPL

Images: (left) reprinted from 'Small science gets to the heart of matter', Science and Technology Review, 2001; (right) C. Mirkin, Northwestern University

Both are direct writing techniques and their main advantages are high resolution and the ability to generate patterns with arbitrary geometries. Like e-beam and ion-beam lithography, SPL and DPN are serial techniques whose main limitation is speed.

Writing 'atom by atom'

A particular feature of an STM is that it can be used for more than just to visualise atoms. Twenty years ago, researchers at IBM were able to demonstrate that they could use the STM tip to carefully move atoms on a surface and write the company logo with atoms, as shown in **Figure 9**.

If one were to write using atoms, letters would be around 1 nm each. With letters of this size, the whole of Encyclopaedia Britannica could be reproduced in an area as small as the tip of a human hair (10^{-4} m^2). Indeed, with letters of this size all the world's books would fit on a single A4 sheet, but it would take incredibly long to write, and in addition they could only be read with the STM.

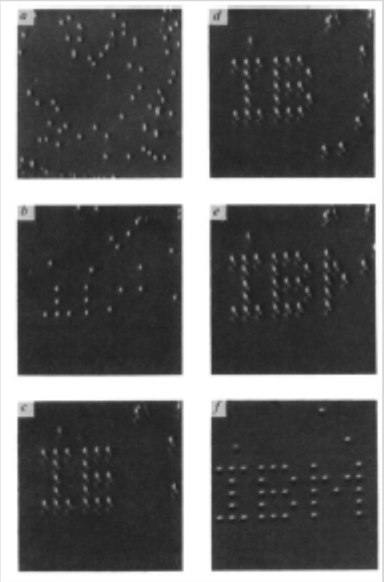


Figure 9: Actual sequence of STM images as reported in the original paper that demonstrated for the first time that writing with the STM is possible

Image: D. M. Eigler., E. K. Schweizer, 'Positioning single atoms with a scanning tunnelling microscope', *Nature*, 5 April 1999, Vol. 344, reprinted with the permission of Macmillan Publishers Ltd, © Nature Publishing Group, 1999

Nevertheless, the ability to move individual atoms using an STM has great potential for the future generation of **data storage devices**. Today, data is stored on CD-ROMs using minute 'bits' of semi-conductors around 0.1 µm (10^{-7} m) in size. If these bits were written with atoms instead, far greater data capacity would be achieved. One of these 'nano-CDs' with 'atomic bits' could contain as much information as one million current CD-ROMs.

The STM allows a material to be built atom by atom independently of its chemistry and physics, as shown in **Figure 10**. This can lead to new materials that most likely have completely new properties. The process is still very slow, since the atoms can be moved only manually, and this must be one atom at a time. Mass production of new nano-materials using this method is thus not yet possible.

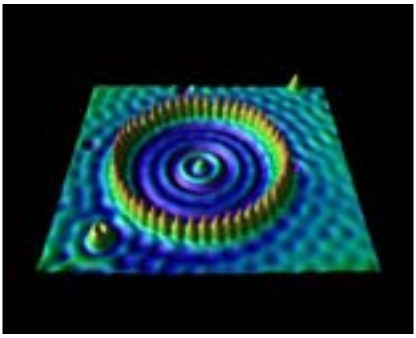


Figure 10: This corral is an artificial structure created from 48 iron atoms (the sharp peaks) on a copper surface. The wave patterns in this scanning tunneling microscope image are formed by copper electrons confined by the iron atoms

Image: D. Eigler, IBM Almaden Research Center, NISE Network (http://www.nisenet.org), reprinted under NISE Network Terms and Conditions

Bottom-up

Bottom-up methods can be divided into gas-phase and liquid-phase methods. In both cases, the nanomaterial is fabricated through a controlled fabrication route that starts from the single atom or molecules:

- gas-phase methods: these include plasma arcing and chemical vapour deposition;
- liquid phase: the most established method is sol-gel synthesis; molecular self-assembly is emerging as a new method.

Plasma arcing

This is the most common method for fabricating nanotubes. The method uses a plasma which is an ionised gas. A potential difference is placed between two electrodes and the gas in between ionises. A typical arcing device is made of two electrodes, and an arc passes from one electrode to the other. The first electrode (anode) vaporises as electrons are taken from it by the potential difference. For instance, a carbon electrode is used to produce carbon nanotubes and this is consumed during the reaction, producing carbon cations. These positively changed ions pass to the other electrode, pick up electrons and are deposited to form nanotubes.

Plasma arcing can also be used to deposit nanolayers on surfaces rather than making new structures. The deposit can be as little as a few atoms in depth (and must be at least 1 nm thick to be considered a nanomaterial). In this sense, plasma arcing is complementary to chemical vapour deposition (described next).

Chemical vapour deposition

In this method, the material to be deposited is first heated to its gas form and then allowed to deposit as a solid on a surface. This method is normally performed under vacuum. The deposition can be direct or through a chemical reaction so that the material deposited is different from the one volatilised. This process is routinely used to make nanopowders of oxides and carbides of metals if carbon or oxygen are present with the metal. The method can also be used to generate nanopowders of pure metals, although not so easy to do.

Chemical vapour deposition is often used to deposit a material on a flat surface. When a surface is exposed to a chemical vapour, the first layer of atoms or molecules that deposit on the surface can act as a template on which material can grow. The structures of these materials are often aligned. During deposition, a site for crystallisation may form in the depositional axis (the axis perpendicular to the surface to be coated). As a result, aligned structures start to grow vertically. This is therefore an example of self-assembly.

Molecular beam epitaxy

This is essentially a very sophisticated evaporation method in which molecular beams interact on a heated crystalline substrate under ultra-high vacuum (UHV) conditions to produce a single crystal film. **Molecular Beam Epitaxy** (MEB) makes it possible to fabricate crystals one atomic layer at a time. The growth process is highly controlled to avoid contaminants being introduced during the crystal growth. A range of surface analysis techniques is used to monitor the growth process and ensure purity of the crystal. MBE is presently used in the semiconductor industry, where the performance of the device (e.g. computer chip) depends on precise control of dopants and on the production of extremely thin crystal layers with hyper-abrupt interfaces. MBE is used for the fabrication of numerous important devices such as light-emitting diodes, laser diodes, field effect transistors, read-write heads for computer drives and more.

Sol-gel synthesis

This method is carried out in the liquid phase. It is a useful self-assembly process for fabricating nanoparticles as well as nanostructured surfaces and three-dimensional nanostructured materials such as aerogels.

A 'sol' is a type of colloid (7) in which a dispersed solid phase is mixed into a homogeneous liquid medium. An example of a naturally occurring sol is blood. As the name suggests, the sol-gel process involves the evolution of networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

The first stage in the sol-gel process is the synthesis of the colloid. The precursors are normally ions of a metal. Metal alkoxides and alkoxysilanes are the most popular since they react readily with water (hydrolysis). The most widely used alkoxysilanes are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) which form silica gels. Alkoxides such as aluminates, titanates and borates are also used, often mixed with TMOS or TEOS. In addition, since alkoxides and water are immiscible, a mutual solvent is used, such as an alcohol.

The sol-gel process involves four steps. First, the hydrolysis reaction, in which the -OR group is replaced with an -OH group. The hydrolysis reaction can occur without a catalyst but is more rapid and complete when catalysts are used. As in any hydrolysis reaction, the catalyst can be a base (NaOH or NH_3) or an acid (HF or CH_3COOH).

After hydrolysis, the sol starts to condense and polymerise. This leads to a growth of particles which, depending on various conditions such as pH, reach dimensions of a few nanometres. The condensation/polymerisation reaction is quite complex and involves many intermediate products, including cyclic structures. The particles then agglomerate: a network starts to form throughout the liquid medium, resulting in thickening, which forms a gel.

All four steps described are affected by the initial conditions for the hydrolysis reaction and the condensation/polymerisation. These conditions include pH, temperature and time of reaction, nature of the catalyst, etc.

The sol-gel process is very commonly used to make silica gels. Other type of gels can also be formed: aluminosilicate gels are special because they form tubular structures. One such product is imogolite which has an external diameter of about 2.5 nm and internal tube diameter of 1.5 nm. These types of nanostructures are known to be good adsorbents of anions such as chloride, chlorate, sulphate

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(7) A colloid is a type of chemical mixture where one substance is dispersed evenly throughout another but the particles of the dispersed substance are only suspended in the mixture, they are not completely dissolved in it. Generally speaking, a colloid is composed of particles 10–200 nm. The dispersed phase can be solid, liquid or gas and the medium in which it is dispersed (called continuous medium) can also be solid, liquid or gas.

and phosphates. The imogolite structure can be dissolved away with hydrofluoric acid (HF). Therefore, these nanostructures can be used for template synthesis: the tube can be filled with atoms and then dissolved away, leaving rows of atoms (2.5 atoms of gold in a row measuring 1 nm).

Sol-gel process for making nanostructured surfaces

Figure 11 summarises the different sol-gel processes. To make the most of the large surface area of nanoparticles, the gel can be placed on a surface. This way a greater bulk-area ratio is obtained. Another strategy is to form an aerogel. These are three-dimensional continuous networks of particles with air (or any other gas) trapped at their interstices. Aerogels are characterised by being porous and very light yet able to withstand 100 times their own weight.

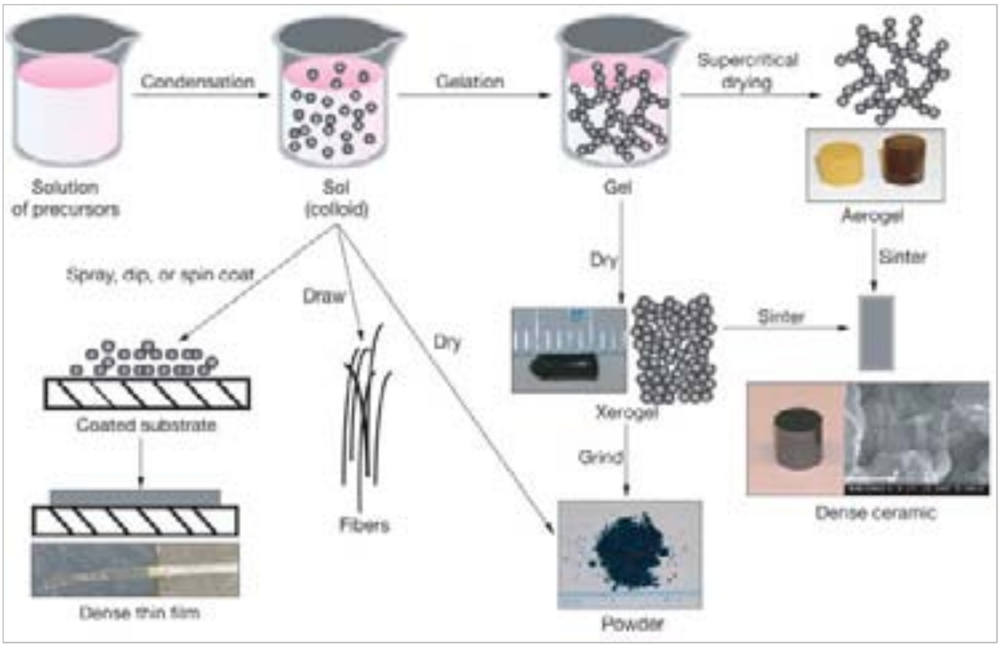

Figure 11: Schematic overview of different materials that can be obtained through a sol-gel process

Image: Lawrence Livermore National Laboratory

A versatile way to create ordered surface nanostructures is to perform the sol-gel synthesis in a liquid which is itself ordered. Liquid crystals are precisely this: they have a crystalline structure but exist in a liquid (rather than solid) phase. Nanostructured silica with controlled pore size, shape and ordering can be made in this way.

The liquid crystalline casting method just described can also be used to produce **nanostructured metals**. This development is very useful for making nanostructured catalytic surfaces, such as platinum or palladium surfaces. Since these metals are very rare and expensive, it is highly advantageous to have surfaces where nearly all metal atoms can take part in the catalytic reaction (being on the surface), and not just surface atoms as in conventional solids.

Functionalised silica glass surfaces

The sol-gel method also allows the incorporation of organic, inorganic and bio-organic molecules within the silica glass structure. Most organic and inorganic molecules cannot be incorporated (doped) in glass because this is prepared using very high temperatures. The sol-gel process occurs at relatively low temperatures (in some cases at room temperature), so these molecules can be incorporated in the process. This makes it possible, for example, to incorporate molecules such as enzymes inside the silica glass. The result is a material that has the advantages of plastics (the product can be made in any form, it can be attached to other materials, etc.) but also many improvements: the glasses are inert, more stable to heat and chemical attack, the entrapped molecules do not leach out, and are protected in their reactivity, and the glasses are transparent (8).

Molecular self-assembly

Self-assembly is the 'fabrication tool' of nature: all natural materials, organic and inorganic, are produced through a self-assembly route. In natural biological processes, molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of the membrane cell from phospholipids. In self-assembly, sub-units spontaneously organise and aggregate into stable, well-defined structures through **non-covalent interaction**. This process is guided by information that is coded into the characteristics of the sub-units and the final structure is reached by equilibrating to the form of the lowest free energy.

TIP FOR TEACHERS: Self-assembly is a concept that can easily be integrated into conventional lessons on genetics or biology. There are various size scales of self-assembly, from the molecular level (from proteins to DNA) to 'macro' level (evolution of a foetus into a baby). Basically, all natural processes are examples of self-assembly.

To date, devices have been fabricated starting from the top (a large piece of metal) and carving down to small pieces; now scientists are considering and studying ways to truly build materials from the bottom up, mimicking nature's own fabrication strategy. Instead of carving nanostructures out of larger materials (which is the typical top-down approach used to fabricate integrated electronic circuits such as micromachining and microlithography), nanostructures could be created bottom-up, from atomic building blocks that self-assemble into larger structures.

It must be noted that this is now possible for extremely small objects. The idea of using a computer-assisted program to actually build a device, such as an electronic circuit, atom by atom, through a self-assembly program is still a vision, but it is possible to fabricate some very small components of an integrated circuit through a self-assembly process (e.g. a nanowire).

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(8) If nanoparticles or even smaller molecules are added to the glass, it remains transparent since nanoparticles do not scatter light — refer to Chapter 4 for more details.

In the laboratory, scientists can make use of this self-organisation of matter as a way of programming the construction of novel structures with specific functions. Thus, the fabrication process is a molecular recognition-directed self-organisation. To build bottom-up, specific patterns are inserted into molecules to form organised supermolecules — nanostructures making use of supermolecular chemistry. This can be understood as a lock-and-key self-organisation of matter: scientists can pre-organise a 'key' in a molecule to fit a 'lock' inanother, or vice versa. Once in proximity, the two (or more) molecules assemble together: the lock-and-key mechanism serves to bind the two molecules together in a specific geometry. In supermolecular chemistry, there are no chemical bonds formed during the self-assembly process: the molecules are held together through metal-ion coordination, hydrogen bonding, donor-acceptor interactions, van der Waals forces and mediation effects (e.g. solvent). **Transition-metal-mediated structures** are a type of supermolecular structure. In the structure, metal cations are the cement that holds the molecules (the 'bricks') together. Interest in supermolecular structures derives from the fact that they can have properties that are dramatically different from those of their components (e.g. change in electric properties). Another method uses the structural motifs and self-recognition properties of DNA to self-assemble pre-designed nanostructures in a bottom-up approach. This field is called DNA nanotechnology.

Two other important types of supermolecular structures that are created through a self-assembly process are **dendrimes** and **cyclodextrins** (Figures 12 and 13).

Figure 12: Dendrimer with 54 ferrocenes attached

Image: Wiki Commons, image for public domain

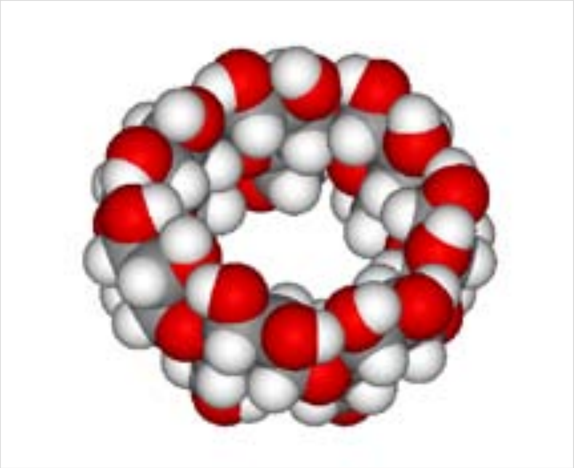

Figure 13: Three-dimensional model of the chemical structure of beta-cyclodextrin

Image: Wiki Commons, image for public domain

DNA nanotechnology

DNA nanotechnology exploits the structural motifs and self-recognition properties of DNA to self-assemble pre-designed nanostructures in a bottom-up approach. Two and three-dimensional structures have been fabricated using this self-assembly method. Recently, the revolutionary **DNA origami method** was developed to build two-dimensional addressable DNA structures of arbitrary shape that can be used as a platform to arrange nanomaterials with high precision and specificity. Researchers at the Centre for DNA Nanotechnology (Aarhus University) have developed a software package to facilitate the design of DNA origami structures and it was initially applied in the design of the dolphins in the former logo of Aarhus University (**Figure 14**).

Figure 14: Researchers began by cutting a dolphin out of the University of Aarhus logo, which was then used as a template to design a dolphin-like DNA structure. After producing this in the laboratory, AFM images were taken of the DNA structure thus formed and an image of the DNA dolphin was reinserted in the Aarhus University logo.

Image: Danish National Research Foundation, Centre for DNA Nanotechnology (cDNA), and the Interdisciplinary Nanoscience Centre (iNANO) at Aarhus University, © 2009

The design program was further applied in the design of a three-dimensional DNA box with dimensions 42 × 36 × 36 nm^3 that can be opened by external 'key' signals (**Figure 15**). The controlled access to the interior compartment of the DNA container opens the way for several interesting applications of the DNA box, for example as a **logic sensor** for multiple sequence signals and for the **controlled release of nano-cargos** with potential applications in the emerging area of nanomedicine.

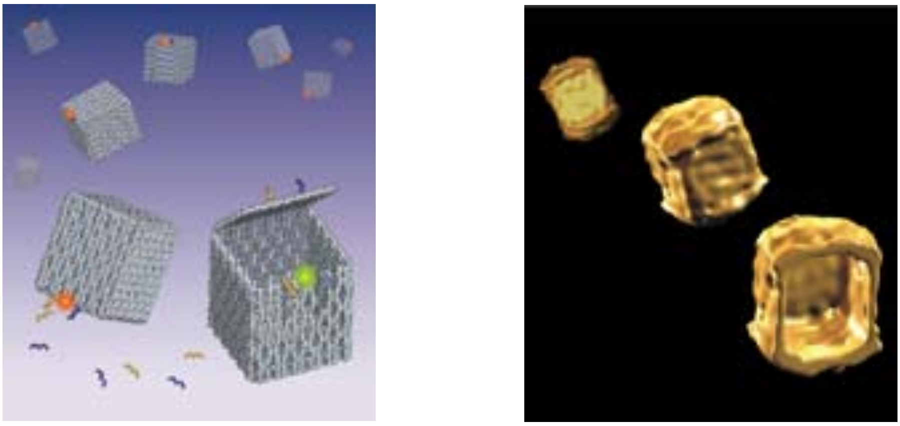

Figure 15: (left) atomic models of DNA boxes with dimensions of 42 x 36 x 36 nm^3 that are large enough to harbour, for example, a whole ribosome; (right) cryo-electron microscopy (cryo-EM) reconstruction of the same DNA boxes

Image: Danish National Research Foundation, Centre for DNA Nanotechnology (cDNA), and the Interdisciplinary Nanoscience Centre (iNANO) at Aarhus University, © 2009

DNA nanotechnology represents one of the latest developments in nanotechnology. It has applications for the fabrication of nano-guides (e.g. waveguides), sensors (for diagnostic and imaging), logic gates, drug release, nano-motors and electronics (wires, transistors). It could lead to bottom-up electronics and DNA computing, which could become the computing of the future.

MODULE 2:

APPLICATIONS AND IMPLICATIONS

Module addressing
the main technological applications
and societal implications

CHAPTER 1:

MEDICINE AND HEALTHCARE

The application of nanotechnologies to the medical sector is referred to as **nanomedicine**. Specifically, this area of application uses **nanometre scale materials and nano-enabled techniques to diagnose, monitor, treat and prevent diseases**. These include cardiovascular diseases, cancer, musculoskeletal and inflammatory conditions, neurodegenerative and psychiatric diseases, diabetes and infectious diseases (bacterial and viral infections, such as HIV), and more. The potential contribution of nanotechnologies in the medical sector is extremely broad and includes new diagnostic tools; imaging agents and methods; drug delivery systems and pharmaceuticals; therapies; implants and tissue engineered constructs.

Why nanotechnologies? Nanomaterials are defined as materials at the nanoscale level, which, in nanomedicine, often goes beyond 100 nm and up to about 500 nm. This is the size range of biomolecules (e.g. proteins, enzymes, DNA) and molecular complexes such as the ion pump. These natural nanomaterials are the constituents of larger hierarchical structures that regulate the function of the cell. Bacteria and viruses are larger (a few micrometres), but their functions (including toxicity to healthy cells) derive from the interactions between the biomolecules that compose them and the surrounding media (including surrounding cells). Basically, nanotechnologies make it possible to create engineering materials (such as drug delivery systems, disease imaging probes, or even tissue engineered constructs) that have dimensions on the scale of biomolecules which, in turn, is the scale that regulates the functions of cells. Nanotechnologies have the potential to improve the whole care process that starts for a patient once a disease is suspected, from diagnosis to therapy and follow-up monitoring. The aim is the development of new materials and methods to detect and treat diseases in a targeted, precise, effective and lasting way, with the ultimate goal of making medical practice safer, less intrusive and more personalised. The timescale from invention of a medical device or drug to release for clinical use is extremely long. In a few cases (such as drug delivery devices), nanotechnology is already in use for improving patient care but, in most of the areas to be discussed, the applications are still some years from being useable products.

Diagnosis

Diagnosis of a suspected disease is one of the most critical steps in healthcare and medicine. Diagnoses are wanted quickly, but must also be reliable, specific and accurate, and with the minimum risk of ‘false positives’. Nanomedicine has the potential to greatly improve the entire diagnostic process. Instead of collecting a blood sample in a vial and sending this to a specialised laboratory for testing (which can take days), doctors will be able to use **miniaturised *in vitro* diagnostic devices** in their surgeries. These are small but highly integrated devices capable of carrying out many tests quickly at the same time using very small quantities of sample to perform the analysis. Some miniaturised *in vitro* diagnostic devices already exist such as the breathalysers that the police carry for alcohol screening or the portable glucosetest devices used by diabetics. These devices can measure ions, small molecules or proteins, or can test for specific DNA sequences that are diagnostic for a particular disease or medical condition. In the last years, there has been a trend to make these devices even smaller, able to perform hundreds of tests at the same time and be easier to use. Nanotechnologies have an important role in this development: nanomaterials, such as nanoparticles or nanotubes, can be integrated into the device. Scientists can engineer nanomaterials to be very specific, so their use will make the device even more accurate and capable of carrying out even more tests simultaneously. Nanomaterials have the characteristic of exhibiting some peculiar quantum effects that can be used to **amplify the signal** arising from the detection. Thus, the use of nanomaterials in miniaturised *in vitro* diagnostic devices will make it possible to improve the specificity of the analysis, its throughput (the number of tests that can be done simultaneously) and its read-out. In the future, these types of devices will make it possible to perform 'point-of-care diagnostics': it will be possible to make a diagnostic test anywhere, not just in the doctor's surgery or hospital. The nature of the sample to be tested will probably change, and become saliva rather than blood, which is much more convenient and safer to handle. This will allow large numbers of patients to be tested, for example in the event of an epidemic, or large numbers of diseases, or the many parameters needed for one specific disease to be considered for the diagnosis of complex medical conditions.

Miniaturised diagnostic devices include biosensors, microarrays and 'lab-on-a-chip' (LOC) devices, also called miniaturised total analysis systems (μTAS). The first two are based on a parallel processing technique, whereas LOC devices are based on a serial processing technique.

Biosensors

Generally speaking, a sensor is a device capable of recognising a specific chemical species and 'signalling' the presence, activity or concentration of that species in solution through some chemical change. A 'transducer' converts the chemical signal (such as a catalytic activity of a specific biomolecule) into a quantifiable signal (such as a change in colour or intensity) with a defined sensitivity. When the sensing is based on biomolecular recognition, it is called a **biosensor**. There are various types of biosensors, such as those based on antibodies/antigens, nucleic acids and enzymes. Furthermore, depending on the technique used in signal transduction, biosensors are classified as optical detection biosensors (as in the example above), electrochemical biosensors, mass-sensitive biosensors or thermal biosensors.

There are numerous **nanoparticles** that can be used as biosensor components. These work as probes recognising an analyte or differentiating between analytes of interest. In such applications, some biological molecular species are attached to the surface of the nanoparticles to recognise the target of interest through a lock-and-key mechanism. The probes then signal the presence of the target by a change in colour, mass or other physical change. Nanoparticles used as elements for biosensors include quantum dots, metallic nanoparticles, silica nanoparticles, magnetic beads and fullerenes, which are hollow cages of carbon atoms, shaped like footballs.

Other biosensors use nanostructured particles as **nano-sieves** through which charged molecules are transported in an electric field. In this case, particles with engineered nanopores are used.

Carbon nanotubes and **nanowires** are also employed for sensing. The latter can be fabricated out of a semiconductor material and their size tuned to have a specific conducting property. This, together with the ability to bind a specific analyte on their surface, yields a direct, label-free electrical read-out. These nanowire biosensors allow the detection of a wide range of chemical and biological species, including low concentrations of protein and viruses, and their application ranges from the medical to the environmental sector. **Figures 1** and **2** illustrate a silicon nanowire biosensor based on biorecognition.

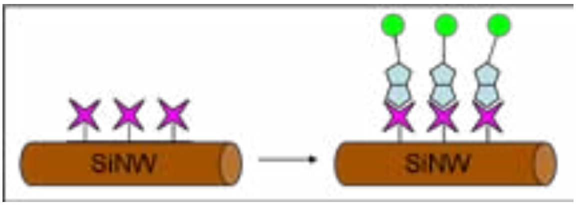

Figure 1: Biorecognition on a silicon nanowire biosensor: the surface of the nanowire is modified with avidin molecules (purple stars) which can selectively bind a streptavidin-functionalised molecule or nanoparticle

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons ShareAlike 3.0

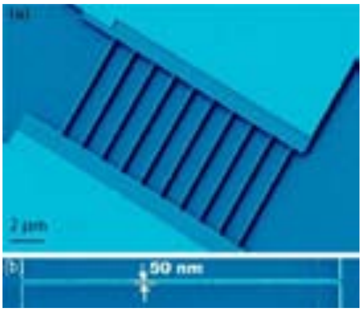

Figure 2: Scanning electron micrograph depicting the functional part of a nano-biosensor containing silicon nanowires

Image: P. Mohanty, Boston University, NISE Network (http://www.nisenet.org), licensed under NISE Network Terms and Conditions

Nanoscale biosensors have the potential to greatly aid in the **diagnosis** of diseases and **monitoring of therapies**. A large number of approaches have been developed in recent years while relatively few have so far been converted into clinical diagnostic tools — their wide application in patient care is foreseen in the next 5–10 years.

Cantilever biosensor

A cantilever biosensor is a biosensor made of numerous 'arms' (called cantilevers) which are tens of micrometres long but very thin (a few micrometres). These devices are fabricated through lithography and etching. The surface of the cantilever is functionalised with a **nanometre-thick layer** of coating which ensures anchorage of the probe material (which can be a DNA strand or a protein, for example). Each cantilever is different and can probe for a different target, as schematised in **Figure 3**. In this type of sensor, the adsorption of the analyte to the specific targets on a cantilever causes a surface stress and bends the cantilever. The most common read-out is optical where the angular disturbance of a laser beam is measured following the bending of the cantilever. Although common, this method suffers from the limitation that measurements are difficult in opaque liquids, such as blood, because of the absorption of the laser light. An alternative to this method is the piezoresistive read-out, where a piezoresistor is integrated into the cantilever. Upon detection of the analyte, the stress applied to the resister changes, which is reflected in a change of its resistance, which in turn is measured as an electrical signal. This approach offers the advantage of allowing the detection in opaque media, the possibility of miniaturising the sensor and incorporating it in portable devices for point-of-use sensing.

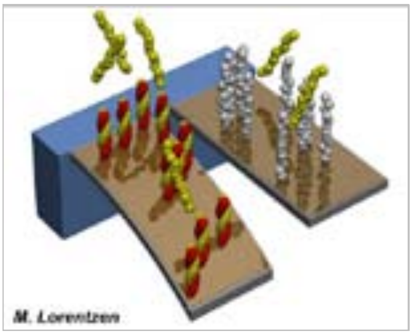

Figure 3: Schematic diagram of a cantilever-based biosensor: the yellow molecules bind specifically to the red molecules on the right-hand cantilever and are detected by the bending of the cantilever

Image: M. Lorentzen, iNANO, University of Aarhus, © M. Lorentzen

Plasmonic biosensors

The optical properties of **noble metal nanoparticles** have received significant research attention in recent years for their potential as components in many applications, including chemical/biochemical sensors. The optical properties of noble metal nanoparticles are dominated by an effect called localised surface plasmon resonance (LSPR), which was described in **Module 1, Chapter 4: Fundamental 'nano-effects'**. One of the consequences of the LSPR effect in metal nanoparticles is that they have very **strong visible absorption** due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold or silver can display colours that are not found in their bulk form, such as red, purple or orange, depending on the shape, size and surrounding media of the nanoparticles. The energy of LSPR is sensitive to the **dielectric function** of the material and the surroundings and to the shape and size of the nanoparticle. This means that if a ligand such as a protein attaches to the surface of the metal nanoparticle, its LSPR energy changes. Similarly, the LSPR effect is sensitive to other variations such as the distance between the nanoparticles, which can be changed by the presence of surfactants or ions. The fact that the LSPR depends on the dielectric environment means that the refractive index can be used as the sensing parameter: changes in the local dielectric environment, induced by the sensing process, are used to detecting the binding of molecules in the particle nano-environment.

In a plasmonic biosensor, the nanoparticles can be dispersed in a medium (in which case the biosensor is a **colloidal plasmonic biosensor**) or supported on a surface (**surface plasmonic biosensor**). Both types of sensors exploit the fact that the sensing event changes the LSPR of the metal nanoparticles, but use different read-out report strategies.

In a **colloidal plasmonic biosensor** (e.g. made of gold nanoparticles), the sensing event results in a change of aggregation among the nanoparticles that form the colloid (**Figure 4**), which can determine a colour change of the colloid. Absorption spectroscopy is used to quantify the biosensing event. In the case of gold colloid, which is normally red, the sensing event can result in the colloid becoming blue. Thus, metal colloids can be used as **plasmonic colorimetric biosensors**. In nanomedicine, this effect is used, for example, in genetic screening, where scientists look for a specific gene sequence in a sample which can be indicative of a specific disease. How is this done? First, the sequence of bases in the target DNA is identified. Then, two sets of gold particles are prepared — one has DNA attached that binds to one end of the target DNA, and the second set carries DNA that binds to the other end. The nanoparticles are dispersed in water. When the target DNA is added, it binds both types of nanoparticle together, linking them to form an aggregate. The formation of this aggregate causes a shift in the light-scattering spectrum from the solution (i.e. a colour change in the solution which can easily be detected). An example is illustrated in **Figure 5**.

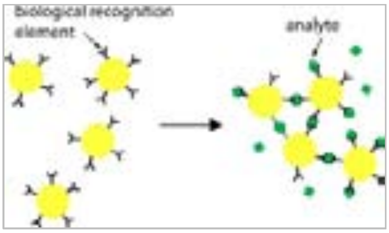

Figure 4: Schematic representation of a colloidal plasmonic biosensor

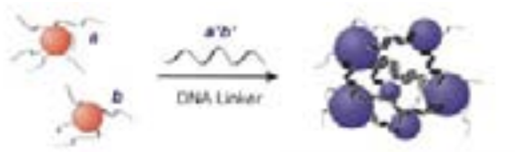

Figure 5: Plasmonic colloidal nanosensor

Image: Jin et al., *Journal of the American Chemical Society*, 2003, 125(6):1643–1654, reprinted with the permission of the American Chemical Society, © 2003

EXPERIMENT C in the **Experiment Module** deals with synthesising and testing a **gold colloidal plasmonic nano-sensor**. In the experiment, students use electrolytes to see the colour change due to the change in aggregation of the nanoparticles as the salt is added to the colloid.

In a **surface plasmonic sensor**, metal nanoparticles are immobilised on a surface as illustrated in **Figure 6**(a). The metal nanoparticles are attached to the surface by means of chemical linkers or prepared by nanolithography (b), and are then modified with the sensor moiety (c). The analyte (the target) attaches from solution specifically on to the recognition function adsorbed on to the particles (d), causing a change in the refractive index around the particle, resulting in an LSPR shift. The LSPR shift is measured through a technique called extinction spectroscopy (e).

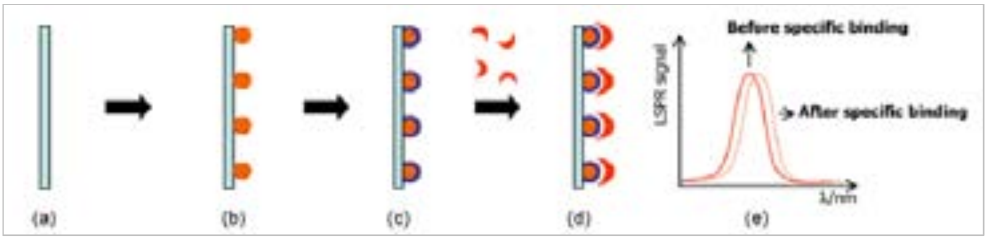

Figure 6: Schematic representation of the preparation and response of LSPR biosensors based on refractive index changes

Image: Borja Sepúlveda et al., 'LSPR-based Nanobiosensors', Nano Today, 2009, 4(3):244–251, reprinted with the permission of Elsevier

Artificial nose biosensor

An artificial nose biosensor is a device that mimics the ability of some mammals, such as dogs, to detect explosives and drugs through their olfactory system. Recent research has shown that this fine capacity in dogs may also be used to detect molecules which, if present, are early indicators of various diseases such as cancer. Numerous research programmes are under way around the world to create an artificial nose: one such is the European project BOND. The application of such types of biosensor ranges from medicine (early disease detection) and security (explosives detection) to the food industry (to measure whether food has gone off). This type of biosensor is an electrochemical sensor that mimics the natural mammal olfactory system. The nose-biosensor, like our own noses, is composed of three main parts, a biomolecule receptor, an electrode and a transducer. When the detector finds the target, a chemical reaction occurs between the detector and the receptor biomolecules for odour. The chemical reaction between the receptor and the substance we smell emits a chemical signal. The electrode translates this chemical signal into electrical signals and transports them to the brain or, in the case of the nose biosensor, they are transported to a transducer. In mammals, the equivalent of the electrodes would be neurons. The transducer (the brain in mammals) receives the electrical signal and translates it into analytical information. In the nose-biosensor, the transducer would give information on a screen.

NANOYOU GAME Students can become'nano-scientists' and fabricate and test a nose biosensor through the NANOYOU Virtual Game (http://www.nanoyou.eu/virtual-lab.html).

NANOYOU DILEMMA Diagnostic nanosensors (cantilever-based, plasmonic, nanowires-based, etc.) will allow for the early detection of various diseases, such as cancer, at the very onset of the symptoms, before the disease is perceived by the patient. Early detection means a higher chance of successfully treating and overcoming the disease. On the other hand, some worry that this will give doctors access to a large amount of personal information. The question is: Where is this information going to be stored, and who will have access to it? Also, what if those devices are used not as a diagnostic tool but as a mean to assess a person's medical condition by other entities, such as insurance companies or job agencies? The dilemma is: Should nanosensors be used to diagnose medical conditions in the early stages when there are still no definite restrictions in place to protect patients' privacy? This dilemma is part of the **NANOYOU role-playing game** (http://www.nanoyou.eu/en/decide).

Microarrays

These devices are used for diagnostic purposes such as DNA analysis (DNA microarray), protein detection (protein microarrays) as well as whole cell analysis. Microarrays are platforms made of hundreds of detection sites that have micron-sized dimensions and allow the specific detection of a (bio)chemical within a mixture or the simultaneous detection of many (bio)chemicals. The detection is related to the chemical functionality on the micron-sized spots in the array and it leads to a single chemical 'yes/no' reaction per spot. Microarrays are used as screening tools, not only for diagnostic purposes but also for **screening new drugs**. Nanotechnology can impact microarray technology by creating densely packed, smaller, nano-sized arrays (nanoarrays) that could allow faster screening of a larger number of (bio) chemicals. There are, however, some problems associated with the handling of ultra-small quantities of liquid so nanotechnologies offer the most promising advantages in sample detection on arrays. The conventional method used for detecting the 'yes/no' reaction at each spot is fluorescence. This technique uses fluorescent probes made of organic molecules attached to the species to be detected (e.g. a protein or a fragment of DNA): when reaction occurs, this is attached to the detection spot, which becomes fluorescent in a 'colour' corresponding to the emission of the fluorescent probe. Fluorescent staining suffers from some disadvantages, mainly fast bleaching of the fluorescent molecules (that is, loss of 'brightness' of the colour in time during imaging); limited numbers of dye molecules that have distinct 'colours' and that can be can be simultaneously imaged; and limited sensitivity. Nanoparticles in the form of **quantum dots** (QD) can be used as an alternative to conventional organic dyes, being more stable, sensitive and monochromatic. A substantial (tenfold) enhancement in sensitivity compared to common fluorescent markers has been accomplished through the use of gold and silver particles of uniform dimensions in the range 40 to 120 nm. Signal amplification is also obtained using metal nanoparticle labels, such as DNA-modified gold nanoparticles. These nano-sized probes have molecules attached to their surface that ensure the selectivity of the detection, while the nano-properties of the probe are responsible for enhancing the signal. The overall effect is an improvement in the sensitivity and selectivity of microarray technology.

Nanobarcodes

The unique properties of nanoparticles, such as the relationship between particle size and colour, can also be used to create multiplexed detection systems in the form of nanobarcodes, for example using quantum dots to create different colour-based codes. Alternatively, fragments of DNA on nanospheres can be used to create a 'bio-barcode', for example for protein detection. A bio-barcode has been used to detect small levels of the cancer marker prostate-specific antigen (PSA) in serum. The results showed an increased sensitivity to the PSA protein compared to conventional protein assays, demonstrating the potential of such approaches for detecting cancers at an earlier stage.

Lab-on-a-chip

These devices are 'miniaturised integrated laboratories' that allow the separation and analysis of biological samples (e.g. blood) in a single device. They are made of microfluidic systems, including micropumps and micro-valves, integrated with microelectronic components. The devices can also integrate one or more sensors. As with microarray technology, the impact of nanotechnologies in this area is in further miniaturisation of these devices, although the handing of ultra-small volumes of samples would pose a problem. Presently, nanotechnologies are making an impact in improving specific components and functions of lab-on-a-chip devices. For example, analysis is commonly done by dielectrophoresis, where non-uniform alternating electrical fields are used to separate and guide small objects through field gradients: this manipulation requires high electrical field strengths that can be obtained using nano-sized electrodes. Another example is nanopore-based separation systems that can be integrated into the membranes used in lab-on-a-chip devices — for example, nanopore-membranes are proposed for DNA sequencing.

Imaging

The second step in the diagnosis of a disease involves *in vivo* imaging, which searches for the symptoms of the disease within the live tissue suspected of being infected without the need to perform surgery. Nanotechnologies are having a very important impact in this area, particularly by developing molecular imaging agents. The latest improvements in the area of imaging deal with the capability of tracking changes at the cellular and molecular level through the analysis of some specific biological markers (a technique called 'targeted molecular imaging' or 'nano-imaging'). A biomarker is an indicator of a biological process or state, such as a disease, or the response to a therapeutic intervention. This can be an altered gene, or a change in protein production, or even a physical feature of a cell. The aim is to detect biomarkers of disease and diagnose illnesses before, or at the onset of, the first symptoms, in this way making *in vivo* imaging a tool for the early detection of a disease. Effective early detection is crucial for planning a therapy with less severe and costly therapeutic demands, especially in diseases such as cancers, where timing is vital for the success of the treatment. Biomarkers could also be used as early indicators of the success of a treatment, thus reducing treatment time and cost. Targeted molecular imaging is important not only for diagnostic purposes, and for monitoring the progress of a therapy, but also for research in controlled drug release, in assessing the distribution of a drug within the patient's body, and for the early detection of unexpected and potentially toxic drug accumulations. The ability to trace the distribution of a drug leads to the possibility of activating it only when and where needed, thus reducing potential drug toxicity.

Diagnostic imaging

Techniques such as X-ray, computer tomography (CT), ultrasound (US), magnetic resonance imaging (MRI) and nuclear medicine (NM) are well established imaging techniques, widely used in both medicine and biochemical research. Originally, imaging techniques could only detect changes in the appearance of a tissue when the symptoms of the disease were relatively advanced. Later, targeting and contrast agents were introduced to mark the disease site at the tissue level, increasing imaging specificity and resolution. It is in this specific area that nanotechnologies are making their greatest contribution by developing better contrast agents for nearly all imaging techniques. The physiochemical characteristics of the nanoparticles (particle size, surface charge, surface coating and stability) allow the redirection and concentration of the marker at the site of interest. An example of nanoparticles used in research for imaging is perfluorocarbon nanoparticles employed as contrast agents for **nuclear imaging**, **magnetic resonance imaging and ultrasound**, with applications in the imaging of blood clots, angiogenesis, cancer metastases and other pathogenic changes in blood vessels. Gadolium complexes have been incorporated into emulsion nanoparticles for the molecular imaging of thrombi, resulting in a dramatic enhancement of the signal compared to conventional MRI contrast agents. **Fullerenes** are also used in magnetic resonance imaging research, filled with smaller molecules that act as contrast-enhancement agents. Metals and silicon nanoparticles are also used to enhance MRI. Silicon particles fabricated into different shapes and coated with conductive layers can have enhanced magnetic resonance interactions with an imaging field.

In **X-ray imaging**, to enhance the signal, an agent must deliver a detectable number of heavy atoms into targeted tissue without toxic effects. Nanoparticles of heavy metals have the highest density of surface atoms but they must be inert and stable. Nanoparticles of inert metals like silver and gold are too expensive and would render the technique not cost-effective. A solution has been proposed by General Electric in the form of **nanoparticles made of heavy metal compounds encapsulated in gold shells**. The added advantage is that organic compounds with sulphide (-S-H) groups (thiols) can easily be attached to the gold surface through the thiol end (forming an S-Au bond). The thiol molecule can be functionalised at the other end with groups that act as receptors for specific binding of antigens, antibodies or even target compounds on the surface of the cell. By targeting receptors unique to a certain type of cancer cell, gold nanoparticles can enhance an X-ray image of a suspected cancer tissue by many orders of magnitude.

Gold nanoshells are a promising material for the optical imaging of cancer. Optical technologies could provide high resolution, non-invasive functional imaging of tissue at competitive costs. However, at present, these technologies are limited by the inherently weak optical signals which come from the endogenous chromophores and the small spectral differences between normal and diseased tissue. Gold nanoshells are made of a dielectric core (silica) covered in a thin metallic (gold) shield. Gold nanoshells possess physical properties similar to gold colloid (as described previously), in particular, a strong optical absorption due to the collective electronic response of the metal to light (the LSPR effect). By changing the relative dimensions of the core and shell, the optical resonance of the nanoparticles can be precisely and systematically varied over a broad region ranging from the near-UV to the mid-infrared (**Figure 7**).This range includes the near-infrared (NIR) wavelength region where tissue transmissivity is higher. Researchers are using these gold nanoshells cells as contrast agents for **Optical Coherence Tomography** (OCT) (9) of cancer cells. As discussed later, gold nanoshells are also capable of treating cancer cells through overheating of the cells. This is discussed in the next section.

Figure 7: (left) SEM image of gold nanoshells each being about 120 nm; (right) optical image of the same nanoshells after being dispersed in water and dried on a microscope slide. The colours are due to selective scattering of light by the nanoparticles.

Images: G. Koeing, University of Wisconsin-Madison, NISE Network (http://www.nisenet.org), licensed under NISE Network Terms and Conditions

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(9) Optical Coherent Tomography (OCT) is a state-of-the-art imaging technique which produces high resolution (typically 10^{-15} μm) real-time cross-sectional images through biological tissues. The method is often described as an optical analogue to ultrasound.

In situ diagnostic devices

In recent years, *in situ* diagnostic devices have been developed, such as wireless capsule endoscopy cameras. These devices are swallowed by the patient and make it possible to closely monitor and locate the site of bleeding and other intestinal problems. Currently, many of these devices, such as the CamPill® produced and sold by Given Imaging Ltd, can only image the problem. In the future, these devices could also incorporate sensors for the detection of specific chemicals, pH, bacteria, viruses, etc. Micro and nanotechnologies now allow the creation of extremely small sensors and research is being conducted on integrating them into swallowable capsules. This will widen their applicability and utility. In the future, they could also be drug-loaded for targeted drug delivery.

Therapy

The same disease, such as cancer, can express itself in many different forms: for example, there are at least 14 different types of breast cancer. Thus, in an ideal world, a therapy should be specific, in order to remove only the 'bad' cells, and effective, both in terms of action and time.

A therapy normally involves a pharmaceutical route (drugs) to treat the disease from the inside of the body, or, when a pharmaceutical therapy is not possible or not effective, other routes to fight the disease from the 'outside' of the body, such as radiative therapies. In some circumstances, surgery is required, and an organ-substitute is inserted into the body in the form of an implant or a donated organ. In all these approaches, which are often used in combination, the aim is always the same: to eliminate selectively the source of the disease in a long-lasting way. Nanotechnologies are making a tremendous impact in this field, with new drugs and new types of treatments under development, some of which have already proven clinically effective and have entered the market.

Drug development and targeted drug delivery

Advances in the field of pharmacology stem from two main concepts: the development of new biologically active drugs (drug discovery) and the development of new drug delivery systems able to reach the specific site of the disease. Drug delivery systems (DDS) are not a new concept: research in this field started in the mid 1960s and resulted in the type of drugs used today (i.e. medicines where the active ingredient is encapsulated and released inside the body by gradual dissolution, osmotic effects, or other mechanisms). Drug delivery systems are in the same form as the 'pills' that are frequently taken and that release their active component gradually in time (slow release drugs) or that dissolve based on some physiological conditions (e.g. acidity of the environment). Drug delivery systems also exist in the form of implants, inserts or other drug-releasing systems.

Drug design and screening

The structure of biological macromolecules defines a three-dimensional nano-environment that mediates specific functions in the cell. The design of new drugs requires a very detailed understanding of this nano-environment. Therefore, gaining insight into the structure of macromolecules on the nanoscale through electron microscopy, nuclear magnetic resonance spectroscopy (NMR) and X-ray crystallography is of fundamental importance tounderstanding biological processes and for the development of new medicines.

One of the bottlenecks in drug discovery is the necessity to screen thousands of candidate drugs for their efficacy in fighting targeted macromolecules in a disease state. Micro and, now, nanotechnologies have enabled the development of microarray platforms and new detection methods (including label-free) to investigate the effects of candidate drugs against disease macromolecules with unprecedented speed.

Targeted drug delivery

Pharmaceutical drugs developed using conventional synthesis routes are limited by problems such as low efficacy, low solubility in water and lack of selectivity. In addition, physiological barriers often prevent the drug from reaching and acting at the target site — a phenomenon called drug resistance. The low solubility and limited bioavailability of conventional drugs is responsible for their limited effectiveness: the body often clears away the drug before its action is complete. The efficacy of drugs is also dependent on the dose used, but dose-dependent side effects often limit their acceptable usage. The lack of selectivity is especially detrimental, for example, in cancer therapies, since anti-cancer drugs, usually distributed in large volumes, are toxic to both normal and cancer cells.

A recognised need exists to improve drug composition, delivery, release and action, and thus to develop new drugs that can act at the specific site of the disease, maximising the drug's therapeutic action while minimising side effects. For drugs to be able to do this, the delivery systems need to be miniaturised to much smaller than the target, and specific in composition to elicit a certain response. With the use of nanotechnologies, targeted drugs (in terms of composition and delivery system) are becoming a reality. In the future, this could lead to targeted therapies and personalised medicine. The aim is to design and deliver drugs in such a way that they can recognise the 'bad' cells at a molecular level, penetrate the cell membrane, and act inside the infected cell. This is often crucial for the efficacy of a drug, since most virus replication and other disease conditions take place across the cell membrane and inside the cell. This way, the treatment will be delivered where it is needed and will be specific, eliminating the problem of the drug killing healthy cells. An example of this approach is siRNA drug delivery.

Targeted drugs and targeted DDS could allow the creation of drug formulations with optimal loading, which deliver to the body only the necessary amount of the drugs and reduce side effects for the patients. Together with the possibility of having nano-DDS that are biodegradable inside the body, this will help to reduce drug toxicity. Drug safety can be further enhanced by the possibility of introducing inside the drug formulation a label that changes colour when the drug reaches its expiry date or is no longer functioning. This will allow for the improvement of drug shelflife and better monitoring of drug safety.

siRNA drug delivery

RNA interference is a natural, fundamental mechanism in gene regulation that occurs in both plants and animals, humans included. Genes carry the genetic material of an individual, the DNA, and are contained in the nucleus of a cell. When genes are express (i.e. activated), the genetic information is copied from DNA to messenger molecules, called messenger RNA (mRNA), which then orchestrate the formation of proteins outside the nucleus of the cell. In 1998, Andrew Fire and Craig Mello discovered that double stranded RNA (dsRNA) can interfere with and break down the mRNA for a specific gene, thus stopping the production of a specific protein. The gene is, therefore, 'silenced' and the production of the protein is turned off. Fire and Mello found that this RNA interference mechanism is specific and can be obtained with a few molecules of dsRNA, and that the effect of dsRNA could spread from cell to cell and from tissue to tissue, and even passed on to offspring. The discovery won the scientists the **Nobel Prize in Medicine in 2006**. Now researchers know that RNA interference plays an important role in switching off genes during an organism's development and controlling cellular functions. But the discovery of RNA interference not only enables scientists to better understand the fundamentals of gene regulation: it also opens new possibilities for genetic engineering in biological and medical research. In the laboratory, scientists can now tailor RNA molecules — silencing RNAs — that activate the breakdown of endogenous mRNAs (i.e. RNA that belongs to that specific cell). When silencing RNA (siRNA) molecules enter the cell, they activate RNA interference and endogenous mRNA molecules that bind to the added siRNA are destroyed. Researchers are now hoping to use RNA interference to treat diseases such as viral infections, cardiovascular diseases, cancer and metabolic disorders. So far, many experiments with RNA interference have yielded promising results, but in order to maximise the therapeutic efficacy of the technique, some fundamental difficulties must be overcome. These include the low stability of siRNA in biological fluids and low specificity of action due to gene off-target effects caused by the similarity in behaviour of synthetic siRNA to natural microRNA produced by the cell. Therefore, there is the need to develop delivery methods capable of overcoming the extracellular and intracellular barriers and getting the siRNA molecules into the right type of cell (targeted delivery) whilst maintaining the stability of siRNA.

Researchers at iNANO (Aarhus University) and other institutions worldwide are developing **nanocarriers for the targeted delivery of siRNA**. For example, they are studying a novel chitosan-based siRNA nanoparticle delivery system for RNA interference *in vitro* and *in vivo*. Chitosan is a naturally occurring cationic polysaccharide that has been widely used in drug delivery systems. It contains positively charged amine groups that can interact with the negatively charged backbone of siRNA and form polyplexes in the form of nanoparticles about 200 nm in size. The protonated amine groups allow transport across cellular membranes and subsequent endocytosis into cells. It has been shown that a chitosan/siRNA nanoparticle delivery system silences genes both *in vivo* and *in vitro* (**Figure 8**). Moreover, this delivery system has been shown to be biocompatible, non-toxic and biodegradable. Another requirement in targeted siRNA delivery is the capability of the carrier to reach a specific cellular compartment and release the cargo (the siRNA) inside that cell. Synthetic vectors based on polycations such as poly-L-lysine have been widely used but have several drawbacks such as high cellular toxicity, sequestration in subcellular compartments and lack of intracellular targeting. In contrast, bioresponsive copolypeptides containing reducible disulfide bridges that respond to intracellular acidity conditions have proven advantageous in delivering nucleic acids into cells. These systems exploit the redox potential gradient existing between the extracellular and the intracellular environment so that the disulfide bridges are broken (and the cargo released) only in one compartment of the cell (in this case, the nucleus). For these reasons, research is being conducted in developing nano-carriers rich in histidine groups.

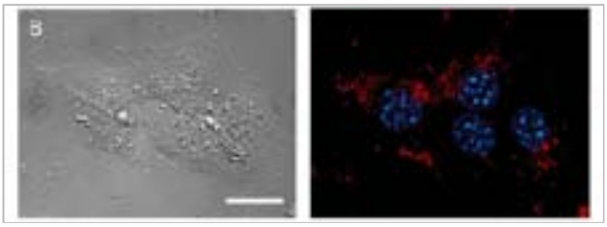


Figure 8: Live cellular uptake of chitosan/siRNA nanoparticles into NIH 3T3 cells: fluorescence microscopy was used to visualise cellular uptake and translocation of Cy5-labelled siRNA within Chitosan nanoparticles after four hours of reaction. Images show fluorescent overlay of siRNA (red Cy5-labelled) and nuclei (blue Hoechst-labelled) adjacent to phase-contrast image (scale bar, 10 µm).

Image: K. A. Howard et al., *Molecular Therapy*, 2006, 14(4):476–484, reprinted with the permission of Macmillan Publishers Ltd, © 2006

Stimuli-activated drug delivery

In this area of research, the idea is to incorporate some specific properties into the delivery system so that the drug can be **activated only on reaching the target**, and the active component released at a controlled rate. This is called stimuli-activated drug delivery. Controlled activation could be linked to some environmental property, such as pH, or ‘lock-and-key’ molecular recognition mechanisms. One example is stimuli-activated gene delivery.

In **gene therapy**, one of the biggest challenges is the targeted delivery of the nuclei acid load to the target (e.g. plasmid-DNA or siRNA) either to silence (RNA silencing) or to activate the expression of a protein as a way to treat a number of diseases. In the previous section, how nanocarrier delivery systems formed by electrostatic interactions between cation polymers and DNA or RNA have been developed to overcome extracellular and intracellular barriers to maximise the delivery of the nucleic acids in the cell was discussed. One way to control the spatial and temporal activity of nucleic acids is to use polymers that change properties in response to stimuli such as temperature and redox potential gradients. This approach to targeted delivery is being investigated at iNANO and is schematically illustrated in **Figure 9**. The idea is to utilise a nanocarrier that passively accumulates in the diseased tissues (e.g. tumours), followed by stimuli-induced activation at the required site (inside or outside the cell). In the case of **thermoresponsive systems**, the application of heat in precise locations of the tissue can induce the deposition of the nanocarrier in the extracellular target region.

Researchers are studying, for example, the use of a thermoresponsive polymer to form a polyplex with plasmid DNA and using AFM to visualise the resulting nanoparticles. They found that the size of the polyplex nanoparticles from around 50 to more than 200 nm could be changed by heating the particles. The AFM images revealed that smaller particles merged to form larger particles during the temperature treatment. Since the ability of polyplexes to cross vasculature endothelial barriers and enter/exit tissues depends on particle size, a thermostimulus could be used to control migration inside tissues. The idea is to apply a thermostimulus in the diseased tissue so as to induce a size increase in the nanoparticles and prevent these from re-entering the bloodstream (**Figure 9**). This general approach could be used for nanocarriers containing drugs or imaging agents for therapeutic and diagnostic applications.

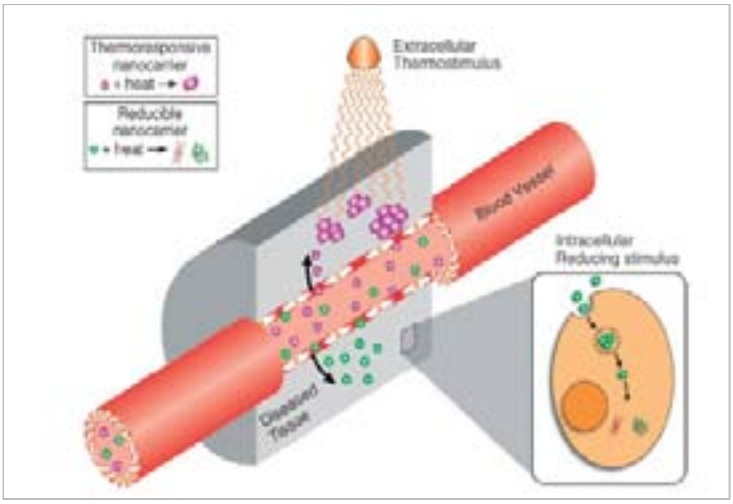


Figure 9: Schematic representation of a nanocarrier thermo-activated for gene therapy

Image: Howard et al., *Small*, 2007, 3(1):54–57, reprinted with the permission of Wiley-VCH GmbH & Co. KGaA, © 2007

Current and future nano-drug carriers

Nano-sized drug carriers currently under development include either materials that self-assemble, or conjugated multicomponent systems, for instance a drug linked to a protein and a polymer (called a polymer-drug conjugate, **Figure 10**). Numerous nanosystems are now being investigated and include micelles, nanoemulsions, nanotubes, nanofibres, liposomes, dendrimers, polymer therapeutics, nanoparticles, nanocapsules, nanospheres and hydrogels. Some of these nano-sized drug carriers are established in the field of drug delivery, such as liposomes: others have made their way to the market in recent years, such as polymer-protein conjugates (polymer pharmaceutics).

Many are now used for treating some forms of cancer, hepatitis, and leukaemia. An example is an anti-cancer drug called DOXIL (Sequus Pharmaceuticals, Inc.).

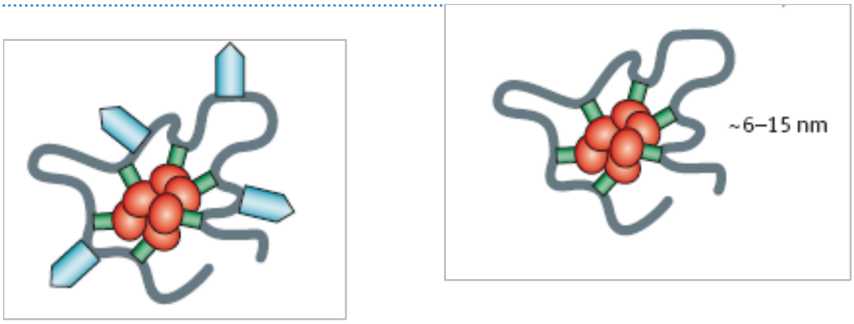


Figure 10: (Left) schematic representation of a polymer-drug conjugate, and of a targeted polymer-drug conjugate (right)

Image: Duncan R., *Nature Reviews Cancer*, 2006, 6(9):688–701, reprinted with the permission of Macmillan Publishers Ltd, © 2006

The future of nano-DDS enabled by nanotechnologies could be miniaturised implantable chips loaded with different drugs that can be released by external stimuli. This could free patients, such as diabetics, from having to administer drugs repeatedly during the day. Research in this area is very active but still requires years for commercial realisation.

Externally activated therapies that use nanoparticles

One of the distinguishing properties of nano-sized drug carriers is their ability to accumulate passively in cancerous solid tumour tissue due to an effect called enhanced permeability and retention (EPR). This passive mechanism has been attributed to the ‘leaky’ nature of tumour vessels. The blood vessels that supply tumours with nutrients have tiny gaps in them that allow nano-DDS (60–400 nm in size) to enter the tumour region and accumulate there. This further enhances the targeted approach to treating infected cells. Moreover, this allows the accumulation of therapeutic agents inside the tumour region with activation by an external source. Based on this concept, some new anti-cancer therapies have been developed and have entered advanced clinical trial stages. In these therapies, nanoparticles are delivered to the tumour site, where they accumulate. An external source is then used to specifically activate the nanoparticles and overheat the tumour region (the therapy is called hyperthermia). Due to the EPR effect, the nanoparticles accumulate only in the tumour region, so the treatment is extremely localised and healthy tissue is not affected. Overheating the tumour site can be achieved, for example, by activating magnetic nanoparticles with an alternating magnetic field so that they start vibrating and thus generate heat. This is the principle on which a new anti-cancer therapy, MagForce®, has been developed: this therapy entered Phase II clinical trials in 2007 for the treatment of prostate cancer. Another approach uses gold nanoshells (as described previously) designed to absorb light in the near infrared (NIR) region. This is the region where light penetration through tissue is optimal (800–1 300 nm). The **nanoshells absorb NIR light**, delivered with a laser, converting light into heat. In animal model studies, the nanoshell treatment has been shown to induce complete resorption of a tumour in 10 days, with all the animals remaining healthy and tumour-free for more than three months after treatment. These examples show the innovative approach to tumour treatment enabled by nanoparticles.

Theranostics

One of the most exciting opportunities that nanotechnologies have brought to the therapeutic field is the possibility of integrating the diagnosis, therapy and follow-up of a disease. This is referred to as theranostics, and could be enabled by nanoparticles incorporated inside a drug that can change some property — such as colour — once the drug has reached the target (e.g. quantum dots). Drugs could therefore have a feedback action. Together with a slow, targeted release system, the nanoparticles could gradually change colour during the drug action, thereby informing doctors of the progress of a therapy. This approach is called 'find, fight and follow' and could become a reality as a result of the parallel progress in the field of molecular imaging. One vision is that, one day, the entire process of diagnosis, pre-imaging, therapy and post-imaging of a specific disease will be integrated. An example of theranostics is the use of gold nanoshells for imaging and treating cancer cells at the same time.

Regenerative medicine

At times, the only way to treat a disease is the removal of the infected organ or tissue. Such loss can also derive from an injury or a congenital condition (e.g. vision or hearing impairment). To compensate for the lost or impaired body function, an artificial construct is implanted in the body. Depending on the type, site and extent of the loss, this construct can be in the form of an engineered tissue or an implant.

Tissue and biomaterial engineering

Tissue engineering deals with the fabrication of **artificial scaffolds to support the growth of donor cells**, which differentiate and grow into a tissue that mimics the lost natural one. This tissue-engineered construct is then implanted in the patient and, in time, resorbed by the body and fully integrated by the host tissue. Current applications of tissue-engineered constructs include engineering of skin, cartilage and bone for autologous implantation (i.e. the implantation of a tissue regenerated by seeding cells of the patient).

The 'scaffold' that supports cell growth is the core of this technique. In the body, cells are supported in their growth and function by a natural scaffold, called the extracellular matrix (ECM). This is a very complex and intricate 'web' of nanofibres that provide the mechanical architecture for cellular growth.

Moreover, the ECM is filled with small molecules (e.g. growth factors) and proteins that direct many cell processes, such as adhesion, migration, growth, differentiation, secretion and gene expression. The three-dimensional spatial organisation of these 'cues' is critical in controlling the entire life cycle of the cell. Ultimately, this three-dimensional nano-architecture guides cells to form tissues as complex as those found in bone, liver, kidney and heart. The biggest challenge in regenerative medicine is the artificial replication of this 'perfect nano-scaffold'. The ability to engineer materials having a similar level of complexity is now becoming a reality through nanotechnology.

Micro-fabrication techniques derived from the semiconductor industry (such as photolithography or ion beam lithography) have long been used for the fabrication of microstructures to support and control cellular growth: one of the pioneering works in this field was published in the late 1970s. In recent years, new nanotechnology techniques have enabled studies at higher and higher resolution, revealing the nanoscale detail of the ECM. Analytical tools, such as the AFM, and nanofabrication tools have allowed scientists to fabricate scaffolds with nanoscale features. A great deal of research is now dedicated to engineering scaffolds with tailored material composition and properties, including nanotopography and controlled alignment, to study how these can support and direct cellular growth. The aim is the fabrication of scaffolds that most closely resemble natural ECM. Researchers now have access to techniques which produce macroscale structures with nanometre details. Conventional polymer chemistry combined with new nanofabrication methods is now used to manufacture a wide range of structures, such as nanofibres of different and well-defined diameters and surface properties; nanofibrous and porous scaffolds; nanowires, nanotubes, nanospheres and nanocomposites.

Close to the field of tissue engineering, and in many cases an integral part of it, is **biomaterial engineering**. Materials used in regenerative medicine are called biomaterials in the sense of being able to trigger and support a biological response. One of the distinguishing features of nanotechnologies is their ability to create new functional materials. This can be exploited in the fabrication of new biomaterials that have better mechanical properties: to increase the implant stability and reduce fatigue failure in orthopaedic implants for example and materials that have enhanced electrical properties, needed in neural prostheses, for example. Nanotechnologies can also be used to fabricate implants made of materials that are more resorbable, to increase functionality and durability. For example, nanocoatings are being studied which will better integrate synthetic implants with the biological tissue, in order to prevent tissue inflammation and the onset of rejection.

Nanotechnologies are also employed in the fabrication of biomaterials that are **responsive to the environment** (e.g. responsive to pH or the presence of specific biomolecules) and, for this reason, are called 'smart biomaterials'. Moreover, research is being conducted to include nanoscale patterns in the biomaterial, which will simulate the natural cues and mimic molecular signalling mechanisms, in order to trigger desired biological events, such as cell adhesion, differentiation and spreading. This could facilitate the fabrication of **dynamic implants** that are not limited to simply replacing a lost organ but truly restore the loss.

Finally, nano-sized sensors could be inserted inside a biomaterial (e.g. nanowire biosensors) functionalised with receptors that can monitor the presence of small organic molecules, proteins, cells (e.g. cancer cells) and viruses. This could be used to collect information on the implant status and activity. This feedback information could be used to maximise the implant efficacy and safety.

Tissue and biomaterial engineering have applications in basically all aspects of regenerative medicine (i.e. neuroprosthetics and neuron regeneration (e.g. spinal cord repair), bone restoration, hearing and vision restoration, motor restoration, etc.).

Nanoengineering bone regeneration

Bones and teeth are material that have to bear complex loads of moving bodies, provide a protective cage for vital organs, anchor tendons and muscles, and act as joints and levers. This functional complexity is reflected in a structural complexity. Bones have a complex hierarchical structure at the nano, micro and macro-levels, which determines their amazing properties.

The 'classic' way to promote the regrowth of bone after injury is to provide a **scaffold** into which bone-forming cells can migrate and grow attached (fused) to the scaffold (**Figure 11**). In the past, numerous scaffolds have been used, mainly coated with hydroxylapatite which is a natural bone component. More recently, research has focused on trying to mimic the nanostructure of the scaffold. This involves working on the topography of the scaffold (surface nano-roughness) but also at anchoring specific biomolecules to the nano-surface of the scaffold. The idea is to mimic the natural fine organisation of natural bone, which is a combination of nano-topography and (bio)chemistry.

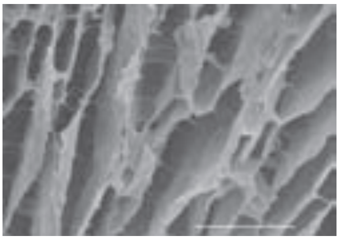


Figure 11: SEM mage showing a hydrogel scaffold grown to study brain tissue engineering and nerve regeneration. The image is 100 μm wide.

Image: D. Nisbet, Monash University, NISE Network (http://www.nisenet.org), licensed under NISE Network Terms and Conditions

A novel approach is the development of '**artificial bone**', which means using macromolecules that self-assemble into large structures that mimic the natural structure of bone. This is a bottom-up approach to bone engineering which leads to materials with nanoscale-level control. For example, some researchers have developed a bone scaffold by biomimetic synthesis of nano-hydrohylapatite and collagen. Collagen is the most plentiful protein in the human body. It is found in most human tissues including bone, cartilage, the heart, eye and skin and gives these tissues their structural strength. These biomaterials assemble into 3D mineralised fibrils that mimic key features of human bone. This material shows some similarities with natural bone in terms of hierarchical micro and nanostructure, and three-dimensional porosity. Cells seeded *in vitro* over this scaffold grew and proliferated well. The advantage of this approach is that the 'building blocks' are biomimetic macromolecules: once assembled, the final 'macro' material can integrate with natural tissues, opening the way to new clinical approaches to bone regeneration.

When these synthetic nanofibres form, they make a gel that could be used as a sort of glue in bone fractures or to create a scaffold for other tissues to regenerate on to. As a result of its chemical structure, the nanofibre gel would encourage attachment of natural bone cells which would help to patch up the fracture. The gel could also be used to improve implants or hip and other joint replacements.

NANOYOU DILEMMA The example of artificial bone is one of the NANOYOU dilemmas, part of the **NANOYOU role-playing game** (http://www.nanoyou.eu/en/decide). The dilemma arises from the fact that if such technology is developed to heal bones, the natural progression might be that it is then used to strengthen otherwise healthy bones to make them almost unbreakable. This solution might not be available for some people (due to cost or accessibility restriction), so it could become a human-enhancement tool only for a few. The dilemma is: Is it acceptable to use processes developed for medical treatment to enhance the human body?

Nanoengineering neuron regeneration

The loss of neuron functions is one of the most dramatic medical conditions in terms of consequences for the patient: it can interfere with basic functions (e.g. movement) and cognitive capabilities. There are numerous neurodegenerative diseases (Parkinson's disease, Alzheimer's disease, etc.) that are connected with neurological damage (**neurodegenerative diseases**). Neuron function loss can also derive from a severe accident (**spinal cord injury**) or a minor one (**peripheral neuron damage**). The loss or impairment of a person's neurological function has detrimental effects on their life. The research in this field is therefore massive, and covers a very wide range of disciplines and sub-disciplines. There are basically two main approaches to neuron regeneration: tissue engineering and neuron prosthetics. Until recently, these two approaches were fairly separate, mainly due to the type of materials employed in the two approaches: 'soft' biomaterials in the first case (biopolymers, proteins, peptides, etc.), and microchip-type materials in the second case (semiconductors, metals, etc.). With the advent of nanotechnologies, these two types of materials are starting to integrate not just in terms of physical attachment (e.g. protein coatings) but in terms of *function*: for example, in nanotechnologies, biomolecules are used as nanoscale motors, or as energy-harvesting materials. Therefore, in the future the approach to neuron regeneration will be in the form of hybrid nanoscale devices. A short review of neuron tissue engineering now follows and neuroprosthetics are discussed in the next section.

Neuron tissue engineering

The use of scaffolds to encourage neuron regrowth after injury is an established method. At first, simple biocompatible polymers were used but, nowadays, the need to engineer the scaffold at the nanoscale level in two ways is recognised: physically, by inserting nanoscale 'paths' to encourage directional growth, and biochemically, by adding 'cues' in the form of neuron growth factors and other essential biomolecules to encourage regrowth (**Figure 12**). These two elements must be engineered so that their coordinated action results in neuron regrowth. In the last few years, the research in this area has been impressive and nanotechnologies have been the enabling tool. For example, researchers at the Stupp Laboratory (Northwestern University, USA) have fabricated a nanogel of elongated micelles arranged in a nanofibre matrix and demonstrated that this can support the directional growth of neurons. The aim of this and other work is to engineer nano-scaffolds that can support the regrowth of neurons to heal patients affected by neurodegenerative disease or severe neuronal losses, as in the case of spinal cord injury.

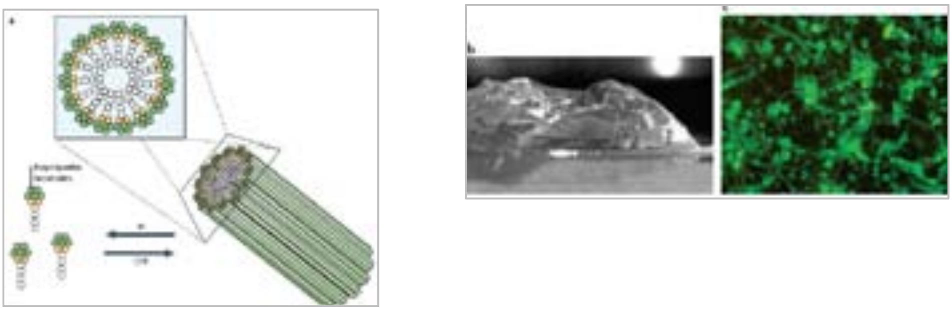


Figure 12: An engineered nanomaterial that supports specific cellular growth and can promote desired neurobiological effects: the material is formed of small bioactive molecules that resemble parts of natural proteins which spontaneously assemble in nanofibres (A) making a macro-gel (B). The gel supports and steers the growth of stem cells (C).

Images: G. A. Silva, *Nature Reviews*, 2006, 7(1), 65–74, reprinted with the permission of Macmillan Publishers Ltd, © 2006

Neuroprosthetics

A 'neuron prosthesis' is a device implanted to restore a lost or damaged neuron function. There are two main kinds of neuron prosthesis: motor and sensory. Much progress in the last decade has been facilitated by miniaturisation. Nanotechnologies offer opportunities to continue this miniaturisation trend but also to introduce new features, such as electrodes that actively interface with the nerves, smaller and more powerful sensors, actuators, and control systems throughout the prosthesis to render it more natural and effective.

A **motor neuroprosthetic device** takes signals from the brain or motor pathway and converts that information to control an actuator device which executes the patient's intentions. Examples include artificial limbs or hands. The task is extremely complicated, since the motor neuroprosthesis must also be integrated with the owner's nervous system. Therefore, prostheses have a sophisticated distributed network of control, actuation and feedback. Limb and hand prostheses also need to be mechanically similar to natural limbs, otherwise the task of learning to use them will be difficult. Therefore, to be effective, the device must be designed with nanoactuators and nanosensors fully integrated into the control system from design to implementation, including the very special ergonomic interface between patient and device.

What can nanotechnologies do? Progress in current motor neuroprosthetic devices has already been made possible by nanotechnologies, which are enabling more natural prosthesis by providing:

- smaller and more affordable **sensors**, processor elements, and the wiring and interconnectors needed to network them in a distributed control system;
- smaller, more powerful, efficient and responsive **actuators** that move smoothly, resembling natural movement — possible because these actuators are based on molecular forces;
- engineering **materials** that match the strength/weight ratios, elasticity/rigidity, and mechanical energy storage characteristics of key components of natural limbs.

A key contribution of nanoscience is in the form of novel materials (e.g. carbon nanotubes) that can become elements of new sensors, computing elements and even artificial muscles. Nanoscale magnetometers, accelerometers, pressure sensors and gyroscopic devices will be able to detect even minute movements and angle changes more precisely. These nanomaterials will support the design of internal movement devices to render the prosthetic movement more natural, and to ensure the accurate transmission of control and feedback information between device and patient. The impact of nanotechnologies will not be in the form of miniaturised robots but rather assemblies of cooperating interconnected networks that compute, communicate, sensing, actuate, etc., to make up a prosthesis that resembles as much as possible the natural lost limb.

Motor neuroprosthetics commonly integrate **sensory neuroprosthetics** as well, since the reconstruction of motor functions needs to be associated with the reconstruction of haptics — the sense of touch (or more specifically, the sense of pressure and force feedback from the body to the brain). Haptics, along with vision, hearing, and balance, is an essential component of the stream of feedback information that the nervous system sends to the brain. So-called **smart materials** (or dynamic materials, meaning materials that change their shape or function in response to an external stimulation) and nanosensors are expected to provide many options to implement sensory neuroprosthetics.

Research in the area of motor and sensory prosthetics is very active and is not only directed to the fabrication of human motor prosthesis but also to **robotics** for computer-assisted surgery, deep-marine investigation, astronomy, etc.

In addition to neuroprosthetics that restore motion functions, **vision and auditory neuroprosthetics** are also extremely important. Both technologies have made enormous progress in the last decade and much has been enabled by micro and nanotechnologies. One such example is **cochlear implants**, which are a type of electronic neuroprosthesis implanted in the middle ear, where they stimulate the ossicles electromechanically, rather than acoustically, through either electromagnetic or piezoelectric transducers. Nanotechnologies have enhanced microelectronics, batteries and micromechanical transducers in cochlear implant devices. Problems in those devices still exist, in particular refinement of the signal processing (e.g. to recognise voice pitch in music), improvement in their long-term biocompatibility (build-up of biofilms and plaques) and prevention of bacterial fungal infections. Nanomaterials are expected to have an important impact in all these areas.

Neuronal stimulation, monitoring and pain management

The cardiac pacemaker is one of the bestknown and most widely used neuroprosthetics. Other types of **electronic stimulators** are cardiac defibrillators, cochlear implants, bone-growth stimulators, neural stimulators for the deep brain to control tremors in Parkinson's disease, neuronal stimulators for spinal cord restoration, sacral and other nerve stimulators. Nanotechnologies are impacting these electronic stimulators through improved battery technologies, biocompatible materials and surface treatments for enclosures and leads, electrode miniaturisation and efficiency improvements, and smaller-sized integrated circuits for control and power with increased speed and processing capabilities.

Electrical stimulation of neural tissue by surgically implanted neuroelectronic devices is already an established modern therapy. Integrated micro and nanoscale devices allow many more electrodes to be applied to the target site with fine resolution and in a coordinated, dynamic way. **Recording of neural activity** is also implemented using nanoscale electrodes, since a much larger number of recording sites is possible. These implanted probes must be resistant to challenging environments, so the nanoscale surface engineering of these probes is essential. In addition to protecting the probes, nanotechnologies are contributing in developing **improved active interfaces** between neurons and electrostimulation devices.

An example of an electronic stimulator is a deep brain stimulator. This device will make it possible to treat patients with severe Parkinson's disease — a disorder of the central nervous system that often impairs the sufferer's motor skills, speech and other functions. It has been found that the uncontrollable tremor of patients can be prevented if a fine nano-size electrode delivering a continuous electrical stimulus is inserted into the brain. This precise electrical stimulus has the effect of eliminating the tremors.

Reduction insize and power requirements with the integration of microelectronic devices makes it feasible in many cases to power an implanted device by RF electromagnetic transmission of power, thus eliminating wires and batteries. This is already the case for implanted pacemakers. Improvements in energy storage through nanoengineered energy materials, such as supercapacitors and conductive polymers, coupled with the low power requirements of nanoengineered electronics, will allow huge improvements in terms of size and the capabilities of such devices. These devices make it possible to perform electrical stimulation at selected points of nervous, sensory and neuromuscular systems. Such improvements might eventually make it possible to use implanted electrical stimulation for bone and tissue grafts, and to stimulate functions in the endocrine system and other organs.

NANOYOU DILEMMA The example of deep brain stimulation is part of the **NANOYOU role-playing game** (http://www.nanoyou.eu/en/decide). The dilemma arises from considering a deep brain stimulator designed to treat Parkinson's disease. Now, this device could also be used to treat other medical and health conditions such as intractable epilepsy, as well as mood and eating disorders. Could this nanotechnology be used to increase the capability of the brain in areas for which it was not originally developed? An example of this might be students enhancing their concentration during exams. The dilemma is: Is it ethically acceptable to use technologies developed for specific medical treatments for others purposes such as improving human capabilities?

Non-invasive brain-machine interfaces

The control of physical objects by the power of thought alone has always captured the imagination of man. Until recently, this possibility was only envisaged in science fiction. Now, with the aid of new technologies, and as a result of decades of studies on neuron activity in the brain, the control of machines and computers by the brain is becoming a reality. Systems are being developed where the patterns of neuronal firing in the brain are translated into electronic controls to support the communication, mobility and independence of paralysed people. This is possible because the firing of neurons and the travel of ion currents along axon membranes generate an electrical current, which, in turn, generates a magnetic field. A steady electrical current generates a static magnetic field, but if the electrical current changes (due to neuronal activity), so does the magnetic field. Conversely, a change in external magnetic field can induce a change in electrical (neuronal) activity. Therefore, magnetism can become a non-invasive communication tool with nerves without implanted electrodes and painful transcutaneous shocks.

The technique is called **magnetic monitoring** and it requires extremely sensitive **magnetometers** because the magnetic fields produced by brain activity are very small. Today, **magnetoencephalography**

(MEG) can map brain activity on a 1 mm grid or less. The first generation of MEG equipment was very bulky, requiring shielded rooms, high power consumption, cryogenic cooling of detectors and significant processing time. The technique has so far been limited to research labs or extremely specialised medical investigations. Nanofabrication is enabling a reduction in size of most of the components of MEG equipment (sensors, magnets, etc.) and new concepts are being developed: in prototypes, this progress has already led to thousandfold improvements in sensitivity and **reductions in size and power requirements** by factors of 10 to 100.

Magnetism can also be used **to induce electrical currents** in the neuron cell membrane such as those induced by implanted electrodes, but without physical contact. **Magnetic stimulation** is a new medical technique which requires strong magnetic fields that must vary or pulse in order to generate an electric field. The impact of nanotechnologies in this case is the nanofabrication of compounds and alloys that produce better high-temperature conducting materials. This will make it possible to reduce the size of the device and the cryogenic environment needed for the performance of superconducting magnets. Nanoparticle thin films are also being developed as shielding materials.

Numerous new **nanoscale magnetometer designs** are being developed, one of which is the **optical atomic magnetometer**. This instrument is based on the interaction of laser light with atoms oriented in a magnetic field in a gas phase. The instrument measures the change in alignment when atoms with a magnetic spin moment interact with a beam of a laser. In the absence of a magnetic field, the atoms will align with the electrical and magnetic field of the laser beam crossing the atoms. Any disturbance by a magnetic field will disorient the alignment with the beam, reducing the amount of light transmitted through the gas. A prototype of such a system has been developed by NIST (USA) containing about 100 billion atoms of rubidium gas in a vial the size of a grain of rice. The change of spin was easily detectable and scalable to much smaller sizes. The NIST prototype was able to detect the heartbeat of a rat. Researchers predict that with their small size and high performance such sensors could lead to **magnetocardiograms** that provide similar information to an electrocardiogram (ECG) without requiring electrodes on the patient's body, even outside clothing. This technique could become a realistic alternative to MRI and PET imaging, without the injection of contrast-enhancement agents or tracers. What is really exciting is that, even with the laser and heating components, this new device uses relatively **low power** and can be extremely small compared to any current magnetic stimulation device. It might one day be possible to use sensors to make portable MEG helmets for brain-machine interfaces.

Although much progress has been made and much research is underway, there are some **major obstacles** to overcome before brain-machine interfaces become a reality. Wireless signal transmission from brain implants is still futuristic, along with wearable magnetic brain-machine interfaces. Another challenge is the optimisation of the microelectrodes that record neuronal activity, which tend to degrade in time due to biofilm formation. **Risk of infection** is also a major problem. Better engineering of interfaces using **nanoengineered materials** is needed to improve biocompatibility and durability and to allow lower stimulation potentials.

ELSA TOPIC Neuroprosthetics raises a number of ELSA issues. Normally, these types of devices are only considered when other pharmacological and neurosurgical options have been exhausted. Bioengineers and medical engineers say that their role should be to compensate for a body's deficit (as result of an accident or a disease), not to replacing any existing function. It should not lead to the enhancement of human capabilities. Nevertheless, nanotechnologies are making these developments more feasible and affordable, obliging researchers in the field, as well as regulators, ethicists and sociologists to reflect on the social, medical and ethical consequences of these devices. The same applies to the concept of cognitive prostheses: a system developed to support and augment the cognitive abilities of its user. Of course, such devices could be extremely useful to people with impaired communication. However, the concept raises the possibility of enhancement of cognitive capabilities for other uses, which brings up many social, ethical and regulatory questions. One such is access to these types of devices. Will these be affordable for everybody, covered by social health systems, or available only to wealthy people? Is it ethical to have a technology that can enhance a person's mental ability, but only if they can afford it? How will this technology be regulated in situations where the mental/cognitive ability of numerous individuals is assessed (job interviews, competitions, etc.)?

CHAPTER 2:

ENVIRONMENT

In industrialised nations, the air is filled with numerous pollutants caused by human activity or industrial processes, such as carbon monoxide (CO), chlorofluorocarbons (CFC), heavy metals (arsenic, chromium, lead, cadmium, mercury, zinc), hydrocarbons, nitrogen oxides, organic chemicals (volatile organic compounds, known as VOCs, and dioxins), sulphur dioxide and particulates. The presence of nitrogen and sulphur oxide in the air generates acid rain that infiltrates and contaminates the soil. The high levels of nitrogen and sulphur oxide in the atmosphere are mainly due to human activities, particularly the burning of oil, coal and gas. Only a small portion comes from natural processes such as volcanic action and the decay of soil bacteria. Water pollution is caused by numerous factors, including sewage, oil spills, leaking of fertilisers, herbicides and pesticides from land, by-products from manufacturing and extracted or burned fossil fuels.

Contaminants are most often measured in parts per million (ppm) or parts per billion (ppb) and their toxicity defined by a ‘toxic level’. The toxic level for arsenic, for instance, is 10 ppm in soil whereas for mercury it is 0.002 ppm in water. Therefore, very low concentrations of a specific contaminant can be toxic. In addition, contaminants are mostly found as mixtures. Consequently, there is a need for technologies that are capable of monitoring, recognising and, ideally, treating such small amounts of contaminants in air, water and soil. In this context, nanotechnologies offer numerous opportunities to prevent, reduce, sense and treat environment contamination. Nanotechnologies can enhance and enable pre-existing technologies and develop new ones.

What can nanotechnologies do? Nanotechnologies offer the ability to control matter at the nanoscale level to create materials with specific properties that can serve specific functions. This is particularly important in environmental issues where pollution often arises from the presence of a specific contaminant within a mixture of materials, in solid, liquid or gas form. The small size of nanomaterials, together with their high surface-to-volume ratio, can lead to very sensitive detection. These properties allow the development of highly miniaturised, accurate and sensitive pollution-monitoring devices (nano-sensors). Nanomaterials can also be engineered to actively interact with a pollutant and decompose it into less toxic species. Thus, in the future, nanotechnology could be used not only to detect contaminated sites but also to treat them. Finally, this technology can be used to reduce the production of harmful wastes in manufacturing processes by reducing the amount of material used, and by employing less toxic compounds.

Another application area is the engineering of coatings that are nanostructured in such a way that they resist the attack of pollutants or have self-cleaning properties so that are easily cleaned by rain water and, therefore, require less detergent to be washed.

The starting point for any discussion on the applications of nanotechnologies to the environment is the ability of nanoscience to create new nanostructured materials with specific properties to serve specific functions. These aspects were previously discussed in **Module 1, Chapters 4 and 5**.

Remediation and mitigation

Soil and groundwater contamination arising from manufacturing processes are a matter of great complexity and concern. Affected sites include contaminated industrial sites (including lakes and rivers in their vicinity), underground storage tank leakages, landfills and abandoned mines. Pollutants in these areas include heavy metals (e.g. mercury, lead, cadmium) and organic compounds (e.g. benzene, chlorinated solvents, creosote). Nanotechnology can develop techniques that will allow for more specific and cost-effective remediation tools. Currently, many of the methods employed to remove toxic contaminants involve laborious, time-consuming and expensive techniques. A pretreatment process and removal of the contaminated area is often required, with consequent disturbance of the ecosystem. Nanotechnology facilitates developing technologies that can perform *in situ* remediation and reach inaccessible areas such as crevices and aquifers, thus eliminating the necessity for costly 'pump-and-treat' operations. In addition, as a result of its ability to manipulate matter at a molecular level, nanoscience can be used to develop remediation tools that are specific to a certain pollutant (e.g. metal), therefore increasing affinity and selectivity, as well as improving the sensitivity of the technique.

Drinking water quality and its contamination from pollutants is another matter of concern. Mercury and arsenic are, in particular, two extremely toxic metals that pose very high health risks. Remediation methods that allow the fast, economic and effective treatment of water polluted with such contaminants is urgently needed. Nanotechnology can introduce new methods for the treatment and purification of water from pollutants, as well as new techniques for wastewater management and water desalination.

Nanomaterials currently being investigated for remediation use include iron and bimetallic nanoparticles, semiconductor nanoparticles, magnetic nanoparticles and dendrimers. Some detailed examples follow.

Remediation using metal nanoparticles

The use of zero-valent (Fe^0) iron nanoparticles for the remediation of contaminated groundwater and soil is a good example of how environmental remediation can be improved with nanotechnology. When exposed to air, iron oxidises easily to rust; however, when it oxidises around contaminants such as trichloroethylene (TCE), carbon tetrachloride, dioxins, or PCBs, these organic molecules are broken down into simple, far less toxic carbon compounds. Since iron is non-toxic and is abundant in the natural environment (rocks, soil, water, etc.), some industries have started using an 'iron powder' to clean up their new industrial wastes. However, the 'iron powder' (i.e. granular zero-valent iron with dimensions in the micron range) is not effective for decontaminating old wastes that have already soaked into the soil and water. Moreover, bioremediation using granular iron powder is often incomplete: some chlorinated compounds, such as PCE or TCE, are only partially treated and toxic by-products (such as DCE) are still found after treatment. This effect is due to the low reactivity of iron powders.

Another matter of concern is the decrease in reactivity of iron powders over time, possibly due to the formation of passivation layers over their surface.

Nanotechnology has offered a solution to this remediation technology in the form of iron nanoparticles. These nanoparticles are 10 to 1 000 times more reactive than commonly used iron powders. They have a larger surface area available for reacting with the organic contaminant and their small size

(1–100 nm) allows them to be much more mobile, so they can be transported effectively by the flow of groundwater. A nanoparticle water slurry can be injected into the contaminated plume where treatment is needed (**Figure 1**). The nanoparticles are not changed by soil acidity, temperature or nutrient levels, so they can remain in suspension maintaining their properties for extended periods of time to establish an *in situ* treatment zone. Experimental results collected both in the laboratory and in the field have shown that nanoscale iron particles are very effective for the complete transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides and PCBs.

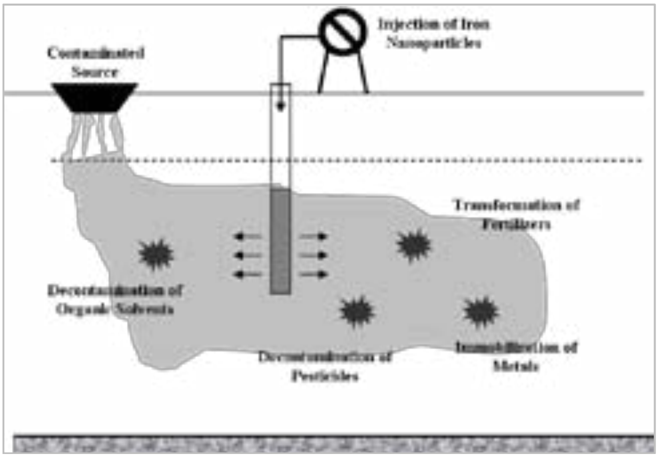


Figure 1: Nanoscale iron particles for *in situ* remediation

When nano-sized iron powders are used, no toxic by-products are formed, a result of the increased reactivity and stability of the nanoparticles compared to the granular iron powder. Contaminant levels around the injection level are considerably reduced in a day or two and nearly eliminated within a few days. As a result of their stability, nano-iron particles remain active in a site for six to eight weeks before they become dispersed completely in the groundwater and become less concentrated than naturally occurring iron. Researchers are assessing whether the technique could also be used for the remediation of dense non-aqueous phase liquid (DNAPL) sources within aquifers, as well as for the immobilisation of heavy metals and radionucleotides.

Bimetallic iron nanoparticles, such as iron/palladium, have been shown to be even more active and stable than zero-valent iron nanoparticles, thus further improving this remediation technology. Finally, iron or bimetallic nanoparticles could be anchored on solid supports such as activated carbon or silica for the *ex situ* treatment of contaminated water and industrial wastes.

Remediation using semiconducting nanoparticles

Semiconducting nanoparticles made of TiO_2 and ZnO are used in **photocatalytic remediation**. Being semiconductors, these materials produce an electron-hole pair when irradiated with a light having energy in the order of the material band gap. TiO_2 has a band gap of 3.2 eV so when the material is irradiated with UV light an electron-hole pair is formed. Both TiO_2 and ZnO are capable of transferring the charge to organic pollutants (such as halogenated hydrocarbons) and induce their oxidation to less harmful by-products, such as CO_2, H_2O and other species. Since TiO_2 and ZnO are readily available and inexpensive, their use for remediation has been studied for many years. Recently, nano-sized TiO_2 and ZnO have been considered, as these have more active surface given the same volume of material. The vision is to create solar photocatalysis remediation systems where TiO_2 or ZnO are used to convert toxic contaminants, such as chlorinated detergents, into benign products using the radiation. There is evidence that these semiconductors can photodegrade numerous toxic compounds, but the technology requires improvements in term of efficiency, since TiO_2 or ZnO only absorb UV light which represents only 5 % of the solar spectrum. In this context, nanotechnology could bring an improvement in two ways.

1. When noble metals like gold and platinum are chemisorbed to the TiO_2 and ZnO nanoparticles, the **photocatalytic activity is accelerated**. The reason is that the presence of the metal helps to keep the electrons and holes from recombining in the semiconductor and thereby increases the efficiency of the photocatalysis.
2. To **increase the photoresponse window** of TiO_2 and ZnO from UV to visible light, the nanoparticles can be modified with organic or inorganic dyes. This is an area of intensive research.

Nanomaterials have also been found able to remove metal contaminants from air. For example, silica-titania nanocomposites are being investigated for use in the removal of elementary mercury (Hg) from vapours such as those from combustion sources. In these nanocomposites, silica acts as a support material and titania transforms mercury to a less volatile form (mercury oxide).

Remediation using dendrimers

Dendrimers are highly branched polymers with controlled composition and nanoscale dimensions. Chelating agents in the form of dendrimers are also studied for the removal of metal contaminants. These can be designed so as to able to act as ‘cages’ and trap metal ions and zero-valent metals, making them soluble in appropriate media or able to bind to certain surfaces. The vision is to use dendrimers as nanoscale chelating agents for polymers supported ultrafiltration systems.

Remediation using magnetic nanoparticles

Another class of nanoparticles that have environmental applications is magnetic nanoparticles. For example, researchers from Rice University’s Centre for Biological and Environmental Nanotechnology (CBEN) have recently shown that nanoparticles of rust can be used to remove arsenic from water using a magnet. The concept is simple: arsenic sticks to rust which, being essentially iron oxide, tends to be magnetic so it can be removed from water using a magnet. Nano-sized rust, about 10 nm in diameter, with its high surface area, has been found to improve removal efficiency while reducing the amount of material used. Compared to other techniques currently used to remove arsenic from contaminated water, such as centrifuges and filtration systems, this method has the advantage of being simple, and most importantly, not requiring electricity. This is very important, given that arsenic-contaminated sites are often found in remote areas with limited access to power. Magnetic nanoparticles modified with specific functional groups are also used for the detection of bacteria in water samples.

Arsenic and arsenate may also be precipitated using nanoscale zero-valent iron (Fe^0) as indicated by recent studies. The removal mechanism in this case involves the spontaneous adsorption and co-precipitation of arsenic with the oxidised forms of Fe^0. As already noted, zero-valent iron is extremely reactive when it is nano-sized, so it is currently considered a suitable candidate for both *in situ* and *ex situ* groundwater treatment.

ELSA and SAFETY TOPIC Although research seems to show that remediation using iron oxide nanoparticles is effective, there are currently some concerns regarding the use of nanoparticles for soil and water remediation. They are related to the fate of the nanoparticles once they are injected into the contaminated site, and the possibility they might be so mobile as to disperse outside the targeted area. It is not clear if such a situation would pose an environmental problem such as interference with plant or animal life cycles. For these reasons, the method is not yet approved and used in the EU. Research is underway to clarify these issues and discussions are taking place on possible strict regulation for this remediation technology.

Remediation using aerogels and solid absorbents

The problem of **oil spills in seawater** is of great concern and has detrimental environmental consequences. Currently, there are numerous bioremediation strategies that use microbial cultures, enzyme additives or nutrient additives to clean up oil spills. The purpose of these additives is to boost the natural nanotechnology of the microbial community to decompose the oil material. Another method gaining acceptance is the use of aerogels (a nanomaterial) modified with hydrophobic molecules to enhance the interaction with the oil. These aerogels have very large surface areas so they can absorb 16 times their weight of oil. They act as a sponge: once the oil has been absorbed, the ‘oil-soaked sponge’ can be removed easily. The problem is that these materials are expensive, so alternatives are under study. The company Interface Scientific Corporation has developed a new nanomaterial modified with self-assembled monolayers (SAMs) which appears to be very effective in remediating oil spills. The company does not provide details of the material but claims that the nanomaterial can absorb 40 times its weight in oil — a method that exceeds any other currently available — and that the oil can be recovered.

As outlined, the use of nanoparticles is very promising in the field of environmental remediation and treatment, precisely because of their small size and reactivity. Nevertheless, some concern exists regarding their use in soil and water treatment: once dispersed in a contaminated site, would the nanoparticles be mobile to a point that they could be taken up by plants or animals at the site and adversely affect them? Biodegradable nanoparticles are likely to be less problematic; nevertheless, there is a need to investigate these safety aspects, and this is the subject of numerous international research programmes. These concerns belong to the more general field of environmental impact assessment of the use of nanoparticles, which includes both risk assessments and life-cycle analysis to understand the short-term and long-term effects of nanoparticles in the environment.

Nanomembranes and nanofilters

Nanotechnology can also be employed for the fabrication of nanofilters, nano-adsorbents and nanomembranes with specific properties to be used for decontaminating water and air. As with other applications, it is the ability to manipulate matter at a molecular level that makes nanotechnology so promising in this field, together with the small size and high surface-to-volume ratio of nanomaterials that are employed in the fabrication of these products.

In principle, ‘**nanotraps**’ designed for a certain contaminant can be produced, for example with a specific pore size and surface reactivity. An example is given by the work carried out at Rice’s CBEN, where researchers are developing reactive iron oxide ceramic membranes (ferroxane membranes) that are capable of remediating organic waste in water (**Figure 2**).

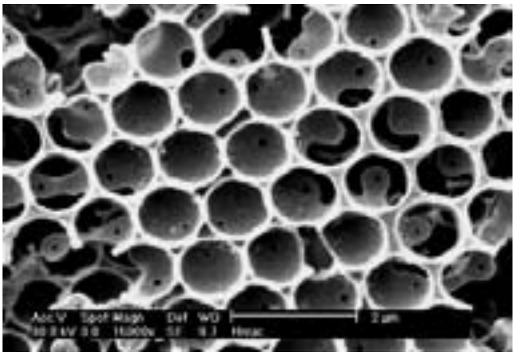


Figure 2: Ceramic nanomembrane

Image: Professor M. Wiesner, Wiesner Laboratory, Duke University

Filters and membranes can also be engineered to be 'active' in the sense of being able not only to trap a certain contaminant, but also to chemically react with it and convert it to a non-toxic product. For example, researchers at the University of Tennessee are investigating a new type of nanofibre for the removal of micro-organisms via filtration that can also kill them on contact.

An interesting application of nanomembranes has been developed by researchers at the University of California Los Angeles (UCLA) in the form of a new reverse osmosis (RO) membrane for seawater desalination and wastewater remediation. The membrane is made of a uniquely cross-linked matrix of polymers and engineered nanoparticles designed to draw in water ions but repel contaminants. This is possible due to the nano-size of the holes forming the membrane, which are 'tunnels' accessible only to the water molecules. Another distinctive feature of this nanomembrane is its ability to repel organics and bacteria, as a result of the chemical composition of the nanoparticles embedded in the membrane. Compared with conventional RO membrane, these membrances are thus less prone to clogging, which increases the membrane lifetime with an obvious economic benefit.

Superhydrophilic filters

In many circumstances, access to clean and safe water is a problem. Nanofilters allow contaminants such as arsenic and other heavy metals to be filtered from water. One commercial reality is the LifeSaver® bottle that has a superhydrophilic filter inside blocks material up to 15 nm in size, which includes viruses and bacteria. The filter is inserted in a plastic bottle and enables contaminated water to be cleaned on-site.

Pollution prevention

Nanotechnologies offer many innovative strategies to reduce pollution in numerous processes including the reduction of waste in manufacturing processes, a reduction of the use of harmful chemicals, reduced emission of greenhouse-effect gases in fuel combustions and the use of biodegradable plastics. These are only a few of the many approaches that can be taken to reduce pollution of the environment. Nanotechnologies are already actively involved in this sector, either as a technology producing advanced materials that pollute less, or as a method to increase the efficiency of certain industrial processes (e.g. catalytic processes).

Materials

Materials that are manufactured in a more environment-friendly way using nanotechnologies include biodegradable plastics made of polymers that have a molecular structure optimal for degradation; non-toxic nanocrystalline composite materials to replace lithium-graphite electrodes in rechargeable batteries; and self-cleaning glasses, such as Activ™ Glass, a commercial product available worldwide from Pilkington. The glass has a special coating made of nanocrystals of TiO_2 which, when exposed to daylight, reacts in two ways. First, it breaks down any organic dirt deposits on the glass and, secondly, when exposed to water, it allows rain to 'sheet' down the glass easily and wash the loosened dirt away. In this product, TiO_2 is found in the form of a thin film 2–20 nm deposited by a high-temperature gas phase. The thickness of the film is essential for ensuring maximum photocatalytic activity and transparency (**Figure 3**).

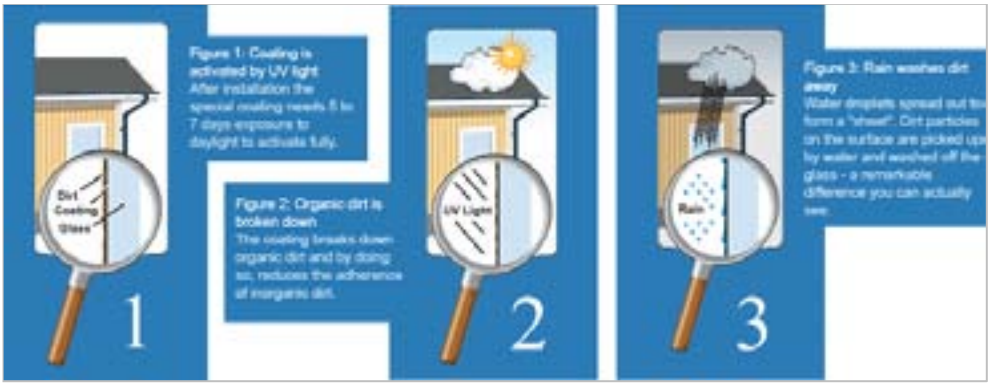


Figure 3: Explanation on how Pilkington Activ™ Self-cleaning Glass works as described by the manufacturer (http://www.pilkington.com)

The coating is hydrophilic (water contact angle (CA) is 20° compared to conventional soda glass for which the CA is 40°). When dirt is deposited, the contact angle of the surface increases, but is then reduced again upon irradiation. The photochemical reaction, which requires oxygen, is quite complex and involves a number of radical sub-products. Titanium oxide is not consumed in the reaction but acts as a catalyst. As a result, organic material is decomposed to CO_2. Concurrently, the contact angle of the surface is further reduced upon irradiation (from 20° to about 15°). After irradiation, dirt can be more easily removed from the glass by rain. The result is that water spreads very effectively (forming a 'layer' over the glass), washing the surface easily. The coating is partially durable to abrasion. Although the name of the product suggests otherwise, this is not a truly 'self-cleaning' layer since it requires water to allow the surface to be cleaned.

Lotus effect® surfaces and textiles

Sometimes, the term 'self-cleaning' is also associated with surfaces that have been engineered to imitate the natural 'self-cleaning' effect found in some leaves, such as the lotus leaf (the effect is described in detail in **Module 1, Chapter 2: Nanoscience in nature**). In this case, the coating is not a uniform layer with a specific chemical functionality (as in the case of photocatalytic coating), but a surface with an engineered topography at the nanoscale level. This leads to a surface which is superhydrophobic (extremely water repellent). Water droplets rolloff the surface and in doing so collect and remove dirt deposited on the surface.

The Lotus effect® has been an inspiration for several innovative materials, such as coatings and textiles. The realisation that certain surface properties can induce water repellence is important in numerous applications. Materials scientists are now engineering numerous types of materials to render them superhydrophobic.

There are many instances where avoiding the wetting of a surface is an advantage, for instance in textiles, which are routinely stained by liquids (juices, coffee, etc.) and solids (mustard, ketchup, etc.). Some companies such as Nano-Tex, Inc., are now commercialising textiles that are engineered to confer superhydrophobic properties on their textiles (**Figures 4** and **5**). This effect is obtained by the presence of 'nano-sized whiskers' on the surface of the fibres that make up the fabric.

Figure 4: Liquid staining on a Nano-Tex®fabric

Image: Nano-Tex, Inc., © Nano-Tex, Inc.

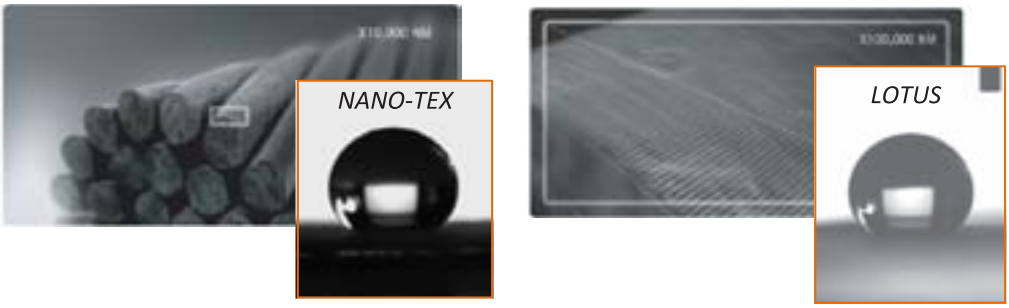


Figure 5: (left) High resolution images of the Nano-Tex® fabric; (right) contact angle images of water droplets on Nano-Tex® fabric and lotus leaf

Images: (left) Nano-Tex, Inc., © Nano-Tex. Inc.; (right) iNANO; Aarhus University, Creative Commons Attribution ShareAlike 3.0)

Experiment D in the **Experiment Module** studies the Lotus effect® and how materials can be engineered to mimic this effect.

The inclusion of TiO_2 nanoparticles in textiles is also being investigated, as this material catalyses the degradation of organic dirt.

Surfaces and materials engineered to mimic the Lotus effect® are useful in construction as they **allow a reduction in the need for cleaning**. Currently, there are various products commercialised or under research that make use of this principle, for example Lotusan®, an exterior paint from the firm Sto launched in 1999. The application of this exterior paint reduces the attack of dirt on the façade to which it is applied, and induces self-cleaning properties when rain droplets roll off and drag dirt away with them.

The above mentioned applications are examples of cases where the superhydrophobic properties of an engineered material, such as a textile or a coating, can reduce cleaning needs, with a consequent reduction in water usage and obvious environmental benefit.

It should be noted that, in contrast to photocatalytic coatings, those based on the Lotus effect® are non-transparent: light is scattered due to the rough nature of the coating. Researchers are thus also investigating transparent superhydrophobic surfaces.

Antimicrobial coatings, textiles and other products

Antimicrobial coatings are needed in many applications, for example to protect medical surfaces and tools, or to reduce microbial attack on the hulls of boats. Sprays and coatings for this use already exist but improvement in this area is needed as many microbes are becoming resistant to the antibiotic treatments that have been used so far. To prevent bacteria attachment, surfaces with nanocoating with specific functionalities and topographies are under investigation. Antifouling surfaces are being investigated for use in the coating of medical utensils and instruments and household appliances, as well as for coating boats. A nanomaterial that is becoming widely used is silver nanoparticles.

Silver is a metal with a long history used for its antibacterial properties — even the Romans used it to dress wounds. This property explains why silver has been used to produce the highest-quality cutlery (silverware) or to store water in vessels in antiquity (even by the Phoenicians). In medicine, 1 % silver nitrate was used in the past as an eye solution to prevent infections in newborn children, and until antibiotics were discovered, silver nitrate was added to germicides and antiseptics as a disinfectant.

The **antibacterial properties** of silver are due to the **silver ions (Ag^+)** released by the bulk metal once this is oxidised. In fact, silver tableware or dishware has antimicrobial activity only if oxidised species are present on their surface. Silver ions induce the oxidative stress of the bacteria cell wall, where many cellular functions are performed, affecting the bacteria's ability to respire and to maintain an intra-cellular environment suitable for life. Silver ions inhibit bacteria growth, suppress respiration and metabolism and basically induce cell death. Silver toxicity has been shown towards **many strains of bacteria**, both gram-negative and gram-positive, and to **fungi** (less towards viruses).

Silver is not considered toxic to the cardiovascular, nervous or reproductive systems in humans. In some people, exposure to silver leads to argyria (or argyrosis) which is due to a process of sequestration of silver ions in an innocuous form which is not reversible and leads to pigmentation or discolouration of the skin. The few cases of death due to silver intoxication have been related to very high concentrations of silver.

In recent years, **silver nanoparticles** (often called 'nanosilver') have been added to numerous consumer products to give them antimicrobial properties. Because of their antibacterial effectiveness and low toxicity towards mammalian cells, silver nanoparticles have become one of the most common nanomaterials used in consumer products. The range of products is quite wide and includes kitchen utensils (pots, pans, etc.), personal wear (socks, shoe liners, underwear), outerwear and sportswear, bedlinen (sheets and mattress covers), appliances (refrigerators, washing machines, air filtration devices, computer keyboards), disinfectant sprays (deodorants) and cosmetics. Nanosilver is incorporated into these different materials through various impregnation techniques (sprayed, painted over the product, incorporated into plastics, etc.).

ELSA TOPIC Silver has been used for centuries so exposure to silver, its ions and associated forms is not new to humans, animals and plants. There is growing concern, however, that the steady increase in consumer products using nanosilver might lead to detrimental environmental consequences. The concern is twofold and involves the possible release of silver nanoparticles from the product and silver ions (and colloids formed with other salts) either through use of the material (e.g. washing of fabrics containing nanosilver), or after their disposal. Currently, it is not clear what is more dangerous for the environment: the actual silver nanoparticles or the ions they release. Since it is known that nanomaterials are normally more reactive than their bulk counterparts, and that they can display new properties, there is concern that silver nanoparticles could behave unexpectedly towards cells (human, bacteria, viruses, plant cells, etc.). Questions have also been raised concerning silver nanoparticle uptake by plants and other systems that might come in contact with nanosilver well before humans through waste water or other water systems. In model experiments, it has been shown that silver nanoparticles are very toxic to the benign bacteria used to remove ammonia in waste water. The concern is that if large quantities of consumable products (e.g. socks, toothbrushes, jackets, etc.) are used, high levels amounts of silver ions, silver nanoparticles or their aggregate forms could be released into rivers and lakes and damage the ecosystem. Many agencies are calling for stricter safety testing of nano-based products and for research on the safety of these products.

NANOYOU DILEMMA The example of silver nanoparticles in a consumer product (socks) is one of the NANOYOU dilemmas included in the **NANOYOU role-playing game 'Antibacterial Socks'** (http://www.nanoyou.eu/en/decide). In this dilemma, students consider the case of **socks with silver nanoparticles** in their fabric to eliminate the bacteria which cause smelly feet and fungal infections. Based on the fact that uncertainty exists regarding the ecotoxicity of nanosilver, students are encouraged to reflect on this product through a benefit versus risk analysis. The dilemma is: Is it right to sell antibacterial socks containing silver nanoparticles when it is not yet known if they are entirely safe for the environment?

The use of **silver nanoparticles in personal hygiene products**, such as toothbrushes, is debated the **NANOYOU NT virtual dilemma 'Nano toothbrush'** (http://www.nanoyou.eu/en/decide). Here, the question asked is if the prolonged use of the toothbrush can cause the degradation of its material and the accidental release of nanoparticles in the saliva, and if this could have some negative health effects.

Anti-fouling coatings for boats are the **NANOYOU NT virtual dilemma 'Boat coating'**. These coatings reduce the attachment of micro-organisms to the surface of the boat, which otherwise reduce its speed. In time, the coating can degrade, so we ask students to consider if this could have an unwanted environmental effect.

Other coatings

A number of products are appearing on the market that can confer some specific property to the surface and which contain nanoparticles (e.g. silica) or other nanomaterials. Examples are anti-graffiti coatings, anti-fog coatings, anti-fingerprint coatings, etc.

NANOYOU GAME Anti-graffiti coatings are used in one of the NANOYOU jigsaw puzzle games (http://nanoyou.eu/en/play-nano.html) — students must match the nanomaterial to its application, connecting it to a specific need.

Fertilisers and wood treatment products

Another area where nanotechnologies are making a contribution is in the development of fertilisers and wood treatment products that are more stable and leach less into the environment. For example, researchers at Michigan State University have incorporated biocides for wood treatment inside polymeric nanoparticles. The small size of the nanoparticles allows them to travel efficiently inside the very fine, sieve-like structure of wood and, at the same time, the biocide, being safely trapped inside a 'nanoshell', is protected from leaching and random degradative processes.

Biomimetic water harvesting

In Module 1, it was shown how natural nanomaterials are inspirational for the fabrication of advanced materials (**Module 1, Chapters 2 and 5**). One example is biomimetic water-harvesting materials. Some plants and insects have the ability to capture water from fog. For example, the Namibian desert dwelling beetle *Stenocara* has bumps on its wing scales with superhydrophobic nanostructured surfaces. The peaks of the bumps are extremely hydrophilic, whereas the slopes of the bumps and the area between them are covered with hydrophobic wax. As a result of this fine nanostructure, as droplets accumulate in size, they roll from the peaks to the waxy channels to a place in the beetle's back that supplies its mouth. A UK company, QinetiQ Ltd, has developed sheets that capture water vapour from cooling towers and industrial condensers based on the nanostructure of the beetle's wing. These materials can capture 10times more water than conventional technology.

Nanocatalysis

A catalyst is a substance that increases the rate of a chemical reaction without being consumed or chemically altered. Conventional catalysts are rare earth metals such as palladium (Pd) and platinum (Pt), which are very expensive. One of the most important properties of a catalyst is its 'active surface' where the reaction takes place. The active surface increases when the size of the catalysts is decreased (**Figure 6**). The greater the catalyst's active surface, the greater the reaction efficiency. Research has shown that the spatial organisation of the active sites in a catalyst is also important. Both properties (nanoparticle size and molecular structure/distribution) can be controlled using nanotechnology. Hence, one area of intense nanoscience research is the development of new nanostructured catalytic surfaces.

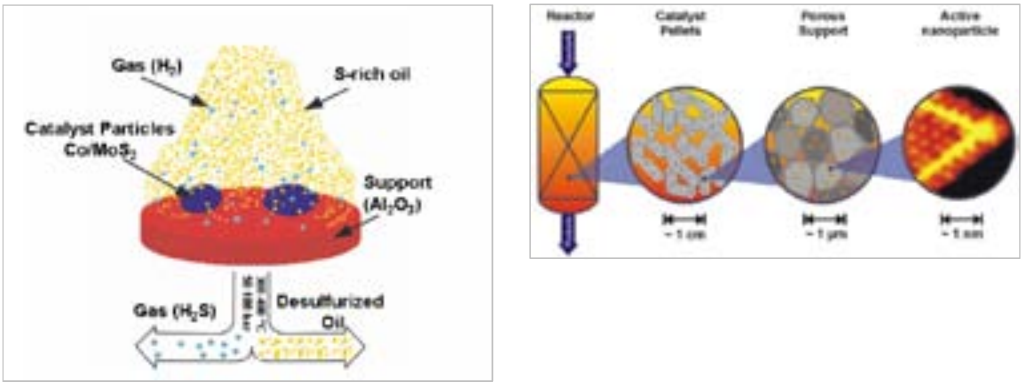


Figure 6: (left) Overview of the hydrodesulphurisation (HDS) catalytic reaction; (right) schematic representation showing how nanoparticles could be included in the catalyst material of a desulphurising fuel reactor. The image on the far right is a real STM image of a MoS_2 nanocrystal on Au(111) showing peculiar atomic distribution at the edges of the crystal.

Images: F. Besenbacher, iNANO, Aarhus University

In the environmental field, nanocatalysis is being investigated, for example, in the **desulphurisation of fuels**, with the aim of developing 'clean' fuels containing very low sulphur products (produced in the fuel during its refining process and responsible for generating sulphuric acid during fuel combustion). Recent nanotechnology research at iNANO has also aided the Danish company Haldor Topsøe A/S in implementing a new generation of hydrodesulphurisation catalysts (BRIM™ Technologies) to be used for sulphur clean-up of fossil fuels worldwide. The hydrodesulphurisation (HDS) catalytic reaction is a reductive hydrogen treatment of fuels to clean up sulphur-containing oil compounds, preventing the emission of many tons of harmful sulphur into the environment on a daily basis.

Another example is Oxonica's Envirox fuel, which uses nano-sized cerium oxide as a catalyst to enhance the efficiency of the fuel combustion. This enhanced-fuel was tested in 2003 and 2004 in 1 000 buses in the United Kingdom (another 500 buses were tracked as control). It was found that the test buses used 5 % less fuel than the controls and that the fuel savings more than paid for the additive.

Nanoscale catalysts are also showing promise in **improving air quality** and for treating particularly challenging **contaminants in water** that must be reduced to a very low level.

Catalytic gold

As a bulk material, gold is notably inert: it does not react with many chemicals (including strong acids and bases). However, when in a nano-size form, gold becomes extremely reactive and this has opened the way for its use in catalytic processes. Conventional materials used in catalysis are rare earth materials such as platinum and palladium, which are extremely expensive. There is great need for catalysts and alternatives are in huge demand. Nano-gold has been shown to be an extremely efficient catalyst in numerous pollution control studies. For example, it has been shown that it is able to remove carbon monoxide from room air under ambient conditions and from fuel cell hydrogen feed gas. Another study has shown that an Au-Pt co-catalyst was able to break down trichloroethylene (TCE) 100 times faster than a catalyst made of a traditional material. Recently, the company Nanostellar Inc. has announced an engineered nano-gold oxidation catalyst which can reduce diesel hydrocarbon emission by 40 % more than commercially available materials. Considering that there are over 14 million light-duty diesel vehicles worldwide, and two million heavy-duty vehicles, the impact of this nanotechnology could be enormous.

Recovery of catalytic material

One of the problems associated with catalysis is that it often makes use of rare earth materials such as palladium (Pd). Natural Pd resources are limited so there is a need to recycle industrial waste from processes that have used Pd as a catalyst. Recycling Pd requires reduction of Pd(II) to Pd(0). For an environmentally friendly alternative to chemical recycling processes, iNANO is investigating the use of bacteria to mediate Pd reduction. The enzyme hydrogenase found in the membrane of many bacteria has the potential to transfer electrons from an organic substrate to Pd(II). In the presence of some bacteria, the Pd is produced as nanoparticles located on the cell surface and in the periplasmic space of Gram-negative bacteria (known as 'bio-Pd'). **Figure 7** shows an example. The catalytic properties of the bio-Pd are similar to commercially available Pd nanoparticles. The hope is to use bacteria to recover catalytically active Pd from industrial waste, and to use recovered Pd for other catalytic processes.

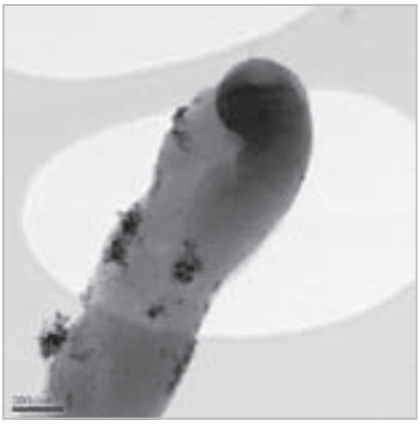


Figure 7: SEMANTIC image of *Desulfovibrio desulfuricans*, a Gram-negative bacterium after palladium recycling. Palladium is produced as nanoparticles (black particles in the image) located on the cell surface and in the periplasmic space of the bacterium.

Image: Rikke Lousie Myer, iNANO, © iNANO

Green manufacturing

Manufacturing processes are always accompanied by the production of diverse waste products, many of which pose a threat to the environment and thus need to be removed and treated. Ideally, manufacturing processes should be designed to minimise material usage and waste production, while ensuring the use of the least amount of energy possible. 'Green manufacturing' is a generic name to broadly cover methods and technologies that are directed towards achieving this goal. It includes the development of new chemical and industrial processes (e.g. water-based rather the solvent-based processes); reduction in the use of unsafe compounds (such as metals); development of 'green' chemicals that are more environment-compatible; and the efficient use of energy. In terms of its application to the reduction of manufacturing waste, nanotechnology can contribute in two ways: by helping the manufacturing to be more controlled and efficient, and by using nanomaterials (such as catalysts) that can raise the manufacturing efficiency while reducing or eliminating the use of toxic materials. Overall, nanotechnology has the potential to make industrial processes more efficient in terms of energy usage and material usage, while minimising the production of toxic wastes. Sometimes the application of nanotechnology to 'greener' manufacturing processes is referred to as 'green nanotechnology' and this includes, for example, bottom-up atomic-level synthesis for developing improved catalysts; inserting information into molecules to build new materials (such as DNA) through highly specific synthesis routes; scaling down material usage during chemical reactions by using nanoscale reactors; and improving manufacturing to require less energy and less toxic materials.

An example of 'green nanotechnology' is the development of aqueous-based microemulsions as an alternative to volatile organic compounds (VOCs) in the cleaning industry. These toxic and potentially carcinogenic compounds, such as chloroform, hexane and percholoroethylene, are conventionally used in the cleaning, textile and oil extraction industries. Microemulsions contain nano-sized aggregates that can be used as 'receptors' for extracting specific molecules at a nanoscale level. Researchers from the University of Oklahoma have synthesised microemulsions with water-attractive and water-repellent 'linkers' inserted between the head and tail parts of a surfactant molecule. The result is a surfactant that has a very low interfacial tension with a wide range of oils. When tested for cleaning textiles from motor oil residues and for extracting edible oil from oilseeds, the microemulsions were found to be very competitive with conventionally used VOCs, both in terms of extraction yield and simplicity of the process.

Environment sensing

Protection of human health and the environment requires the rapid, sensitive detection of pollutants and pathogens with molecular precision. Accurate sensors are needed for *in situ* detection, both as miniaturised portable devices and as remote sensors, for real-time monitoring of large areas in the field. Generally speaking, a sensor is a device built to detect a specific biological or chemical compound, usually producing a digital electronic signal on detection. Sensors are now being used for the identification of toxic chemical compounds at ultra-low levels (ppm and ppb) in industrial products, chemical substances, water, air and soil samples, or in biological systems. Nanotechnologies can improve current sensing technology in various ways. By using nanomaterials with specific chemical and biological properties, the sensor selectivity can be improved, thus making it possible to isolate a specific chemical or biological compound with little interference. Hence, the accuracy of the sensors is improved. As with other nano-engineered products discussed in this document, the high surface-to-volume ratio of nanomaterials increases the surface area available for detection, which, in turn, has a positive effect on the limit of detection of the sensor, thereby improving the sensitivity of the device. Nanosensors are generally faster, as they can detect the targeted analyte (e.g. bacteria) at a lower concentration than a conventional sensor, so the positive response arrives quicker. Scaling down using nanomaterials allows detection sites to be packed into the same device, thus allowing the detection of multiple analytes. This scaling-down capability, together with the high specificity of the detection sites obtainable using nanotechnology, will allow the fabrication of super-small 'multiplex' sensors, thus lowering the cost of the analysis and reducing the number of devices needed to perform the analysis with an economic benefit. Advances in the field of nanoelectronics will also allow the fabrication of nanosensors capable of continuous, real-time monitoring.

Research in the field of nanosensors encompasses various areas such as: synthesising new nanomaterials with specific detection sites able to recognise a certain pollutant; developing new detection methods to increase the limit of detection of the sensors while ensuring a 'readable' electrical signal; and miniaturising the size of the sensor elements while integrating them with larger parts of the device.

An example of how nanoscience can be applied to sensing technology is shown in **Figure 8**, which schematises the operational principle of a heavy-metal nanosensor developed for monitoring heavy metals in drinking water. The sensor is made of an array of electrode pairs fabricated on a silicon chip and separated by a few nanometres. When the electrodes are exposed to a solution of water containing metal ions, these deposit inside the nano-gap between the electrodes. Once the deposited metal bridges the gap, a 'jump' in conductance between the electrodes is registered. The size of the gap, being only few nanometres, allows the detection of a very low concentration of metal ions. This type of sensor is called a 'nanocontact sensor'.

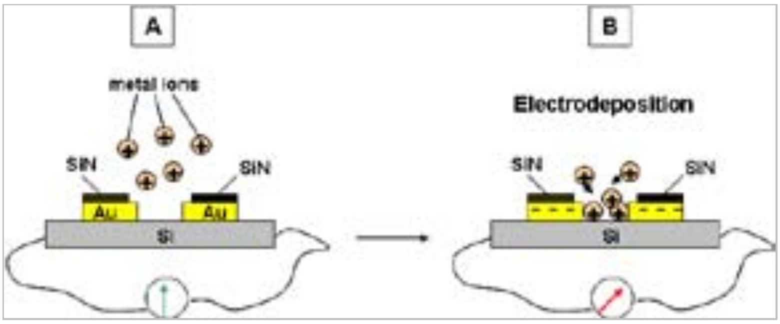


Figure 8: Schematic representation of a nanocontact sensor: (A) a drop of sample solution containing metal ions is placed onto a pair of nanoelectrodes separated with an atomic scale gap on a silicon chip; (B) holding the nanoelectrodes at a negative potential, electrochemical deposition of a single or a few metal atoms into the gap can form a nanocontact between the two nanoelectrodes and result in a quantum jump in the conductance

Image: adapted from *Proceedings — Nanotechnology and Environment: Applications and Implications — Progress Review Workshop III*, 26–28 October 2005, p. 67

Nanowire and nanotube-based sensors

Some nanomaterials in the form of nanowires or nanotubes offer outstanding opportunities as sensor elements in chemical and biological sensors. Individual single-walled carbon nanotubes (SWNTs) have been demonstrated to exhibit a faster response and a substantially higher sensitivity, for example towards gaseous molecules (such as NO_2 and NH_3) than that of existing solid-state sensors. In this case, the mechanism involved in sensing is the direct binding of the gaseous molecule to the surface of the SWNT, upon which the electrical resistance of the SWNT dramatically increases or decreases. Moreover, this sensitivity has been registered at room temperature, whereas conventional solid-state sensors operate at very high temperatures (200–600 °C) to achieve enhanced chemical reactivity between molecules and the sensor material.

Although SWNTs are promising candidates as nanosensors, they also have some limitations that could curb their development. First, existing synthesis methods produce a mixture of metallic and semiconducting nanotubes with only the latter being useful as sensors. Second, in order to be able to sense a variety of chemical and biological species, the surface of nanotubes needs to be modified to have specific functionalities to bind those species. Flexible methods to modify the surface of nanotubes to bind a large variety of analytes are not yet well established. Conversely, nanowires of semiconductors such as silicon do not have these limitations: they are always semiconductors and there is established knowledge for the chemical modification of their surface. Boron-doped silicon nanowires (SiNWs) have been used for the sensitive real-time electrical detection of proteins and antibodies. The small size and the capability of these semiconductor nanowires to detect a wide range of analytes in real time could be used to develop sensors to detect pathogens, chemical and biological agents in water, air and food.

Cantilever sensors

A cantilever sensor is a device made of an array of silicon cantilevers, each coated with a nano-layer which is sensitive to a specific pollutant. The cantilevers are typically 10–500 µm long, but have a thickness of a few micrometres or less. The pollutant-specific layer on top of the cantilever 'arm' is at the nanoscale level. The interaction of the pollutant with the 'arm' of the cantilever causes this to bend as a consequence of a change in surface stress. A laser beam detects this minute bending, which can also lead to quantitative mass measurement of the pollutant detected. Cantilever sensors have been developed to detect VOCs, heavy metals, pesticides and harmful bacteria like salmonella.

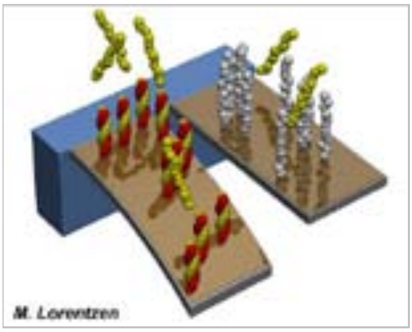


Figure 9: Schematic diagram of a cantilever-based biosensor: the yellow molecules bind specifically to the red molecules on the right-hand cantilever and are detected by the bending of the cantilever

Image: M. Lorentzen, iNANO, University of Aarhus, © Lorentzen

Food packaging and monitoring

Nanotechnology may have a tremendous impact on the way food is produced, packaged, stored and transported. Applications include improved processing and packaging, enhanced flavour and nutrition, tracking of products and ingredients from farm to shelf, and monitoring of taste, ripening, and microbiological contamination. These areas are of major public and industrial interest and technical solutions require that profound insights from materials science are combined with a thorough understanding of chemical, molecular, and physical composition of foods and their nutritional effects. Hopes are high that nanotechnology can provide solutions to many of these diverse challenges. Meeting these challenges is, for example, the mission of the NanoFOOD consortium at iNANO (Aarhus University). One project in particular focuses on the characterisation and exploitation of **proteins immobilised on surfaces**. Immobilisation strategies need to be developed to ensure the surface attachment of functional proteins in order to modify surface properties to include enzymatic activity. Such enzymatic surfaces have huge potential in many applications including food production, healthcare and environmental control. An example of the latter is the development of substitutes **for the ecotoxic tributyltin antifouling paint used on ships**. This paint must not be used after 2008, and the race is on to find effective and environmentally friendly alternatives. Scientists are working to develop surfaces and paint formulations with antifouling properties. Apart from marine vessels, such surfaces and paint may find applications in food production and hospitals. The approach is to engineer surfaces with antifouling effects against a wide range of organisms by immobilising enzymes that either degrade key components of biofilms or have toxic effects on the fouling organisms. The hope is that such properties will inhibit bacterial adhesion and growth. Long-term functionality and sustained release of active compounds are key goals.

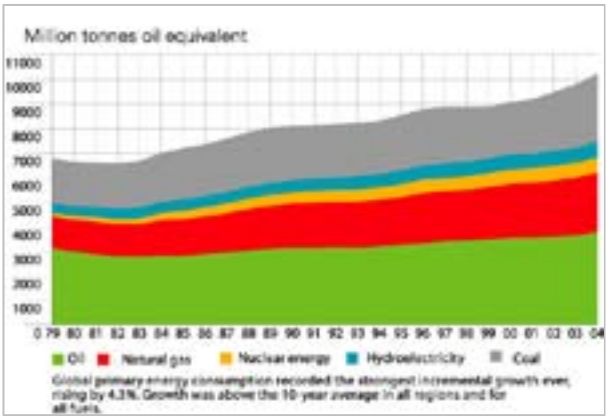
Another area where nanotechnology will have an important impact **is food packaging and tracking**. The vision is to be able to create packaging systems that are 'smart' in the sense of being able to detect the freshness of the food they contain, report any spoilage, and allow tracking of the package through the entire supply chain. Some technologies already exist that combine the plastic of the package with a dye which changes colour in the absence or presence of a specific chemical, such as oxygen or ethanol (two gases that are indicative of spoilage), therefore visually alerting the consumer that the package is compromised, even before there are visible signs of spoilage. Latest advancements in this field consider the use of nanomaterials, such as nanoparticles, or nanofibres, embedded in the inner side of the plastic used in the packages and in combination with dyes. Nanosensors such as the one described in the previous section could be used, capable of detecting ultra-small quantities of material. Nanomaterials have the advantage of having high surface areas, so they are very reactive, and can be functionalised to be very sensitive to detect a specific chemical species, such as oxygen, and provide a fast response. In a similar way, nanoparticles could be used to detect other chemicals that indicate food spoilage, such as ethanol, or even the presence of bacteria. This nanosensor could even be engineered to continuously wireless communicate the status of the product it contains to the manufacture.

NANOYOU DILEMMA The use of nanosensors to monitor food quality and freshness during its storage and retail forms one of the NANOYOU dilemmas included in the **NANOYOU role-playing game 'Nanotechnology in food packaging'** (http://www.nanoyou.eu/en/decide). Currently, there is little knowledge on the degradation process of materials containing nanoparticles. Numerous studies exist to provide life-cycle analysis of nanomaterials, but this type of research requires time. In the meantime, should these materials be disposed of as normal plastic, or is a different waste system needed? The dilemma is: Should nanoparticles be used in our food or pharmaceutical packages to detect freshness, when we still do not know the full ramifications of the using them?

CHAPTER 3:

ENERGY

Today, the world's energy demands are satisfied mainly via the combustion of fossil fuels. Of the 210 million barrels of oil equivalent per day used worldwide, about 85 million barrels come from oil; the rest comes from coal (23 %), gas (17 %), biomass (17 %), some fission (5 %), a small amount from hydroelectric power (6 %) and almost none from renewable resources (**Figure 1**).



Global primary energy consumption recorded the strongest incremental growth ever, rising by 4.3%. Growth was above the 10-year average in all regions and for all fuels.

Figure 1: Global primary energy consumption

It is estimated that by 2050, twice the amount of energy that is burned or consumed today (about 14 Terawatts, TW) will be needed and that most energy will have to come from solar, wind and geothermal (50 %) energy. By then, it is expected that the world's population will rise from today's 6.3 billion to 9 billion people. Relying on fossil fuels (oil, coal and natural gas) to 'feed' the world's future energy needs is not a responsible environmental option, since there is some evidence that the combustion of fossil fuels is the main cause of the high levels of greenhouse gases such as carbon dioxide (CO_2) that are accumulating in the atmosphere, with consequent dramatic worldwide climatic changes.

But, the problem is not limited to the environmental impact of using fossil fuels. The availability of fossil fuels is limited and the supply is presently decreasing; consequently, as the demand for energy increases, so does the cost of fossil fuels. Affordable energy is instrumental in basically every aspect of our present societies, including preserving global peace. In fact, in the list of the most important problems facing humanity in the next 50 years, energy is at the top (**Table 1**). The reason is that affordable energy is fundamental for dealing with the other problems listed: the availability of clean water and food right down to poverty and education.

Ranking	Problem
1	Energy
2	Clean water
3	Food
4	Environment
5	Population
6	Disease
7	War/terrorism
8	Poverty
9	Education
10	Land

Table 1: List of the most important problems facing humanity in the next 50 years

Adapted from R. E. Smalley, 'Future Global Energy Prosperity: The Terawatt Challenge', *Materials Matters Bulletin*, June 2005, 30:412–417

So, the world is presently facing an 'energy challenge' and there is an urgent need for alternative energy resources to fossil fuels. Of these, renewable energy sources that are CO_2-neutral (10) (solar, wind, geothermal, hydro, etc.) are an option. However, a tremendous technology breakthrough will need to occur in the next years to make the conversion of these energy resources an efficient and economically viable option. Solar energy is an excellent example. Every day, the Earth is hit by 165 000 TW of solar power; in the words of Nobel Prizewinner Richard E. Smalley, every day 'we are bathed in energy' (11). The problem is that renewable energy sources like solar energy are not constant in time and evenly distributed geographically (**Figure 2**). Therefore, solar energy collection, conversion, storage and distribution are major challenges: the entire process needs to be efficient and cost effective. Current solar panels have about 15–20 % energy conversion efficiency and they are very expensive. Since solar light is only available during part of the day, suitable storage solutions also need to be found.

Another alternative energy carrier is hydrogen, but hydrogen fuel cell technology will have to face a number of issues (e.g. hydrogen extraction, hydrogen storage, fuel cell lifetime and cost) before a hydrogen economy can become a reality. Solving the future energy challenges requires not only advances in the field of energy conversion and storage, but also energy savings, considering how much energy is wasted today using conventional incandescent lights. As discussed in this document, nanotechnologies not only have the potential to solve many of the issues that the energy sector is facing, but their application to this sector has already resulted in advanced research projects and some commercial realities.

Solar energy

Among the renewable sources of energy, solar energy holds great potential. Solar light, however, is not constant, it is only available during part of the day, and it is geographically uneven: some countries receive a much higher illumination than others. **Figure 2** gives an idea of the area that should be covered worldwide in order to produce a little more than the world's current total primary energy demand (assuming a conversion efficiency of 8 %). The main problem associated with this form of energy is not its supply, but the development of devices that will allow its efficient and cost-effective conversion into electric current.

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(10) Here, CO_2-neutral designates an energy carrier that does not directly produce CO_2 upon conversion (like solar energy or hydrogen).

(11) 'Energy challenge' discussed by Professor R. E. Smalley (http://smalley.rice.edu).

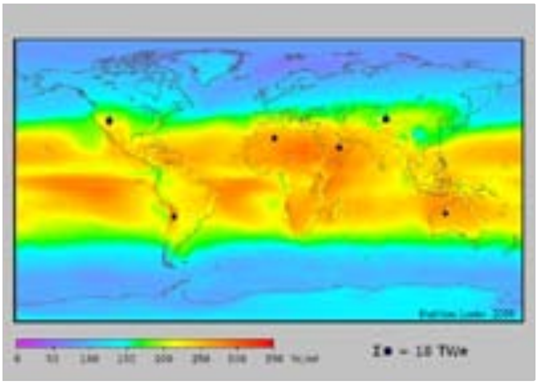

Figure 2: Solar power systems installed in the areas defined by the dark disks could provide a little more than the world's current total primary energy demand (assuming a conversion efficiency of 8 %). Colours in the map show the local solar irradiance averaged over three years.

Image: http://www.ez2c.de/ml/solar_land_area/

The second biggest problem is its storage and efficient transport. The areas that are most irradiated are deserts, therefore, in most cases, remote from the main urban centres, so transporting this energy to where it is most needed becomes a challenge. Making solar energy a viable alternative to fossil fuels therefore requires a series of advances that will most likely be possible through fundamental research into solar energy conversion, storage and transport. Many of these advances are likely to be enabled by nanotechnologies.

Photovoltaics

A photovoltaic (PV) device is a device which converts solar energy into electricity. In a **conventional photovoltaic cell** there are two separate material layers, one with a reservoir of electrons that functions as the negative pole of the cell, and the other lacking electrons, the electron holes that function as the positive pole. When sunlight or other light sources are absorbed by the cell, enough energy is provided to the cell to drive the electrons from the negative to the positive pole, creating a voltage difference between them. In this way, the cell can serve as a source of electrical energy. The efficiency of a PV device depends on the type of semiconductor it is made of, and on its absorbing capacity. All semiconductors absorb only a precise 'energy window' (the 'band gap') which is **just a fraction of the entire solar energy available**. Presently, maximum energy conversion efficiency (15–20 %) in a PV cell is obtained when it is made of crystalline silicon (Si). This is an excellent conducting material, abundant and widely used in electronics, but has the main drawback of being very expensive to produce, which is reflected in the high cost of current PVs. This has limited their use. Alternative, cheaper materials, such as titanium dioxide, can be used in PV technology. Titanium dioxide is a well-known non-toxic semiconducting material, but has the characteristic of absorbing only the UV region of the solar spectrum, which represents only about 5 % of the total solar energy available. This material, therefore, leads to cheaper PVs but with lower energy conversion efficiency.

As will be discussed, nanotechnologies offer the possibility to introduce alternative materials and fabrication methods to produce cells with tailored absorption characteristics in order to absorb a larger portion of the solar energy spectrum. In order to meet the 'energy challenge' through solar energy, conversion efficiencies in the order of 45 % are needed, so research in this area is very intense and numerous different types of nanomaterials are being investigated. In order to reach this ambitious goal, devices must be made of materials that absorb the visible part (representing about 46 %) of the solar spectrum.

There are basically two approaches being investigated.

- Development of silicon nanocrystals engineered to absorb more solar energy.
- Biomimetic approaches, where the photovoltaic device is engineered to mimic the best known solar-conversion process ever made, the natural photosynthesis molecular machine.

Nanocrystals

The limitation of silicon is not only related to its processing cost. Due to its indirect band gap, silicon is weak in absorbing light — only a fraction of the solar spectrum is absorbed. This is where nanoscience can help: in sufficiently small nanocrystals, the band gap becomes quasi-direct, which gives rise to strong light absorption. Thus, the optical properties of silicon can be improved by adding nanocrystals. One such example is silicon-based tandem solar cells, where the top cell is based on nanocrystals, while the bottom cell is a standard silicon cell. Inside the solar cells, the nanocrystals are used to increase the generation of current.

Biomimetic approaches using nanotechnologies

Nature has developed a 'splendid molecular machine' (12) that enables the conversion of solar energy into chemical energy through a process called photosynthesis. In this process, solar energy is converted into stored chemical energy (in the form of carbohydrates). The process is an amazing example of a natural nanotechnology which serves as an inspiration for the creation of biomimetic devices capable of converting solar energy into other forms of energy. In photovoltaics, the aim is the conversion of solar energy into electricity to be used for powering electrical appliances. In photosynthesis, light is 'captured' by light-harvesting antennae (e.g. chlorophyll) in which photons are absorbed, exciting electrons to higher energy states. **The pigment in the 'antenna' absorbs strongly in most of the visible region of the solar spectrum**. The energised electrons are transferred to a series of reaction centres which are called Photosystem I and Photosystem II. In these reaction centres, a series of photochemical electron transfer reactions occur involving quinines. Eventually, the energy is transferred through proton bonds to another reaction centre where the energy is stored in the bonds of the ATP molecule, which reacts further to form nicotinamide adenine dinucleotide phosphate (NADP+). In the final step of the process, hydrogen is taken from water (forming NADPH), releasing oxygen as a by-product. The NADPH stores energy until it is used in the next step of the reaction to provide energy for the formation of C-C bonds, consuming carbon dioxide in the process. The end product is carbohydrates. Therefore, the overall process consumes water and carbon oxide, and produces carbohydrates, which are the fixed form of carbon that is the food base for all animal life.

Artificial photosynthesis

Some researchers have been able to extract the complex Photosynthesis I from spinach and use it to power solid-state electronic devices. This represents an example of a biomimetic solid-state photosynthetic solar cell. Creating the interface is not trivial because, in the plant, the complex requires salts and water to function, which obviously cannot be used in electronic devices, so surfactants are used instead. The device is made of alternating layers of conducting material (gold), biological material, semiconducting layer, and a conducting layer on top. The conversion efficiency of the device is 12 %.

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(12) Boyer, P. D., 'The ATP synthase — a splendid molecular machine', Annual Review of Biochemistry, July 1997, 66:717–49.

Dye-sensitised solar cell

The second approach is a hybrid between conventional photovoltaics, which uses semiconducting materials, and artificial photosynthesis. To date, this seems the most promising approach to improve PV efficiency. In this approach, some other strongly absorbing species (dye) which mimic the function of the chlorophyll are attached to the surface of the semiconductor (e.g. TiO_2). These types of cells are called dye-sensitised cells, or Gräztel cells after the name of their inventor, or **photoelectrochemical cells** (PEC). The complex dye molecules (called sensitisers) are attached to the surface of a mesoporous titanium oxide. These are different from a classic thin-film PV in that light is absorbed in a semiconductor layer, whereas in **the Gräztel cell, absorption occurs in the dye molecules**.

The *dye molecules* act somewhat like an antenna (mimicking chlorophyll), meaning that more of the light of a particular colour can be captured but also that a wider range of colours of light can be absorbed compared to pure TiO_2, thus increasing the efficiency of the device (**Figure 3**).

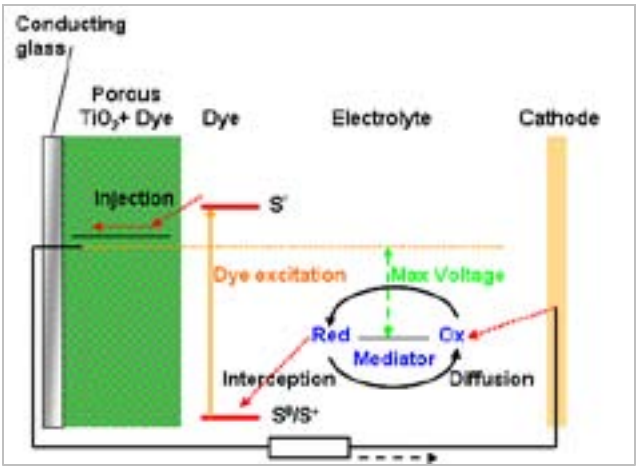

Figure 3: Schematic representation of the operation of the dye-sensitised electrochemical photovoltaic cell (Gräztel cell)

Image: L. Filipponi, iNANO, Aarhus University, own work

In the Gräztel cell, the anode is made **of mesoporous dye-sensitised TiO_2** and receives electrons from the photo-excited dye which is thereby oxidised. The oxidised dye in turn oxidises the mediator, a redox species that is dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. The mesoporous nature of the titanium oxide provides an enormous internal surface area, thereby reducing the amount of material needed in the cell. The titanium oxide films are produced from a nanoparticle suspension (which is synthesised to form a stable porous material). Specific synthetic dyes are under development to increase light absorption. These cells are extremely promising because they are made of low-cost materials and do not need elaborate apparatus to manufacture. Current scale-up of production utilising polymer materials and roll-to-roll continuous production has the potential to produce the large areas of solar cells required to capture significant amounts of solar energy. Some companies, such as DyeSol, are already producing and selling these types of solar cells, with conversion efficiencies of about 12 % (**Figure 4**).

Figure 4: A dye solar cell (DSC) commercialised by DyeSol

Image: http://www.dyesol.com

Quantum-dot-sensitised solar cells

Another possibility is to use semiconductor nanocrystals (known as quantum dots, QDs) instead of the photosensitive dyes used in the Gräztel cell. For example, CdS, CdSe, InP and InAs quantum dots have been combined with mesoscopic networks of TiO_2 nanoparticles to obtain **quantum-dot-sensitised solar cells (QDSSCs)**. In general, QDs offer several advantages compared to organic dyes such as those employed in a Grätzel cell: **they provide the ability to match the solar spectrum better because their absorption spectrum can be tuned with particle size**. An important nanotechnology discovery with great potential to increase the efficiency of these types of solar cells was reported in May 2006 by a team at the Los Alamos National Laboratory (USA). Researchers in this group found that when nanoparticles of less than 10 nm in diameter made of lead and selenium (PbSe nanoparticles) are illuminated with light they absorb one photon of light but produce up to three electrons. When today's photovoltaic solar cells absorb one photon of sunlight, the energy is converted to one electron, and the rest of the photon's energy is lost in heat. Therefore, PbSe nanoparticles produce at least twice the number of electrons compared to conventional semiconductors, a process known as 'carrier multiplication'. This nanotechnology discovery could boost the efficiency of today's solar cells from 20–30 to 65 %.

NANOYOU DILEMMA The use of nanomaterials in photovoltaic devices promises to greatly improve the efficiency of these devices. When nanomaterials are encapsulated or contained within a photovoltaic cell, the risk of them coming into contact with the user is very low. The problem may occur when the device comes to the end of its lifetime. There may be problems with disposal of the device, especially if the regulation and control of these devices lags behind their development. In the **NANOYOU role-playing game 'Nano-based solar cell'** (http://www.nanoyou.eu/en/decide), students consider the question: Should solar cells incorporating nanoparticles be commercially manufactured before any associated risks are fully established?

Lotus-mimicking PV coatings

The lotus leaf is characterised by being extremely water-repellent, so much so that water simply rolls off its surface dragging dirt with it. The consequence is the extreme cleanliness of the leaf, which is a symbol of purity in some Indian cultures. The superhydrophobic properties of the lotus leaf are a consequence of its micro and nano-topography, as well as its surface chemistry (see **Chapter 2**).

Superhydrophobic surfaces are useful in **improving the performance of solar cells**. One of the problems with this technology is that the cells are outside and, therefore, prone to becoming very dirty. This layer of dirt 'masks' the catalytic areas of the solar cells and so reduces their efficiency and lifetime. Coating the solar panel with a superhydrophobic coating keeps the panel considerably cleaner. Because of the nano-surface roughness, the coating is transparent to UV light, a necessity for these types of devices. The superhydrophobic coating is also durable, which further improves the solar panel lifetime.

In one research project, PV cells have been coated with a nanostructured coating which increases the absorption of light. The coating mimics the lotus leaf, so it is superhydrophobic, with the effect of also conferring self-cleaning properties on the PV surface.

Solar energy storage

Storage of electrical power is critical for making solar energy a primary power source. The best place to provide this storage is locally, near the point of use. Ideally, every house, business and building should have its own local electrical energy storage device, an uninterruptible power supply capable of handling the entire needs of the occupiers for 24 hours. If this were done using today's lead-acid storage batteries, such a unit for a typical house capable of storing 100 kWh electrical energy would take up a small room and cost over USD 10 000. Through advances in nanotechnology, it may be possible to shrink an equivalent unit to the size of a washing machine, and reduce the cost to less than USD 1 000.

Solar heating

Solar energy can also be used as a heating source to produce hot water, and heat homes and offices. Current systems are able to convert 25–40 % solar radiation into heat. The principle of solar heating is straightforward: a material absorbs sunlight energy and releases it in the form of heat directly to a water source or a heat exchange element (heat pump). Any material that can enhance surface area or have improved absorption properties would improve this technique: numerous nanomaterials do so. Since the sun is a variable source that produces a diffuse energy, controlling the incident solar radiation is difficult because of its changing position. Nanotechnologies can be used to fabricate complex nano-structured mirrors and lenses to optimise solar thermal collection. Furthermore, aerogels with nanopores are used as transparent and thermally isolating materials for the cover material of solar collectors.

Hydrogen society

Hydrogen (H_2) can, in principle, be a future environmentally friendly energy carrier when it is produced from renewable energy. The ideal scheme would be to produce hydrogen by splitting water molecules using solar light (**Figure 5**). Hydrogen could then be used as an energy carrier to provide electricity in our homes, fuel our cars, etc.

The idea of a fuel cell was first conceived in 1839 by Sir William Grove who thought that **electricity could be produced by reversing the process of electrolysis**, in which hydrogen and oxygen are produced by the electrolysis of water.

Hydrogen fuel cells use hydrogen and oxygen as fuel to generate electricity. The fuel molecules in the cell must be ionised to react. The ionisation must be catalysed by the electrodes, and an electrolyte must conduct the formed ionic species so that they can react (**Figure 6**). The sub-product of this reaction is only water — no CO_2 is produced during the conversion of hydrogen to electricity. The result of the electrochemical process is a maximum of 1.2 V and 1 W cm^{-2} of power.

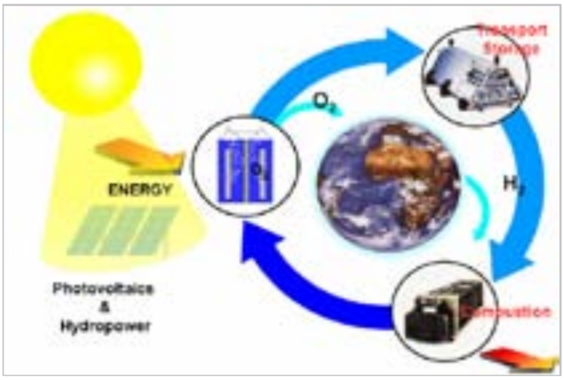

Figure 5: The ideal combination of photovoltaic and hydropower

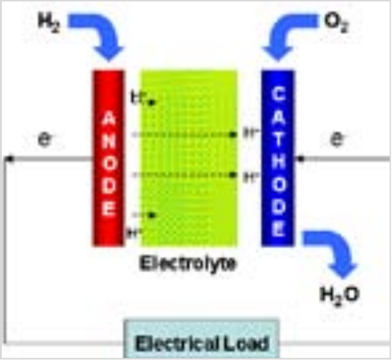

Figure 6: Schematic representation of a hydrogen fuel cell

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

The three fundamental elements of a hydrogen fuel cell are therefore the fuel (H_2 and O_2), the catalyst and the electrolyte. At present, there are problems associated with each of these elements, making the fabrication and operation of hydrogen fuel cells technically challenging and very expensive. However, the technology is developed enough and the worldwide research so intense that consumer goods powered by fuel cells are likely on a large scale.

Hydrogen production

The first problem is associated with the nature of the fuel, hydrogen. Although hydrogen is abundant in nature it is not freely available, it needs to be extracted from a source, such as hydrocarbons (e.g. methane), which produce CO_2 on extraction, or water. Extraction of hydrogen from water is better. Ideally, hydrogen should be extracted using a renewable energy source (solar, wind, geothermal, etc.). One of the most promising methods of hydrogen generation is its photochemical extraction from

Source	USD/ GJ
H_2 from coal/oil/natural gas	1–5
H_2 from natural gas minus CO_2	8–10
H_2 from coal minus CO_2	10–13
H_2 from biomass	12–18
H_2 from nuclear energy	15–20
H_2 from wind energy (via land)	15–25
H_2 from wind energy (via sea)	20–30
H_2 from solar cells	25–50

Table 2: Comparison of the cost of different types of hydrogen sources: for a sustainable economy to exist, the price must be less than USD 5/GJ

Adapted from T. R. Jensen, 'Hydrogen Fuel Cells', *Aktuel Naturvidenskab*, 2004 (http://www.ird.dk), reprinted with the permission of the author

water using sunlight. The idea is to use sunlight to split water into hydrogen and oxygen. This is accomplished routinely and has been for over 3.5 billion years by photosynthetic organisms, but to make it happen artificially is a real challenge!

Nanotechnologies for improving photoinduced water splitting

In principle, visible light at wavelengths shorter than 500 nm has enough energy to split water into hydrogen and oxygen. However, water is transparent to this visible range and does not absorb this energy. Therefore, the combination of a light-harvesting system with a water-splitting system is necessary to implement the use of sunlight to split water.

Simple as the concept might sound, several technical challenges must be overcome before this technology can become commercially viable. **Table 2** compares the cost of producing hydrogen from a series of sources, and shows how, to date, only extraction from fossil fuels is economically viable. Therefore, fundamental research is necessary to overcome the limitations of photochemical water decomposition to produce hydrogen.

In 1972, A. Fujishima and K. Honda demonstrated the photoelectrolysis of water with a TiO_2 photoanode using platinum as a counter-electrode. Although the reaction is possible, before it can become viable (i.e. both economic and efficient) as a source of hydrogen, two main problems need to be solved.

The first is the limited light absorption of wideband gap semiconductors (such as TiO_2) in the visible range of the solar spectrum. This problem has already been mentioned in the section on photovoltaics as it applies to both technologies. Basically, photovoltaics and photoinduced water splitting implement the same concept of using sunlight to excite electrons but they differ in how the excited electron (e-h pairs) are used: to drive a current (in PVs) or to drive a chemical redox reaction (in photoinduced water splitting).

As discussed in the previous section, nanotechnology is leading the way in solving some of the problems associated with solar energy conversion with the introduction of nanostructured materials that have high solar energy absorption rates. Along this approach, the group under the direction of Dr Misra at the University of Nevada has developed **titanium dioxide (TiO_2) nanotube arrays** having a modified band gap for generating hydrogen by splitting water using sunlight.

The second problem in photoinduced water splitting is the fast electron-hole recombination, which lowers the efficiency of the process. In simple terms, photocatalysis involves harvesting solar photons in a semiconductor (the TiO_2 surface) and subsequent conversion of these photons to electronic excitations, which then induce the desired water-splitting reaction. The excited electron-hole pair, though, has a high tendency to recombine. Nanostructures offer the opportunity to minimise the distances (and thus the times) over which charges have to survive and be transported after excitation. Deposition of small noble metal islands (< 5 nm) or metal nanoparticles enhances the photocatalytic activity of systems that use TiO_2 as the photocatalytic surface. This effect is due to the charge separation across the metal-semiconductor interface. More recent nanotechnology approaches include the use of carbon-doped titania nanotubes arrays, SWCNTs and nanostructured hematite films.

Hydrogen storage

The combustion of hydrogen is straightforward with no detrimental by-products: $H_2 + ½ O_2 \rightarrow H_2O$. However, a problem exists that relates to its **storage** and **transport** which need to be both efficient and safe. The problem is easily seen by comparing the energy-to-volume ratio for gaseous hydrogen (3.0 MJ/L) to that of conventional gasoline (32.0 MJ/L). This means that, given the same volume, the energy produced by hydrogen is about 10 times lower than that from conventional gasoline. This obviously represents a problem for storing hydrogen in a vehicle: a big, heavy tank would be required to store and transport the required amount of hydrogen (**Figure 7**). Some possible solutions are to use liquid hydrogen (8.5 MJ/L), compressed hydrogen or to store hydrogen in a solid metallic support such as metal complexes (hydrides).

The use of compressed hydrogen implies using liquid tanks that must be made of a very strong yet lightweight material. This material should also have outstanding insulating and pressurisation properties in order to avoid hydrogen leakage. This problem can potentially be solved using nanotechnology to develop new materials with exceptional properties in terms of strength and density.

Figure 7: Volume of 4 kg hydrogen compacted in different ways, relative to the size of a car

Image: L. Schlapbach, A. Züttel, 'Hydrogen storage materials for mobile applications', *Nature*, 2001, 414:353–358, reprinted with the permission of Macmillan Publishers Ltd, © 2001

Solid metallic nanostructured supports

Solid metallic supports are probably the most viable option for hydrogen storage. In this approach hydrogen is 'loaded' to a solid support and extracted from it when needed. The main challenges here are the material loading capacity and the regeneration kinetics to re-extract the hydrogen from the support The best material would achieve an optimum compromise between having hydrogen too weakly bonded to the storage material, which means a low storage capacity, and a too strongly bonded to the storage material, which would require high temperatures to release hydrogen. Nanotechnology can contribute in this field by developing new molecules that allow high hydrogen loading capacity and acceptable regeneration kinetics. Researchers aim to develop nanomaterials that are light in weight, low in volume, have high loading capacities, good regeneration kinetics, and are low in cost.

Two candidate materials are complex metal hydrides, which have an intermediate bonding of hydrogen, and nanostructured carbon-based materials, such as carbon nanotubes. The properties of some complex metal hydrides as hydrogen storage materials, such as $LiBH_4$, $NaBH_4$ and $NaAlH_4$, are summarised in **Table 3**. In **Figure 8**, the schematic representation of sodiumaluminium hydride ($NaAlH_4$) is shown. The structure can be visualised as a salt made of sodium ions (Na^+, yellow) and a complex ion of aluminium (Al, orange) and hydrogen (blue), AlH_4^- (other examples of complex ions are the ion sulphate SO_4^{2-} and the ion phosphate PO_4^{3-}).

	H_2 — in hold		Pressure/ temperature
	Mass-energy density (weight %)	Volume-energy density (g/L)	$p(H_2)$ (bar) (1)
Pressure tank	4.6	25	300
	ca. 6	58	700
Metal hydride			Temperature (°C) (2)
MgH_2	7.6	110	350
$LaNi_5H_6$	1.4	121	ca 50
$TiFeH_2$	1.9	107	ca 50
Complex metal hydrides			
$LiBH_4$	18.5	121	380
$NaBH_4$	10.7	114	400
$LiAlH_4$	10.6	87	> 125
$NaAlH_4$	7.5	94	210
Mg_2FeH_6	5.5	150	320

Table 3: Comparison between various hydrogen storing systems

(1) Hydrogen pressure in a gas tank (700 bar is the target).

(2) Temperature for H_2 release at $p(H_2) = 1$ bar, without catalyser.

Adapted from T. R. Jensen, 'Hydrogen Fuel Cells', *Aktuel Naturvidenskab*, 2004 (http://www.ird.dk), reprinted with the permission of the author

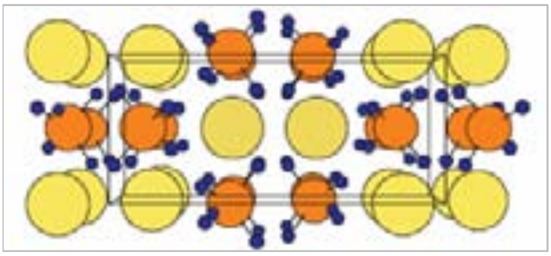

Figure 8: Schematic representation of sodiumaluminumhydride ($NaAlH_4$), a promising complex hydride for hydrogen storage

Image: T. R. Jensen, 'Hydrogen Fuel Cells', *Aktuel Naturvidenskab* (http://www.ird.dk), Naturvidenskab 2004

The hydrogen fuel cell

In order for hydrogen fuel cells to become an economically viable alternative to combustion chambers, two other main problems need to be addressed: the **nature of the catalyst** and that of the **electrolyte** in the cell.

Currently, the electrodes in a fuel cell are made of a metal such as platinum (Pt), which is a rare, expensive metal, also sensitive to the CO and sulphur species that are dispersed in the atmosphere. These deactivate the platinum surface (a phenomenon called 'poisoning of the catalyst'). Fuel cells operate at high temperatures (> 70 °C) since the poisoning agents at these temperatures tend to de-adsorb. Nanotechnology is already actively involved in addressing some of the issues concerning fuel cell catalysts. Improvements in this area through nanotechnology concern (a) increasing the material catalytic activity; and (b) reducing the use of rare metals. Since the current generated at an electrode is proportional to the active surface of the catalyst, fuel cells that have higher power density can be formed from nanomaterials, which have a higher surface area to volume ratio. Electrocatalytic material properties are also proportional to particle size, so nanoparticles and nanomaterials have increased catalytic activity compared to bulk materials. This characteristic can lead to a reduction in the use of rare metals, for example by using carbon nanomaterials as a support for the dispersions of nano-sized platinum, thereby reducing the weight of platinum needed to produce the same surface area of active Pt catalyst. Carbon nanomaterials are particularly suitable since they act both as a support for the platinum nanomaterial and as a conductor. Suitable carbon nanomaterials are carbon foams containing nanopores, different types of nanotubes and single-walled nanohorns.

Proton exchange membrane fuel cell

The electrolyte conventionally used in fuel cells is aqueous KOH operating at about 70 °C (liquid alkaline cell). It leads to corrosion of the electrodes, reducing the cell lifetime, and operates at high temperatures, decreasing the thermodynamic efficiency of the cell. A solid electrolyte is preferred, therefore **modern hydrogen fuel cells use a proton-permeable membrane made of a polymer** (e.g. Nafion®), which has a high proton conductivity due to the presence of water molecules in its structure. In a Proton Exchange Membrane Fuel Cell (PEMFC), the proton ions generated at the platinum anode pass through the proton conducting membrane to the platinum cathode, where they combine with oxygen and form water (**Figure 9** illustrates the operational principle of a PEMFC).

Proton Exchange Membrane Fuel cells (PEMFC) are the most likely fuel cells to achieve commercialisation for automotive purposes as a result of their low operating temperatures and their inherent properties of being lightweight, producing high current densities and containing no corrosive materials.

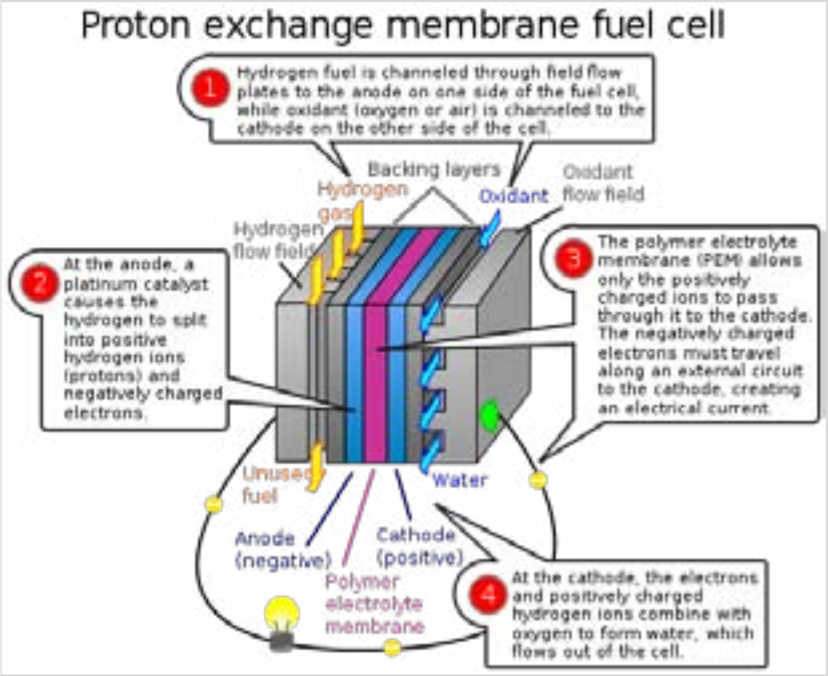

Figure 9: Diagram of a proton exchange membrane fuel cell

Image: Wiki Commons, Public image

An area where improvement is urgently needed, however, is the nature of the solid membrane. Nafion®, for example, is expensive, subject to degradation through dehydration at operating temperatures above 100 °C, and is not fabricated with nanoscale control; therefore, it has pores that are not uniform in size and distribution, so that the active sites on the membrane surface (directly involved in proton binding) are randomly exposed. Other 3D solid electrolytes have been investigated, but they have the problem of either very low conductivity (reducing the efficiency of the cell) or requiring high temperatures to operate.

In this context, nanotechnologies can aid in the development of nanostructured solid membranes to increase proton conductivity, cell efficiency and durability. These include ceramic electrolyte membranes (e.g. metal-oxane membranes) and nanostructured solid electrolytes or fillers fabricated with nanoscale control. In addition, fuel cell assembly, durability and cost could, in principle, be improved by employing nanotechnology to fabricate sturdier cells able to withstand the large changes in temperature required in some applications, such as automotive operation.

Thermoelectricity

Thermoelectric materials (TE) are functional materials that have the double property of being able to convert heat to electricity, and vice versa. Thermoelectricity can be generated in all conductive materials. When a temperature gradient is applied across a wire, electrons diffuse from the hot to the cold part due to the larger thermal speed of the electrons in the hot region. Consequently, a charge difference builds up between the hot and cold regions, creating a voltage and producing an electric current. Alternatively, a current can be applied to the wire to carry heat away from a hot section to cooler areas.

Thermoelectric materials can, therefore, be used either for cooling or power generation. Although current devices have a low conversion efficiency of around 10 %, they are strongly advantageous compared to conventional energy technologies, since the converters have no moving parts and are thus both reliable and durable. Furthermore, they are scalable and hence ideal for miniature power generation, and no pollutants are released into the environment. If significantly improved thermoelectric materials can be developed, thermoelectric devices may replace the traditional cooling systems in refrigerators. They could also make power generators in cars obsolete by utilising heat from the exhaust gases, or they could possibly be used to convert huge amounts of industrial waste heat into electricity.

Despite their enormous potential, thermoelectric materials have not yet fulfilled their huge promise, and are currently only employed in niche applications, most notably by NASA to generate electricity for spacecraft that are too far from the sun for solar cells to operate (**Figure 10**). The problem is that for the process to be efficient, the thermoelectric materials need to be good electrical conductors but poor thermal conductors, so that the temperature difference inside the material remains. More specifically, thermoelectric materials are ranked by their figure of merit, ZT, which is defined as $ZT = S2\sigma T/k$, where S is the thermopower (or Seebeck coefficient), σ is the electrical conductivity, k is the thermal conductivity and T is the absolute temperature. To be competitive with conventional refrigerators and generators, thermoelectric materials with $ZT > 3$ must be developed. Yet in five decades of research, the room temperature ZT of bulk semiconductors has increased only marginally, from 0.6 to about 1.0. The challenge lies in the fact that S, T and k are interdependent: changing one alters the others, making optimisation extremely difficult.

However, in the last years, there have been reports of dramatic increases in the properties of thermoelectric materials. In all these cases, the material has been found to be nanostructured. Researchers are studying these nanomaterials in detail to understand whether this is a result of quantum confinement or photon dynamics and transport. What is clear is that to have optimum properties, the material needs to have high symmetry at the nanoscale level, and needs to incorporate heavy elements because of itslow thermal conductivity.

Some examples of nanostructured thermoelectric materials are half-heuster alloys (ZrNiSn), Zn_4Sb_3, skutterudines, and novel PbTematerials (e.g. LAST-18, SALT-20 and LASTT).

Figure 10: Clathrate crystals produced at iNANO are among the target materials for NASA's high-temperature thermoelectric converters for future Mars missions. Heat for the converters will be provided by radioactive sources.

Image: iNANO, Aarhus University

Rechargeable batteries

Rechargeable batteries are energy storage devices used to power small electronic equipment such as mobile phones and personal computers, where high power and light weight are important. These same attributes are required for electric vehicles, hybrid electric vehicles, power tool and backup power subsystems. In simple terms, a battery is an electrochemical device that generates direct current through a coupled set of reduction-oxidation (redox) reactions. The positive electrode is reduced (captures electrons) and the negative electrode is oxidised (releases electrons). The battery consists of a positive electrode facing a negative electrode divided by a porous separator that prevents the electrodes from touching, and an ionic electrolyte, which is a conducting medium that ensures movement of the ions from one electrode to the other. Intercalation-based batteries using the small lithium (Li+) ion are the most used (**Figure 11**). These batteries have at least one redox-active electrode with an open crystal structure with 'holes' capable of intercalating Li+. For example, oxidation of cobalt in $LiCoO_2$ expels Li+ which is taken up in a graphite electrode. When the battery is charged, the Li+ moves from the positive electrode to the negative one via the electrolyte. On discharge, the opposite occurs, releasing energy in the process. Ideally, the structure of the redox-active crystal should be capable of reversibly intercalating the small Li+ ion.

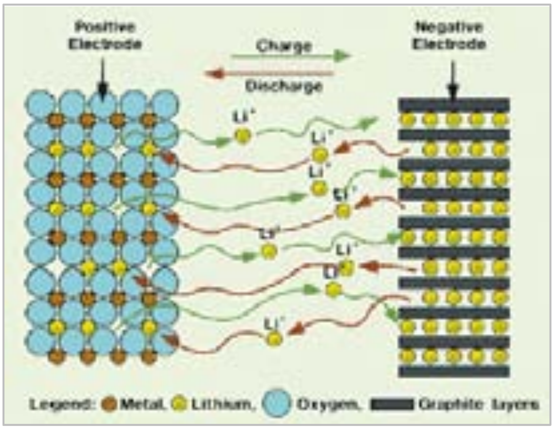

Figure 11: Schematic representation of a lithium-ion battery

Nanotechnologies to impact energy capacity, battery power, charge rate and lifetime

Current problems with lithium rechargeable batteries involve a number of issues, the first being the battery energy capacity: in order to allow ions and electrons to move quickly into and out of the active material (allowing fast charging and discharging), the material must be deposited as a thin film. This limits the amount of active material that can be incorporated into the battery (energy capacity). For high-capacity batteries, thickness is increased in order to provide more energy storage but with the drawback of slower charging.

The second issue concerns the battery power: an important attribute of large format batteries is their capability to deliver power quickly. Power is restricted by the ion removal capability in lithium batteries, which depends on the electrochemical properties of the battery. Then there is the problem of charge rate: batteries need to be recharged, and recharging times are now in the order of hours. The time of charge is restricted by the incorporation rate capabilities of Li+ inside the graphite electrode.

Lithium battery lifetime also needs to be improved: in current batteries, every time Li+ enters/exits the graphite electrode, the pores of the electrode need to expand or shrink. This repeated expansion and shrinkage fatigues the graphite particles, which break apart as a result, reducing battery performance.

Nanomaterials as alternatives to conventional electrodes

Nanocrystalline composite materials and nanotubes can be used to replace the conventional graphite or Li-graphite electrode. These can be fabricated to house voids having the same size as the lithium ions they have to accommodate. This allows much more active material to be packed into an electrode, increasing energy capacity. A nanostructured electrode with voids having the same size as the lithium ions increases the battery life and also ensures high charge rates. In the future, nanotechnology will also allow a move away from flat layers of electrode materials to positive and negative electrodes that interpenetrate. This 3D nano-architecture could improve the mobility of ions and electrons, thereby increasing battery power.

In this context, it is interesting to note the work reported in December 2007 by Yi Cui et al. at Stanford University (USA), on the use of silicon nanowires as anode material. Bulk silicon has been investigated in the past as an alternative material to graphite since it has a low discharge potential and the highest theoretical charge capacity (more than 10 times that of existing graphite anodes). However, silicon bulk anodes (containing silicon films or large silicon particles) have shown short battery lifetime and capacity fading due to pulverisation and loss of electrical contact between the active material and the current collector. These problems arise from the fact that the volume of silicon anodes changes by about 400 % during battery cycling as a result of the anode swelling (battery charging) and shrinking (battery discharging) as lithium ions enter and exit the anode.

The group at Stanford University replaced a conventional bulk silicon anode with one formed of silicon nanowires (SiNW), grown directly on the metallic current collector. In this way, they were able to achieve the theoretical charge capacity of silicon anodes (10 times that of current ion-lithium batteries) and to maintain a discharge capacity close to 75 % of this maximum. The work has been patented and the discovery has great potential for commercial high-performance lithium batteries.

'Paper battery'

Some exciting work recently reported by scientists at Rensselaer Polytechnic Institute (USA) uses a composite material that combines high energy capacity with flexibility. The researchers found that they could combine nanotubes (which are highly conductive) with a layer of cellulose, the material used to make paper. In this way, they were able to obtain 'paper batteries' which can be rolled or folded just like paper without any loss of efficiency. This opens the door to batteries moulded to assume a particular form. Like all batteries, the paper version comprises electrodes, electrolyte, and a separator. The first electrode is formed by vertically aligned multi-walled carbon nanotubes, deposited on silicon substrates. Plant cellulose is cast on top of this layer, solidified, and dried to form the porous separator. The middle paper layer is then impregnated with an ionic liquid which acts as the electrolyte; this can be an organic salt that is liquid at room temperature. The ionic liquid contains no water, so there is nothing in the batteries to freeze or evaporate. This expands the working temperature range of the battery, which can withstand extreme temperatures from 195 K to 450 K. To make a battery, the second electrode is formed by coating the paper side with lithium oxide. Interestingly, the same material can be used to make a supercapacitor simply by folding the paper in half, so that there is a carbon electrode at both the top and bottom. The team were also able to fabricate dual-storage devices containing three electrodes that act as both supercapacitors and batteries.

Battery operation range, lifetime and safety

Lithium batteries are, at present, limited in their operating temperature range. Below 0 °C and above 50 °C the batteries cannot be recharged, and above 130 °C they become unsafe due to thermal runaway. Thermal runaway, which is due to reaction of the graphite with the electrolyte, can also occur due to battery impurities. Finally, lithium batteries are made of toxic metals and are, therefore, harmful for the environment.

Battery safety can be increased if the graphite electrode in a lithium battery is replaced with a nanostructured material that is inert towards the electrolyte. Nanotechnology can also be employed to use alternative active materials which are less expensive and non-toxic to the environment. For example, the non-toxic magnetite (Fe_3O_4) has been employed as the active material in a high-capacity Cu nano-architectured electrode (**Figure 12**). Nanostructured lithium batteries are becoming a commercial reality, such as the Altairano NanoSafe™ and 123 Systems Batteries.

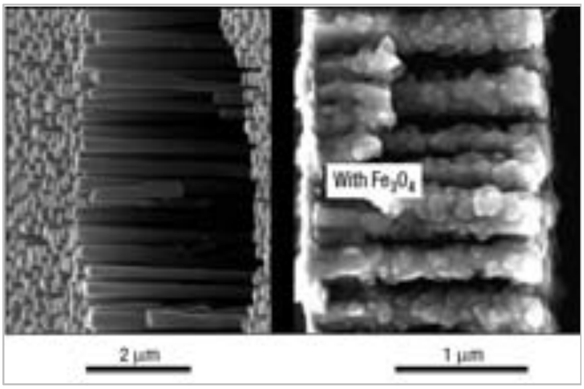

Figure 12: Cross-sectional views of Cu-nanostructured current collector before (left) and after (right) Fe_3O_4 deposits

Image: P. L. Taberna et al., 'High rate capabilities Fe_3O_4-based Cu nano-architectured electrodes for lithium-ion battery applications', *Nature Materials*, 2006, 5:567–573, reprinted with the permission of Macmillan Publishers Ltd, © 2006

Supercapacitors

Supercapacitors are another way of storing electricity that can benefit from nanotechnology. They are needed in devices that require rapid storage and release of energy, for instance hybrid-electric and fuel cell-powered vehicles. They are constructed of two electrodes immersed in an electrolyte, with an ion permeable separator between them. Each electrode-electrolyte interface represents a capacitor, so the complete cell can be considered as two capacitors in series. The focus in the development of these devices has been on achieving high surface area with low matrix resistivity. The most remarkable property of a supercapacitor is its high power density, about 10 times that of a secondary battery. The maximum power density of a supercapacitor is proportional to the reciprocal of its internal resistance. A number of sources contribute to the internal resistance and are collectively referred to as Equivalent Series Resistance (ESR). Contributors to the ESR include the electronic resistance of the electrode material and the interfacial resistance between the electrode and the current-collector. Carbon, in its various forms, is currently the most extensively used electrode material in supercapacitors. A typical commercial supercapacitor can produce a power density of approximately 4 kW/kg. Nanotubes can be used to increase the power density of supercapacitors, since the nanoscale tubular morphology of these materials offers a unique combination of low electrical resistivity and high porosity in a readily accessible structure. Single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) are under investigation. Research has shown that the use of thin-film electrodes with multi-walled aligned nanotubes increases the specific power density (laboratory results of 30 kW/kg have been reported), as a result of the reduction inESR.

Energy savings

Energy savings can be achieved in numerous ways, such as improving insulation of residential homes and offices; more efficient lighting; and using lighter and stronger materials to build devices which would then require less energy to operate. Moreover, a large portion of energy is lost during its transport, so there is a need for a more efficient electric grid to transport energy. Nanotechnologies can potentially be applied to all of these energy-saving materials and technologies.

Catalysis

Catalysis is of vital importance in our society and constitutes a cornerstone of life from biological processes to the large-scale production of bulk chemicals. The availability of plentiful and inexpensive chemicals relies on industrial catalytic processes and, without them, it would be impossible to maintain the current living standard of the present human population. Other technologies also depend on catalysis, including the production of pharmaceuticals, means of environmental protection, and the production and distribution of sustainable energy. As already discussed in some of the previous sections, many technological advances required to **make alternative energy carriers to fossil fuels — such as sunlight and hydrogen — an economically viable option rely on optimising a catalytic process**.

For example, for water to be split into hydrogen and oxygen with sunlight to feed a fuel cell, researchers need to improve the activity of the catalyst (e.g. TiO_2).

A typical heterogeneous catalyst consists of a few nanometre-wide catalytically active nanoparticles dispersed on a highly porous support material which can have surface areas up to 250 m^2/g. The manufacturing of structures on the nanometre scale has been a central issue in catalysis research and development for decades. This fact relates to the structure of a heterogeneous catalyst, which requires control of materials ranging from macroscopic dimensions down to the nanoscale. Heterogeneous catalysis, therefore, has, in a sense, always had a nanoscience component. Since catalytic action takes place at a surface, and catalytic materials are often very expensive (as they use rare materials such as platinum), the goal for chemists has always been to fabricate catalysts with as high a surface-to-volume ratio as possible, so as to maximise the surface exposed to the reaction and minimise the amount of catalyst required.

Advanced materials

Nanotechnology can offer some indirect energy saving solutions by developing materials with better properties. One example is materials with improved strength which make constructions leaner and thus lighter, with an indirect energy saving, for example in the transport sector (both on the road and in the air). Since a large fraction of the fuel consumption in a car is weight-related, making cars with lighter materials would be a very efficient way of saving energy. Higher tensile strength can be exploited as well as higher possible loads, so that with the same amount of material, stronger components can be built. For example, wind turbines could be capable of sustaining higher wind speeds if they were made of high-strength nanomaterials. Better creep resistance is an advantage in virtually any system for thermal power generation due to the higher operating temperature allowed and the concurrent higher efficiency. Nanocoatings with improved corrosion properties have a longer service life in aggressive environments and thus have potential for energy saving throughout their entire life cycle (e.g. extraction, production, operation, disposal and recycling).

Insulators and 'smart' coatings

Insulation is a very effective way of minimising energy consumption, for example in homes and offices. Nanotechnology offers the possibility of developing new materials with improved insulating properties. One example is nanoporous aerogels to improve thermal insulation. A commercial example is represented by Aspen Aerogels products. This company produces flexible aerogel nanoporous insulation blankets (e.g. Cryogel™) designed for cryogenic applications (e.g. insulating pipes and tanker ships). These insulation blankets can be cut just like normal textiles and installed faster than traditional materials, and their low thermal conductivity requires less material to be used. Additionally, Aspen's products are resistant to compression and inherently hydrophobic so they can be exposed to water for long periods without damaging the products' outstanding thermal properties. Nanotechnology applied to indirect energy saving can be found in the form of 'smart' materials such as electrochromic and photochromic coatings used for darkening window. They reduce indoor heating in summer, so less air-conditioning is required to keep the atmosphere cool, with consequent energy saving. Another example of nanotechnology applied to smart coatings is the use of a family of wavelength-selective films used to manufacture 'heat mirrors'.

One of these materials is indium tin oxide (ITO), an infrared absorber. A 0.3 nm ITO coating on glass provides more than 80 % transmission for the wavelengths predominant in sunlight. The transmission properties of the window can be varied by changing the thickness and material composition of the coating, so that a combination of materials could be used to produce smart windows that reflect solar energy in summer but transmit solar energy in winter.

Energy-harvesting materials

Numerous innovative electronic devices under development have nanoscale components (see **this module, Chapter 4: Information and Communication Technologies**). Nanodevices do not use much energy, and if the little they need could be scavenged from vibrations associated with footsteps, heartbeats, noises and airflow, a whole range of applications in personal electronics, sensing and defence technologies would open up. In order to do this, an 'energy-scavenger' having nanoscale dimensions would have to be included in the device. Furthermore, energy gathering of this type requires a technology that works at low frequency range (below 10 Hz), ideally based on soft, flexible materials. A group working at Georgia Institute of Technology (USA) has now come up with a system that converts low-frequency vibration/friction energy into electricity using piezoelectric zinc oxide nanowires grown radially around textile fibres. A piezoelectric material that makes uses of piezoelectricity was discovered in 1883 by Pierre Curie and his brother Jacques. They showed that electricity was produced when pressure was applied to selected crystallographic orientations. Piezoelectricity is thus the induction of electrical polarisation in certain types of crystals due to mechanical stress. Zinc Oxide nanowires are such a type of piezoelectric nanomaterial. In the work just mentioned, researchers have grown ZnO nanowires radially around a fibre of Kevlar, which is a material known for its strength and stability (**Figure 13**). By entangling two fibres and moving them by sliding them back and forth, a relative 'brushing motion' is created, which in turn produces an output current.

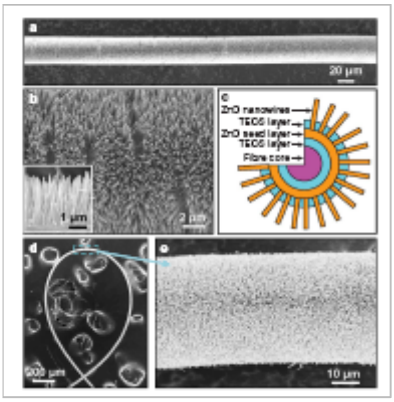

Figure 13: Kevlar fibres coated with ZnO nanowires: (a) SEM image of a Kevlar fibre covered with ZnO nanowire arrays along the radial direction; (b) higher magnification SEM image and a cross-section image (inset) of the fibre, showing the distribution of nanowires; (c) diagram showing the cross-sectional structure of the TEOS-enhanced fibre, designed for improved mechanical performance; (d) SEM image of a looped fibre, showing the flexibility and strong binding of the nanowire layer; (e) enlarged section of the looped fibre, showing the distribution of the ZnO nanowires at the bending area.

Image: Qin et al., 'Microfibre-nanowire hybrid structure for energy scavenging', *Nature*, 2008, 451:809–13, reprinted with the permission of Macmillan Publishers Ltd, © 2008

The mechanical energy (sliding motion) is converted into electricity via a coupled piezoelectric-semiconductor process. This work shows a potential method for creating fabrics which scavenge energy from light winds and body movement. In the future, these types of nano-energy scavengers could be incorporated in textiles to power personal electronics.

Efficient lighting

Another important application of nanotechnology in the area of energy saving is the production of more efficient lighting devices. Conventional incandescent lights are not energy efficient, a large portion of their energy being dispersed in heat. Solid-state light devices in the form of light-emitting diodes (LEDs) are attracting serious attention now as low-energy alternatives to conventional lamps. The need is to engineer white-light LEDs as a more efficient replacement for conventional lighting sources. One proposed solution is to use a mixture of semiconductor nanocrystals as the intrinsic emitting layer in an LED device. Simply mixing several colours of nanocrystals together to achieve white light is a possibility, but this would result in an overall reduction indevice efficiency through self-absorption between the various sizes of the nanocrystal. An important result that can potentially resolve this problem has recently come from the work of some researchers at Vanderbilt University (USA). They found that crystals of cadmium and selenium of a certain size ('magic-sized' CdSe) emit white light when excited by a UV laser, a property that is the direct result of the extreme surface-to-volume ratio of the crystal. This material could, therefore, be ideal for solid-state lighting applications.

Organic light-emitting diodes (OLEDs) represent a promising solution for lighting applications as well as for low cost, full-colour flat panel displays quantum dots (QD) are another class of nanomaterials that are under investigation for the manufacture of more efficient displays and light sources (QD-LEDs). Quantum dots are characterised by emitting saturated and monochromatic light; the colour emitted depends on the size of the quantum dot and the light is emitted under certain conditions (e.g. when current passes to them via conductive polymer films). Recently, even white-emitting quantum dots have been fabricated. Therefore, quantumdot-based LEDs are promising light sources and could be useful for use in flat-panel displays. The structure and properties of OLEDS and of QD-LEDs is described in detail in **this module, Chapter 4: Information and Communication Technologies**.

NANOYOU DILEMMA The use of quantum dots in polymer composites for new forms of light-emitting devices (QD-LEDs) is extremely promisingin the development of alternatives to conventional light bulbs. In the **NANOYOU role-playing game 'Revolution for the light bulb'** (http://www.nanoyou.eu/en/decide), students reflect on the safety aspects of these devices. Like other materials used in electronics (e.g. transistors), quantum dots are often made of toxic metals like cadmium, although in extremely small amounts. Therefore, QD-LEDs would need to be properly managed once disposed of, as is the case for all electronics, but even more so in this case. However, it is not yet known what method should be used to dispose of them, what sub-products could be produced, and if disposed of improperly, could they represent an environmental hazard. The dilemma is: Do we implement the quantum dot technology within an energy efficient light source even though some health and environmental risks remain unanswered?

Efficient energy transport

One area where there is a large margin for improvement is in the transport of electric current. As the world's power demand increases, the burden on the electricity infrastructure grows. This has been shown recently in some nationwide blackouts such as those that occurred in the north-east USA in 2003, and in Italy in the same year. Therefore, a major challenge is to develop new transmission-line materials that are lighter and have less energy loss than copper. Single carbon nanotubes (CNT) have the remarkable property of weighing one sixth as much as copper but with similar or even better conductivity and negligible eddy current loss. This material thus has the potential to overcome some of the limitations of current transmission materials. Before this can become a reality, however, advances in the production of CNTs are needed. At present, scientists produce CNTs often less than 100 nm in length and with widely varying electrical conduction properties. The challenge for the future is, therefore, to produce nanotubes with controlled properties. Moreover, the manufacturing must be cost-effective and able to produce cables of fibres with the desired electrical properties. At present, therefore, this application remains a vision.

CHAPTER 4:

INFORMATION AND COMMUNICATION TECHNOLOGIES

Nanotechnology is, in many respects, **already a key player in Information and Communication Technologies** (ICT) research and development, both in academia and industry. Computer microprocessors and memory storage devices have followed a path of miniaturisation over the last 20 years that has 'naturally' brought transistors to have dimensions lower than 100 nm. There are now challenges to meet to continue this miniaturisation: as the materials of semiconductors, metals and insulators are reduced to nano-size, quantum effects start to predominate and to determine their properties and this is resulting in a number of issues. Nanotechnology offers the opportunity to exploit, rather than avoid, quantum effects in the development of the next generation of integrated circuits. As miniaturisation cannot proceed forever with the methods and tools that have been used so far, new approaches will be needed. Nanomaterials, precisely for their quantum properties, and nanotechnology tools allow for the creation of new data storage and processing methods. These developments are discussed in the sections on integrated circuitsanddata storage. The section on photonics looks in details at this emerging technology for opto-communication. Another essential contribution of nanotechnology is in the field of displays, which are becoming thinner, lighter and less energy-consuming. The contribution of nanotechnology in this area is covered in the sectionon displays.

But the evolution of the ICT sector will most likely go beyond what is considered 'electronics' today (i.e. devices that perform a task). There are visions of electronics embedded in our clothing and in the environment around us in what is conceived as a network of devices that create 'ambient intelligence'. Although still more a vision than reality, there is intense research to bring to fruition the tools required to realise 'ambient intelligence'.

This chapter looks at these various areas of applications in the ICT sector and considers what the impact of nanotechnologies could be in each.

Integrated circuits

In the late 1960s, Gordon E. Moore, co-founder of Intel Corporation, made a memorable observation that later became known as Moore's Law. He observed that the number of transistors on a chip roughly doubled every 18 months. Originally, this was only an observation but was later adopted as an industry goal. The progression in transistor density on a chip overthe last 40 years has, indeed, followed Moore's law (**Figure 1**). In order to keep up with this law, transistors have become smaller and smaller. The first transistor was about 1 cm high and made of two gold wires 0.02 inches apart on a germanium crystal. The latest transistors from Intel® (Penryn and Nehalem) have 45 nm feature sizes and in a quad-core configuration have over 731 million transistors! These numbers give an idea of the enormous miniaturisation efforts that have been achieved by the semiconductor industry.

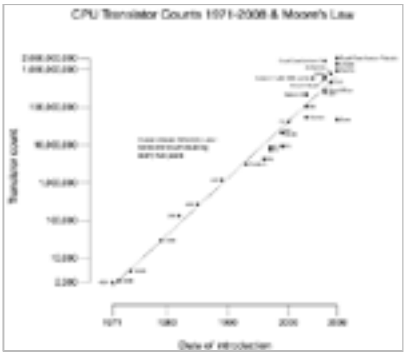

Figure 1: Curve showing the increase in the number of transistors on computer chips, which follows Moore's prediction of doubling every 18 months

Image: http://commons.wikimedia.org/wiki/User:Wgsimon, Creative Commons Attribution ShareAlike 3.0

The scaling-down of transistors has been the driving force for a number of reasons. Transistors are the basic building blocks of the elements in an integrated circuit (microprocessor, mass memory, logic gates, etc.). Integrated circuits are the core of the information and memory storage devices that are an essential part of all electronics used: from computers to refrigerators, cars, mobile phones, etc. As the size of the transistor is reduced, its density on a chip increase, which increases the speed, the amount of memory stored per area, and the number of functions that can be integrated on a single device.

TIP FOR TEACHERS: To illustrate this, ask students to describe the size and function of the first mobile phone they can remember. In the early 1990s, it was just a phone, quite bulky and heavy. Later it became smaller, lighter, and with many more functions. Nowadays, there are all-in-one devices that are phones, digital music players, radios, video cameras, Internet platforms, and more!

The enormous advances in computing that have characterised the last 15 years (including the advent of the Internet and the 'Information Age') have come about as a result of the miniaturisation of all the elements in computer chips. In the future, high performance computing is expected to deliver tools that not yet available, such as a real-time language translator or ubiquitous sensing.

The scaling down of transistors cannot go on indefinitely with the tools and materials now available. Experts say that Moore's law will last until the year 2015, perhaps a few years beyond. Eventually, a point will be reached where the transistor is so small that quantum effects start to predominate. In a transistor the 'on' and 'off' state are determined by the flow (or not) of electrons through the n-p junction (gate). At very low dimensions (e.g. 1 nm) electrons will be able to pass through the gate via tunnelling, which is a fundamental quantum effect (for details see **Module 1, Chapter 4: Fundamental 'nano-effects'**.

Another issue is **power consumption** and **heat generation**. This is an issue that everyone using a modern mobile phone experiences daily. As the number of functions integrated into a mobile phone has increased, so has the amount of power it consumes (the type and battery lifetime has become determinant tothe quality and performance of the device and its cost). This also leads to heat generation, which, at smaller scales, becomes even more important and is considered a research priority. Reducing power consumption is also critical, not just for the performance of the device but also for environmental considerations (energy saving).

In simple terms, by continuing to use the current technology, a stage of development will be reached where further scaling down will create effects opposite to those intended — such as growing energy consumption in standbymode and performance restrictions in active mode. New technologies will be needed to allow the miniaturisation of electronic devices along Moore's curve.

WHAT CAN NANOTECHNOLOGIES DO? Current transistors are already below 100 nm, so technically the semiconductor industry already makes use of nanotechnologies. Continued miniaturisation of transistors using the complementary metal-oxide-semiconductor (CMOS) platform (More Moore technology) has already produced transistors smaller than 100 nm. This threshold was crossed around the year 2000, and today transistors are 45 nm. Although the **More Moore** approach does involve working with materials with nanoscale sizes (and related fabrication methods), it has the task of scaling existing CMOS processes and reaching the 'CMOS limit' (i.e. the size limit obtainable with this technology). Some consider this not to be 'true nanotechnology', since it does not make explicit use of the unique properties of nanomaterials (quantum effects etc.). This development course (i.e. developing fundamentally new approaches to information processing and data storage, beyond that which used today, such as self-assembly, or totally new materials such as molecular electronics) belongs to the domain called **Beyond CMOS**. In addition to these two domains, is the **More than Moore** domain, meaning technologies that provide functionality beyond traditional computing (such as intelligent systems that can interface with the user and the environment). Without going into the technical details too deeply, the next sections outline the impact of nanotechnologies in these **domains of technology innovation**.

More Moore

Semiconductor components (microprocessors, mass memories, logic gates, etc.) will need to follow the miniaturisation trend described by Moore's law to keep up with the industry demand (More Moore). This means introducing new materials and new device architectures. One of the most critical elements in current transistors is the **insulating layer** between the two gate electrodes. This layer is currently made of silicon oxide: as the transistor is made smaller, the thickness of this layer is reduced to a point where leakage (the passage of electrons between the two electrodes when voltage is off (i.e. tunnel leakage current)) becomes a problem. In the latest processors, silicon dioxide is replaced with a **high-permittivity material (high-k)** for lower power consumption. Hafnium compounds are the most promising high-k materials and are currently used in Intel® 45 nm technology generation (node).

As the materials used in transistors change and smaller features are needed, the **fabrication methods** used in CMOS also need to evolve. In general, the limit of the smallest size that can be created depends on the tool used. Features about 500 nm in size could be fabricated using optical lithography but, in order to create smaller features, extreme-UV lithography is needed. Advances in CMOS technology have always implied enormous investments for the development of fabrication techniques able to deliver the required transistor size. As new materials are introduced into CMOS technology, new fabrication technologies also need to be integrated. For example, the 45 nm node is madeusing a fabrication process different from the conventional top-down lithography approach. Hafnium materials are normally deposited using the **atomic layer deposition** method (ALD) which is a bottom-up fabrication method (for a review of fabrication methods used in nanotechnologies, see **Module 1, Chapter 7: Fabrication methods**). The method is believed to be used in the latest generation of Intel® processors. Another nanofabrication method that is being considered to pursue Moore's law of miniaturisation is **nano imprint lithography**. Although there are numerous fabrication techniques that can be used to make nanoscale features (of which the scanning tunnelling microscope is the most powerful), in the context of the semiconductor industry only a few are feasible candidates. Any new fabrication technique (different to conventional lithography) must satisfy a number of stringent requirements: resolution, defect rate, throughput (i.e. being capable of producing many features quickly), and must be easily integrated into current fabrication facilities (otherwise massive financial investments would be needed). Nano imprint lithography seems to be the technology that, at the moment, can best satisfy these needs and will most likely be the technology used for the future 32 nm and 22 nm nodes.

Another key element in integrated circuits starting to create problems is the copper **connectors between the transistors**. The effective resistivity of copper increases at smaller dimensions and the integrity of the signal as it travels along the connector is becoming a major issue. **Nanotubes and nanowires** are now being considered as alternatives to conventional copper. Carbon nanotubes are considered an ideal material since they can be outstanding conductors (with almost zero resistance and heat dissipation), and they are extremely strong mechanically and inert to chemicals. The current problem is fabrication (pure carbon nanotubes are hard to produce) and alignment.

More than Moore

The 'More than Moore' domain refers to the development of functional components beyond the traditional computing ones (microprocessors and memory). **Future electronics will integrate an interface with the real word** (so-called ambient intelligence) and will need to integrate not just a processor and memory, but also sensors, actuators, RF interfaces, etc. They will also need to satisfy a number of requirements, such as low power consumption, flexibility, thermal management, and last but not least, cost. Nanotechnologies are going to have an essential role in all those systems. In the last part of this chapter, some ideas of what 'ambient intelligence' might do for us and what this might imply in terms of social and ethical consequences are discussed.

A detailed analysis of the technical elements that will be integrated into these systems is not covered here as it would be too advanced for secondary school level; however, the new materials and fabrication methods that will be needed in order to integrate these smart multifunctional systems and connect them to the outside word are outlined. Various nanodevices based on different technologies and processes will need to coexist within the same package. This is conceptually very different from the current concept of 'multifunctionality' where different 'packages' with specific functionalities are separated and added together only the end of the manufacturing process. In the future, there will be 'system in a package' solutions where the different functionalities are integrated in one 3D architecture as the package is constructed (nanosensors, nanoactuators, processors, etc.). This requires the **heterogeneous integration of electrical and non-electric components**, which, in turn, requires the development of new materials (e.g. plastic electronics). In the short term, nanotechnologies will probably contribute to improve the properties of current materials, for example with the addition of nanoparticles to adjust parameters such as electrical resistance, thermal conductivity, coefficient of thermal expansion, etc. In the long term, nanotechnologies are expected to be used to develop nanoscale interconnectors and self-assembly technologies that to go beyond current architectures.

Beyond CMOS

It has been mentioned already that the miniaturisation of microprocessors and memory cells cannot continue indefinitely, and Moore's law will necessarily come to a halt, if the same CMOS technology is used. On the other hand, miniaturisation and system integration will surely continue to be fundamental in our communication society, even more than today. Ubiquitous sensing, ambient sensing, 'constant' networking and communication in an 'always connected' state will most likely be part of our future.

For this to be possible, new materials and processing methods will be required once the dimensions of transistors become so small that quantum effects start to predominate. Nanotechnologies will allow us to exploit these effects and realise the future generation of electronics to store and process information where quantum effects and other nano-effects determine the property and functionality of the device. Without going into too much detail, there now follows some information on the fundamental developments that researchers are working on to ensure that miniaturisation can continue beyond the intrinsic limits of the CMOS technology.

New data storage and processing nanotechnologies

Microprocessors work by processing information through the passage of an electrical signal. In the future, information processing will be done using a state variable other than electric charge, such as spin (spintronics), molecular states (molecular electronics), photons (photonics), mechanical state, resistance, quantum state (including phase) and magnetic flux. These new state variables will require new materials to be used (e.g. relying on spin implies using magnetic materials rather than a semiconductor) and new functional organisation of the device (architecture).

The following is a list of some new concepts that are being developed for processing and data storage that make use of state variables other than the 'conventional' used in CMOS (electric charge).

- **Spintronics**: This is a new type of technology that exploits the spin of the electron (rather than only its charge) to store and process information. It requires thin layers of magnetic materials. The **giant magnetoresistance effect (GMR)** represents the first type of this new technology, and is used in the new-generation memory devices such as the Magnetic Random Access Memory or **MRAM** used, for example, in the Apple iPod. The GMR and data magnetic storage devices based on this effect are discussed in the next section,Data storage.
- **Photonics**: Another possibility is the use of photons (rather than electrons) in the visible or IR range to transmit and process data (**optical communication**). In this case, semiconductors (e.g. silicon) can no longer be used since they cannot emit and transport light efficiently. Other materials (photonic crystals) engineered at the nanoscale need to be used. Photonic crystals and their use in optical communication are discussed in the sectionon photonics in this chapter.
- **Quantum electronics**: This term means the explicit use of the **tunnelling effect** to transport electrons from the source to the drain of the transistor. One such transistor exists and is called the **single-electron transistor** (SET). In this type of transistor, three is a quantum dot between the source and the drain: electrons must tunnel through this dot in order to get from the source to the drain. In simple terms, this is like having two electrodes (source and drain) separated by a thin insulating barrier with a third electrode (the quantum dot, or **quantum island**) in the middle of this insulating gap. The transport of charge from the source to the quantum island and then from the quantum island to the drain occurs via the quantum mechanical process of tunnelling.
- **Carbon nanotube transistors**: In many ways, carbon nanotubes are considered a 'dream' material when it comes to electronics: they can be conductive or insulating depending on their chirality (and when they are conductive, they are extremely good electronic conductors, with little resistance and, consequently, little heat dissipation); they are strong (mechanically) and chemically inert; they are resistant to high temperatures; and they can be functionalised with specific molecules to act as anchoring points. Carbon nanotubes are 1–2 nm in width and they are as narrow as the double stranded DNA molecule (the molecule that carries our genetic information). So arranging nanotubes into electronic circuitry could allow miniaturisation by a factor of about 100 over the current limit.

- **Molecular electronics**: molecules in natural systems (plants, animals) are arranged in macromolecular systems (nanostructures) that perform numerous tasks which involve the transmission of charges, photons, etc. These macromolecular systems have developed over millions of years of evolution and are an example of excellence when it comes to efficiency! Examples included the electric flow in nervous signalling, the control of charges in the ionic pump, and the absorption of light and transmission of photons and charge in plant chlorophyll, and many more. Molecular electronics is a branch of nanoscience that aims to make explicit use of molecular assemblies for the transmission and storage of data. The field includes molecular wires, molecular switchers, molecular sensors and other 'hardware' components of electronics. The idea is to assemble molecules in nanostructures that can perform a specific function (e.g. the transport of charge) depending on its configuration. An example is a two-terminal transistor having three benzene rings that act as the charge transfer site. The central benzene ring is functionalised with two groups (NH_2 and NO_2) that make the overall molecule very susceptible to an electronic field. The electric field can induce the distortion (twisting) of the molecule. In simple terms, this gives rise to an electronic device where if a voltage is applied, the molecule twists in such a way that the current flow is stopped; when the voltage is turned off, the molecule springs back to its native conformation and current flows again. This is just one of many molecular electronic devices under research. In order to fabricate and test such small devices, nanotools such as the STM are needed. These types of devices are still ata very early stage of development because of the time required to fabricate and test them. Furthermore, in order to make any useful molecular circuit, a vast number of devices need to be orderly arranged and securely fixed to a solid support to prevent them from interacting randomly with one another. In the future, molecular wires (e.g. made of conductive polymers such as polypyrrole) or carbon nanotubes could be incorporated into integrated circuits, which would notably reduce the size of computer chips (wires used today use about 70 % of the real space on a chip!).

Data storage

Data storage is a key component of many devices in use every day: computers (which contain both a hard drive and RAM), mobile devices (in which the memory medium is normally a memory card — such as digital cameras), and portable media players (e.g. iPods and mobile phones that use Flash memory).

Data storage technologies include two main groups, **hard disk drives** (having a mechanical component) **and solid-state data storage devices**, which can be further divided in volatile and non-volatile. 'Volatile' means that memory is lost once the power is turned off; 'non-volatile' means that memory is retained when the power of the device is switched off.

- Volatile memory storage devices today include mainly **static random access memory** (SRAM) and **dynamic random access memory** (DRAM).
- Non-volatile memory storage devices, such as **Flash memory**, are used in mobile devices and portable media players.

Each type of memory has its advantages and disadvantages: DRAM has a smaller memory cell size than SRAM and can, therefore, store more data but needs to be refreshed periodically, consuming power and lowering speed; SRAM can store less data but is faster; flash memory is non-volatile, making it ideal for devices where the power is often turned off.

Memory storage devices are described by their capacity (amount of data in MB), memory density (a function of the capacity and the size of the memory cell), lifetime (how many read/write cycles it can perform before it degrades), read/write speed and cost.

The concept of a universal memory

The need for memory storage devices with an ever-increasing density capacity has been the driving force in this industry. The motivation has been the need to keep pace with Moore's law (and therefore reduce the size of the memory devices), and the proliferation of mobile devices which demand low power operation and batteries that have a low consumption in standby mode. These two trends have catalysed the search for a universal memory, meaning a memory storage device that addresses the major technical challenges of existing memory technology (DRAM, Flash memory, etc.), while combining the valuable properties of each — speed, density and non-volatility. Although a universal memory is still a concept, research towardsits realisation is intense and new technologies that have been developed are trying to go in this direction. Nanotechnology is an essential part of all of these.

Nanotechnology developments in data storage

In the last few decades, the dimension of memory storage cells has decreased, following Moore's law. This continuing size reduction has, however, led to memory cells with extremely small transistors. At the current 90 nm process node, SRAM and DRAM are beginning to suffer from a number of scaling issues. As the semiconductor is reduced in size, quantum effects come into play, and electrons can 'jump' from the source to the drain by tunnelling or just by thermal motion. Moreover, other elements become critical, such as charge leakage due to silicon substrate crystalline defects. In Flash memory, an insulating layer of silicon oxide 'wraps' the gate architecture and serves as a barrier for storing the change. As this layer becomes thinner, the charge can start to leak out of the device. These are only a few of the problems facing memory storage development today.

To deal with these challenges, new concepts that make use of fundamental nano-concepts and nanotechnology tools have recently been introduced:

- **magnetoresistive random access memory (MRAM)**, where each memory cell is made of two ferromagnetic thin layers separated by an insulating layer;
- **ferroelectric RAM (FeRAM)**, similar in architecture to MRAM, but where a ferroelectric layer replaces the dielectric layer;
- **resistive RAM (RRAM)**, in which a conduction path is created through a dielectric material;
- **phase transition memory**, also known as **phase change memory (PCM)**, which uses the phase transition of a material from crystalline to amorphous;
- **nanotube RAM**, a trademark of the company Nantero (NRAM™), which uses carbon nanotubes to determine memory states.

Each of these technologies is at a different level of maturity and time will be needed before they can compete with Flash memory. However, development in this sector is very rapid and it is projected that by 2012, nanotechnology-enabled storage devices will account for 40 % of the total memory market.

MRAM

Magnetic materials are used in **magnetoresistive random access memory** (MRAM), in which each memory cell consists of two magnetic thin-film materials separated by an isolating layer.

Magnetic multilayer nanocomposites (very thin films made of magnetic materials) display **magnetoresistance** properties. Magnetoresistance is a phenomenon whereby the application of a DC magnetic field changes the resistance of a material. In metals, this effect occurs only at very high magnetic fields and low temperatures. In 1988, it was discovered that a very pronounced effect, now known as the **giant magnetoresistance effect** (GMR), could be obtained in materials made of alternating layers of nanometre thick ferromagnetic material and non-magnetic but conducting material (**Figure 2**). The magnetisation vector can be aligned (parallel) or not (anti-parallel)in the magnetic layers forming the multilayer, as shown in **Figure 2**. Polarity is persistent, therefore the device is **non-volatile**. If current flows through the device and the layers have a parallel configuration, the resistance is lower than if the layers are anti-parallel. In the MRAM memory cell, the two thin layers of metals are separated by a thin insulating material. This gives rise to another effect called the **tunnelling magnetoresistance effect** (TMR). In contrast to GMR, TMR uses ultra-thin non-conducting spacer layers, which renders the ferromagnetic layers electrically isolated. Electrons can thus tunnel through this barrier (13). As in the GMR effect, the passage of a current changes the polarity of the magnetic material causing either a high or a low resistance across the insulating barrier, which can be read as a ‘1’ or a ‘0’. To write data in such memory cells, a current is passed through the cell, which alters the polarity of the magnetic layers.

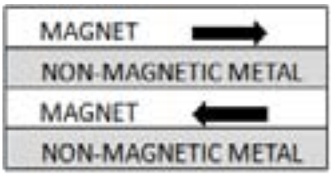

Figure 2: Arrangement for producing giant magnetoresistance: layers of non-magnetic (but conductive) material alternating with oppositely magnetised (arrows) ferromagnetic layers

Some materials have been discovered having even larger magnetoresistive effects than layered materials and this phenomenon is called **colossal magnetoresistance** (CMR). These materials (e.g. LaSr- and LaCa-manganites) have a peculiar crystal structure that is responsible for the CMR effect and could have a number of applications in memory storage devices.

NRAM^{TM}

The company Nantero Inc. has introduced a new type of non-volatile random access memory, NRAM^{TM}, where the N stands for ‘nanotube’ since it uses carbon nanotubes. The nanotubes are assembled as fibres and are suspended perpendicularly across trenches of etched silicon wafers. At the end of the silicon trench, there is a contact electrode. When a potential is applied between the fabric and the electrode, the fabric bends and touches the electrodes. The interaction is based on van der Waals forces and remains

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(13) The tunnelling effect is a quantum mechanical effect which occurs when a small particle penetrates a barrier by using a classically forbidden energy state. This effect is based on the fact that particles (e.g. electrons) should be treated more as a wave than a hard sphere. As a result of the tunnelling effect, an electric current will flow through a thin isolating barrier when a voltage is applied.

even after the power is turned off. When the fibre is far away from the electrode, the junction has a high resistance and this is read as a '0' state. As current is passed, and the fibre touches the electrode, the junction resistance is lowered, and this is read as a '1' state. Carbon nanotubes are produced using an alternative to the conventional method (chemical vapour deposition, CVD) and which does not require high temperatures. The process developed by Nantero, Inc. allows the production of pure carbon nanotubes at room temperature. This is an added advantage to the technology as CVD requires temperatures so high as to damage the other constituents of the memory device. The NRAM™ is considered a very important development towards the concept of universal memory, and it has the advantage that it is fabricated using current CMOS technology platforms: this ensures immediate manufacturability.

Phase-change memory

Phase-change memory (PCM) (also called **phase random access memory**, PRAM) is another new and promising concept in **non-volatile memory storage**. It uses a material, chalcogenide glass, which can be 'switched' between two states, crystalline and amorphous, through the application of heat. The amorphous state has high resistance and is used to represent '0', whilst the crystalline state has lower resistance and is associated with the state '1'.

Overall, PRAM (or PCB) is considered the most promising advancement in non-volatile memory solutions. In February 2008, Nymonyx started shipping the first PCM prototypes for customer evaluation. The product, Alverstone, is a 128 MB PRAM produced on a 90 nm CMOS fabric. Nymonyx is the new company formed by STMicroelectronics and Intel®, producing non-volatile memory. Progress in this technology is fast and, in December 2009, Nymonyx announced a paper showing the scaling of PCM to the 45 nm lithography node for the first time on a 1 GB product with an effective cell size of 0.015 μm^2. Nymonyx researchers report good electrical properties and reliability results, confirming that PCM has reached the maturity to become a mainstream technology for high density non-volatile memory applications.

Photonics

Photonics is the study of the interaction of light with matter. The field was opened up in the 1960s with the invention of the laser. Ten years later, the invention of the optical fibre as a means of transmitting information via light formed the basis for **optical communication**. The field is now enormous and consists of many sub-disciplines and applications, such as laser technology, biological and chemical sensing, display technology, optical computing, fibre optics, photonic crystals and more.

In 1987, Eli Yablonovitch at Bell Communications Research Centre created an array of 1 mm holes in a material with a refractive index of 3.6. It was found that the array prevented microwave radiation from propagating in any direction. This discovery launched the research on photonic crystals, but it took more than a decade to fabricate photonic crystals that do the same in the near-IR and visible range. Nowadays, photonics crystals are an important nanomaterial being investigated for numerous applications including, in particular, optical communication.

Photonic crystals

A photonic crystal consists of a periodic structure made of dielectric materials that affects the propagation of light. Essentially, photonic crystals contain **regularly repeating internal regions of**

high and low dielectric constant. Photons (behaving as waves) propagate through this structure — or not — depending on their wavelength. The periodicity of the photonic crystal structure has to be of the same length scale as half the wavelength of the electromagnetic waves (i.e. approximately 200 nm (blue) to 350 nm (red) for photonic crystals operating in the visible part of the spectrum. Such crystals have to be artificially fabricated by methods such as electron-beam lithography and X-ray lithography.

Photonic crystals exist in nature. For example, in **Module 1, Chapter 2: Nanoscience in nature** it was shown how the beautiful blue wings of some butterflies owe their colour to their internal nanostructure, which is in fact a photonic crystal structure: another example is opals.

Applications in communication

Photonic crystals are now receiving much attention because of their potential particularly in the **optical communication industry**. The current explosion in information technology has been enabled by semiconductor technology and the ability to fabricate materials where the flow of electrons can be controlled in the most intricate ways. Photonic crystals promise to give us similar control over photons — with even greater flexibility because scientists have far more control over the properties of photonic crystals than they do over the electronic properties of semiconductors. The goal of putting more transistors on a chip (to make smaller and faster integrated electronic circuits) requires further miniaturisation. This, unfortunately, leads to higher resistance and more energy dissipation, putting a limit on Moore's law. Researchers are considering using **light and photonic crystals** (as an alternative to electrons travelling in wires) for the new generation of integrated circuits. Light can travel much faster in a dielectric medium than an electron in a wire, and it can carry a greater amount of information per second. Given the impact that semiconductor materials have had on every sector of society, photonic crystals could play an even greater role in the 21st century.

Properties of photonic crystals

Photonic crystals are designed to confine, manipulate and control the propagation of photons in three dimensions. The properties of a photonic crystal are determined by the radius of the holes (or other features such as dielectric rods) forming the array, the periodicity of the holes (or rods), the lattice structure, the thickness of the material and the refractive index.

The properties of photonic crystals can be understood by considering an analogy with semiconductors. In general, in a semiconductor, the valence or conduction electrons can move in a periodic potential arising from the positively charged ion cores (the nucleus). The potential is characterised by two areas of allowed energy, which are separated by a region of forbidden energy, called the energy gap, which means that there are certain wavelengths that will not propagate in the lattice (i.e. no electrons will be found in the band gap region). This is true for a perfect silicon crystal. However, in real materials, the situation is different: electrons can have energy within the band gap if the periodicity of the lattice is broken. This can be the result of a missing silicon atom, or the presence of an impurity atom occupying a silicon site, or if the material contains interstitial impurities (additional atoms located at non-lattice sites). Doping of semiconductors is intentionally done in microelectronics.

Now consider photons moving through a block of transparent dielectric material containing a number of tiny air holes arranged in a lattice pattern. The photons will pass through regions of high refractive index — the dielectric — alternating with regions of low refractive index — the air holes. This is analogous to the periodic potential that an electron experiences when travelling through a silicon crystal. If there is a large differencein refractive index between the two regions, then most of the light will be confined either within the dielectric material or the air holes. This confinement results in the formation of allowed energy regions separated by a forbidden region — the so-called **photonic band gap**. Since the wavelength of the photons is inversely proportional to their energy, the patterned dielectric material will block light with wavelengths in the photonic band gap, while allowing other wavelengths to pass freely.

In a semiconductor, it is possible to break the perfect periodicity of a silicon-crystal lattice by introducing defects (doping), and to have electrons in the forbidden energy gap region. Similarly, it is possible to **create energy levels in the photonic band gap** by changing the size of the holes (or rods) forming the photonic crystals. This introduces an 'allowed frequency' (i.e. an allowed wavelength) in the photonic band gap, and the photonic crystal then acts like a waveguide.

Therefore, in simple terms, semiconductors consist of periodic arrays on the atomic scale that control the flow of electrons; photonic crystals consist of periodic arrays on the scale of wavelength of dielectric material that control the propagation of light waves. Periodic structures made of materials having different dielectric properties (high and low refractive index materials) serve as waveguides. Optical properties can be kept absolutely under control by controlling the structure and material composition of the photonic crystal.

Fabrication of photonic crystals

There are different approaches to building a photonic crystal. The first researchers to report this idea were Yablonivich and John in 1987, who fabricated a crystal at microwave wavelengths. The fabrication consisted of covering a block of dielectric material with a mask consisting of an ordered array of holes and drilling through these holes in the block on three perpendicular facets. The material, which became known as 'Yablonovite', prevented microwaves from propagating in any direction — in other words it exhibited a 3D photonic band gap. Despite this early success, it has taken over a decade to fabricate photonic crystals that work in the near-infrared and visible regions of the spectrum. For example, for visible light, a lattice dimension of approximately 500 nm would be required, which means fabricating a material with holes separated by 500 nm. This is an extremely difficult task which requires suitable materials and processing techniques.

Instead of drilling holes on a surface, another approach to creating a photonic crystal is to build the lattice out of isolated dielectric materials that are not in contact, as illustrated in **Figure 3**.

If an entire line defect is introduced in the lattice in **Figure 3** by removing an entire row of rods, the regions where the rods have been removed act like a waveguide, and an allowed energy level is created in the photon gap. A waveguide is like a pipe that confines electromagnetic energy, enabling it to flow in only one direction. One interesting characteristic of such a waveguide is that light passing though it can turn very sharp corners, which is not true in an optical fibre.

If only one rod is eliminated in the lattice in **Figure 3** (or if its diameter is changed), a resonant cavity is formed, which also puts an energy level into the gap. As already mentioned, this energy gap depends on the radius of the rod, which provides an opportunity to tune the frequency of the cavity. This ability to tune the light and concentrate it in small spaces makes photonic crystals useful for **filters and couplers in lasers**.

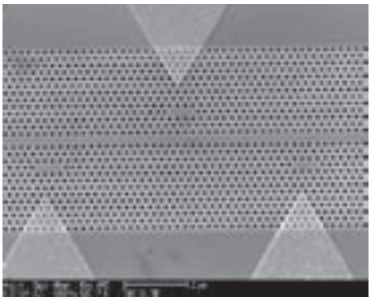

Figure 3: SEM image of a photonic crystal: the periodic arrangement of the holes in the material controls the movement of light within the crystal. Each hole has a diameter of about 200 nm.

Image: A. Faraon, Stanford University, NISE Network (http://www.nisenet.org), licensed under NISE Network Terms and Conditions

In theory, photonic crystal applications reach across the entire electromagnetic spectrum, from UV to radio waves. In practice, the challenge is the nanofabrication of these devices. Novel nanofabrication methods, including self-assembly approaches, will play an essential role in the development of this field.

Displays

Display technology has progressed enormously in the last decade. Until a few years ago, there were bulky televisions with cathode ray tube (CTR) technology, and mobile phones with black and white displays that could only show text. Nowadays, LCD televisions are becoming the norm and mobile phones that can show photos and movies are the norm, many even with touch displays. This progress has been enabled by intense research in the field, driven by a billion-dollar industry and the constant need for more functional devices combining image and video quality, low power consumption and low cost. Thickness and flexibility are also becoming an important requirement. Here, some of the latest advances in display technology and the impact that nanotechnologies have had in their development are reviewed. **Organic light-emitting diodes** (OLEDs), **quantum dot light-emitting diodes** (QD-LEDs) and **electronic paper** (e-paper) are described in detail. Another area of development is **field emission display** (FED), which, in a sense, is the progression of the old cathode ray technology to the nanoscale. Field emission display uses an element, such as carbon nanotubes, as a source of electrons that strike a coloured phosphor. This technology is not commercial yet and remains at prototype level.

OLEDs

Current displays rely mainly on two approaches: liquid crystal displays (LCD) and plasma display panels (PDP). These two technologies have basically replaced the old cathode tube technologywhich is being phased out. Plasma display panels require much more energy than liquid crystal displays to operate and are currently not as successful as LCDs, especially at a time when energy consumption is a major concern. LCD technology, on the other hand, is becoming extremely common due to a considerable price drop in the last few years.

Liquid crystal displays offer a number of advantages compared to the old cathode tube technology: first of all, displays are much thinner and less bulky due to their inherent structure and assembly, and they provide a much better image quality. However, **LCD**s have two main problems connected to their inherent composition: first, LCD displays can be **difficult to see at oblique angles**, as laptop computer users are well aware; second, they require backlight, which consumes power.

The need for backlight explains why, in an LCD, black looks more like deep grey than true black.

Organic light-emitting diodes have emerged as a new technology offering a number of advantages over LCDs (**Figure 4**). In this technology, the display is formed of an emissive and conductive layer sandwiched between an anode and a cathode. A voltage is applied across the OLED so that the *anode is positive* with respect to the cathode. This creates a flow of electrons from the anode to the cathode: therefore, electrons are removed from the conductive layer and added to the emissive layer. The conductive layer becomes positively charged and the emissive layer negatively charged. This causes electron holes to appear at the boundary between the two layers: electrostatic forces induce electrons and holes to get closer and they recombine, emitting energy as a photon. Emission is in the visible region and this is what generates the colours in the display.

Figure 4: OLED films about 200 nm thick

Image: R. Ovilla, University of Texas at Dallas, NISE Network (http://www.nisenet.org), licensed under NISE Network Terms and Conditions

Molecules used in OLEDs — as the name suggests — are organic molecules such as organo-metallic chelates and conjugated dendrimers (two types of macromolecules that can reach the nanoscale). The molecules can be directly evaporated or printed on the polymer substrate, which is a notable advantage, and can lead to very complex multilayer structures. The molecules are deposited in rows and columns onto the flat carrier (simply by printing) and the resulting **matrix of pixels can emit different colours**.

Therefore, the **colour generation in an OLED** is fundamentally different from that in an LCD, which is powered by a fluorescent lamp (backlight) colour-filtered to produce red, green and blue pixels. Thus, when an LCD screen displays full white colour, two thirds of the light is absorbed by the filters. This explains some fundamental **advantages of OLEDs over LCD**.

- **OLED pixels directly emit light**, they do **not require backlight**, thus consuming less power than LCDs. When in the OFF mode, the OLED elements produce no light and consume no power.
- OLEDs have a much better picture quality because they **naturally achieve a higher contrast ratio**. For a viewer, the most noticeable effect is that the black areas in an OLED appear true black.
- OLEDs can be much **thinner and lighter** than LCD panels. In addition, OLED can be printed onto any suitable substrate using an inkjet printer so they can, theoretically, be incorporated into flexible substrates, which opens up numerous new display possibilities (roll-up displays or displays included in fabrics).
- Unlike LCDs, OLED panels can be seen well **under sunlight** and at different angles.

OLED technology is currently used in small displays (OLEDS are used in numerous colour mobile phones) but it is not yet established in television panels due to some **challenges** presented by the OLED technology. Many of these challenges can be addressed with the use of nanomaterials and nanotechnologies.

First, the organic molecules used in the OLED have an inherent tendency to degrade in time. Increasing the **lifetime** of OLEDs is a research priority. This is particularly true for the colour blue (e.g. the lifetime of a blue OLED is 14 000 hours, whereas a typical LCD panel has a lifetime of 60 000 hours). Much research is being dedicated to the synthesis and testing of new organic molecules that can increase the lifetime of OLEDs. The problem of OLED lifetime is particularly important in those electronics that require a long lifetime (e.g. televisions). In devices that are used intermittently (mobile phones etc.), lifetime is less important. This explains why OLED technology is already fairly well diffused in mobile devices.

A second problem is in the nature of the top cathode layer of the OLED, which needs to be a transparent electrode. Currently, ITO (indium tin oxide) is used since it offers a combination of conductivity and transparency. The problem is the availability of ITO, which is declining, and in the way it is processed, which is by chemical vapour deposition (CVD). This deposition method requires very high temperatures which limit the type of substrate that can be used. ITO is slightly opaque and this affects image quality. A very active field of research is the search for **suitable nanomaterials to replace ITO** in OLED cathodes. One possibility is carbon nanotubes. Currently, there are numerous methods to fabricate CNTs (alternatives to CVD) such as spray coating and roll-to-roll printing. Furthermore, numerous companies are emerging that produce CNTs and the price is dropping.

Another issue in OLEDs is that the organic molecules contained within them are **very sensitive to water** and other substances. Therefore, the coating and packing of the OLED components is of fundamental importance. One of the problems is that current packaging materials are either too brittle (which is a problem in flexible screens) or require too high a temperature during the production process, which would destroy the device. Currently, alternating layers of organic and inorganic materials are used. This gives some degree of flexibility and blocks the entry of foreign substances (although not totally). **Nanomaterials** could help solve this challenge: for example, a method was recently developed whereby nanoparticles are used to fill the pores in these organic and inorganic layers and this markedly improved the packaging of these devices.

Application of OLEDs

Organic light-emitting diodetechnology can be used for two main applications: displays and light sources. The possibility of using OLEDs instead of traditional light bulbs is very attractive in terms of energy consumption (conventional incandescent lights lose most of their energy as heat). OLED technology is thus being considered for use in lights and signs. The potential of OLED technology in the energy sector is discussed in **this module, Chapter 3: Energy**.

The second mainstream application is in the **display industry**. Currently, they are used as small screens for mobile phones, portable digital audio players (MP3), car radios, digital cameras, etc. **OLED technology in TV** is just appearing on the market. The first commercial OLED TV was the Sony XEL-1, commercialised in 2007 (at a cost of about USD 2 500 in the United States). In October 2008, Samsung announced the world's largest OLED Television (40 inch) with a full HD resolution of 1 920 x 1 080 pixels. The same company showcased the thinnest OLED display, only 0.05 mm (i.e. thinner than paper). This opens up numerous opportunities. Clearly, all major display companies are investing hugely in this new technology.

The fact that OLEDs can be fabricated on flexible substrates opens the door to **OLEDs in textiles**, **labels** and other flexible materials.

Quantum dot light-emitting diodes (QD-LED)

Quantum dots (QD) are another class of nanomaterials under investigation in the manufacture of more efficient displays and light sources (QD-LEDs). Quantum dots are nanoscale semiconductor particles characterised by emitting a specific colour based on the size of the nanoparticle. A minute change in particle size results in a totally different colour being emitted; for instance a 6 nm-diameter particle would glow red, while another of the same material but only 2 nm wide would glow blue. Light emission from a QD is monochromatic, therefore it is very pure. As a consequence, their use in displays would lead to images of exceptional quality. The most exciting property of QD-LEDs, however, is that they use much less power than the currently used LCDs where light is filtered by numerous polarisers. Like OLEDS, QD-LEDs emit light, rather than filtering it, so, for this reason, QD-LEDs are expected to be more energy efficient. In June 2006, QD Vision announced a first proof of concept of a quantum dot display.

Electronic paper (e-paper)

e-paper is a display technology that aims to mimick the appearance of ordinary ink on paper. There are various technologies to create e-paper, among which **electrophoretic paper** is the most established. Unlike conventional flat panel displays, electrophoretic displays rely on reflected ambient light, rather than the emission of light from the display, and can retain text or images without constant refreshing, thereby requiring much less power. This also means that they can be used under sunlight without the image fading. e-paper is also very **light** and **flexible**.

e-paper has numerous commercial applications, such as **e-books** (i.e. e-readers that can display the digital version of a book), **e-papers**, **electronic labels**, general signage, timetables at bus stations, etc.

The first electronic paper was invented in the 1970s by Nick Sheridon (Xeron) and was called Gyricon (**Figure 5**). The technology behind electrophoretic paper is fundamentally different to that behind other displays. In this case, the information display is formed by the rearrangement of charged pigment particles in an applied electric field: **titanium oxide** (TiO_2) particles about 1 μmin diameter are dispersed in oil with a **dark-coloured dye** together with surfactants and charging agents. The mixture is placed between two parallel conductive plates and a voltage applied. The charged particles move electrophoretically towards the plate with their opposing charges. When the particles are on the front side of the display, they scatter light and appear white; if they are at the back of the display, the display looks black because the incident light is absorbed by the dye. The back electrode is divided into a number of small picture elements, the pixels, so the image is formed by delivering the appropriate voltage to the pixel (resulting in a white or black pixel). Therefore, the image is created by a repeated pattern of reflecting (white) and absorbing (black) regions.

Developers imagine that e-paper will be used as a support (imagine a roll to keep in your pocket that opens up on command) on which to download information (from an overhead satellite, a mobile phone network or an internal memory chip) and then as a reading support which does not require power and can be seen under sunlight etc. (**Figure 6**). Once reading is done, the device can be rolled up again, placed in the pocket and reused.

Figure 5: Rolled up Gyricon e-paper

Image: Eugeni Pulido, Wiki Commons, Creative Commons Attribute ShareAlike 3.0

Figure 6: Example of an e-paper device

Image: Manuel Schneider, Wiki Commons, Creative Commons Attribute ShareAlike 3.0

At present, the technology is limited to black and white but numerous companies are investing resources to develop a coloured e-paper solution. Another issue is the low refresh rate, making electrophoretic paper **unsuitable for displaying animation or video**. Some newspapers are already offering their subscriber's e-paper versions of their print editions.

Nanotechnologies for e-paper

Some new materials are emerging as elements of e-paper. In May 2008, Unidym and Samsung produced the first active matrix **e-paper device incorporatingcarbon nanotubes** as the transparent electrodes. Other approaches use photonic crystals, liquid crystals and other nanomaterials.

Another development uses a **thermochromic display** (**Figure 7**) which can easily be fabricated using soft lithography. The thermochromic material is a microencapsulated powder mixed inside a polymer (PDMS). The thermochromic material is dark green at room temperature but turns white when heated above 60 °C. Once the two components have been mixed, they form a polymer composite that can be spin-coated over a substrate and, once it is cured, this forms a thin polymeric sheet that has the characteristic (inherent to PDMS) of being very flexible but also resistant to stretching etc. The thermochromic display is basically made of a single layer of thermochromic sheet in which a conductive wire, shaped in the logo desired, is embedded. When a voltage is applied, an electric current is generated in the wire, which creates a localised heat. Above 60 °C, the colour of the thermochromic composite in the area corresponding to where the wire is becomes white, and the image of the logo appears. The main limitation of this technology is that the image is created through a wire, and not pixels.

Figure 7: Thermochromic display under development at the Hong Kong University of Science and Technology

Image: Liu et al., 'Paperlike thermochromic display', *Applied Physics Letters*, 2007, 90:213508, reprinted with the permission of the American Institute of Physics, © 2007

Information storage devices

Numerous miniaturised devices now exist that can store and transmit data. Two examples are 'smart cards' and 'smart tags'. These devices have been created to meet the need to collect and transmit data using less space (chips) and wirelessly. The application of these devices covers personal data cards (e-patents, e-health cards, credit cards, etc.), tags for package protection and tracking, etc. The trend in the development of these devices has been that opened up by miniaturisation: integration of more functions in a smaller space. In the future, this trend will continue and nanotechnology will most likely be the enabling technology.

Nanotechnologies in tags

Products are most commonly **identified and tracked** using a label, which is also a code: the one still commonly in use is the barcode. In the last years, the emergence of another labelling and tracking system has been seen — radio frequency identification (RFID). An RFID is a small, wireless integratedcircuit (IC) chip (**Figure 8**) with a radio circuit and an identification code embedded in it. The advantages of the RFID tag over other scannable tags (e.g. barcodes) are that the RFID tag is small enough to be embedded in the product itself (not just on its package); it can hold much more information; it can be scanned at a distance (and through materials, such as boxes or other packaging); and many tags can be scanned at the same time. RFID tags are already being used in many ways, for example for **livestock tracking** (attached to the ear or injected into the animal) or in the latest **e-passports**. They are used in libraries, schools, transport systems (toll roads), tickets (parking tickets), sports (race timing), etc. Developers of the technology envision a world where they can 'identify any object anywhere automatically.'

The current size of the RFID chip is about the size of a dust mite, the smallest is about 50 x 50 µm. There are already some developments that make use of nanotechnology, in particular tags directed towards the authentication and tracking of valuable products such as drugs. The goal is to avoid counterfeiting and to make sure that the drug is not released into the wrong market (e.g. black market). One example is a technology developed by NanoInk®, the company that owns the patent of the Dip Pen Nanolithography® (DPN®) (14) instrument, which was invented by the company owner. The company

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(14) For details on the DPN® and its function, see Module 2, Chapter 7: Fabrication methods.

had developed a technique for **encrypting pills** using the DPN. Each pill can be encrypted with information about place and day of manufacture, target market and expiry date. To make this encrypting technology fully workable, the same encrypting should be placed on the package of the drugs. Another method developed at the National Physics Laboratory in the UnitedKingdom makes use of electron beam lithography to encrypt pills. This way, the pill carries information in a very secure way: a special reader is needed for it to be decoded. Furthermore, the information is so tiny that it cannot be seen with the naked eye, making it ideal for covertly marking things.

Figure 8: RFID chip on a stick with barcode on the opposite site

Image: Wiki Commons, Public image

Another strategy for authentication, developed particularly for packing, has been advanced by Nanoplex Technologies, Inc. (USA) in the form of nanobarcodes. These are made of nanoparticles of gold, silver and platinum, which are grown into stripes. Each stripe has a different metal combination which leads to a different reflectivity of the stripe. A special microscope reader is needed to decode the information. **Nanoplex** can create different codes by alternating the stripe order so billions of different codes can be made. Each unique code can be associated with an item, which allows the company to track where the item is or has been.

ELSA TOPIC Developers of RFID technology imagine that, one day, an RFID invisible tag will be on every object, to identify its location and follow its transport, but also to ensure (in the case of food packages) the product integrity, etc. RFID technology could be the ultimate solution to theft and fraud. However, in some cases, RFID chips have been implanted in humans; for example, in 2004, the Mexican Attorney General's office implanted 18 of its staff members with one such chip (the VeriChip) to control access to a secure data room. The use of RFID implantable chips is strongly opposed by privacy advocates and some human rights movements, such as Friends of the Earth, warning of potential abuse. They have denounced these devices as 'spychips'which could be used by governments, leading to an increased loss of civil liberties. If private employers were to use this type of chips on their employees, they would have access to an incredible amount of private information. In addition, privacy advocates say that the information contained in this chip could easily be stolen, so that storing anything private could lead to identity theft. In terms of safety, in 2004, the Food and Drug Administration warned that these chips pose potential medical problems. Electrical hazards, MRI incompatibility, adverse tissue reaction, and migration of the implanted transponder are just a few of the potential risks the FDA has identified with the VeriChip ID implant device.

The video **Titina tag** deals with the topic of nano-tags and the possibility of tracking a person without their knowledge (http://www.youtube.com/watch?v=9sngsNmOl9E&feature=player_embedded). Although in Italian, the video is fun!

Wireless sensing and communication

At present, 'electronics' basically means devices — pieces of equipment — that offer a service (computation, information, entertainment and communication). The development path over the last years has been adding performance and complexity to these devices. One of the visions ofthe ICT industry is the concept of **ambient intelligence**: computation and communication always available and ready to serve the user in an intelligent way (i.e. satisfying certain requirements). The vision is that electronics will be embedded in the natural surroundings of life (clothes, books, doors, etc.), present whenever needed, enabled by simple and effortless actions, attuned by users' senses, adaptive to users' needs and actions, and totally autonomous. The concept of ambient intelligence is partly still a science fiction vision, and technologies are not yet developed that allow this vision to be realised. However, the vision of actively interfacing humans and electronics is not totally abstract: consider, for example, Wii system, which allows a person to command (and play with) software simply by moving at a distance, or virtual reality games and communication tools. The vision of ambient intelligence, however, is even more ambitious. Scientific progress and industrial investment are likely to make ambient intelligence (or at least some of its concepts) a reality in the future.

Electronic devices in the 'intelligent ambient world' will become a gateway between the user and the environment. A fundamental requirement is **ubiquitous sensing and computing**: devices must be highly miniaturised, integrated in the environment, autonomous, robust, and require low power consumption. They should be created easily and survive without particular management. All of these requirements are likely to be met with the use of nanotechnologies: some key elements are now listed.

- **Miniaturisation and system integration**: Numerous different functions (logic, memory, radio frequency, sensors and software) will need to be integrated in a single component. This implies new and severe demands on the microelectronic, opto-electronic and microsystem components that are the 'building blocks' of the Information Society technologies. It means developing new manufacturing technologies and materials that can make it possible to reach this advanced system integration at feasible costs. Nanotechnologies allow use of nano-sized material (carbon nanotubes, molecular electronics, etc.) and realise nanosystem transistors hundreds of times smaller than the current ones. Miniaturisation is the gateway to a number of key elements: mobility, low power consumption, more performance, small sizes and low weight, low cost, high reliability, more flexibility and ubiquity.
- **From 'chips' to embedded 'soft' electronics**: Presently, electronics are in the form of solid, rigid 'wafers' or 'chips'. To realise the concept of ambient intelligence, a key requirement is the embedding of electronics in many different types of materials, from plastics to textiles. Organic electronics (i.e. meaning naturally conducting molecules, such as polypyrrole) will have an important role. At the moment, organic materials are used in OLEDs (see the OLED section in this chapter), organic solar cells (discussed in **this module, Chapter 3: Energy**), and in organic transistors (still at a proof-of-concept stage). Although all these systems are still in development, research is very intense and it is likely that organic electronics will become a key

component in our future electronic devices. The reason is that organic electronics are produced by depositing and patterning thin films of organic conductors, semiconductors or insulators. Organic films can be deposited in a vacuum, but also inexpensively from solution or via high-resolution inkjet printing. Processing temperature is always low (below 200 °C) meaning that organic thin films can be integrated with soft materials such as plastics, opening the way to flexible organic electronics.

- **Embedded sensors**: One of the key enablers of ambient intelligence is the presence of sensors embedded in the user and in the environment with which it needs to communicate to gather information and communicate data wirelessly. Nanotechnologies may render this possible by enhancing the sensory skills of humans based on **wearable or embedded sensors** (e.g. in clothing) and the ability to process this enormous amount of sensory data through powerful computers. In order to achieve a true integration between the sensor element and the physical object, the device should adapt to the environment that surrounds it: so those devices should become 'intelligent' in the sense that learning should be a key property of their systems, similar to the way systems grow and adapt in the biological world. Ambient sensors should also be robust, survive in harsh environments or, in the case of wearable electronics, survive washing, be inexpensive and be ecologically sustainable.
- **Integrated power sources**. Power supply is crucial for all embedded electronics, whether wearable (e.g. electronics in clothing, shoes) or embedded in objects surrounding the user. For example, in the case of wearable electronics, where low power is required, the electrical power could either be body heat or body movement. Although the field is in its infancy, research is very intense and some systems have been demonstrated in laboratories in the form of miniaturised thermogenerators or miniaturised energy scavenger systems (these are discussed in **Module 2, Chapter 3: Energy**).

ELSA TOPIC Clearly the realisation of the vision of ambient intelligence requires numerous scientific and technical challenges to be met. The time frame from 'vision' to reality could be decades. In addition, the concept itself brings about a number of fundamental ethical and social questions: What does it mean to be human? What does it mean to 'sense'? Is it ethical to enhance (and interfere with) the way humans interact with their environment? Does human progress 'need' this technology? Questions of personal data privacy also arise. The questions are numerous and intense discussion on these fundamental ethical issues is already taking place. Nanotechnologies, being an enabler of the ambient intelligence vision, are necessarily part of these discussions.

Wearable sensing textiles

Sensors could be inserted inside clothes to gather information about the wearer's location and other environmental conditions around them, such as temperature, pressure, etc. This would enormously facilitate the task of locating missing people. For example, a jacket (or other wearable textile) with an integrated GPS sensor could become a standard part of children's clothing to ensure their safety. Other electronics could become integrated as well, such as phones, music devices, etc. With the advancement of nanoelectronics, these types of clothing could become a reality.

NANOYOU DILEMMA The example of the jacket with an embedded GPS is the subject of a NANOYOU dilemma, part of the **NANOYOU role-playing game** (http://www.nanoyou.eu/en/decide). Consider the children's clothing with an integrated GPS sensor: it would allow parents to always know the location of their children and, if they get lost, they could be immediately located. However, would it make them feel that were under constant surveillance? Is this against the fundamental human right of freedom?

Intelligent sensors are already a reality in the form of **wearable sensing textiles** that can monitor fundamental physiological parameters such as heart rate, temperature, respiratory rate, etc., with applications in monitoring and prevention of cardiovascular risk. For example, the Italian company Smartex has developed a prototype that measures all of these parameters, including posture. The information registered by the sensing textile is sent to a computer via Bluetooth. The company is also part of a new European project, Biotex, which aims to create wearable textiles with even more sophisticated sensing capabilities. The aim is to create **biosensing clothes** that remotely monitor physiological and metabolic functions in order to improve early diagnoses. The approach aims to develop sensing patches adapted to various targeted body fluids and biological species to be monitored, where the textile itself is the sensor.

MODULE 3:
EXPERIMENTS

Module including experiments for teachers and students

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to MSDS specifications and according to specific school safety rules. Personal protection must be taken as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

EXPERIMENT A:

NATURAL NANOMATERIALS

MATERIAL INCLUDED IN THIS EXPERIMENT PACKAGE

For teachers:

TEACHER RESOURCES — EXPERIMENT A: NATURAL NANOMATERIALS

For students:

STUDENT BACKGROUND READING — EXPERIMENT A: NATURAL NANOMATERIALS

STUDENT LABORATORY WORKSHEET — EXPERIMENT A: NATURAL NANOMATERIALS

LEVEL OF EXPERIMENT: Simple

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to MSDS specifications and according to specific school safety rules. Personal protection must be taken as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

TEACHER RESOURCES

NATURAL NANOMATERIALS

AIM: There are numerous **natural nanomaterials around us** and in this experiment, students will learn that two very common materials, gelatin and milk, are two of these nanomaterials. Milk, as we know, is white and its appearance is connected to the presence of numerous proteins which are self-assembled in specific nanostructures, called casein micelles, 50–300 nm in size. When milk is heated and an acid such as vinegar is added, this molecular organisation is disrupted and milk agglomerates and a 'curd' precipitate forms. Interestingly, if the same procedure is carried out using cold milk, only thickening occurs, no precipitate is formed. Students will learn that this is due to the fact that the stability of casein micelles in milk is due to both electrostatic and hydrophobic interactions: therefore, depending on the degree of disruption of these interactions different effects are obtained. Overall, the experiment will show how appearance (colour, odour) and **function of a material such as milk is profoundly connected to its molecular supra-organisation (nanostructures)**. By altering this organisation, new materials are obtained (in the example of milk processing, these are cheese, yogurt, etc.). This is a fundamental concept of nanoscience.

FIELD OF NANOTECHNOLOGY APPLICATION: Fundamental concepts in nanoscience

EXTRA TEACHER READING: Module 1, Chapter 2: Nanoscience in nature, and Chapter 4: Fundamental 'nano-effects', in the NANOYOU Teachers Training Kit in Nanotechnologies

REQUIRED STUDENT PRE-KNOWLEDGE:

- Light absorbance and scattering
- Protein structure (primary, secondary, etc.) and relationship between protein structure and function

STUDENT READING:

- NANOYOU Student Background Reading — Experiment A: Natural nanomaterials

EXPECTED OUTCOMES:

- Existence of natural nanomaterials: gelatin and milk as examples of natural colloids
- Light interaction with colloids
- Protein self-assembly into nanostructures
- Relationship between the 'macro' properties (colour, smell, taste, consistency) of milk and its molecular structure and how these can be manipulated to obtain different products (cheese, yogurt, etc.)

STUDENT ASSESSMENT:

- NANOYOU Student Laboratory Worksheet — Experiment A: Natural nanomaterials

BACKGROUND INFORMATION

Natural nanomaterials

By natural nanomaterials, we mean materials that **belong to the natural world** (animal and mineral), without human modification or processing, and that have remarkable properties because of their **inherent nanostructure**.

The chemical identity and properties of a substance depend on its molecular structure. The nanostructure of a biological material is due to its supramolecular organisation — the arrangement of tens to hundreds of molecules into shapes and forms in the nanoscale range. The interaction of light, water and other materials with these nanostructures gives the natural materials remarkable properties that can be appreciated at the macroscale.

There are **hundreds of examples of nanoscience under our eyes daily**, from geckos that walk upside down on a ceiling, apparently against gravity, to butterflies with iridescent colours, to fireflies that glow at night. In nature, there are some outstanding solutions to complex problems in the form of fine nanostructures with which precise functions are associated.

Natural nanomaterials provide an **inspiring way to bring nanoscience into the classroom**. Many natural materials with which students will be very familiar **owe their properties to nanostructures in their composition**. In this experiment, the natural nanomaterials that will be analysed are **gelatin and milk**. Both are types of **colloids**. A colloid is another type of chemical mixture where one substance is dispersed evenly throughout another but **the particles of the dispersed substance are only suspended in the mixture**, they are not completely dissolved in it (unlike a solution). This occurs because the particles in a colloid are larger than in a solution. Generally speaking, a **colloid is composed of particles 10–300 nm**. They are small enough to be dispersed evenly and maintain a homogenous appearance, but large enough to **scatter light**. The particles in a colloid can be so well dispersed that they have the appearance of a solution (e.g. transparent).

Figure 1: Examples of natural nanomaterials: (from top left, clockwise) butterfly, the foot of a gecko, nasturtium leaves, milk

Images: (top left) Wiki Commons, Creative Commons Attribute ShareAlike 3; (top right) A. Dhinojwala, University of Akron, NISE Network, reprinted under NISE Network Terms and Conditions; (bottom left) Wiki Commons, Creative Commons Attribute ShareAlike 3.0; (bottom right) iNANO, University of Aarhus, Creative Commons Attribution ShareAlike 3.0

A simple way to test if a mixture is a solution or a colloid is to **shine a laser beam though the mixture**: the light will be scattered only by the colloid.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

In this experiment, students will realise that **without these nanostructures, common materials like milk lose their appearance and function**.

In this experiment students will:

1. Prepare gelatin and test it with a laser pen to confirm its colloidal nature.
2. Confirm that milk is a colloid and treat it with acid to induce its aggregation. This experiment will give students practical evidence of the link between structure and function, and how manipulation of the molecular organisation of a material, such as milk, leads to materials with different colour, odour and taste!

Gelatin

Gelatin is a tasteless solid substance, derived from the collagen inside the skin and bones of animals. It is used as a gelling agent in food products (cakes etc.), in pharmaceuticals (e.g. gelatin capsules), in cosmetic products and photography.

Gelatin is a **protein** produced by **partial hydrolysis of collagen** found in the bones, connective tissues, organs and some intestines of **mammalian animals** such as pigs. However, gelatin from **fish** is also becoming a common source.

During the partial hydrolysis of collagen, some molecular bonds between individual collagen strands are broken down into a form that rearranges more easily (gelatin). For this reason, gelatin chemical composition is, in many respects, very similar to that of its parent collagen.

Gelatin is often found in the form of powder. When mixed with water, it forms a solution of high viscosity, which sets to a gel on cooling, forming a **colloid gel**. Gelatin gel melts to a liquid when heated and solidifies when cooled again. Therefore, its existence as a gel is limited to a **specific temperature window**.

Figure 2: Testing a gelatin sample with a laser pen

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

The fact that gelatin is a colloid rather than a solution can easily be seen by using a **laser pen and shining light through the gel**. A path of scattered light is clearly visible (Tyndall effect). This effect is due to the scattering of light by the nanoparticles inside the colloid and students will test this effect.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

HOW IS IT 'NANO'?

Recent studies with the **Atomic Force Microscope (AFM)** have shown that gelatin is, indeed, formed by numerous **nanostructures** which have various shapes depending on the type of gelatin being analysed. For example, AFM analysis of gelatin extracted from catfish (*Ictalurus punctatus*) skin has revealed the presence of **annular pores** with diameters averaging 118 nm and **spherical nanoaggregates** with diameters around 260 nm. It is hypothesised that these structures are formed during the penetration of water inside the collagen molecules during hydrolysis. **The presence of these nanostructures proves that gelatin is a colloid and explains its light scattering behaviour**.

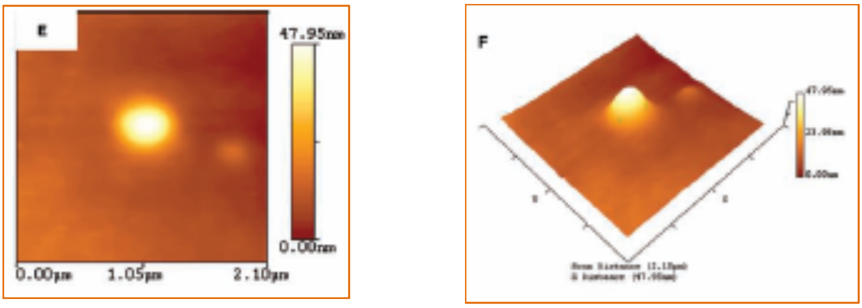

Figure 3: AFM images of gelatin extracted from catfish revealing the presence of spherical nanostructures

Images: Yang et al., *Journal of Food Science*, 2006, 72(8):c430-c440, reprinted with the permission of Wiley-Blackwell Publishing Ltd, © 2006

Milk

Bovine milk contains a number of biomolecules, such as lipids and proteins, which are dispersed in water. The amount of proteins is between 2.5 and 3.5 % depending on the animal breed, of which about 80 % are **caseins** (the rest being whey or serum proteins). Four proteins comprise the casein group and are: α_{s1}-casein, α_{s2}-casein, β-casein and k-casein. The caseins are characterised by the fact that they are **phosphoroproteins** that precipitate at pH 4.6 (isoelectric point, IP), at which pH whey proteins remain soluble. Another property of caseins is their existence as **casein micelles** which are **50–300 nm in size**. Micelles contain the caseins combined with calcium, phosphate and small amount of citrate. As such, **milk is a colloid** (a mixture of nanoparticles evenly dispersed but only suspended in a liquid medium). The presence of these micelles (together with other biomolecules like lipids) determines the **white colour of milk** due to their light scattering.

Although milk is a colloid, it is not transparent: therefore, if you shine a light through milk in a glass, the Tyndall effect is not visible. However, if milk is diluted (1 % milk in water) the effect is seen. Students will see this effect.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

FROM STRUCTURE TO FUNCTION

The fine molecular self-organisation of proteins and minerals in milk is fundamental to realise its natural function of transporting calcium from the mother to the offspring. Numerous studies have revealed that this organisation results in nanostructures which have precise functions (**casein micelles**). In the next section, how this organisation is determined not only by electrostatic interactions but also hydrophobic interactions between the proteins that constitute milk, and some minerals that are associated with the proteins are also described. Without this fine organisation, calcium would not be 'trapped' inside the milk micelles and the biological function of milk would not be realised.

MILK PROCESSING

Processing of milk with various treatments is widely used in the dairy industry. For instance, yogurt is a fermented milk product obtained by the controlled growth of specific micro-organisms, mainly bacteria that convert lactose (milk sugar) into lactic acid. By lowering the pH of milk, its consistency and taste change. In cheese-making, enzymes are used to induce the aggregation and precipitation of caseins. As discussed in the next section, in all milk processing methods, **the molecular organisation of caseins is altered**, which leads to thickening, precipitation and other effects. The appearance, taste and other 'macro' properties of milk are deeply connected to its supra-molecular (nano) structure. **In this experiment, students will use vinegar and heat to alter the properties of milk.**

CASEINS

Caseins are one of the types of proteins found in milk. Casein in milk (which has a pH near to neutral, about 6.7) are negatively charged (IP = 4.6). All caseins, except k-casein, possess the ability to **bind to Ca^{2+} which occurs mainly through their phosphate residues**. The binding of Ca^{2+} is fundamental for milk to fulfil its function (i.e. to transport calcium (and other nutrients) from the mother to the offspring). Each casein is composed of a different peptide sequence and, therefore, has a different secondary and tertiary structure.

The precise **structure** of casein is still a matter of debate and study within the scientific community. This arises from the fact that **caseins cannot be crystallised** (as opposed to other types of proteins) and NMR structural studies have so far extended to peptide analysis. The current model of casein tertiary structure is based on numerous studies performed using circular dichroism, Raman spectroscopy and FTIR analysis.

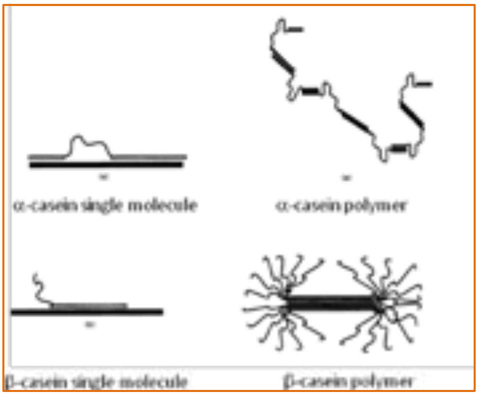

Figure 4: Schematic structures of caseins and their polymers (rectangles in the images represent hydrophobic regions)

Image: D. S. Horne, *International Dairy Journal*, 1998, 8(3), 171–177, reprinted with the permission of Elsevier

The most current model of casein tertiary structure is based on considering **caseins as block copolymers**. In the case of α-casein, the protein has **two hydrophobic regions separated by a hydrophilic core**. It is predicted that this protein self-assembles into a 'train-loop-train structure' as illustrated in **Figure 4**. It is believed that this protein links inter-molecularly to form a worm-like polymeric chain. On the other hand **β-casein** has a **highly charged N-terminal region and a hydrophobic C-terminal region** and it is believed it assumes a tail-train structure. Self-association of these molecules is believed to lead to a 'micellar polymer' with a hydrophobic core and a hydrophilic 'hairy' outside. **K-caseins** have a structure which is a mirror image of β-casein, and thus have a **hydrophobic neutral N-terminal region and a highly charged C-terminal** peptide. K-caseins do not have the ability to bind Ca^{2+} but have a stabilising function.

CASEIN MICELLES: STRUCTURE AND FUNCTION

Caseins in milk are believed to exist as **casein micelles 50–300 nm in size**. Micelles contain the **caseins combined with calcium, phosphate and small amount of citrate**. The structure of casein micelles (like that of casein itself) is still a matter of debate and intense research. Since all caseins possess a hydrophobic region and a polar region, it is believed that hydrophobic interactions as well as electrostatic interactions play a role in the self-association of caseins to form casein micelles. Casein micelles differ from the polymers of the individual caseins in one crucial aspect: they contain inorganic calcium phosphate, which exists in the form of small microcrystalline inclusions termed **calcium nanoclusters**. The fact that the stability of casein micelles is not due only to electrostatic interaction has been demonstrated by the fact that **casein micelles can be dissociated using urea**, which is an agent that does not rupture the calcium phosphate linkages.

Two types of linkages between casein in the casein micelles have been postulated.

The first linkage is **hydrophobic**, where two or more hydrophobic regions from different molecules (α-caseins and β-caseins) form a bonded cluster. These are indicated as a **rectangular bar** in **Figure 6**.

The second linkage of **hydrophilic charged regions** containing phosphoserine clusters which bind to colloidal calcium phosphate nanoclusters (indicated as CCP in **Figure 6**).

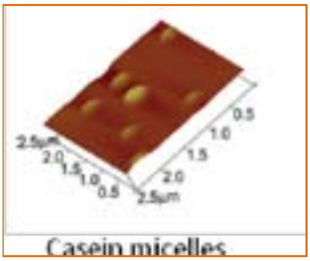

Figure 5: AFM image of milk casein micelles

Image: K. Shekar et al., *Proceedings of the National Academy of Sciences* (USA), 23 May 2006, 103(21):8000–8005, reprinted with the permission of the National Academy of Sciences, USA, © 2006

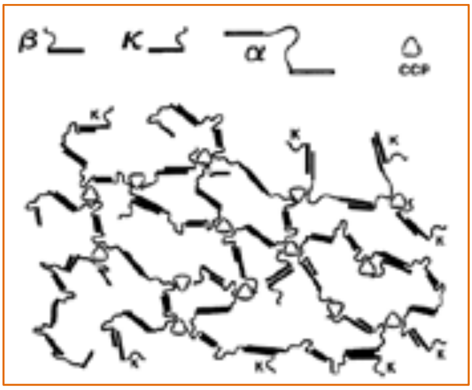

Figure 6: Dual bonding model in casein micelles, with α, β and k-casein depicted as indicated

Image: D. S. Horne, *International Dairy Journal*, 1998, 8(3), 171-177, reprinted with the permission of Elsevier

The k-caseins do not have the phospheroserine group to link with the calcium nanocluster, therefore their association is only possible through hydrophobic interactions. Furthermore, the micelle cannot grow further beyond the k-caseins, which therefore act as an outer layer in the micelle. The **role of k-caseins is to stabilise the casein micelle**, preventing excessive growth and micellar aggregation which would otherwise lead to precipitation.

CASEIN MICELLES DISSOCIATION AND AGGREGATION

As already discussed, casein micelles are believed to have an intricate structure which is an interplay of hydrophobic and electrostatic interactions. Maintenance of micellar integrity is a balancing act and numerous methods exist to disrupt this balance. These methods are widely used in the dairy industry to make cheese and fermented products such as yogurt. These methods are now briefly reviewed: the aim here is not to detail the production of milk products (but the interested teacher can find more information at the end of this document in the Further reading section).

- **Increasing the pH (to about 8)** leads to casein **micelle dissociation**, and the effect is that heated milk becomes more translucent. The reason for this is that increasing the pH from the natural neutral point converts the phosphoseryl groups from singly to doubly charged units which are no longer capable of linking the calcium phosphate nanoclusters. The increased negative charge of the micelle induces electrostatic repulsion, and the micelles dissociate.

- **Decreasing the pH to the isoelectric point (4.6)** induces dissociation of the casein micelles. The reason for this is that calcium micelles only exist because of the presence of calcium phosphate; therefore, its dissolution necessarily causes changes in the stability of the micelle. The consequence of lowering the pH is the titration of the phosophoseryl and carboxyl groups in the proteins. Without their negative charge these groups cannot link to the colloidal calcium phosphate nanoclusters, so these are released from the micelle. It should be noted that this does not necessarily cause the caseins to dissociate from the micelles and lead to precipitation. At temperatures below 25 °C, increasing dissociation occurs, but otherwise the caseins remain in the micelles. This effect will be tested in this experiment by adding vinegar (a source of acid) to cold milk. The reason lies in the fact that the stability of casein micelles is not entirely connected to electrostatic interaction, but also to hydrophobic interactions. The latter are extremely temperature-dependent: hydrophobic interactions are stronger at higher temperatures. **Therefore, hydrophobic interactions maintain the stability of casein micelles in cold milk even when its pH has been lowered to the isoelectric point.** On the other hand, **if acidification occurs after milk has been warmed (to about 60 °C), micelles are dissociated (calcium phosphate is released from the micelle) and will aggregate due to increased electrostatic forces and increased hydrophobic interaction**. This will be tested in this exercise by adding vinegar to warm or cold milk.
- **Attack by chymosin leads to micelle precipitation and formation of a curd**. This process is employed in **cheese-making**. Chymosin is a proteolytic enzyme which is the active ingredient in rennet, the extract of calves' stomachs used in cheese-making. Chymosin specifically attacks a single bond in the k-casein, breaking the molecule into two peptides: one remains attached to the micelle, while the other diffuses in solution. As already mentioned, the presence of k-caseins is fundamental for the overall stability of the casein micelle; therefore, its disruption leads the micelle to lose stability, aggregate and eventually form a curd.
- The controlled addition of **lactic acid bacteria** (bacteria that produce lactic acid such as *Lactobacillus, Lactococcus* and *Leuconostoc*) under specific processing conditions leads to fermented milk products such as yogurt. This process differs from simple acidification as milk is heat-treated and whey proteins are also incorporated. The coagulation is induced by the acidification but does not lead to the formation of a curd but to a product which is more viscous than plain milk.

TIP FOR TEACHERS: The phenomenon of aggregation of milk can easily be seen in milk that is old and has long passed its sell-by date. In this case, it is lactic acid bacteria that are responsible for the acidification of milk and consequent aggregation to form acid-smelling lumps. **In this experiment, students will use vinegar (a source of acid) and heat to alter the properties of milk**.

WHAT CAN THIS EXPERIMENT TEACH ABOUT NANOTECHNOLOGY?

Through this exercise, students will learn about two fundamental concepts.

- **Structure means appearance**: materials in the 'real' natural world, such as milk, appear as they do because of the fine nanostructures they possess. Milk is white because it contains colloidal nanoparticles (micelles). If the structure of these micelles is altered, some of the 'macro' properties of milk such as the **colour** and **odour** will be changed.
- **Structure means function:** natural materials have very specific functions which are dictated by the fine supra-organisation of their molecules (nanostructures). If this structure is altered, a material with a new function can be produced. In cheese production, altering the casein micelles through specific processes (e.g. chymosin treatment or lactic acid bacteria

fermentation) leads to different products (cheese, yogurt, etc.). **This is exactly the concept of nanotechnologies**: to engineer new materials with new functions from the manipulation of their molecular organisation.

THIS EXPERIMENT IN CLASS

1. Start with a discussion on natural nanomaterials. What are they? Let the students think of materials they know already and/or discuss examples such as the gecko, butterflies, bones, or biological nanostructures such as DNA, ferritin, chlorophyll.
2. Discuss the relationship between structure and function. This can start at the macro-level (e.g. the structure of a building to serve its function to resist an earthquake) and move to the nanoscale.
3. Discuss with the students what they know about gelatin and milk. What happens when you heat these substances? Or cool them? What happens if milk is left in a fridge way past its sell-by date?
4. Proceed with the experiment as outlined in the next section.
5. Conclude with a discussion on other natural colloids such as blood, custard, smoke. Nano is all around us!

MATERIALS

The material below is indicated assuming students will work in pairs.

Materials for the entire class (to be shared)

- gelatine from pig skin (Sigma-Aldrich No G1890, 100 g costs about EUR 34)
- 1 l white vinegar
- laser pen (to be shared by the class; ideally more than one should be available)
- water kettle if hotplates are not available for students to use

Materials for each student pair

- hotplate
- 2x beaker 50 ml
- 1x beaker 200 ml
- 2x beaker 500 ml
- 0.5 g gelatin powder
- tablespoon
- 800 ml skimmed milk
- 4 tablespoons white vinegar
- thermometer
- spatula
- latex gloves
- safety glasses

SAFETY NOTE: This experiment does not use chemicals, simply common liquids and solids. Nevertheless, staining is possible so wash hands and surfaces thoroughly after handling. Use appropriate clothing protection, gloves and eye protection. Collect all liquids and washing water in glass/plastic containers and dispose down the sink. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

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PROCEDURE

1. Is gelatin a colloid?

In this part of the experiment, students prepare gelatin and test it with a laser pen to confirm its colloidal nature.

STEP 1

Prepare a 10 mg/ml gelatin sample by mixing 0.5 mg gelatin powder with 50 ml cold water. Place on the hotplate and heat the water and gelatin mixture. Stir with the spatula as the mixture heats up. Bring close to the boil (check the temperature with the thermometer), then turn off the hotplate and let the gelatin cool down.

SAFETY NOTE: Do not touch the beaker immediately as it will be very hot. After it has cooled down, remove it from the hotplate and place on the bench safely. Otherwise use safety gloves.

STEP 2

Once the gel is formed, test it with a laser pen. Place a piece of white paper on the far side of the beaker. Shine the laser beam through the gelatin sample and ask students to record their observations.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

STEP 3

Repeat the laser test using a beaker ofplain water. Does plain water scatter light?

Students should complete Q1 and Q2 of the student laboratory worksheet

2. Milk and its properties

Milk is a natural colloid and students will confirm this as they did with gelatin, using a laser pen (using diluted milk). They will then treat the milk with acid to disrupt its molecular nanostructure and induce aggregation.

STEP 1

Milk is a natural colloid but unlike gelatin it is not transparent. Pour 400 ml of milk into a beaker. Try to test it with a laser pen as you did with gelatin, can you see a path of scattered light? No, because the light is reflected back (back scattering).

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

Now ask the students to dilute milk. Take 150 ml of distilled water in a beaker or glass, and add 1–2 droplets of milk (using a pipette). Mix and let the solution stand for a couple of minutes (so the air bubbles can dissipate). The solution will look pale grey. Now ask the students to test it again using the laser pen. They will see a path of scattered light.

Students should complete Q3 and Q4 of the student laboratory worksheet

STEP 2

With the use of a pH paper, record the pH of skimmed milk.

Now place the same beaker containing milk used in **STEP 1** on a hotplate, turn the hotplate on and warm the milk up to about 60 °C. If a hotplate is not available, the milk can be heated using water that has been boiled separately and added to the water bath container (as shown in the image).

TIP FOR TEACHERS: A **microwave oven** can be used as an alternative but the milk should **not boil nor become too hot**: therefore, a test should be done beforehand to assess the time required for heating the milk to about 60 °C when using that specific microwave oven.

STEP 3

- To the hot milk (about 60 °C) add two tablespoons of white vinegar stirring well. It will be seen that milk will immediately aggregate and form a 'milk ball'. Make sure students wear gloves as they do this (the beaker will be hot).

- Ask the students to record the pH of the liquid.
- Students should write down their observations.

SAFETY NOTE: Aggregated acid-milk should not be tasted by the students!

STEP 4

- Repeat the test but without heating the milk. Give each pair of students another 400 ml cold milk, and ask them to add two tablespoons of white vinegar. The milk will not agglomerate but only become a bit thicker.
- Ask the students to record the pH of the liquid.
- Ask the students to record their observations.

The reason why the milk only becomes a bit thicker but does not agglomerate should be discussed.

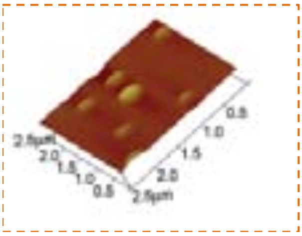
Students should complete Q5 and Q6 of the student laboratory worksheet

TIP FOR TEACHERS: This part of the experiment can be used to connect it with the process of making yogurt.

Why does this happen? In normal milk (pH close to neutral), the casein micelles are formed of caseins (charged negatively, IP = 4.6), which are neutralised by calcium clusters resulting in a stable micelle. In addition to electrostatic interaction, hydrophobic interactions among the caseins stabilise the micelle. By adding vinegar, the pH of milk is lowered enough to induce dissociation of the casein micelles because calcium phosphate is released from the milk micelles. The reason for this is that lowering the pH to the isoelectric point leads to the titration of the phosophoseryl and carboxyl groups in the proteins. Without their negative charge, these groups cannot link to the colloidal calcium phosphate nanoclusters, so these are released from the micelle.

When vinegar is added to warm milk, a curd is formed because the proteins that make up the micelles are no longer charged and aggregate due to hydrophobic interactions. This aggregation leads to precipitation because the milk is warm. In fact, if the vinegar is added to cold milk, an increase in viscosity is noted (sign of a coagulation of the micelles) but a curd is not formed. This is because at temperatures below 25 °C, acidification of milk leads to an increase in micelle dissociation but otherwise the caseins remain in the micelles. The reason lies in the fact that the stability of casein micelles is not entirely connected to electrostatic interactions but also to hydrophobic interactions. The latter are extremely temperature-dependent: hydrophobic interactions are stronger at higher temperatures. **Therefore, hydrophobic interactions maintain the stability of casein micelles in cold milk even when its pH has been lowered to the isoelectric point.** On the other hand, **if acidification occurs after milk has been warmed (to about 60 °C), micelles are dissociated (calcium phosphate is released from the micelle) and will aggregate due to increased electrostatic forces and increased hydrophobic interaction**.

ANSWERS TO QUESTIONS



Q1: Yes, gelatin is a colloid since a path of scattered light is visible through it.

Q2: No, water is not a colloid since no path of scattered light is visible.

Q3: Yes, milk is a colloid since a path of scattered light is visible through it.

Q4: Image should be the one represented here (15).

Q5: When vinegar is added to warm milk, a curd is immediately formed. When vinegar is added to cold milk, no curd is formed: it only becomes a bit thicker. The difference is very evident.

Q6: The fact that the reaction is temperature-dependent is an indication that the stability of casein micelles is not only due to electrostatic interactions (which can be altered through the addition of an acid) but also to some other form of physical interactions among the molecules that form the micelles. In this case, it is hydrophobic interactions, which are very temperature-dependent.

FURTHER READING

Dalgleish, D. G., ‘Bovine milk protein properties and the manufacturing quality of milk’, *Livestock Production Science*, 1992, 35:75–93.

Horne, D. S., ‘Casein interactions: casting light on the black boxes, the structure of dairy products’, *International Diary Journal*, 1998, 8:171–7.

Horne, D. S., ‘Casein structure, self-assembly and gelation’, *Current Opinion in Colloid and Interface Science*, 2002, 7:456–61.

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(15) Image: K. Shekar et al., *Proceedings of the National Academy of Sciences* (USA), 23 May 2006, 103(21):8000–8005, reprinted with the permission of the National Academy of Sciences, USA, © 2006, no further use possible without written approval of copyright holder.

STUDENT BACKGROUND READING

NATURAL NANOMATERIALS

There are many **natural nanomaterials around us** and in this experiment, you will learn that two very common materials, milk and gelatin, are two of these nanomaterials. The properties of these materials are directly connected to their molecular supra-organisation, which includes nanostructures.

In this experiment you will:

1. Prepare gelatin and test it with a laser pen to confirm its colloidal nature.
2. Confirm that milk is a colloid and treat it with acid to induce its aggregation. This experiment will give you practical evidence of the link between structure and function, and how manipulation of the molecular organisation of a material, such as milk, leads to materials with different colour, odour and taste!

BACKGROUND INFORMATION

Natural nanomaterials

Many materials that **belong to the natural world** (animal and mineral) have properties which are the result of **inherent nanostructures**.

The interaction of light, water and other materials with these nanostructures gives the natural materials **remarkable properties which we can see with our eyes**. These nanostructures arise from the supra-molecular organisation of the material: tens to hundreds of molecules which are arranged into shapes and forms in the nanoscale range. There are **hundreds of examples of nanoscience under our eyes daily**, from geckos that walk upside down on a ceiling, apparently against gravity, to butterflies with iridescent colours, to fireflies that glow at night.

In nature, there are some outstanding solutions to complex problems in the form of fine nanostructures with which precise functions are associated.

In this experiment, the natural nanomaterials that you will analyse are **gelatin and milk**. Both are types of **colloids**. A colloid is a type of chemical mixture in which one substance is evenly dispersed throughout another but **the particles of the dispersed substance are only suspended in the mixture**, they are not completely dissolved in it (unlike a solution). This occurs because the particles in a colloid are larger than in a solution. Generally speaking, a **colloid is composed of particles 10–300 nm**. They are small enough to be dispersed evenly and maintain a homogenous appearance, but large enough to **scatter light**. The particles in a colloid can be so well dispersed that they have the appearance of a solution (e.g. transparent).

A simple way to test if a mixture is a solution or a colloid is to **shine a laser beam though the mixture**: the light will be scattered only by the colloid.

Figure 1: Examples of natural nanomaterials: (from top left, clockwise) butterfly, the foot of a gecko, nasturtium leaves, milk

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WARNING: Never shine a laser beam near the eyes nor look straight into the beam! You should wear **safety glasses** when doing this test.

In this experiment, you will realise that **without these nanostructures, common substances like milk lose their appearance and function**.

Gelatin

Gelatin is a tasteless solid substance, derived from the collagen inside the skin and bones of animals. It is used as a gelling agent in food products (cakes etc.), in pharmaceuticals (e.g. gelatin capsules), in cosmetic products and in photography.

Gelatin is a **protein** produced by **partial hydrolysis of collagen** found in the bones, connective tissues, organs and some intestines of **mammals** such as pigs. However, gelatin from **fish** is also becoming a common source.

Gelatin is often found in the form of powder. When mixed with water it forms a solution of high viscosity, which sets to a gel on cooling, forming a **colloid gel**. Gelatin gel melts to a liquid when heated and solidifies when cooled again. Therefore, its existence as a gel is limited to a **specific temperature window**.

HOW IS IT 'NANO'?

Recent studies with the **Atomic Force Microscope (AFM)** have shown that gelatin is, indeed, formed by numerous **nanostructures** which have various shapes depending on the type of gelatin being analysed. For example, AFM analysis of gelatin extracted from catfish (*Ictalurus punctatus*) skin has revealed the presence of **annular pores** with diameters averaging 118 nm and **spherical nanoaggregates** with diameters around 260 nm. **The presence of these nanostructures proves that gelatin is a colloid and explains its light-scattering behaviour**.

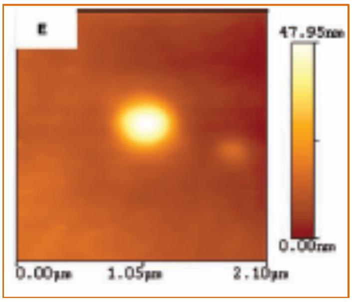


Figure 2: AFM images of gelatin extracted from catfish revealing the presence of spherical nanostructures

Image: Yang et al., *Journal of Food Science*, 2006, 72(8):c430–c440, reprinted with the permission of Wiley-Blackwell Publishing Ltd, © 2006

Milk

Bovine milk contains a number of biomolecules, such as lipids and proteins, which are dispersed in water. The amount of proteins is between 2.5 and 3.5 % depending on the animal breed, of which about 80 % are **caseins** (the rest being whey or serum proteins). Four proteins comprise the casein group and are: α_{s1}-casein, α_{s2}-casein, β-casein and k-casein. The caseins are characterised by the fact that they are **phosphoroproteins** that precipitate at pH 4.6 (isoelectric point, IP), at which pH whey proteins remain soluble. Another property of caseins is their existence as **casein micelles** which are **50–300 nm**. Micelles contain the caseins combined with calcium, phosphate and small amount of citrate. As such, **milk is a colloid** (a mixture of nanoparticles evenly dispersed but only suspended in a liquid medium). The presence of these micelles determines the **white colour of milk** due to their light scattering.

FROM STRUCTURE TO FUNCTION

The fine molecular self-organisation of proteins and minerals in milk is fundamental to realise its natural function of transporting calcium from the mother to the offspring. Numerous studies have revealed that this organisation results in nanostructures which have precise functions (**casein micelles**). The next section describes how this organisation is determined not only by electrostatic interactions but also hydrophobic interactions between the proteins that constitute milk; some minerals associated with the proteins are also described. Without this fine organisation, calcium would not be ‘trapped’ inside the milk micelles and the biological function of milk would not be realised.

MILK PROCESSING

Processing of milk with various treatments is widely used in the dairy industry. For instance, yogurt is a fermented milk product obtained by the controlled growth of specific micro-organisms, mainly bacteria that convert lactose (milk sugar) into lactic acid. By lowering the pH of milk, its consistency and taste change. In cheese-making, enzymes are used to induce the aggregation and precipitation of caseins. As discussed in the next section, in all milkprocessing methods, **the molecular organisation of caseins is altered**, which leads to thickening, precipitation and other effects. The appearance, taste and other ‘macro’ properties of milk are deeply connected to its supra-molecular (nano) structure.

In this experiment, you will use vinegar (a source of acid) and heat to alter the properties of milk.

CASEINS

Casein in milk (which has a pH near to neutral, about 6.7) is negatively charged (IP = 4.6). All caseins, except k-casein, possess the ability to **bind to Ca^{2+} which occurs mainly through their phosphate residues**. The binding of Ca^{2+} is fundamental for milk to fulfil its function (i.e. to transport calcium (and other nutrients) from the mother to the offspring). Each casein is composed of a different peptide sequence and, therefore, has a different secondary and tertiary structure.

CASEIN MICELLES: STRUCTURE AND FUNCTION

Caseins in milk are believed to exist as **casein micelles** of **50–300 nm**. Micelles contain the **caseins combined with calcium, phosphate and small amount of citrate**. The structure of casein micelles (like that of casein itself) is still a matter of debate and intense research. Since all caseins possess a hydrophobic region and a polar region, it is believed that hydrophobic interactions as well as electrostatic interactions play a role in the self-association of caseins to form casein micelles. Casein micelles differ from the polymers of the individual caseins in one crucial aspect: they contain inorganic calcium phosphate, which exists in the form of small microcrystalline inclusions termed **calcium nanoclusters**. The fact that the stability of casein micelles is not due only to electrostatic interaction has been demonstrated by the fact that **casein micelles can be dissociated using urea**, which is an agent that does not rupture the calcium phosphate linkages.

Two types of linkages between caseins in the casein micelles have been postulated.

The first linkage is **hydrophobic**, where two or more hydrophobic regions from different molecules (α-caseins and β-caseins) form a bonded cluster. These are indicated as a **rectangular bar** in **Figure 3**.

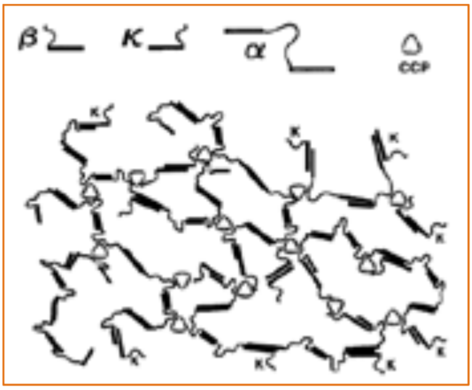


Figure 3: Dual bonding model in casein micelles, with α, β and k-casein depicted as indicated

Image: D. S. Horne, *International Dairy Journal*, 1998, 8(3), 171–177, reprinted with the permission of Elsevier

The second linkage is of **hydrophilic charged regions** containing phosphoserine clusters which bind to colloidal calcium phosphate nanoclusters (indicated as CCP in Figure 3).

The k-caseins do not have the phospheroserine group to link with the calcium nanocluster, therefore their association is only possible through hydrophobic interactions. Furthermore, the micelles cannot grow further beyond the k-caseins, which therefore act as an outer layer in the micelle. The **role of k-caseins is to stabilise the casein micelles**, preventing excessive growth and micellar aggregation which would otherwise lead to precipitation.

CASEIN MICELLE DISSOCIATION AND AGGREGATION

As already discussed, casein micelles are believed to have an intricate structure which is an interplay of hydrophobic and electrostatic interactions. Maintenance of micellar integrity is a balancing act and numerous methods exist to disrupt this balance. These methods are widely used in the dairy industry to make cheese and fermented products such as yogurt etc.

- **Increasing the pH (to about 8)** leads to casein **micelle dissociation**, and the effect is that heated milk becomes more translucent. The reason for this is that increasing the pH from the natural neutral point converts the phosphoseryl groups from singly to doubly charged units which are no longer capable of linking the calcium phosphate nanoclusters. The increased negative charge of the micelles induces electrostatic repulsion, and the micelles dissociate.
- **Decreasing the pH to the isoelectric point (4.6)** induces dissociation of the casein micelles. The reason for this is that calcium micelles only exist because of the presence of calcium phosphate; therefore, its dissolution necessarily causes changes in the stability of the micelles. If an acid (a proton-donor) is added to milk, the phosophoseryl and carboxyl groups in the proteins become protonated, so they are no longer capable of interacting electrostatically with calcium phosphate nanoclusters, and these are released from the micelles. It should be noted that this does not necessarily cause the caseins to dissociate from the micelles. At temperatures below 25 °C, increasing dissociation occurs, but otherwise the caseins remain in the micelles. This effect will be tested in this experiment by adding vinegar (a source of acid) to cold milk. The reason lies in the fact that the stability of casein micelles is not exclusively connected to electrostatic interaction, but also to hydrophobic interactions. The latter are extremely temperature-dependent: hydrophobic interactions are stronger at higher temperatures. **Therefore, hydrophobic interactions maintain the stability of casein micelles in cold milk even when its pH has been lowered to the isoelectric point.** On the other hand, **if acidification occurs after milk has been warmed (to about 60° C), micelles are dissociated (calcium phosphate is released from the micelle) and will aggregate due to increased electrostatic forces and increased hydrophobic interaction**. This will be tested in this exercise by adding vinegar to warm or cold milk.
- **Attack by chymosin leads to micelle precipitation and formation of a curd**. This process is employed in **cheese-making**. Chymosin is an enzyme which is the active ingredient in rennet, the extract of calves' stomachs used in cheese-making. Chymosin specifically attacks a single bond in the k-casein. As already mentioned, the presence of k-caseins is fundamental for the overall stability of the casein micelle; therefore its disruption causes the micelle to lose stability, aggregate and eventually form a curd.
- The controlled addition of **lactic acid bacteria** (bacteria that produce lactic acid, such as *Lactobacillus*, *Lactococcus*, and *Leuconostoc*) under specific processing conditions leads to fermented milk products such as yogurt. This process differs from simple acidification as the milk is heat-treated and whey proteins are also incorporated. The coagulation is induced by the acidification but does not lead to the formation of a curd but to a product which is more viscous than plain milk.

WHAT CAN THIS EXPERIMENT TEACH ABOUT NANOTECHNOLOGY?

Through this exercise, you will learn about two fundamental concepts.

- **Structure means physical properties (colour, odour, etc.)**: materials in the 'real' natural world, such as milk, appear as they do because of the fine nanostructures they possess. Milk is white because it contains colloidal nanoparticles (micelles). If the structure of these micelles is altered, some of the 'macro' properties of milk like **colour** and **odour** will be changed.
- **Structure means function**: natural materials have very specific functions which are dictated by the fine supra-organisation of their molecules (nanostructures). If this structure is altered, a material with a new function can be produced. In cheese production, altering the casein micelles through specific processes (e.g. chymosin treatment or lactic acid bacteria fermentation) leads to different products (cheese, yogurt, etc.). **This is exactly the concept of nanotechnologies**: to engineer new materials with new functions from the manipulation of their molecular organisation.

STUDENT LABORATORY WORKSHEET

Natural Nanomaterials

Student name:.........................

Date:..

AIM:

- Learn about the existence of natural nanomaterials
- Light interaction with colloids
- Gelatin and milk as examples of natural colloids
- Relationship between the ‘macro’ properties (colour, smell, taste, consistency) of milk and its molecular structure
- Understanding of the relationship between molecular structure of milk (nanostructures) and its properties, and how these can be manipulated to obtain different products (cheese, yogurt, etc.)

BEFORE YOU FILL IN THIS WORKSHEET

- Read STUDENT BACKGROUND — EXPERIMENT A: NATURAL NANOMATERIALS
- Ask your teacher any questions you have

MATERIALS

- hotplate
- 2x beaker 50 ml
- 1x beaker 200 ml
- 2x beakers 500 ml
- 0.5 g gelatin powder (Sigma-Aldrich No G1890)
- 1 tablespoon
- 800 ml skimmed milk
- 4 tablespoons white vinegar
- thermometer
- spatula
- latex gloves
- safety glasses

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to MSDS specifications and according to specific school safety rules. Personal protection must be used as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

IMAGES: Images on page 273 were kindly provided by: (A) Christoph Gösselsberger, image is from O. Hekele, C. G. Goesselsbergerand, I. C. Gebeshuber 'Nanodiagnostics performed on human red blood cells with atomic force microscopy', *Materials Science and Technology*, 2008 24(9); (B) AFM image of bacteria cells collected at iNANO, Aarhus University, image courtesy of Park Systems XE-Bio; (C) K. Shekar et al., *Proceedings of the National Academy of Sciences* (USA), 23 May 2006, 103(21):8000-8005, reprinted with the permission of the National Academy of Sciences, USA, © 2006; (D) AFM image of DNA double strands on mica surface, reprinted with the permission of JPK Instruments AG. No further use of these images is allowed without the written approval of the copyright holders.

PROCEDURE

1. Prepare and test gelatin

In this part of the experiment, you will prepare gelatin and test it with a laser pen to confirm its colloidal nature.

STEP 1

- Prepare a 10 mg/ml gelatin sample by mixing 0.5 mg of gelatin powder with 50 ml of cold water. Place on the hotplate and heat the water and gelatin mixture. Stir with the spatula as the mixture heats up. Bring close to boil (check temperature with the thermometer), then turn off the hotplate and let the mixture cool down.

SAFETY NOTE: Do not touch the beaker immediately as it will be very hot. After it has cooled down, remove it from the hotplate and carefully place it on the bench safely. Otherwise use safety gloves.

STEP 2

- Once the gel is formed, test it with a laser pen. Place a piece of white paper on the far side of the beaker. Shine the laser beam through the gelatin sample and record your observations.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! You must wear **safety glasses** when doing this test.

STEP 3

- Repeat the laser test using a beaker of plain water.

Q1: Based on the laser test, is gelatin a colloid? Why?

....

Q2: Based on the laser test, is water a colloid? Why?

2. Milk and its properties

Milk is a natural colloid and you will confirm this as you did with gelatin, using a laser pen (using diluted milk). You will then treat the milk with acid to disrupt its molecular nanostructure and induce aggregation. You should wear safety glasses and gloves during the entire experiment.

STEP 1

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! You must wear **safety glasses** when doing this test.

- Wear safety glasses
- Milk is a natural colloid but, unlike gelatin, it is not transparent. Pour 400 ml of milk into a beaker. Try to test it with a laser pen as you did with gelatin, can you see a path of scattered light?

....

Now dilute the milk. Take 150 ml of distilled water in a beaker or glass, and add 1–2 droplets of milk (using a pipette). Mix and let the solution stand for a couple of minutes (so the air bubbles can dissipate). The solution will look pale grey. Now test it again using the laser pen.

Can you see the path of scattered light?...

Q3: Based on your visual observation, is milk a colloid?

....

Q4: Milk owes its properties to the existence of casein micelles, which are nanostructures of 50–300 nm. Select from the images provided at the end of this worksheet the AFM image that you think corresponds to casein micelles. Paste the image here.

STEP 2

- Use the same beaker containing the milk that you used in STEP 1. With the use of a pH paper, record the pH of skimmed milk (in the table provided).
- Now place the same beaker containing the milk on a hotplate, turn the hotplate on and warm the milk to about 60 °C. If a hotplate is not available, the milk can be heated using water that

has been boiled separately and poured into a water bath container. Your teacher will instruct you on how to warm up the milk.

STEP 3

– To the hot milk (about 60 °C) add two tablespoons of white vinegar stirring well. Remember that the beaker will be hot! What happens? Record your observations in the table provided. Record the **pH of the liquid** (in the table provided).

SAFETY NOTE: You should not taste aggregated acid-milk!

STEP 4

– Repeat the test but without heating the milk. Take a clean beaker and add another sample of 400 ml cold milk. Without heating, add two tablespoons of white vinegar and stir. What happens? Record your observations in the table provided. Record the **pH of the liquid** (in the table provided).

Milk before test: pH ...

	Temperature of milk	Effect of adding vinegar	pH
TEST 1			
TEST 2			

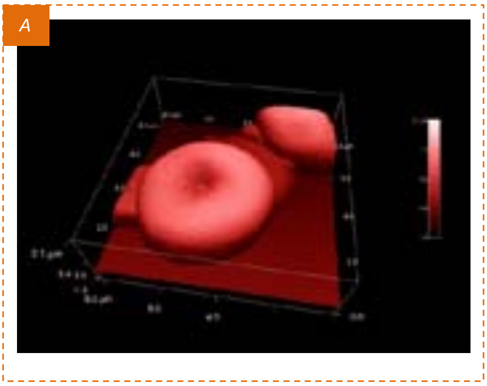
Q5: Was there a clear difference when you added vinegar to warm milk and to cold milk? If yes, describe.

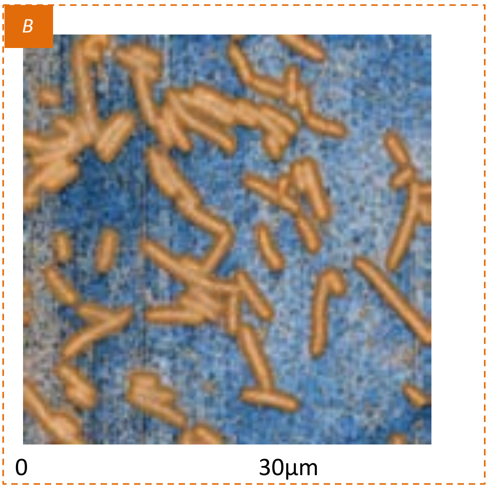
....

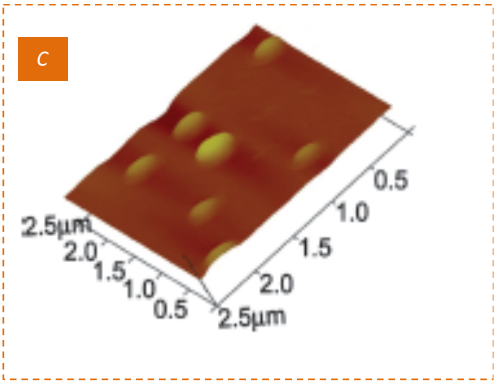
....

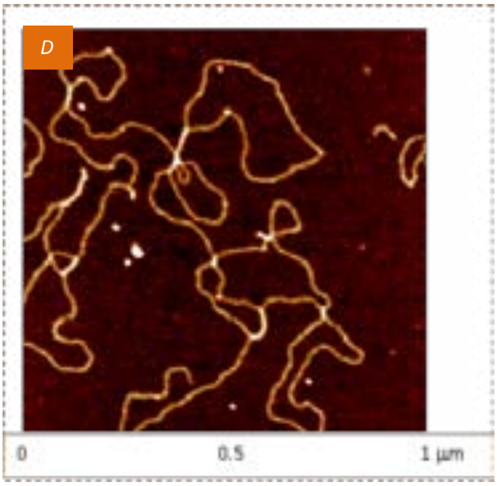
Q6: Based on the results of the test of adding vinegar to warm milk and to cold milk, do you think the reaction that takes place is entirely an acid-base reaction? Explain.

....









Images for question Q4

Cut out the image you think is the right one and paste it in the space provided in Q4.

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EXPERIMENT B:

LIQUID CRYSTALS

MATERIAL INCLUDED IN THIS EXPERIMENT PACKAGE

For teachers:

TEACHER RESOURCES — EXPERIMENT B: LIQUID CRYSTALS

For students:

STUDENT BACKGROUND READING — EXPERIMENT B: LIQUID CRYSTALS

STUDENT SYNTHESIS PROCEDURE — EXPERIMENT B: LIQUID CRYSTALS

STUDENT LABORATORY WORKSHEET — EXPERIMENT B: LIQUID CRYSTALS

LEVEL OF EXPERIMENT: Medium

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to the MSDS specifications and according to specific school safety rules. Personal protection must be taken as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assumes no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

TEACHER RESOURCES

LIQUID CRYSTALS

AIM: Liquid crystals (LCs) are an example of **self-assembled molecules** that are sensitive to external factors, such as temperature, and that change their assembly as a consequence of these variations. The effect in some types of liquid crystals is a change of colour. This experiment will show students two fundamental concepts: (a) that the way a material behaves at the macroscale depends on its structure at the nanoscale; and (b) that the nanoscale, liquid crystals are self-assembled molecules that organise themselves into nanostructures which have specific optical properties.

FIELD OF NANOTECHNOLOGY APPLICATION: Fundamental concepts in nanoscience

EXTRA TEACHER READING: Module 1, Chapter 5: Overview of nanomaterials, in the NANOYOU Teachers Training Kit in Nanotechnologies

REQUIRED STUDENT PRE-KNOWLEDGE:

- Electromagnetic radiation, colour and absorbance
- Concept of self-assembly
- Concept of chirality

STUDENT READING:

- NANOYOU Student Background Reading — Experiment B: Liquid crystals

EXPECTED OUTCOMES:

- Understanding of concept of self-assembly
- Understanding that the way a material behaves at the macroscale is affected by its structure at the nanoscale
- Learning about liquid crystals and how they work
- Testing a real thermotropic liquid crystal and see how its colour changes with temperature
- Creating a liquid crystal thermometer

STUDENT ASSESSMENT:

- NANOYOU Student Laboratory Worksheet — Experiment B: Liquid crystals

BACKGROUND INFORMATION

Self-assembly

The concept of self-assembly derives from observations that, in natural biological processes, molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of membrane cells from phospholipids. In self-assembly, sub-units spontaneously organise and aggregate into stable, well-defined structures through non-covalent interaction. This process is guided by information coded into the characteristics of the sub-units and the final structure is reached by equilibrating to the lowest free energy state. An external factor, such as a change in temperature or a change in pH, can disrupt this organisation. For example, a protein self-assembles in a specific structure but, if exposed to conditions such as high heat or high acidity, it can denature, which means that its structure is damaged, and the protein unfolds. This means that the protein loses its function as its structure is damaged. So, in nature, self-organised structures have specific functions.

Molecules in nature change conformation and move from one self-organised structure into another as they bind to certain ions or atoms. Many examples can be given, such as haemoglobin (which captures and releases an iron ion), or the potassium-sodium pump, chlorophyll, etc.

In this experiment, students will see an example of a self-assembled macromolecule, a liquid crystal. Liquid crystals have properties that are directly connected to the way their long molecules self-assemble into nanostructures. Although these nanostructures cannot be seen with the naked eye, macroscale changes in the optical properties (colour) of the liquid crystal as its temperature is changed can be seen. When the temperature of a liquid crystal changes, its molecules self-assemble into a different nanostructure: this influences the way light is reflected by the liquid crystal, and so that a different colour is observed. **Therefore, this colour change is a direct consequence of a change in the self-organisation of the liquid crystal molecules.**

What is a liquid crystal?

A liquid crystal is a fourth state of matter: it has properties between those of a conventional liquid and those of a solid crystal. Liquid crystals are partly ordered materials, somewhere between their solid and liquid phases. This means that liquid crystals combine the fluidity of ordinary liquids with the interesting electrical and optical properties of crystalline solids.

Liquid crystals are temperature-sensitive since they turn to solid if it is too cold and to liquid if it is too hot. This phenomenon can, for example, be observed on laptop screens when it is very hot or very cold.

The molecules in a liquid crystal are often shaped like rods or plates or some other forms that encourage them to **align collectively along a certain direction** (**Figure 1**).

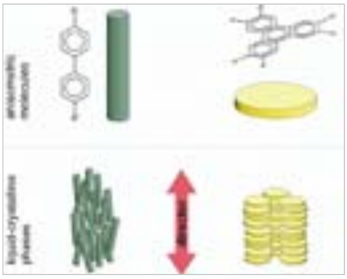

Figure 1: Examples of the self-organisation of anisometric (i.e. with asymmetrical parts) molecules in liquid-crystalline phases: (left) rod-like molecules form a nematic liquid, in which the longitudinal axes of the molecules are aligned parallel to a common preferred direction (director); (right) disc-like (discotic) molecules arrangedinto molecule-stacks (columns), in which the longitudinal axes are also aligned parallel to the director. As a result of their orientational order, liquid crystals exhibit anisotropic physical properties, just like crystals.

Image: http://www.ipc.uni-stuttgart.de/~giesselm/AG_Giesselmann/Forschung/Fluessigkristalle/Fluessigkristalle.html

A liquid crystal is formed by the self-assembly of molecules into ordered structures, called phases.

An external disturbance, such as a change in temperature or magnetic field, even very small, can induce the liquid crystals to assume a different phase. The molecules in liquid crystal displays, for instance, are reoriented by relatively weak electrical fields. Different phases can be distinguished by their different optical properties (**Figure 2**).

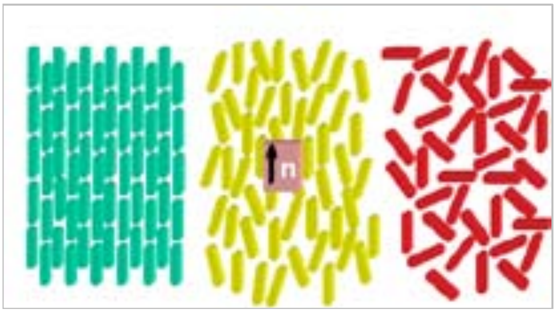

Figure 2: Schematic representation of molecules in a solid (left, molecules are well organised); in a liquid crystal (centre) molecules have a long range distance order); and in a liquid (right) molecules are not ordered

Image: © IPSE Educational Resources, University of Wisconsin-Madison

Liquid crystals (LCs) are divided into three groups:

- **thermotropic liquid crystals** consist of organic molecules, typically having coupled double bonds, and exhibit a phase transition as temperature is changed (**Figure 3, left**),
- **lyotropic liquid crystals** consist of organic molecules, typically hydrophilic (water-loving) and exhibit a phase transition as a function of both temperature and concentration of the liquid crystal molecules in a solvent (typically water) (**Figure 3, right**),
- **metallotropic liquid crystals** are composed of both organic and inorganic molecules, and their liquid crystal transition depends not only on temperature and concentration but also on the organic-inorganic composition ratio.

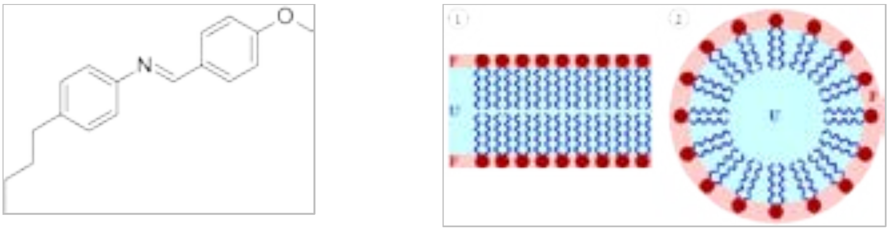

Figure 3: (left) Chemical structure of N-(4-methoxybenzylidene)-4-butylaniline (MBBA); (right) structure of lyotropic liquid crystal: (1) is a bilayer and (2) is a micelle (the red heads of the surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue).

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

Lyotropic liquid-crystalline phases are **abundant in living systems**, such as biological membranes, cell membranes, many proteins (e.g. the protein solution extruded by a spider to generate silk), as well as tobacco mosaic virus. Soap is another well-known material which is in fact a lyotropic liquid crystal. The thickness of the soap bubbles determines the colours of light they reflect.

In this experiment, students will study the properties of a **thermotropic liquid crysta**l meaning that its properties change with changes in temperature.

Liquid crystals that change colour when temperature is changed

Liquid crystal phases that respond to certain temperature ranges are called **thermotropic liquid crystals**. Many thermotropic liquid crystals exhibit a variety of phases as temperature is changed, as illustrated in **Figure 4**. The ordering inside a thermotropic liquid crystal exists in a specific temperature range. At high temperatures, the thermal motion will destroy the delicate cooperative ordering of the liquid crystal phase, pushing the material into a conventional isotropic liquid phase. At too low a temperature, most liquid crystal materials will form a conventional (though anisotropic) crystal. These intermediate phases have some level of order, which is progressively lost as the temperature rises. In the smectic phases, which are found at lower temperatures than the nematic, molecules form well-defined layers that can slide over one another. The smectics are thus positionally ordered in one direction. In the nematic phase, molecules have no positional order but they have long-range orientational order. This means that the molecules move quite randomly but they all point in the same direction (within each domain).

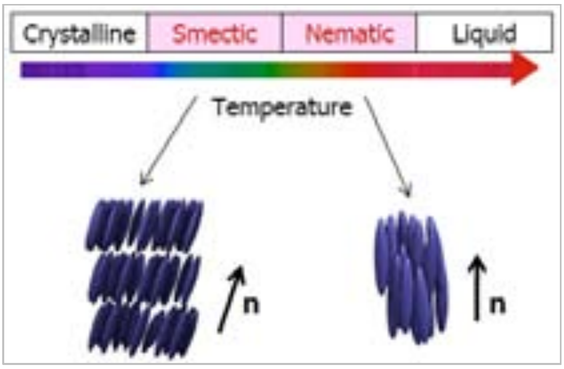

Figure 4: Schematic representation of the structure transition of a thermotropic LC from the smectic to the nematic phase as the temperature is increased

Image: Own work adapted from Wiki Commons, Creative Commons Attribution ShareAlike 3.0 and IPSE Educational Resources 'Liquid crystals', University of Wisconsin-Madison

What is important to note is that some specific structural and optical properties are associated with each liquid crystal phase: **as the temperature is changed, the colour of the liquid crystal changes**. Thus, changing the temperature of the material allows the material to move from one phase to the other, so that the material exhibits these different colours. This type of liquid crystal is used in thermometers and in miniaturised temperature sensors (e.g. to locate short circuits on circuit boards).

A particular type of liquid crystal phase is the **chiral nematic phase**. The chiral nematic phase exhibits chirality (handedness). This phase is often called the **cholesteric phase** because it was first observed in cholesterol derivatives. In this experiment, students will analyse this type of liquid crystal (**Figure 5**).

Only **chiral molecules** (i.e. those that lack inversion symmetry) can give rise to such a phase. In this phase, the molecules are **stacked in rotating layers, like a spiral staircase (helix)**. On each 'step' of the staircase, the molecules are arranged in a specific order, but there is a finite angle between each 'step' and the next (**Figure 6**).

Figure 5: Schematic representation of ordering in chiral liquid crystal phases: a chiral nematic phase (also called the cholesteric phase) in a liquid crystal

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

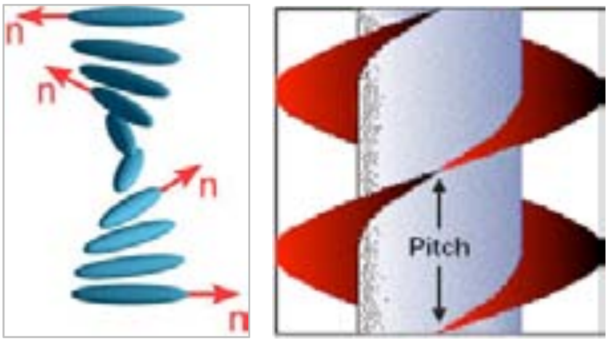

Figure 6: (left) Schematic representations of stacked rotating layers in a chiral liquid crystal forming a 'spiral staircase' having a pitch p; (right) schematic representation of the pitch in a chiral liquid crystal

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

The **chiral pitch**, p, refers to the distance over which the liquid crystal molecules undergo a full 360° twist. As the temperature of the liquid crystal changes, the pitch changes, which leads to tighter or looser helixes.

What gives the colour to the liquid crystal?

When light strikes a liquid crystal, some of the light is reflected. **What is seen is the reflected light**. The colour (i.e. the wavelength) of the reflected light depends on how tightly the helix is twisted. If the pitch in the liquid crystal is of the same order as the **wavelength of visible light (400–700 nm)**, then interesting optical interference effects can be observed. The colour of the light reflected depends on the pitch in the liquid crystal (i.e. **how tightly the helix is twisted**). When the helix is tightly twisted, the pitch is smaller, so it reflects smaller wavelengths (blue end of the spectrum); when the liquid crystal is less twisted, it has a larger pitch, so it reflects larger wavelengths (red end of the spectrum).

An increase in temperature leads to a decrease in the pitch. By increasing the temperature of the liquid crystal, a colour change should be expected from the red end of the spectrum to the blue end of the spectrum, so from orange, to yellow, green, blue and violet (**Figure 7**).

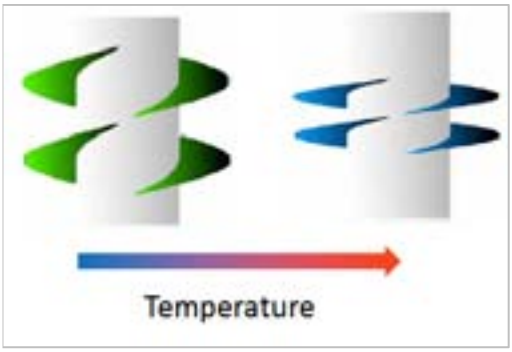

Figure 7: Representation of a change in pitch in a chiral liquid crystal as the temperature is changed

Image: adapted from IPSE Educational Resources 'Liquid crystals', University of Wisconsin-Madison

The chiral twisting that occurs in chiral liquid crystal phases also makes the system respond differently in right and left-handed circularly polarised light. These materials can thus be used as polarisation filters.

WHAT CAN THIS EXPERIMENT TEACH ABOUT NANOTECHNOLOGY?

The properties of materials at the macroscale are affected by the structure of the material at the nanoscale. Changes in a material's molecular structures are often too small to see directly, but sometimes changes can be seen in the properties of the material. Liquid crystals are an excellent example, in particular the type used in this experiment, since their optical properties (colour) change visibly as the temperature of the liquid crystal is changed. In nanotechnology, scientists take advantage of the peculiar properties of materials at the nanoscale to engineer new materials and devices.

Liquid crystals are **an example of self-assembled molecules which change their spatial organisation depending on external factors** such as temperature. Self-assembly is another fundamental concept in nanoscience.

THIS EXPERIMENT IN CLASS

1. Start with a discussion on self-assembly. What other molecules self-assemble in organised structures? (e.g. proteins, DNA). Discuss how the structure is fundamental for the function of the macromolecule.
2. Talk about the fact that the way a material behaves at the macroscale is affected by its nanostructure. Although this cannot be seen with our eyes, changes in the material properties, such as its colour, can be seen. Liquid crystals are such an example: they are self-assembled molecules which have specific properties, such as colour, depending on the structure they have.
3. Liquid crystals that change colour with temperature. Discuss how they work. Give examples (small flat thermometers, sensors, etc.).
4. Run the experiment in the lab (details below) dividing students into groups of two or more as required.

OVERVIEW OF SAMPLES TO BE PREPARED

Table 1 indicates the quantities of materials needed to make four samples of liquid crystals each sensitive to a different temperature interval. Depending on the class level, students can synthesise four different liquid crystal mixtures, or the instructor could prepare them in advance for the class.

NB: Synthesis is very quick and takes little time, but it requires weighing three different solids four times, which might be time-consuming. The class could be divided in two, with each half making only two mixtures, and then ask the students to swap the vials. **Each vial will have enough material for up to 4–6 students (2–3 pairs).**

Table 1:

Liquid crystal	Cholesteryl oleyl carbonate	Cholesteryl pelargonate	Cholesteryl benzoate	Temperature (°C)
Type 1	0.65	0.25	0.10	17–23
Type 2	0.45	0.45	0.10	26.5–30.5
Type 3	0.40	0.50	0.10	32–35
Type 4	0.30	0.60	0.10	37–40

MATERIALS

The following is an indication of the materials needed for each pair of students.

- cholesteryl oleyl carbonate (Sigma-Aldrich No 151157, 25 g costs about EUR 60), see table for quantity
- cholesteryl pelargonate (Sigma-Aldrich No C78801, 100 g costs about EUR 115), see table for quantity
- cholesteryl benzoate (Sigma-Aldrich No C75802, 25 g costs about EUR 40), see table for quantity
- 4x 10 ml glass vials
- plastic funnel
- hotplate (no stirring needed) or a heat gun or hairdryer
- paper to clean
- balance (if possible with 0.01 g resolution)
- plastic vessels (for measuring solids on the balance)
- 1 glass Pasteur
- safety glasses
- latex gloves
- spatula

SAFETY NOTE: Follow school laboratory safety guidelines. Before using any materials, read the MSDS sheetscarefully. Use these materials with normal chemical precautions according to the MSDSs. Wear eye protection and gloves. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling any chemicals. After preparing the liquid crystals, keep in a closed glass vial and do not open and inhale. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

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PROCEDURE

1. Synthesis of four different liquid crystal mixtures

- Measure the weights of solids needed using a scale and three different plastic vessels.

  NB: Clean the spatula well between measurements using some paper!

- Mix the three solids in the large glass vial using a plastic funnel.

  TIP: Secure the funnel on the mouth of the glass vial with clear wrapping tape to make sure the funnel stays in place when the students add the solids.

  Note that the solids (particularly cholesteryl oleyl carbonate) are quite sticky so be sure to gently push the solids down the funnel and remove as much solid as possible from the funnel walls. If a lot of solid remains on the spatula or funnel walls, keep both of these in place as you heat the glass vial, so the solid can melt and is not lost.

- Heat the glass vial using a hotplate or a heat gun. The hotplate should be set at 185 °C. If neither of these heat sources are available, use a hairdryer at the higher temperature and flow. It might take a while to induce melting. Be patient! **Finally, the liquid crystal should look transparent and have the consistency of honey.**

  WARNING: Caution is needed when using a hotplate or heat gun. These should be operated only in the presence of a teacher. The mouth of a heat gun can become very hot, so do not touch it, do not touch the vial as it is heating up, and do not touch it immediately after the heat gun has been turned off. Wait a few minutes before doing so, and always wear gloves.

- While the sample is still liquid, gently move the vial around at an angle (see image) so that the liquid crystal spreads around the vial walls.
- **Clearly mark the vial** with a number corresponding to the type of liquid crystal you have made ('1' for Type 1 etc.).
- Students should observe the **colour change as the liquid cools down**.

Prepare (or let the students do so) the four different vials and then let the students test them!

Students should follow the instructions in the Student Laboratory Worksheet — Experiment B: Liquid crystals

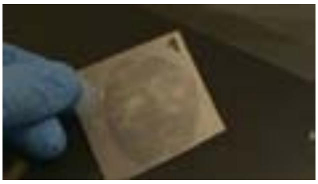
2. Preparation of four liquid crystal sheets and testing in a water bath

MATERIALS

The following is an indication of the materials needed for each pair of students.

- four vials of liquid crystal mixture, each containing a different mixture
- water bath (hotplate, Pyrex glass water container half-filled with water, thermometer)
- sheet of clear contact paper
- clothes peg
- spatula
- pair of scissors
- A4 sheet of black cardboard
- A4 size sheet of foam
- paper cutter
- gloves
- safety glasses
- tissue paper
- room thermometer

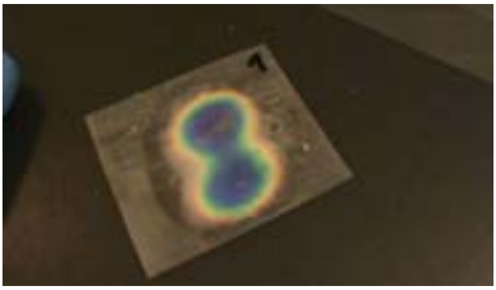
Prepare four different crystal liquid sheets: Cut two pieces of transparent contact paper (about 10 x 10 cm), peel off the backing paper and place on the laboratory bench. With a spatula, place some liquid crystal type 1 in the centre of the sheet. If the liquid crystal is very cold and has turned solid, heat the vial first with a hairdryer (it should be



the consistency of honey). Two to three spatulas of material will be needed. Place the second piece of contact paper on top of the first, so that the two sticky parts attach to each other. Gently press the centre where the liquid crystal is to distribute it evenly. A thin layer of liquid crystal about 4 x 4 cm is needed. Do not press too hard or the material will come out from the edges. Cut the sheet at the end around the edges. With a permanent marker, mark the number corresponding to the type of liquid crystal (‘1’ for Type 1 etc.) in the corner of the sheet.

Students should complete Q1 and Q2 of the student laboratory worksheet

- **Test the liquid crystal sheets with your fingers.** Place the four liquid crystal sheets you have just made on a piece of **white A4 paper**. Wait few seconds ... What do you see? Now press against each of the liquid crystal sheets with a finger (wear gloves). Repeat the experiment putting the sheets on the **black A4 cardboard**. In order to compare the different sheets, the finger should be kept on each sheet for the same time. Students should record their observations.



Students should complete Q3 and Q4 of the student laboratory worksheet

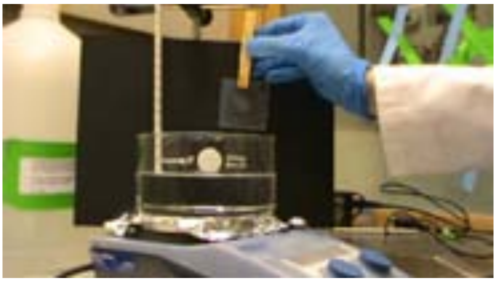
- **Test each liquid crystal sheet in a water bath**: The temperature of the water bath should initially be 15 °C, and then gradually increased to reach the working temperature of each liquid crystal mixture.

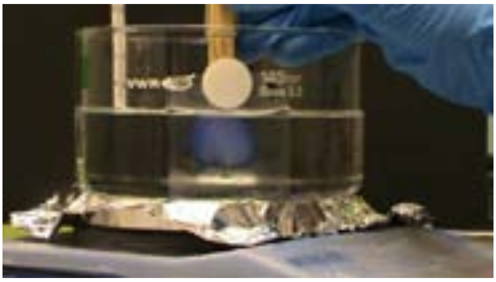
Liquid crystal	Water temperature range (°C)
Type 1	15–23
Type 2	23–30
Type 3	30–35
Type 4	35–40

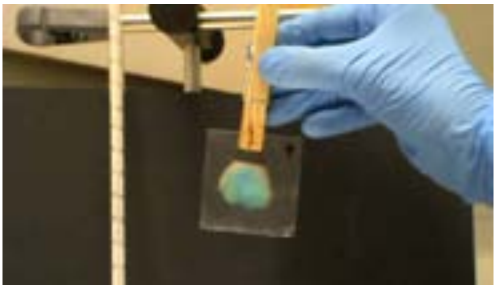
Students should **observe the colour change of each liquid crystal as the water temperature increases** (it is best to test the samples one at the time, so students can monitor closely what happens in each sample).

To help see the effect, place a black A4 card safely at the back of the water bath.

NB: it should not touch the hotplate!







Students should complete Q5 to Q12 of the student laboratory worksheet as they test the different sheets of liquid crystals

- To confirm the sensitivity of the liquid crystals to temperature, students should test sheet 1 (Type 1) at higher temperatures and/or sheets 2 to 4 at lower temperatures (compared to their working temperature).
- When finished, the water bath should be turned off.
- Use **Video 1** if the experiment cannot be performed in class, or as an additional class tool.

3. Fabrication of a liquid crystal room thermometer

Now, prepare a **liquid crystal room thermometer**. Use the liquid crystal sheets made in the previous part of the experiment (make new ones if necessary).

SAFETY NOTE: Wear gloves as you or the students make the thermometer. Be careful not to squeeze the liquid crystal sheets and push the liquid crystal outside the sheet. If this happens, clean up immediately with paper towel.

NB: The material listed above will make one thermometer. The teacher can choose to ask each pair of students to make a thermometer, or make just one per class.

- Write on the white foam the word NANO. You will need to 'fill' each letter with one liquid crystal sheet, so make sure the single letters are large enough (see picture).

- With a paper cutter, cut the four letters from the foam board.
- Attach a different liquid crystal sheet to the back of each letter, following this order:

N — Type 1; A — Type 2; N — Type 3; O — Type 4

- Secure each letter one at a time using long strips of clear contact paper or use transparent tape. Make sure that the liquid crystal sheets do not overlap inside the letters. **The idea is that each letter should contain only one liquid crystal sheet**.
- Once all the liquid crystals sheets are attached, attach the white foam to the black cardboard (placing the side where the liquid crystal sheets are against the cardboard).
- **Now you have a room thermometer!**
- If no colours are displayed, then the room is at less than 17 °C. If there is a radiator in the room, place the thermometer over it ... and see what happens!
- Another test, if the room is too cool to get a response from the thermometer, is to place it over a working laptop computer ... it will show what we all know, that laptops generate heat!
- You can use the thermometer throughout the year: when is hot, take it outside in the sun, or place it on the classroom window.

ANSWERS TO QUESTIONS

Q1 and **Q2**: Depending on the temperature of the room, answers will be different. If the room is 18–20 °C, the sample Type 1 should be able to detect the room temperature (and thus be coloured even without touching it). If the room is below 17 °C, none can be used (they are all clear at room temperature).

Q3: The colour seen is a consequence of reflected light: therefore, a black background is needed to see it. This is why in order to see the colours, students need to place the sample on a piece of black paper.

Q4: In order to display some colour, each liquid crystal sheet tested must be touched by an object that has a temperature in its working temperature range. Hands are no more than 36 °C, so Type 3 and Type 4 liquid crystals will not show any colour. If the sheet is rubbed (rather than just pressed with the finger) enough heat may be generated to warm it to the working temperature, and hence show a colour. But, most likely this will still not be enough for Type 4.

Q5: Sheet 1 (Type 1) liquid crystal will start to display some colour around 17 °C. Since the reading of the thermometer is subject to error, and the temperature of the sheet will most likely not be identical to that of the water bath, the colour might appear few degrees before or after 17 °C. If this is reported by the students, it should be critically discussed.

Q6: All liquid crystal sheets will display a colour gradient throughout their working temperature window which is directly related to the wavelength scale of visible radiation. The colour gradient will be from the red end of the spectrum to the blue end of the spectrum (as temperature increases). This is because the colour of the light reflected depends on the pitch in the liquid crystal (i.e. how tightly the helix is twisted). When the helix is tightly twisted, the pitch is smaller, so it reflects smaller wavelengths (blue end of the spectrum); when the liquid crystal is less twisted, it has a larger pitch, so it reflects larger wavelengths (red end of the spectrum). An increase in temperature leads to a decrease in the pitch so, on increasing the temperature of the liquid crystal, a colour change from the red end of the spectrum to the blue end of the spectrum should be expected, from orange, to yellow, green, blue and violet.

Q7: When the crystal liquid sheet Type 1 is removed from the water bath, it gradually changes colour. If the room where the experiment is being performed has a temperature less than 17 °C, it will gradually become transparent.

Q8: The temperature of the water bath is around 17 °C.

Q9: No, because 30 °C is outside the Type 1 working temperature (which is 17–23 °C).

Q10: Yes, it is the same for the reasons explained in the answer to Q6.

Q11: Sheet 3 and Sheet 4 are sensitive to higher temperatures than Sheet 1. When they are taken out of the water bath, they lose their colour very quickly because the room temperature is totally out of their working temperature range. On the other hand, Sheet 1 has a working temperature range which includes room temperature (normally room temperature is around 18 °C), so Sheet 1 will be much slower to lose its colour and will possibly retain some colour (if RT is between 17 and 23 °C).

Q12: Type 4, because it has a working temperature range equal to the fever range (37–40 °C).

Q13: If no colour appears on the first 'N' it means that the room is at a temperature lower than 17 °C.

CREDIT: This experiment was adapted from the activity 'Preparation of Cholesteryl Ester Liquid Crystals' (http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/index.htm) and the 'Exploring materials: Crystal Liquids' activity developed by the NISE (Nanoscale Informal Science Education) Network (Creative Commons Attribution ShareAlike 3.0) (http://www.nisenet.org). The activity was developed for the NISE Network with funding from the National Science Foundation under Cooperative Agreement #ESI-0532536. Any opinions, findings, conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Foundation.

REFERENCES

Kato, T., 'Liquid crystals: self-assembled soft materials', *Current Opinion in Solid State and Materials Science*, 2002, Vol. 6, p. 513.

Liquid crystal (http://en.wikipedia.org/wiki/Liquid_crystal).

Whitesides, G. M., 'Self-assembly at all scales', *Science* 2002, Vol. 295, pp. 2418–21.

STUDENT BACKGROUND READING

LIQUID CRYSTALS

Liquid crystals (LCs) are an example of **self-assembled molecules** that are sensitive to external factors, such as temperature, and that change their assembly as a consequence of variations in these factors. In this experiment you will see how some **liquid crystals change colour as their temperature is changed**. You will learn two **fundamental concepts of nanoscience**: (a) that the way a material behaves at the macroscale depends on its structure at the nanoscale; and (2) that liquid crystals are self-assembled molecules that organise themselves into nanostructures which have specific optical properties. These can be employed for making numerous 'macro' objects such as displays and thermometers.

In this experiment you will:

- prepare different mixtures of liquid crystals that are sensitive to different temperature windows,
- create a number of liquid crystal sheets and test them in various water baths,
- make a liquid crystal thermometer.

This document provides the background information for this laboratory exercise.

What is a liquid crystal?

You have probably learned that there are three states of matter: gas, liquid and solid. A liquid crystal is a fourth state of matter: it has properties between those of a liquid and of a solid. The molecules in a liquid crystal can move independently, as in a liquid, but remain a bit organised, as in a crystal (solid).

Liquid crystals are **partly ordered materials**, somewhere between their solid and liquid phases (**Figure 1**). This means that liquid crystals combine the fluidity of ordinary liquids with the interesting electrical and optical properties of **crystalline solids**.

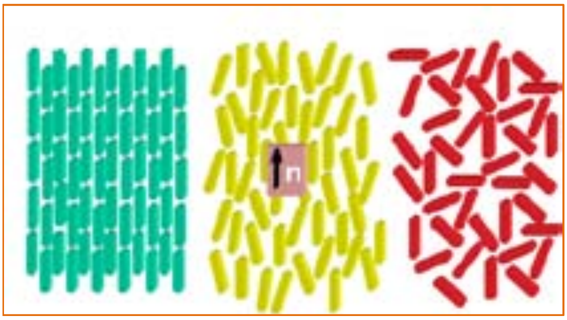


Figure 1: Schematic representation of molecules in a solid (left), molecules are well organised; in a liquid crystal (centre), molecules have a long range distance order; and in a liquid (right) molecules are not ordered

Image: © IPSE Educational Resources, University of Wisconsin-Madison

The order of liquid crystals can be manipulated with mechanical, magnetic or electric forces. What is interesting is that this change of order can be obtained with **very small variations of these forces**. The molecules in liquid crystal displays, for example, are reoriented by relatively weak electrical fields.

Liquid crystals are **temperature-sensitive** since they turn to solid if it is too cold and to liquid if it is too hot. This phenomenon can, for example, be observed on laptop screens when it is very hot or very cold.

A liquid crystal is an example of a self-assembled nanostructure

Liquid crystals are made of molecules that have the shape of rods or plates or some other forms that encourage them to **align collectively** along a certain direction. They assume a **self-assembled** (or self-organised) structure. This process is guided by information that is coded into the characteristics of the molecules and the final structure is reached by equilibrating to the form of the lowest free energy. The concept of self-assembly is the basis of natural biological processes, where molecules self-assemble to create complex structures with nanoscale precision. Examples are the formation of the DNA double helix or the formation of the membrane cell from phospholipids.

A **liquid crystal is formed by the self-assembly of molecules into ordered structures**, or phases. An external disturbance, such as a change in temperature or magnetic field, even very small, can induce the liquid crystal to assemble in a different way and assume a different phase. Different phases can be distinguished by their **different optical properties**.

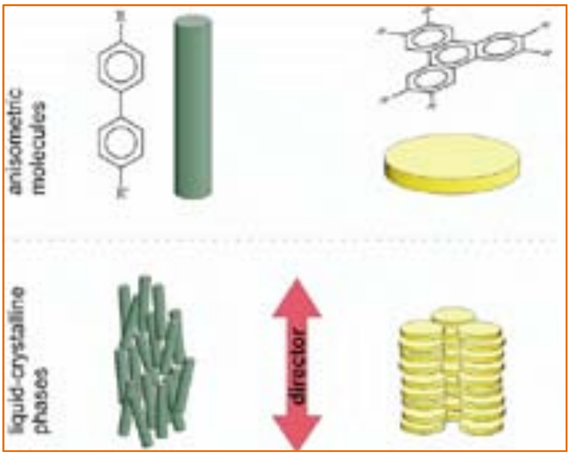


Figure 2: Examples of the self-organisation of anisometric (i.e. with asymmetrical parts) molecules in liquid-crystalline phases: (left) rod-like molecules form a nematic liquid, in which the longitudinal axes of the molecules are aligned parallel to a common preferred direction (director); (right) disc-like (discotic) molecules arrangedinto molecule-stacks (columns), in which the longitudinal axes are also aligned parallel to the director. As a result of their orientational order, liquid crystals exhibit anisotropic physical properties, just like crystals.

Image: http://www.ipc.uni-stuttgart.de/~giesselm/AG_Giesselmann/Forschung/Fluessigkristalle/Fluessigkristalle.html

Are there any natural liquid crystals?

Yes! Some forms of liquid crystals are **abundant in living systems**, such as biological membranes, cell membranes, many proteins (e.g. the protein solution extruded by a spider to generate silk), as well as the tobacco mosaic virus. Soap is another well-known material, which is in fact a lyotropic liquid crystal. The thickness of soap bubbles determines the colours of light they reflect.

Thermotropic liquid crystals

In this experiment, you will study and test the properties of a **thermotropic liquid crysta**l. This type of liquid crystal responds to changes in temperature by changing its colour. As the temperature increases, the colour of the liquid crystal changes from orange, to yellow, green, blue and purple. The change in colour is a direct consequence of the change of the molecular organisation of the liquid crystal as the temperature is increased.

How does this work? Liquid crystals are made of molecules that are shaped like rods or plates which tend to align collectively along a certain direction and assume a somewhat **ordered molecular structure**, called a phase. The type of liquid crystal that you will study here is made of long molecules that tend to organise in rotating layers, like a spiral staircase (a helix). This phase is a chiral phase because the overall structure lacks inversion symmetry. This phase is often called the **cholesteric phase** because it was first observed in cholesterol derivatives (**Figure 3**).

Figure 3: Schematic representation of ordering in chiral liquid crystal phases: a chiral nematic phase (also called the cholesteric phase) in a liquid crystal

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

On each 'step' of the staircase, the molecules are arranged in a specific order, but there is a finite angle between each 'step' and the next (**Figure 4**).

The chiral **pitch**, p, refers to the distance over which the liquid crystal molecules undergo a full 360° twist. As the temperature of the liquid crystal changes, so the pitch changes, which leads to more tightly or more loosely twisted helixes.

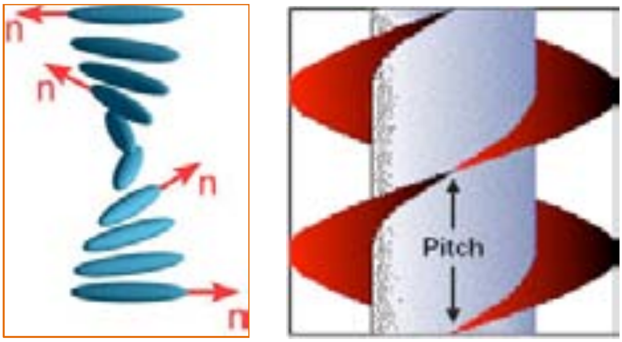


Figure 4: (left) Schematic representations of stacked rotating layers in a chiral liquid crystal forming a 'spiral staircase' having a pitch p; (right) schematic representation of the pitch in a chiral liquid crystal

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

How is this related to the colour change?

When light strikes a liquid crystal, some of the light is reflected. **What we see is the reflected light**. The colour (i.e. the wavelength) of the reflected light depends on how tightly the helix is twisted.

If the pitch in the liquid crystal is of the same order as the **wavelength of visible light (400–700 nm)**, then interesting optical interference effects can be observed. The colour of the light reflected depends on the pitch in the liquid crystal (i.e. **how tightly the helix is twisted**). When the helix is tightly twisted, the pitch is smaller, so it reflects smaller wavelengths (blue end of the spectrum); when the liquid crystal is less twisted, it has a larger pitch, so it reflects larger wavelengths (red end of the spectrum).

An increase in temperature leads to a decrease in the pitch; therefore, by increasing the temperature of the liquid crystal, one should expect a colour change from the red end of the spectrum to the blue end of the spectrum, so from orange to yellow, green, blue and violet (**Figure 5**).

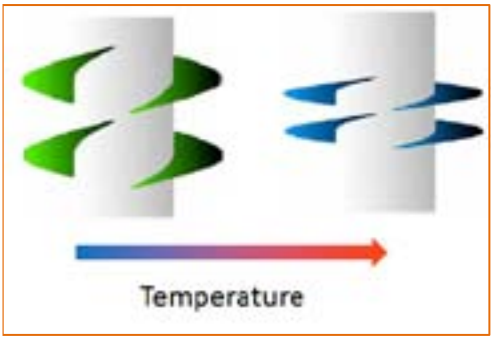


Figure 5: Representation of a change in pitch in a chiral liquid crystal as the temperature is changed

Image: adapted from IPSE Educational Resources 'Liquid crystals', University of Wisconsin-Madison

HOW IS THIS 'NANO'?

The properties of materials at the macroscale are affected by the structure of the material at the nanoscale. Changes in a material's molecular structures are often too small to see directly with our eyes, but sometimes we can see changes in the material's properties. Liquid crystals are an excellent example, in particular the type used in this experiment, since their optical properties (colour) change visibly as the temperature of the liquid crystal is changed. In nanotechnology, scientists take advantage of the peculiar properties of materials at the nanoscale to engineer new materials and devices.

Liquid crystals are an example of self-assembled molecules which change their spatial organisation depending on external factors such as temperature. Self-assembly is another fundamental concept in nanoscience.

Applications of liquid crystals

The chiral twisting that occurs in chiral liquid crystal phases also makes the system respond differently in right- and left-handed circularly polarised light. These materials can thus be used as polarisation filters. Liquid crystals are routinely used in displays for mobile phones, cameras, laptop computers and other electronics. In these displays, an electric field changes the orientation of the molecules in the liquid crystal, and affects the polarisation of light passing through them.

Because of their sensitivity to temperature, and their colour-changing property, they are also used in thermometers. In miniaturised sensors, liquid crystals can detect certain chemicals, electric fields and changes in temperature.

Researchers are now investigating the addition of nanoparticles to liquid crystals to induce new electrical and optical properties in the liquid crystal, for applications in photovoltaics, optical waveguides, light-emitting diodes and sensors.

In this experiment, **you will make a room thermometer** which you can use in class throughout the year to check the temperature of your classroom, or the temperature outside!

STUDENT SYNTHESIS PROCEDURE

LIQUID CRYSTALS

The synthesis procedure for EXPERIMENT B: Liquid crystals included in the Experiment Module of the NANOYOU Teachers Training Kit in Nanotechnologies for students aged 14–18 now follows.

SAFETY NOTE: Follow school laboratory safety guidelines. The chemicals used in this experiment must be used according to the MSDS specifications. Personal protection must be used as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

MATERIALS

- cholesteryl oleyl carbonate (Sigma-Aldrich No 151157), see table for quantity
- cholesteryl pelargonate (Sigma-Aldrich No C78801), see table for quantity
- cholesteryl benzoate (Sigma-Aldrich No C75802), see table for quantity
- 4x 10 ml glass vials
- plastic funnel
- hotplate (no stirrer needed) or a heat gun or hairdryer
- paper for cleaning
- balance (if possible with 0.01 g resolution)
- plastic vessels (for measuring solids on the balance)
- safety glasses
- latex gloves
- spatula

The following table indicates the quantities of materials needed to make four **different mixtures of liquid crystals**.

Liquid crystal	Cholesteryl oleyl carbonate	Cholesteryl pelargonate	Cholesteryl benzoate	Temperature (°C)
Type 1	0.65	0.25	0.10	17–23
Type 2	0.45	0.45	0.10	26.5–30.5
Type 3	0.40	0.50	0.10	32–35
Type 4	0.30	0.60	0.10	37–40

SPECIFIC PRECAUTIONS

Before using any materials, read the MSDS sheets carefully. Use these materials with the normal chemical precautions according to the MSDSs. Use appropriate clothing protection and, gloves and eye protection. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. After preparing the liquid crystals, keep in a closed glass vial and do not open or inhale.

PROCEDURE

- Measure the amounts of the **three solids** that are needed using a scale and three different plastic vessels. **NB:** Clean the spatula well between measurements using some paper!
- Mix the three solids in the glass vials using a plastic funnel. Note that the solids (particularly cholesteryl oleyl carbonate) are quite sticky, so be sure to gently push the solids down the funnel and remove as much of the solid as possible removed from the funnel walls. If a lot of solid remains on the spatula or funnel walls, keep both in place as you heat up the glass vial, so it melts and you don't lose it.
- Heat the glass vial using a hotplate or a heat gun. The hotplate should be set at 185 °C. If you don't have either of these, use a hairdryer set at the highest temperature and highest flow. It might take a while to melt the solids. Be patient! **Finally, the liquid crystal should look transparent and have the consistency of honey.**

  WARNING: Caution should be taken when using a hotplate or heat gun. These should be operated only in the presence of a teacher. The mouth of a heat gun can become very hot, so do not touch it, do not touch the vial as you heat it, and do not touch it immediately after you have turned the heat gun off. Wait a few minutes before doing so, and always wear gloves.

- While the sample is still liquid, gently move the vial around at an angle with your hands (see image) so that the liquid crystal spreads around the vial walls.
- **Clearly mark the vial** with a number corresponding to the type of liquid crystal you have made ('1' for Type 1 etc.)

Prepare the four different vials and then test them!

Continue the experiment following the instructions in Student Laboratory Worksheet — Experiment B: Liquid crystals

……

CREDIT: This experiment was adapted from the activity ‘Preparation of Cholesteryl Ester Liquid Crystals’ (http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/index.htm)and the ‘Exploring materials: Crystal Liquids’ activity developed by the NISE (Nanoscale Informal Science Education) Network(Creative Commons Attribution ShareAlike 3.0) (http://www.nisenet.org). The activity was developed for the NISE Network with funding from the National Science Foundation under Cooperative Agreement #ESI-0532536. Any opinions, findings and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Foundation.

STUDENT LABORATORY WORKSHEET

LIQUID CRYSTALS

Student name:.........................

Date:.......................................

AIM:

- Understanding of the concept of self-assembly
- Understanding that the way a material behaves at the macroscale is affected by its structure at the nanoscale
- Learn about liquid crystals and how they work
- Test a real thermotropic liquid crystal and see how its colour changes with temperature

BEFORE YOU FILL IN THIS WORKSHEET

- Read STUDENT BACKGROUND READING — EXPERIMENT B: LIQUID CRYSTALS
- Ask your teacher any questions you have

MATERIALS

- four vials of liquid crystal mixture, each containing a different mixture
- water bath (hotplate, Pyrex glass water container half-filled with water, thermometer)
- sheet of clear contact paper
- clothes peg
- spatula
- pair of scissors
- A4 sheet black cardboard
- A4 foam sheet
- paper cutter
- gloves
- safety glasses
- tissue paper
- room thermometer

SAFETY NOTE: The chemicals used in this experiment must be used according to MSDS specifications. Personal protection must be used as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

PROCEDURE

1. Prepare four different liquid crystal mixtures

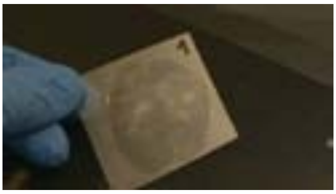
Follow the synthesis procedure described in the **document 'Synthesis of liquid crystal mixtures'** and prepare four different liquid crystal mixtures according to the table below. Each mixture is expected to be sensitive to different ranges of temperatures. If you are not performing the synthesis yourself, collect four vials containing the mixtures from your instructor/teacher. **Do not inhale the contents of the vials.**

Liquid crystal	Cholesteryl oleyl carbonate	Cholesteryl pelargonate	Cholesteryl benzoate	Temperature (°C)
Type 1	0.65	0.25	0.10	17–23
Type 2	0.45	0.45	0.10	26.5–30.5
Type 3	0.40	0.50	0.10	32–35
Type 4	0.30	0.60	0.10	37–40

2. Prepare four different liquid crystal sheets

Cut out two pieces of transparent contact paper (about 10 x 10 cm), peel off the backing paper and place on the laboratory bench. With a spatula, place some Type 1 liquid crystal in the centre of the sheet. If the liquid crystal is very cold and has turned into a solid, heat the vial first with a hairdryer (it should be the consistency of honey). You will need 2–3 spatulas of material. Place the second piece of contact paper on top of the first, so that the two sticky parts attach to each other. As you do so, gently press the centre where the liquid crystal is to distribute it evenly. You need to create a thin layer of liquid crystal about 4 x 4 cm. Do not press too hard, otherwise the material will come out from the edges. Cut the sheet at the end around the edges. With a permanent marker, mark the number corresponding to the type of liquid crystal ('1' for Type 1 etc.) in the corner of the sheet.

Repeat the same procedure for the fourtypes of liquid crystals.



Q1: What is the temperature of the room you are in?

....

Q2: Can any of the four liquid crystal mixtures you have made be used for sensing the temperature in your room? If yes, which one?...

....

3. Now test the four different liquid crystal sheets!

Place the four liquid crystal sheets you have just made on an **A4 sheet of white paper**. Wait few seconds. What do you see? Now press with your finger (wear gloves) against each of the liquid crystal sheets. Repeat the experiment putting the sheets on an **A4 sheet of black cardboard**. In order to compare the different sheets, you should keep the finger on each sheet for the same time. Record your observations in the table provided.

	White paper	Black paper
Sheet 1 (Type 1)		
Sheet 2 (Type 2)		
Sheet 3 (Type 3)		
Sheet 4 (Type 4)		

Q3: Why do you get a different result when you test the liquid crystal sheets against white and black paper?

....

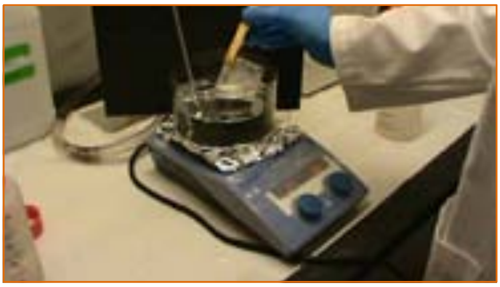
Q4: Did all the sheets display some colour? If not, why is that? What can you do to make these sheets display colour?

....

Now rub your hands together and test again each of the sheets. Do you see any difference?

....

Now, turn the water bath on and set it to a water temperature of 15 °C. To be able to see the colour changes, place an A4 sheet of black cardboard safely behind the water bath. **NB: The paper and cardboard should not touch the hotplate!**



Hold the first liquid crystal Sheet 1 (Type 1) with a clothes peg and immerse it the water bath (see image). Do you see any colour? Now increase the hotplate temperature so that the water reaches 23 °C. Record the colours that you see as the temperature increases:

Sheet 1 (Type 1)		
Temperature (°C)	**Colour**	**Comments**
16		
17		
18		
19		
20		
21		
22		
23		

Q5: At what temperature do you start to see some colour (Sheet 1)? Does this correspond to the predicted temperature (according to Table 1)?

....

Q6: Does the scale of colours that you have recorded in the table above match a wavelength scale? If so, why?

....

....

Q7: When you take the liquid crystal sheet out of the water bath, does it lose its colour immediately? If not, why do you think this is?

....

....

Q8: Imagine putting Sheet 1 (Type 1) in a water bath and you don't know the temperature of that water bath. The sheet turns orange. What temperature is the water bath?

....

Continue the experiment testing the other liquid crystal sheets you have made.

- **Place Sheet 2 in the water bath you have just used (now at 23 °C) and increase the temperature so that the water gradually reaches 30 °C.** What happens? Record your observations in the table provided.

Sheet 2 (Type 2)		
Temperature (°C)	**Colour**	**Comments**
22–23		
23–24		
25		
26		
27		
28		
29		
30		

- **When the water temperature reaches 30 °C, test Sheet 1 (Type 1) again.**

Q9: Can Sheet 1 detect temperatures around 30 °C? Why?..

Continue the experiment testing the other liquid crystal sheets you have made.

- **Test Sheet 3 (Type 3):** Place Sheet 3 in the water bath you have just used (now at 30 °C), increase the temperature so that the water gradually reaches 35 °C. What happens? Record your observations in the table provided.

Sheet 3 (Type 3)		
Temperature (°C)	**Colour**	**Comments**
30		
31		
32		
33		
34		
35		

- **Now test Sheet 4 (Type 4):** Increase the temperature of the hotplate so that the water temperature increases from 35 to 40 °C. Record your observations in the table provided.

Sheet 4 (Type 4)		
Temperature (°C)	Colour	Comments
35		
36		
37		
38		
39		
40		

Q10: Was the colour sequence that you observed for Sheet 3 and Sheet 4 the same as for Sheet 1? Why/Why not?

………………………………………………………

Q11: When you take liquid crystal Sheet 3 or Sheet 4 out of the water bath, does it behave like Sheet ? What is the difference? Why?

………………………………………………………

Q12: Which of the liquid crystals among the four types that you have would you use for checking whether you have a fever? Why?

………………………………………………………

3. Making a liquid crystal room thermometer

Now you can make a **liquid crystal room thermometer**. You can use the liquid crystal sheets made in the previous part of the experiment or make new ones if necessary.

SAFETY NOTE: Wear gloves as you make the thermometer. Be careful not to squeeze the liquid crystal sheets so that the liquid crystal is pressed outside the sheet. If this happens, clean immediately with paper.

- Write on the white foam the word NANO. You will need to ‘fill’ each letter with one liquid crystal sheet, so make sure the single letters are large enough (see image).
- With a paper cutter, cut the four letters from the foam board.
- Attach a different liquid crystal sheet on the back of each letter, following this order:

N — Type 1; A — Type 2; N — Type 3; O — Type 4

- Secure each letter one at a time, using long pieces of clear contact paper. Alternatively, you can use transparent tape. Make sure that the liquid crystal sheets do not overlap inside the letters. **The idea is that each letter should contain only one liquid crystal sheet**.
- Once you have attached all the liquid crystals sheets, attach the white foam to the black cardboard (placing the side where the sheets are against the black card).
- **Now you have a room thermometer!**

Q13: Does your room thermometer show any colour? If not, why not?

……………………………….

If you don’t see any response on the thermometer, try placing it over a working laptop computer … It will show what we all know, that laptops generate heat!

- You can use your thermometer throughout the year. In the summer, take it outside under the sun, or you can place it on the classroom window.

……

CREDIT: This experiment was adapted from the activity ‘Preparation of Cholesteryl Ester Liquid Crystals’ (http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/index.htm)and the ‘Exploring materials: Crystal Liquids’ activity developed by the NISE (Nanoscale Informal Science Education) Network (Creative Commons Attribution ShareAlike 3.0). The activity was developed for the NISE Network with funding from the National Science Foundation under Cooperative Agreement #ESI-0532536. Any opinions, findings, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Foundation.

EXPERIMENT C:

COLORIMETRIC GOLD NANOSENSOR

MATERIAL INCLUDED IN THIS EXPERIMENT PACKAGE

For teachers:

TEACHER RESOURCES — EXPERIMENT C: COLORIMETRIC GOLD NANOSENSOR

For students:

STUDENT BACKGROUND READING — EXPERIMENT C: COLORIMETRIC GOLD NANOSENSOR

STUDENT SYNTHESIS PROCEDURE — EXPERIMENT C: COLORIMETRIC GOLD NANOSENSOR

STUDENT LABORATORY WORKSHEET — EXPERIMENT C: COLORIMETRIC GOLD NANOSENSOR

LEVEL OF EXPERIMENT: **Advanced**

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used accordingto MSDS specifications and according to specific school safety rules. Personal protection must be usedas indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

TEACHER RESOURCES

COLORIMETRIC GOLD NANOSENSOR

AIM: Plasmonic colorimetric nanosensors are used in nanomedicine because they allow the precise detection of specific analytes with high sensitivity and without the need for a label. In a colloidal plasmonic biosensor (e.g. a sensor made of gold nanoparticles), the sensing event results in a change of aggregation in the colloid, which can determine a colour change of the colloid. The aim of this experiment is to synthesise and test a plasmonic colorimetric sensor. First, the students will synthesise a colloid of gold nanoparticles and learn that the colour of the gold colloid is ruby-red, rather than golden as for bulk gold, so they will have direct evidence that the size of a material at the nanoscale is fundamentally important in determining its properties. The gold colloid prepared is then tested as a chemical colorimetric sensor: by adding a salt to the colloid, its agglomeration changes, which results in a change in colour (from ruby-red to blue). In the experiment, students test other solutions, such as sugar, and observe the effect on the colloid. The last test involves the use of a protein and shows how these can coat the nanoparticles to a point they can no longer aggregate.

FIELD OF NANOTECHNOLOGY APPLICATION: Medicine

EXTRA TEACHER READING: Module 1, Chapter 4: Fundamental 'nano-effects', and Module 2, Chapter 1: Medicine and healthcare, in the NANOYOU Teachers Training Kit in Nanotechnologies

REQUIRED STUDENT PRE-KNOWLEDGE:

- Electromagnetic radiation, colour and absorbance, light scattering
- Concept of bio-recognition

STUDENT READING:

- NANOYOU Student Background Reading — Experiment C: Colorimetric gold nanosensor

EXPECTED OUTCOMES:

- Understanding of the effect of size on the properties of a familiar material such as gold
- Properties of colloids; optical properties of gold nanoparticles
- Understanding of the use of metal colloids for sensing and in particular medical diagnostics

STUDENT ASSESSMENT:

- NANOYOU Student Laboratory Worksheet — Experiment C: Colorimetric gold nanosensor

BACKGROUND INFORMATION

In this experiment, students use a plasmonic colorimetric sensor made of nanoparticles: the gold colloid (containing gold nanoparticles) is the sensing material, and the addition of an analyte (such as salt or sugar) induces a change in the aggregation of the nanoparticles in the colloid, which is reflected in a change in its colour. Here, some background information is provided on the properties of gold nanoparticles and their use in medical diagnostics; some details of the synthesis of the gold colloid are also provided.

1. About gold

In this experiment, the sensor is made of **gold nanoparticles**. Most students will be very familiar with the colour of bulk gold and with some of its properties, but not with its properties at the nanoscale. Gold (Au, atomic number 79), is the most malleable and ductile of all metals, it can be beaten to very thin sheets of material and rolled or bent as desired. Gold creates alloys with many metals. The colour of pure gold is metallic yellow (golden), but other colours can be conferred by alloying gold with metals such as copper and silver. For example, 'rose gold' is an alloy of gold and copper in high mass percentages (**Figure 1**).

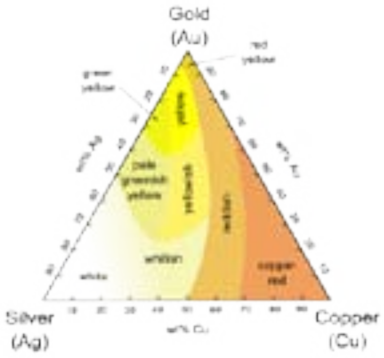


Figure 1: Approximate colours of Ag-Au-Cu alloys

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

NOTE: Some gold alloys have a colour different to the metallic yellow of pure gold but this is due to the presence of two metals in the alloy. Colloids of gold nanoparticles might have colours such as red, purple or blue, but are made only with gold.

Gold is very stable and non-toxic and, for this reason, is widely used in jewellery and dentistry because it is air-inert and is not affected by most reagents. Gold is also a good conductor of heat and electricity (due to the fact that conduction electrons are free to move around the nucleus); it is also corrosion resistant so it is used for electrical contacts and other electronic applications. Gold has also numerous other applications; for example, thin layers of gold (so thin as to be transparent) are applied to the windows of large buildings to increase the reflectivity of sunlight (and reduce transmittance), so that less air conditioning is required in summer to keep the building cool.

2. From bulk metals to nano-sized metals (nano-metals)

One of the distinguishing properties of metal nanoparticles in general is their optical properties, which are different to those of their bulk counterpart. This is due to an effect called localised surface plasmon resonance (LSPR), which is described in **Module 1, Chapter 4: Fundamental 'nano-effects'**. One of the consequences of the LSPR effect in metal nanoparticles is that they have very **strong visible absorption** due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold or silver can display colours which are not found in their bulk form, such as red, purple or orange, depending on the shape, size and surrounding media of the nanoparticles. The energy of LSPR is sensitive to the **dielectric function** of the material and the surroundings and to the shape and size of the nanoparticle. This means that if a ligand, such as a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes. Similarly, the LSPR effect is sensitive to other variations such as the **distance between the nanoparticles**, which can be changed by the presence of surfactants or ions. The fact that LSPR depends on the dielectric environment means that the refractive index can be used as the sensing parameter: changes in the local dielectric environment, induced by the sensing process, are used to detect the binding of molecules in the particle nano-environment.

3. Plasmonic colorimetric gold colloid sensor

In a plasmonic biosensor, the nanoparticles can be dispersed in a medium (in which case, the biosensor is a **colloidal plasmonic biosensor**) or supported on a surface (**surface plasmonic biosensor**). Both types of sensors exploit the fact that the sensing event changes the LSPR of the metal nanoparticles, but they use different read-out report strategies.

In a **colloidal plasmonic biosensor** (e.g. made of gold nanoparticles), the sensing event results in a change of aggregation among the nanoparticles that form the colloid (**Figure 2**), which can determine a colour change of the colloid. Absorption spectroscopy is used to quantify the biosensing event. In the case of gold colloid, which is normally red, the sensing event can result in the colloid becoming blue. Thus, metal colloids can be used as **plasmonic colorimetric biosensors**. In nanomedicine, this effect is used, for example, in **genetic screening**, where scientists look for a specific gene sequence in a sample which can be indicative of a specific disease. **How is this done?** First, the sequence of bases in the target DNA is identified. Then two sets of gold particles are prepared — one has DNA attached that binds to one end of the target DNA, and the second set carries DNA that binds to the other end (**Figure 3**). The nanoparticles are dispersed in water. When the target DNA is added, it binds both types of nanoparticle together, linking them together to form an aggregate. The formation of this aggregate causes a shift in the light-scattering spectrum from the solution (i.e. a colour change in the solution that can easily be detected). The example is illustrated in **Figure 3**. Since the colloid changes colour as a result of the sensing event, this is called **colorimetric sensing**. Gold colloids can be used for colorimetric sensing specifically because they have different colours depending on the environment that surrounds them.

The method is not limited to sensing DNA strands and can sense also other complementary biomolecules such as antigen-antibody systems; it is used to study the stability of proteins.

In this experiment, students will only use a qualitative approach: the outcome of the sensing process is a change in colour of the solution which is visible with the naked eye (visible absorption).

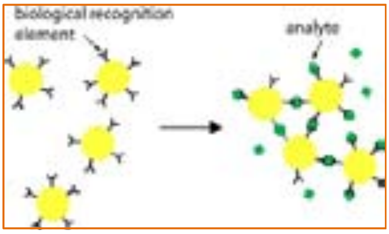


Figure 2: Schematic representation of a colloidal plasmonic biosensor

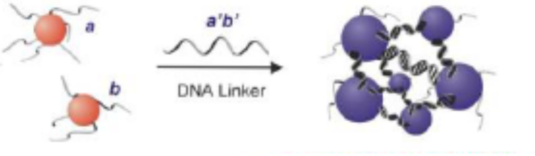


Figure 3: Plasmonic colloidal nanosensor

Image: Jin et al., *Journal of the American Chemical Society*, 2003, 125(6):1643–54, reprinted with the permission of the American Chemical Society, © 2003

4. Does nano-gold have other properties different to bulk gold?

Yes, it does. Nano-gold is extremely reactive and is now being studied as a **new catalyst**. Nano-gold has been shown to be an extremely efficient catalyst in numerous pollution control studies. For example, a company has announced an engineered nano-gold oxidation catalyst which can reduce diesel hydrocarbon emission 40 % more than commercially available materials. Considering that there are over 14 million light-duty diesel vehicles worldwide, and two million heavy-duty vehicles, the impact of this nanotechnology could be enormous.

5. About the gold colloid synthesis

In **this experiment**, students will prepare a colloid of gold nanoparticles in water starting from a solution of **gold chloride hydrate and a solution of sodium citrate**. This is the simplest reaction to synthesise gold nanoparticles and was pioneered by J. Turkevich et al. in 1951 and refined by G. Frens in the 1970s. The method described in this reaction is adapted from 'Color my nanoworld', *Journal of Chemical Education*, 2004, 81(4). This synthesis method generally produces nanoparticles 10–20 nm in size, so the end-product is a **gold colloid** (16). In the reaction, the citrate acts as a weak reducing agent (reducing $AuCl^{4-}$to Au) and as a stabiliser. A layer of citrate anions adsorbs around each nanoparticle and prevents these from aggregating: the electrostatic repulsion of the anions keeps the nanoparticles separated. In this state, the colloid appears ruby-red owing to the absorption of light by the free electron oscillations (the surface plasmon). The position of the surface plasmon λ_{max} for colloid gold is between 500 and 600 nm depending on the particles' size and shape, as well as the solvent refractive

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(16) In a colloid, one substance is dispersed evenly throughout another but the particles of the dispersed substance are only suspended in the mixture, they are not completely dissolved in it. The particles have dimensions in the 10–100 nm range. Natural colloids are in the form of emulsions (milk), gels (gelatin), aerosols (fog), etc.

index and inter-particle distance. In this experiment, λ_{max} is around 520 nm (green) and the solution appears red. A colour wheel can be used to show the correlation between the colour a substance absorbs and the colour it appears.

If the anion layer is removed, the nanoparticles start to approach and agglomerate. This effect can be used to sense a certain chemical (**Figure 4**). If a strong electrolyte is added, such as NaCl, the ions of the salt shield the negative charges on the particles, allowing them to approach and aggregate into larger and larger clumps. The formation of agglomerates is reflected in a change of the optical spectrum and the appearance of a second absorbance peak around 650–750 nm, causing the solution to **turn deep blue**. If a high concentration of salt is added, the nanoparticles aggregate to a point at which they precipitate, and the solution becomes clear.

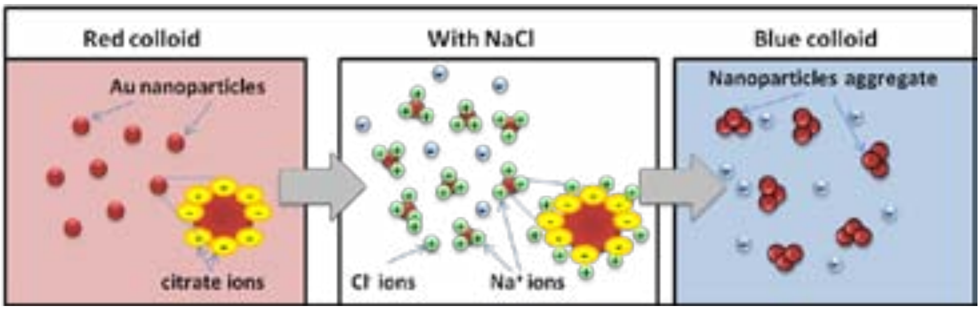


Figure 4: Schematic representation of the optical changes of a colloidal gold as a solution of salt is added

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Other disturbances that can be easily observed now considered.

- **If a stabiliser of high molecular weight**, such as a protein or polyethylene glycol, is added, it adsorbs to the surface of the nanoparticles with the effect of inhibiting aggregation, even at high salt concentration (**Figure 5**). In this exercise, egg white is used as a very economic source of protein (mainly ovoalbumin).
- **If a weak or non-electrolyte is added** (e.g. sugar), the electrostatic repulsion between the gold and the citrate ions is not disrupted and the solution remains red. A small change in colour (e.g. from ruby-red to slightly pink) can be observed, the consequence of a very small agglomeration that occurs as the protein is added (**Figure 6**).

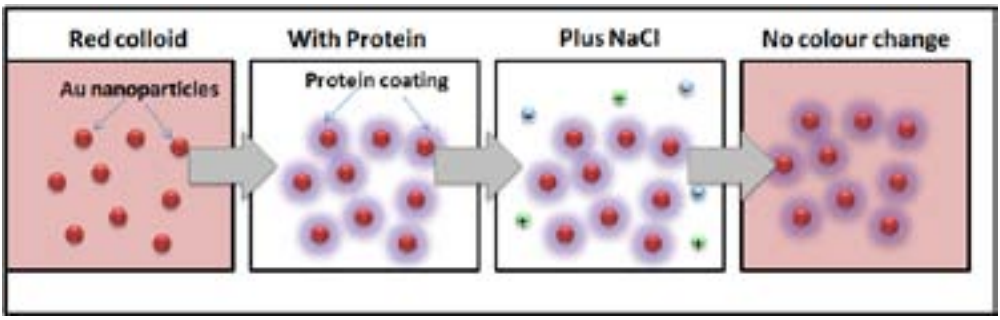


Figure 5: Schematic representation showing that a protein coats the gold nanoparticles and prevents them from aggregating as salt is added to the colloid

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

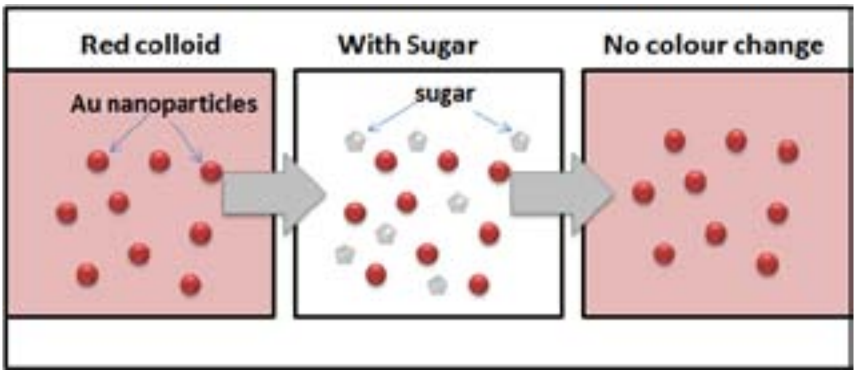


Figure 6: Schematic representation of the optical changes of colloidal gold as a solution of sugar is added

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

One peculiarity of this synthesis is the colour change observed as the citrate is added to the gold chloride hydrate solution before it reaches the final ruby-red colour. The reaction starts with a solution which is yellowish (solution of $HAuCl_4$) and, after the citrate is added, the colour changes first to clear, then light grey, dark blue-grey, then purple, dark purple, and finally ruby-red. Only recently have these intermediate colours been understood and correlated to the **formation of intermediate nanostructures before the formation of the final gold nanoparticles**. Specifically, TEM images have shown that after few seconds of citrate addition, **gold nanowires 5–8 nm are formed**, which are responsible for the dark purple colour. Beyond a certain threshold, the nanowires disintegrate into nanoparticles, and the solution turns ruby-blue. Although the chemistry and kinetics of this reaction would be too advanced for class teaching, this rapid and dramatic colour change during the reaction should be closely observed and this observation used to further support the notion that **size and shape at the nanoscale are very important factors** (**Figure 7**).

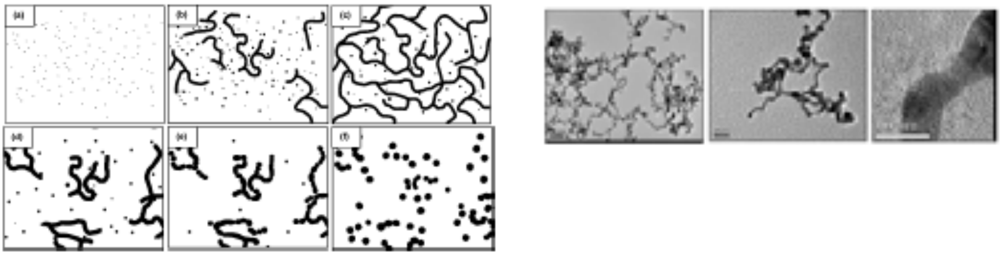


Figure 7: (left) Growth mechanism of nanospherical gold particles synthesised by reduction of aqueous $AuCl_4$ by sodium citrate; (right) TEM images of the dark intermediate showing an extensive network of gold nanowires which were isolated from the dark purple solution

Image: Pong et al., *Journal of Physical Chemistry*, reprinted with the permission of the American Chemical Society, © 2003

THIS EXPERIMENT IN CLASS

Depending on the class level and time available, this experiment module can be used in different ways. The authors suggest the following.

1. Start with a general discussion on gold, asking students what they know about gold.

- What are the properties of gold? As a metal? Is it a catalyst?
- What colour is gold?
- What is gold used for?

Here, teachers can also discuss other aspects of the chemistry curriculum, such as:

- the properties of metals and metal alloys,
- the electromagnetic spectra and colour.

Students should complete Q1 and Q2 of the student laboratory worksheet

2. Introduce the concept of colloids

- What is the difference between a colloid and a solution?
- Discuss the light scattering of colloids
- Optical properties of metal colloids and in particular of gold colloids (LSPR effect)
- Applications of gold colloids (link with Module 2, Chapter 1: Applications of nanotechnology — Medicine and healthcare)

3. Synthesis of a gold colloid

Divide the students intopairs and ask them to follow the synthesis procedure (students should have the Experiment C — Student Synthesis Procedure: Colorimetric gold nano-sensor). The procedure is described below. Instructors should encourage students to closely monitor the colour change of the solution during the synthesis and record their observations in the table in their student laboratory worksheet.

MATERIALS

Chemicals:

- 0.1 g $HAuCl_4*3H_2O$ (Sigma-Aldrich No G4022, 1 g costs about EUR 144.50)
- 0.5 g $Na_3C_6H_5O_7*2H_2O$ (Sigma-Aldrich No S4641, 25 g costs about EUR 24)
- 1 litre distilled water

Glassware/labware:

- eye protection
- latex or nitrile gloves
- paper towels
- cylinders: 10 ml, 50 ml and 500 ml
- glass pipettes: 5 ml and 25 ml
- 50 ml Erlenmeyer flask or beaker
- four disposable plastic capsules for measuring solids
- spatula
- glass bottles: 500 ml, two small bottles 25 ml or two beakers 25 ml
- aluminium foil
- laser pen
- stirring hotplate
- magnetic stir bar

Also needed for laser test:

- glass of milk

SAFETY NOTE: The experiments described in the following training kit use chemicals which must be used according to the MSDS specifications and according to specific school safety rules. Personal protection must be usedas indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

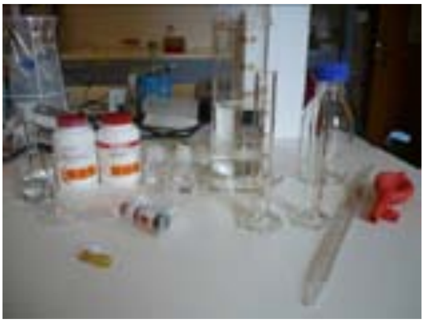
SPECIFIC PRECAUTIONS

Use these materials with the normal chemical precautions according to the MSDSs. Use appropriate clothing protection, gloves and eye protection. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. **Be aware that $HAuCl_4$*$3H_2O$ is corrosive and must be handled with caution**.

DISPOSAL OF THE GOLD COLLOID

After the experiment, dispose of any remaining gold colloidas follows: add enough NaCl solution to the colloid to induce precipitation. Leave the solution for at least 30 minutes (a black residue will form as in the image). Filter the residue through filter paper and then dispose of it with normal solid waste. Dispose of the clear liquid down the sink with plenty of water.

PROCEDURE (PROTOCOL FOR TEACHERS)



1. Preparation of stock solutions (to be made by the students or by the teacher depending on time). Preparation time is 30 minutes. Solutions indicated are enough for 25 students.

NB: All glassware used should be clean and dry.

- **1.0 mM hydrogen tetrachloroaurate**: Dissolve 0.1 g $HAuCl_4$*$3H_2O$ (orange solid) in 500 ml distilled water. Solution appears light yellow.

  NB: This stock solution of gold(III) ions can be prepared in advance if stored in a brown bottle or in a bottle well covered (including cap) in aluminium foil. Stored in this way, the solution will last a couple of months. **This 500 ml stock solution is sufficient for 25 experiments.**

- **1 % trisodium citrate**: Dissolve 0.5 g $Na_3C_6H_5O_7$*$2H_2O$ in 50 ml distilled water.

  NB: This 50 ml stock solution is sufficient for 25 experiments

- **Approximately 1 M NaCl**: Dissolve 0.5 g NaCl (or table salt) in 10 ml distilled water.
- **Approximately 1 M sugar solution**: Dissolve 2 g sugar in 10 ml distilled water.

2. Synthesis procedure for the gold colloid

(a) Add 20 ml 1.0 mM $HAuCl_4$ stock solution to a 50 ml Erlenmeyer flask on a stirring hotplate (turned off). The solution appears light yellow. Add a magnetic stir bar to the flask. Turn the stirring and the temperature on. Bring the solution to the boil.

COMMENTS: After the temperature is turned on, some bubbles are seen forming at the bottom of the flask, then they become more and more evident. This is when the citrate should be added, even if full bubbling is not seen. The reaction should ideally be performed under reflux conditions, as evaporation occurs which leads to a volume loss.

(b) To the boiling solution, add (all at once) 2 ml of a 1 % solution of trisodium citrate dihydrate, ($Na_3C_6H_5O_7{*}2H_2O$). The gold colloid gradually forms as the citrate reduces the gold(III). Students should observe the colour change as the citrate is added.

Figure 8: Addition of the citrate — note that immediately after the addition, the solution appears clear (right)

COMMENTS: The solution starts slightly yellow, then it becomes clear as soon as the citrate is added, then grey, dark grey, purple, dark purple, then ruby-red. The entire reaction (from when the hotplate is turned on) takes about 10–15 min. To minimise the volume loss due to evaporation, reduce the temperature to about 100 °C once the solution is boiling.

1 minute into the reaction

2 minutes into the reaction

3 minutes into the reaction

4 minutes into the reaction

In the images above, the colour shift from deep purple to ruby-red at the end of the reaction can be seen.

The reaction is complete after about **6 minutes of total reaction** (from the addition of the citrate). The time of reaction might vary depending on the temperature and freshness of the citrate solution.

Appearance of final colloid:

(c) Once the solution is ruby-red, turn the hotplate off and stop the stirring. Remove the flask from the hotplate.

WARNING: The flask will be hot so use a safety glove to avoid burning your fingers! Place the flask on a safe surface (e.g. table bench with a piece of aluminium foil).

TIP FOR TEACHERS: If you decide to prepare the gold colloid in advance, you can use the **NANOYOU Video 2 — Gold colloid** to show the synthesis to the students.

CLASS DISCUSSION

After the synthesis, students can test the gold colloid to understand its properties.

Let the students test the ruby-red colloid with a laser pen.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! Students should wear **safety glasses** when doing this test.

A scattered light path through the colloid is clearly visible. Compare the effect of shining the laser through water or stock solutions: the light will not be scattered.

- Students should also analyse other familiar liquids such as milk (a natural colloid), and/or other solutions like a salt solution.

NOTE! If you test milk, it must be diluted. Place 150 ml of water in a beaker and add 2 droplets of milk; stir and let it settle for a couple of minutes. Plain milk will back scatter all the light. All solutions (e.g. salt solution) should be made with distilled water and should left to settle before testing (any air bubbles in the solution might give erroneous results).

Students should complete Q3 to Q7 of the student laboratory worksheet

4. Gold colloid as a plasmonic colorimetric sensor

In nanomedicine, gold colloids are now being investigated as colorimetric sensors, for example to detect specific DNA fragments. Here, a simpler experiment is suggested. The key elements of this type of sensor are that it is very sensitive and it **does not require the use of a label**.

The colloid should be tested with different solutions to see how it can be used for sensing certain species (these tests are described in the next section).

- Strong ionic solutions induce a colour change from ruby-red to blue (e.g. NaCl). Therefore, it can be used to detect the presence of **electrolytes**.
- Weak or non-ionic solution does not induce this change (e.g. sugar).
- Surfactants or proteins coat the colloid to such a point that it is no longer affected by strong ionic solutions (e.g. adding a white egg solution followed by NaCl does not induce a colour change).
- Teachers can suggest testing the gold colloid in other solutions, such as vinegar (which is a mild acid) and ask the students to guess what change to expect.
- Teachers can prepare a ‘test’ solution without telling the student its contents and ask the students to guess what this ‘test’ solution is made of depending on its effect on the colour of the gold colloid.

MATERIALS

The material indicated below is intended for students working in pairs.

Chemicals:

- the gold colloid prepared in the synthesis (Part 3), should be about 15 ml
- 0.5 g NaCl (Sigma-Aldrich No S7653, 250 g costs about EUR 32), fine kitchen salt can be used as alternative
- 2 g sugar
- a fresh egg
- 1 litre distilled water

Glassware/labware:

- safety glasses
- latex or nitrile gloves
- paper towels
- cylinders: 10 ml, 50 ml and 500 ml
- glass pipettes: 5 ml, 25 ml, 10x Pasteur pipettes
- 50 ml Erlenmeyer flask or beaker
- two disposable plastic capsules for measuring solids
- spatula
- glass bottles: 500 ml, two small bottles 25 ml or two beakers 25 ml
- six glass vials
- a transparent plastic container

SPECIFIC PRECAUTIONS

Use these materials with the normal chemical precautions according to the MSDS. Use appropriate clothing protection, gloves and eye protection. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals.

DISPOSAL OF THE GOLD COLLOID

After the experiment, dispose of any remaining gold colloid as follows: add enough NaCl solution to the colloid to induce precipitation. Leave the solution for at least 30 minutes (a black residue will form as in **Figure 11**). Filter the residue through filter paper and then dispose of it with normal solid waste. Dispose of the clear liquid down the sink with plenty of water.

METHOD:

1. Divide the ruby-red gold colloid into five vials each containing about 3 ml.
2. Use one vial as control, and the other four to perform different plasmonic colorimetric tests.

- **TEST 1**: Add 6 droplets NaCl solution: the colloid becomes blue (if it is general kitchen salt, it looks more grey-blue). **Why does this happen**? In the colloid citrate, ions act as stabilisers: they cover the surface of the nanoparticles and prevent their aggregation. When a strong ionic solution (NaCl) is added, its ions shield the charges on the particles, allowing them to approach and aggregate. The formation of agglomerates is reflected in a change of the optical spectrum causing the solution to turn deep blue.

Figure 11: Colour change as salt is added to the gold colloid

- **TEST 2**: Add 15–20 droplets NaCl: the colloid becomes dark grey, and a black precipitate starts to appear (**Figure 11, left**). If the sample is left for some time (30 minutes), the solution becomes clear and much black precipitate forms (**Figure 12**). **Why does this happen?** If a high concentration of ionic solution (NaCl) is added, the nanoparticles aggregate to a point they precipitate, the solution becomes clear and a black precipitate is clearly seen forming (**Figure 12, left**). If the vial is left to rest for about 30 minutes, aggregation continues until a big precipitate forms, and the solution appears clear (**Figure 12, right**).

Figure 12: Precipitation of a gold aggregate as an excess of NaCl is added to the gold colloid

- **TEST 3**: Add 10 drops sugar solution: the colloid doesn't change colour and it remains ruby-red. **Why does this happen?** Sugar is anionic; therefore, the citrate ions covering the gold nanoparticles remain undisturbed.

Figure 13: Effect of adding a solution of sugar to the gold colloid (vial on the far right). The middle shows the vial to which salt solution was added to the gold colloid, and on the left is a control (pure gold colloid).

- **TEST 4**: Crack open a fresh egg and with a Pasteur extract some egg white (about 1 ml or 2–3 full Pasteurs), place it in an empty glass vial and add one Pasteur distilled water. Mix gently together: it will form a foam so let it stand for a minute to reduce the foam, then take the solution from the very bottom to avoid the foam/bubbles. Add this water-egg white mixture to the gold colloid: the colloid turns dark pink and an 'emulsion' is seen. **Why does this happen?** As the protein is added to the gold colloid, the nanoparticles become coated with a layer of protein, which acts as a stabiliser. Nevertheless, during the addition of the protein, a little aggregation might occur, which is reflected in a colour change (dark pink instead of ruby-red). More sophisticated addition methods (e.g. using stirring) might prevent this from happening.

Figure 14: Addition of egg white to the gold colloid (left is the control, right is the test vial)

- **TEST 5**: If NaCl (6 drops) are added to the above solution (**TEST 4**), the colour does not change; it does not turn blue. If more NaCl is added, the colour still doesn't change. **Why not?** The protein (mainly ovoalbumin) in the egg white acts as a surfactant, shielding the gold nanoparticles from the ions, in a sense 'protecting' the nanoparticles. The NaCl ions don't have access to the gold nanoparticle surface and therefore do not induce a change in their aggregation.

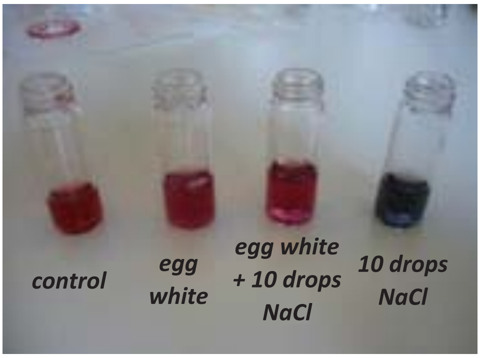


Figure 15: Overview of the test experiments (left to right): control (only colloidal gold); colloidal gold and the tested species of egg white, egg white plus 10 drops NaCl, and just 10 drops of NaCl

After the test, students should complete Q8 to Q15 of the student laboratory worksheet

5. Gold colloid as a medical diagnostic tool

Students should reflect on how a gold colloid can be used as a diagnostic colorimetric tool. The general idea is that any diagnostic process that induces a change in aggregation can (potentially) induce a visible colour change. To quantify this change, a spectrophotometer would be needed to measure the absorption of the solution. To be relevant in diagnosis, the process must be specific, based on a biomolecular recognition system, which can be the complementarity of DNA strands, or other processes such as antigen-antibody recognition.

Compared to other diagnostic tools, gold colloid has the advantage of not requiring a label, since the detection reaction is visible. This is an advantage because labelling is normally a long process; therefore, a label-free detection method is faster and requires fewer consumables, thus lowering the cost of the process.

Students should complete Q16 and Q17 of the student laboratory worksheet

6. Additional topics for class teaching

Depending on the needs and level of the class, instructors can use this experiment to discuss a number of additional science topics:

- solutions versus colloids;
- bulk metals and nano-sized metals: differences in bonding, conductivity properties, etc.;
- electromagnetism and properties of light (reflection, scattering, etc.);
- optical spectra of a substance and optical properties of a nanomaterial;
- science and art: examples of ancient artefacts containing nanotechnology;
- proteins and their sources (e.g. egg white).

ANSWERS TO QUESTIONS

Q1: Gold alloys are made of bulk gold mixed with other metals. In this form, gold alloys have different colours (e.g. ‘white gold’, ‘pink gold’).

Q2: A metal colloid can have different colours depending on the size of the nanoparticles that form the colloid. The metal colloid can be red, purple or blue. The colour is due to the presence of surface plasmons.

Q3: Because there are some intermediate nanostructures that are formed during the reaction.

Q4: In a colloid, the substance is only dispersed (not dissolved) in the solution.

Q5: Because nanoparticles scatter light, so a scattered path can be seen through the colloid.

Q6: Milk, gelatin.

Q7: Milk and the gold colloid.

Q8: Blue.

Q9: In the gold colloid, citrate ions act as stabilisers; they cover the surface of the nanoparticles and prevent their aggregation. When a strong ionic solution (NaCl) is added, its ions shield the charges on the particles, allowing them to approach and aggregate. The formation of agglomerates is reflected in a change of the optical spectrum, causing the solution to turn deep blue.

Q10: The colloid aggregates so much that a black precipitate forms.

Q11: The colloid remains nearly the same colour; it shifts a bit towards pink, but it does not become blue. The reason is that sugar is anionic, so the citrate ions covering the gold nanoparticles remain fairly undisturbed. The fact that the colloid is pink rather than ruby-red indicates that a small change in aggregation has occurred.

Q12: Egg is a source of protein (ovoalbumin).

Q13: Adding egg to the colloid does not change its colour.

Q14: The colloid remains red. The protein (mainly ovoalbumin) in the egg white acts as a surfactant, shielding the gold nanoparticles from the ions, in a sense ‘protecting’ the nanoparticles. The NaCl ions do not have access to the gold nanoparticle surface and therefore do not induce a change in their aggregation.

Q15: When salt is added directly to the gold colloid, the ions of the salt shield the charges on the particles, allowing them to approach and aggregate. When a protein is added instead, it forms a shield around the nanoparticles, so the ions of the salt can no longer interact with the citrate around the nanoparticles.

Q16: The fact that a change of agglomeration in colloids leads to a colorimetric change can be used to detect a specific biomolecule. The lock-and-key mechanisms of some biomolecules, such as antigen-antibody, can be used. For example, if a gold colloid probe having gold nanoparticles functionalised with antigen A and then a colloid target containing various antibodies is added and a colour change is seen, it indicates that antibody A is present in the target.

Q17: Labelling is a time-consuming procedure, and labels are also expensive.

REFERENCES

'Color my nanoworld', *Journal of Chemical Education*, 2004, 81(4).

A more detailed description of the synthesis of colloid gold is given by Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–55.

For the colour change as the synthesis of the gold colloid proceeds and the formation of intermediate nanostructures, such as gold nanowires, see Pong et al., *Journal of Physical Chemistry* C, 2007, 111:6281–7.

……

CREDIT: This exercise was partly adapted from the experiment reported in 'Color my nanoworld', *Journal of Chemical Education*, 2004, 81(4), and the experiment 'Citrate synthesis of gold nanoparticles', University of Wisconsin-Madison (http://www.mrsec.wisc.edu/Edetc/curriculum/index.html); a more detailed description of the synthesis of colloid gold is given by Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–955.

STUDENT BACKGROUND READING

COLORIMETRIC GOLD NANOSENSOR

In this experiment, you will synthesise and test a plasmonic colorimetric nanosensor made of nanoparticles of gold. Here some background information is provided so you can make the most of this experiment.

What do you know already about gold?

Think of gold as you know it. Gold (Au, atomic number 79) is the most malleable and ductile of all metals; it can be beaten to very thin sheets of material and rolled or bent as desired. This has been known and done for centuries. The **colour of pure** gold is metallic yellow (golden). You have probably seen or heard of ‘rose gold’ or ‘white gold’, but these are not made of pure gold; these are alloys of gold, they contain other metals such as copper and silver (**Figure 1**).

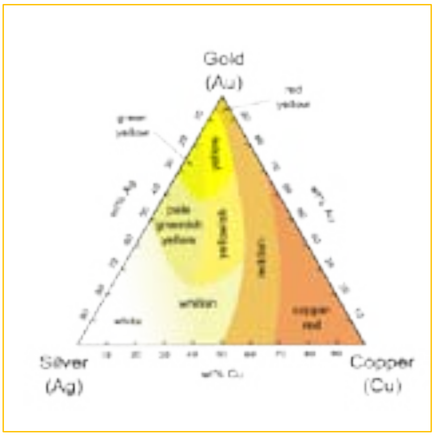


Figure 1: Approximate colours of Ag-Au-Cu alloys

Image: Wiki Commons, Creative Commons Attribution ShareAlike 3.0

What about gold´s reactivity? Gold is **very stable and non-toxic** and, for this reason, is widely used in jewellery and dentistry because is air-inert and is not affected by most chemicals. Gold is also a **good conductor of heat and electricity** (which is due to the fact that conduction electrons are free to move around the nucleus); it is **corrosion-resistant** so it is used for electronic contacts and other electronic applications. Gold has also numerous other applications: for example, thin layers of gold (so thin as to be transparent) are applied to the windows of large buildings to increase the amount of sunlight reflected by the window. This way, less air conditioning is required in summer to keep the building cool. **In this experiment, nanoparticles of gold (or ‘nano-gold’) will be investigated.**

Is nano-gold different from the gold we are familiar with?

Yes, it is! The properties of nano-gold are very different and it all has to do with the size of the nanoparticles.

When gold nanoparticles are inside a medium, such as water, they create a **colloid**. A colloid is different from a solution. A solution is a chemical mixture where onesubstance is evenly dispersed in another (such as a salt solution); a colloid is another type of chemical mixture: the particles of the dispersed substance are only suspended in the mixture: they are not completely dissolved in it. This occurs because the particles in a colloid are larger than in a solution. A colloid is composed of particles in the range of 10–100 nm. Gold colloids can have many different colours, ranging from ruby-red, to purple, to blue. And these are not alloys, they are made of pure gold nanoparticles! A characteristic of colloids is that they **scatter light**.

Colloids exist in nature and can be in the form of emulsion (such as milk), gel (gelatin), aerosol (fog), and many other forms. Even custard is a colloid! Where are the nanoparticles in these materials? For example, milk is an emulsion of macromolecules (casein micelles and liposomes) in water. Casein micelles and liposomes are a type of natural nanomaterial.

A simple way to **test if a mixture is a solution or a colloid** is to shine a laser beam though the mixture: the light will be scattered only by the colloid. To be visible, the colloid must be relatively transparent. For example, milk is a natural colloid but it is opaque. So, to perform this test you need to dilute the milk.

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! You must wear **safety glasses** when doing this test.

What determines the colour in gold colloids?

Metal nanoparticles, including gold nanoparticles, have optical properties which are very different from the properties of the corresponding bulk (macro) material. This is due to an effect called **localised surface plasmon resonance** (LSPR). In a conventional metal, electrons are free to move in all directions. When a beam of light (an electromagnetic radiation) hits the material, the energy is absorbed by the conduction electrons, which start to oscillate, generating a plasmon (**Figure 2**). In a bulk material, the plasmon quickly dissipates in heat as the electrons more around and no effect is seen. Conduction electrons in a metal nanoparticle are not so free to move, they are confined in space. When light hits a metal nanoparticle, a plasmon is also generated by the surface conduction electrons, but this time the movement of the electrons is confined in space. Therefore, a surface localised plasmon is generated. **The plasmon oscillates periodically in a confined space**. When the frequency of this oscillation is the same as the frequency of the light that it generated it (i.e. the incident light), the plasmon is said to be in resonance with the incident light. For this reason, the effect is called the localised surface plasmon resonance effect (LSPR). **The consequence of the LSPR effect is that there is an enhanced electromagnetic field close to the surface/particle.**

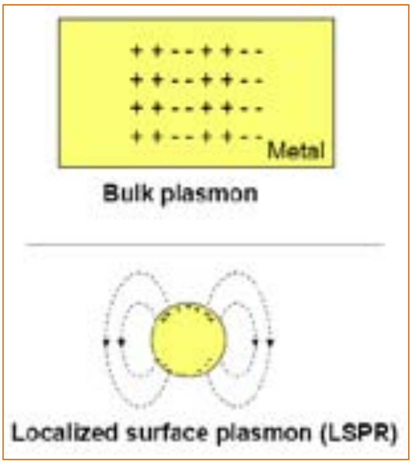


Figure 2: Formation of plasmons in bulk metal (top) and in nanoparticles (bottom)

Image: D. Sutherland, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

The energy of LSPR is **sensitive to the dielectric function of the material and the surroundings and to the shape and size of the nanoparticle**. This means that if a ligand, such as a protein, attaches to the surface of the metal nanoparticle, its LSPR energy changes. Similarly, the LSPR effect is sensitive to other variations such as the distance between the nanoparticles, which can be changed by the presence of surfactants or ions. The LSPR effect has been observed not only in metal nanoparticles but also in nanorings, voids in metal films and other nanostructures

One of the consequences of the LSPR effect in metal nanoparticles is that they have **very strong visible adsorption** due to the resonant coherent oscillation of the plasmons. As a result, colloids of metal nanoparticles such as gold or silver can display **colours which are not found in their bulk form**, such as red, purple or orange, depending on the shape, size and surrounding media of the nanoparticles. **In this experiment, you will see that nano-gold is not golden in colour but ruby-red!**

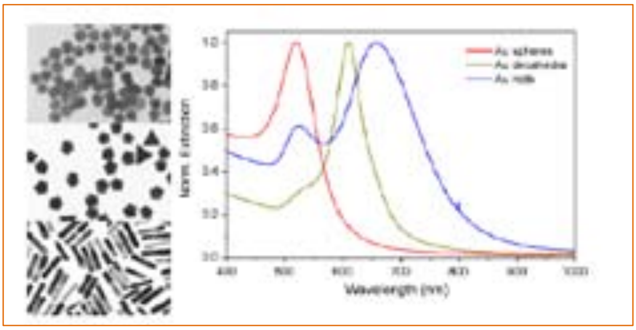


Figure 3: Transmission electron micrographs and UV-vis spectra of gold nanoparticle colloids with various geometries: (top) spheres; (middle) decahedra; and (bottom) rods

Image: Borja Sepúlveda et al., 'LSPR-based Nanobiosensors', *Nano Today*, 2009, 4(3), 244–251, reprinted with the permission of Elsevier

Figure 4: Dependence of colour on gold size

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Medieval artisans used it! Without knowing it, artisans have been using nano-gold through history. The beautiful **stained glass windows produced during the medieval time**, and visible in numerous churches, are made of a composite of glass and nano-sized metal particles. The 'ruby-red' glasses often seen are a mixture of glass with ultrafine (nano-sized) gold powder.

Does nano-gold have other properties different from bulk gold?

Yes, it does! Nano-gold is extremely reactive and is now being studied as a **new catalyst**. Nano-gold has been shown to be an extremely efficient catalyst in numerous pollution control studies. For example, a company has announced an engineered nano-gold oxidation catalyst which can reduce diesel hydrocarbon emission 40 % more than commercially available materials. Considering that there are over 14 million light-duty diesel vehicles worldwide, and two million heavy-duty vehicles, the impact of this nanotechnology could be enormous.

What is the application of nano-gold in medicine?

Gold is now studied in many nanomedicine applications. Here the focus in on just one use: a colorimetric biosensor. Generally speaking, a sensor is a device capable of recognising one or more specific chemical species within a mixture and 'signalling' its presence through some chemical changes. A 'transducer' converts the chemical signal into a quantifiable signal with a defined sensitivity. A biosensor is a device that is capable of detecting a specific biomolecule, such as a type of antibody, a fragment of DNA, etc. The presence of these specific biomolecules is indicative of the presence of a certain type of virus or bacteria which is responsible for a specific disease. One area of very active research is the development of future miniaturised biosensors that doctors can use in their office to test if their patient has a specific disease. This is 'point-of-care-diagnostics'. Nanomaterials have most of their atoms on the surface and, therefore, have a large area (compared to their volume) available for detection. Furthermore, as will be seen in this experiment, nanomaterials have peculiar optical properties which make their use advantageous. For this and other reasons, nanomaterials are very useful in the engineering of miniaturised biosensors.

In a gold colloidal plasmonic biosensor, the sensing event results in a **change of aggregation among the nanoparticles that form the colloid** (**Figure 5**).

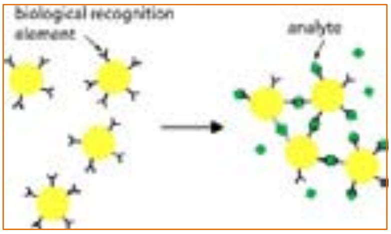


Figure 5: Schematic representation of a colloidal plasmonic biosensor

This change of aggregation can determine a colour change of the colloid. Absorption spectroscopy is used to quantify the biosensing event. For this reason, the sensor is called colorimetric (from the word ‘colour’). In the case of gold colloid, which is normally ruby-red, the sensing event can result in the colloid becoming blue. In nanomedicine, this effect is used, for example, in **genetic screening** where scientists look for a specific gene sequence in a sample. The gene sequence can be an indication of the presence of a specific pathogen, such as a virus. First, the sequence of bases in the target DNA is identified. Then two sets of gold particles are prepared — one has DNA attached that binds to one end of the target DNA, and the second set carries DNA that binds to the other end. The nanoparticles are dispersed in water. When the target DNA is added, it binds both types of nanoparticle together, linking them together to form an aggregate. The formation of this aggregate causes a shift in the light-scattering spectrum from the solution (i.e. a colour change in the solution that can easily be detected). The example is illustrated in **Figure 6**.

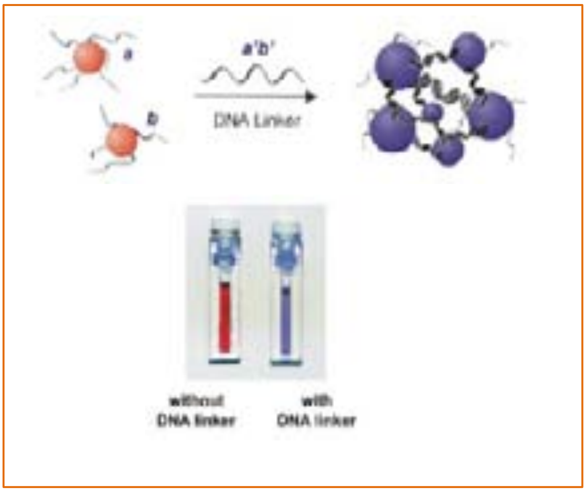


Figure 6: Plasmonic colloidal nanosensor

Image: Jin et al., *Journal of the American Chemical Society*, 2003, 125(6):1643–54, reprinted with the permission of the American Chemical Society, © 2003

Other techniques use the key-and-lock mechanism of antigen-antibodies, or enzymes that can bind to specific biomolecules. Basically, this technique combines the general concept of biorecognition (which is common to all biosensors) with a peculiar nano-effect (the fact that as the aggregation of gold nanoparticles changes, the colour changes).

In this experiment, you will test a colloid gold nanosensor to see if it can detect an electrolyte, such as salt.

You will perform the synthesis of a gold colloid starting from a solution of **gold chloride hydrate** and a **solution of sodium citrate**. This is the simplest reaction to synthesis gold nanoparticles and generally produces **gold nanoparticles 10–20 nm in size**. In the reaction, the citrate acts as a weak reducing agent (reducing $AuCl^{4-}$ to Au) and as a stabiliser. A layer of citrate anions adsorbs around each nanoparticle and prevents these from aggregating: the electrostatic repulsion of the anions keeps the nanoparticle separated. In this state, the colloid appears ruby-red owing to the absorption of light by the free electron oscillations (the surface plasmon). In this experiment, λ_{max} is around 520 nm (green) and the solution appears red.

If the anion layer is removed, the nanoparticles start to approach and agglomerate. This effect can be used to sense a certain chemical. If a strong electrolyte is added, such as NaCl, the ions of the salt shield the negative charges on the particles, allowing them to approach and aggregate into larger and larger clumps. The formation of agglomerates is reflected in a change of the optical spectrum causing the solution to **turn deep blue**. If a high concentration of salt is added, the nanoparticles aggregate to a point at which they precipitate, and the solution becomes clear.

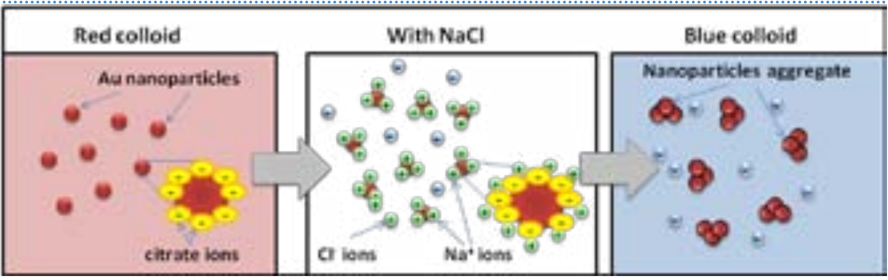


Figure 7: Schematic representation of the optical changes of a colloidal gold as a solution of salt is added

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

- **If a weak or non-electrolyte is added** (e.g. sugar), the electrostatic repulsion between the gold and the citrate ions is not disrupted and the solution remains red.
- **If a stabiliser of high molecular weight is added**, such as a protein or polyethylene glycol, it adsorbs to the surface of the nanoparticles with the effect of inhibiting aggregation, even at high salt concentration. In this exercise, egg white is used as a very economic source of protein (mainly ovoalbumin).

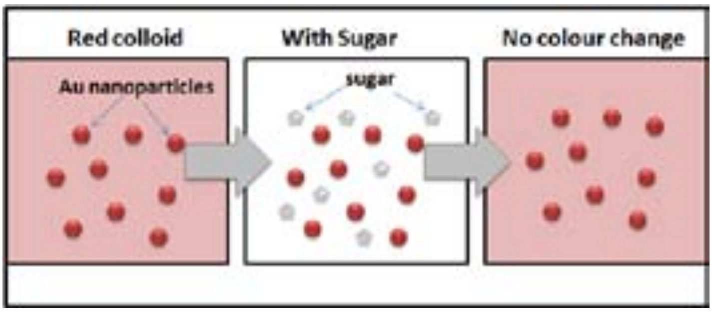


Figure 8: Schematic representation of the optical changes of a colloidal gold as a solution of sugar is added

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution Non-Commercial ShareAlike 3.0

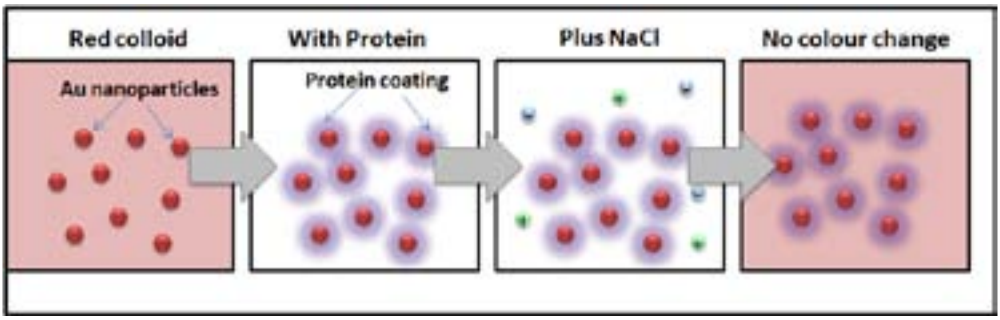


Figure 9: Schematic representation showing that a protein coats the gold nanoparticles and prevents them from aggregating as salt is added to the colloid

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution Non-Commercial ShareAlike 3.0

CREDIT: This exercise was partly adapted from the experiment reported in 'Color my nanoworld', *Journal of Chemical Education*, 2004, 81(4), and the experiment 'Citrate synthesis of gold nanoparticles', University of Wisconsin-Madison (http://www.mrsec.wisc.edu/Edetc/curriculum/index.html); a more detailed description of the synthesis of colloid gold is given in Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–955.

STUDENT SYNTHESIS PROCEDURE

COLORIMETRIC GOLD NANO-SENSOR

The synthesis procedure for EXPERIMENT C: Colorimetric gold nano-sensor included in the Experiment Module of the'NANOYOU Teachers Training Kit in Nanotechnologies'for students aged 14–18 now follows.

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to MSDS specifications and according to specific school safety rules. Personal protection must be used as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments will be carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

MATERIALS

Chemicals

- 0.1 g $HAuCl_4*3H_2O$ (Sigma-Aldrich No G4022)
- 0.5 g $Na_3C_6H_5O_7*2H_2O$ (Sigma-Aldrich No S4641)
- 1 litre distilled water

Glassware/labware

- eye protection
- latex or nitrile gloves
- paper towels
- cylinders: 10 ml, 50 ml and 500 ml cylinder
- glass pipettes: 5 ml and 25 ml
- 50 ml Erlenmeyer flask or beaker
- four disposable plastic capsules for measuring solids
- spatula
- glass bottles: 500 ml, two small bottles 25 ml or two beakers 25 ml
- aluminium foil
- laser pen
- stirring hotplate
- magnetic stir bar

Also needed for laser test

- glass of milk

SPECIFIC PRECAUTIONS

Use these materials with the normal chemical precautions according to the MSDS. Use appropriate clothing protection, gloves and eye protection. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. **Be aware that $HAuCl_4$*$3H_2O$ is corrosive and must be handled with caution.**

DISPOSAL OF THE GOLD COLLOID

After the experiment, dispose of any remaining gold colloid as follows: add enough NaCl solution to the colloid to induce precipitation. Leave the solution for at least 30 minutes (a black residue will form). Filter the residue through filter paper and then dispose of it with normal solid waste. Dispose of the clear liquid down the sink with plenty of water.

PROCEDURE:

1. Preparation of stock solutions

- **1.0 mM hydrogen tetrachloroaurate**: Dissolve 0.1 g $HAuCl_4$*$3H_2O$ (orange solid) in 500 ml distilled water. Solution appears light yellow.
- **1 % trisodium citrate**: Dissolve 0.5 g $Na_3C_6H_5O_7$*$2H_2O$ in 50 ml distilled water.
- **Approximately 1 M NaCl**: Dissolve 0.5 g NaCl (or table salt) in 10 ml distilled water.
- **Approximately 1 M sugar solution**: Dissolve 2 g sugar in 10 ml distilled water.

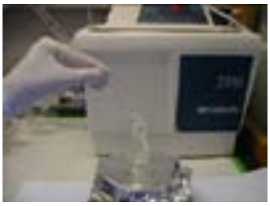
Your teacher might have prepared those solutions for you. In that case, skip part A and go to part B.

2. Synthesis procedure of the gold colloid

(a) Add 20 ml 1.0 mM $HAuCl_4$ stock solution to a 50 ml Erlenmeyer flask on a stirring hotplate (turned off). The solution appears light yellow. Add a magnetic stir bar to the flask. Turn the stirring and the temperature on (about 120 °C). Bring the solution to the boil. To minimise the volume loss due to evaporation, once the solution is boiling, reduce the temperature to about 100 °C.

(b) To the **boiling solution**, add (all at once) 2 ml 1 % solution of trisodium citrate dihydrate, ($Na_3C_6H_5O_7$*$2H_2O$). The gold colloid gradually forms as the citrate reduces the gold(III). Observe the colour change as the citrate is added. Once the solution is ruby-red, turn the hotplate off and stop the stirring. Remove the flask from the hotplate.

WARNING: The flask will be hot, so use an oven glove to avoid burning your fingers! Place the flask on a safe surface (e.g. table bench with a piece of aluminium foil).



Before reaction

End of reaction

CREDIT: This exercise was partly adapted from the experiment reported in ‘Color my nanoworld’, *Journal of Chemical Education*, 2004, 81(4), and the experiment ‘Citrate synthesis of gold nanoparticles’, University of Wisconsin-Madison (http://www.mrsec.wisc.edu/Edetc/curriculum/index.html); a more detailed description of the synthesis of colloid gold is given by Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–955.

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STUDENT LABORATORY WORKSHEET

GOLD COLORIMETRIC NANOSENSOR

Student name:........................

Date:.......................................

AIM:

- Understanding of the effect of size on the properties of a familiar material such as gold
- Properties of colloids
- Optical properties of gold nanoparticles
- Understanding of the use of gold colloids in biosensors and in particular for medical diagnostics

BEFORE YOU FILL IN THIS WORKSHEET

- Read STUDENT BACKGROUND READING — EXPERIMENT C: COLORIMETRIC GOLD NANOSENSOR
- Ask your teacher questions you have

DISCLAIMER: The experiments described in the following training kit use chemicals which must be used according to the MSDS specifications and according to specific school safety rules. Personal protection must be used as indicated. As with all chemicals, take precautions. Solids should not be inhaled and contact with skin, eyes and clothing should be avoided. Wash hands thoroughly after handling chemicals. Dispose of materials as indicated. All experiments must be conducted in the presence of an educator trained in science teaching. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

PROCEDURE

1. Gold and its properties

Complete this table about the **properties of gold.**

	COLOUR	CONDUCTIVITY and REACTIVITY	APPLICATIONS
BULK GOLD			
NANO-GOLD			

Add comments here if the space in the table is not enough:......................................

....

Q1: Can ‘bulk’ gold have colours different from the normal golden colour? If yes, in what form?

....

Q2: What colour can a metal colloid be? Why?

....

....

2. Synthesise a gold colloid

Follow **EXPERIMENT C — Student synthesis procedure: Colorimetric gold nano-sensor** and write down your observations as the synthesis proceeds. Read the table provided before starting the synthesis so you know what to look for as the reaction proceeds. Observe carefully the colour change during the time of the reaction.

Record your observations in the table provided.

Colour of $HAuCl_4$ solution (before reaction)	Colour immediately after the addition of the citrate	Colour of the final gold colloid	Did you notice any intermediate colours? Which one(s)?	Time of reaction

Q3: Why do you think some intermediate colours are seen during the reaction?

....

3. Learn the properties of a gold colloid

Q4: A colloid is different from a solution. What is the difference?

………………………………

Q5: The presence of nanoparticles can be confirmed using a laser pen. Why?

………………………………

Q6: Are there any natural colloids? If yes, name a few.

………………………………

Now use a **laser pen** to confirm the presence of gold nanoparticles in your and other samples. Record your observations

WARNING: Never shine a laser beam near the eyes nor look straight into the beam! You must wear **safety glasses** when doing this test.

Sample	Observed effect	Additional comments
Water		
Diluted milk (1)		
Gold colloid synthesised in class		
Salt solution		

(1) Use 2 droplets milk in 150 ml distilled water.

Q7: Based on your observations, which of the materials you have tested is a colloid?

………………………………

4. Test the gold colloid as a colorimetric nanosensor

MATERIALS NEEDED

Chemicals

- the gold colloid prepared in the synthesis (Part 3), should be about 15 ml
- 0.5 g NaCl (Sigma-Aldrich No S7653, 250 g costs about EUR 32), fine kitchen salt can be used as alternative
- 2 g sugar
- 1 fresh egg
- 1 litre distilled water

Glassware/labware

- safety glasses
- latex or nitrile gloves
- paper towels
- cylinders: 10 ml, 50 ml, 500 ml
- glass pipettes: 5 ml, 25 ml pipette, 10x Pasteur pipettes
- 50 ml Erlenmeyer flask or beaker
- two disposable plastic capsules for measuring solids
- spatula
- glass bottles: 500 ml, two small bottles 25 ml or two beakers of 25 ml
- six glass vials
- a transparent plastic container

DISPOSAL OF THE GOLD COLLOID

After the experiment, dispose of any remaining gold colloidas follows: add enough NaCl solution to the colloid to induce precipitation. Leave the solution for at least 30 minutes (a black residue will form). Filter the residue through filter paper and then dispose of it with normal solid waste. Dispose of the clear liquid down the sink with plenty of water.

METHOD:

1. Divide the ruby-red gold colloid into **5 vials** each containing about 3 ml.
2. Use one vial as control, and the other four to perform different plasmonic calorimetric tests.

SAMPLE	TEST	EFFECT OBSERVED
Control vial	—	
Vial 1	Add 6 droplets NaCl solution	
Vial 2	Add 15–20 droplets NaCl	
Vial 3	Add 10 droplets sugar solution	

Q8: What is the colour of Vial 1 after the test?

………………………………

Q9: Why did this happen?

………………………………

………………………………

Q10: What happened when you added more salt? Why?

…………………………………

Q11: What happens when you add sugar instead of salt? Why?

....

....

The plasmonic sensor you are testing is based on the fact that some molecules induce a change in the aggregation of the nanoparticles. Some molecules, such as proteins, prevent this from happening. Test it! Complete the table provided.

SAMPLE	TEST	EFFECT OBSERVED
Vial 4	Add some egg white (read **note** below)	
Vial 5	Add 6 droplets NaCl to Vial 4	

NB: Crack open a fresh egg and with a Pasteur pipette extract some egg white (about 1 ml or 2–3 full pipettes), place it in an empty glass vial and add one Pasteur of distilled water. Mix together gently: it will foam, so let it stand a minute to reduce the foam, then take the solution from the very bottom to avoid the foam/bubbles. Add this water/egg white mixture to the gold colloid.

Q12: Why did you add egg white to Vial 4?

....

Q13: What was the effect?

....

Q14: What happens when you add salt after having added egg white?

....

Q15: How is this different from what happened when you added salt directly to the gold colloid (Vial 2)?

....

5. Application in nanomedicine

Q16: Gold colloids are used in nanomedicine as plasmonic colorimetric sensors. Based on the fact that the colour change is due to a change in nanoparticle aggregation, how can this effect be used to detect the binding of biomolecules, such as DNA or antibodies?

....

....

Q17: A colorimetric sensor has the advantage over other types of sensors that it does not require a label. Why is this beneficial?

....

Notes

....

....

CREDIT: This exercise was partly adapted from the experiment reported in ‘Color my nanoworld’, *Journal of Chemical Education*, 2004, 81(4), and the experiment ‘Citrate synthesis of gold nanoparticles’, University of Wisconsin-Madison (http://www.mrsec.wisc.edu/Edetc/curriculum/index.html); a more detailed description of the synthesis of colloid gold is given by Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–955.

EXPERIMENT D:

SUPERHYDROPHOBIC MATERIALS

MATERIAL INCLUDED
IN THIS EXPERIMENT PACKAGE

For teachers:

TEACHER RESOURCES — EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS

APPENDIX I EXPERIMENT D

For students:

STUDENT BACKGROUND READING — EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS

STUDENT LABORATORY WORKSHEET — EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS

Supporting videos (http://www.nanoyou.org):

NANOYOU VIDEO 3 — LOTUS EFFECT®, PART 1

NANOYOU VIDEO 4 — LOTUS EFFECT®, PART 2

LEVEL OF EXPERIMENT: **Medium**

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TEACHER RESOURCES

SUPERHYDROPHOBIC MATERIALS

AIM: The aim of this experiment is to show students some innovative materials that are **highly water repellent, stainless and require less cleaning due to their surface nanoengineering**. These materials have been developed using nature as inspiration, since some plant leaves (such as the lotus leaf or nasturtium (*Tropaeolum*)) leaf have the exceptional property of being superhydrophobic due to nanostructures present in their surface composition. Water simply rolls off these leaves! The effect is due to the interplay of surface chemistry and surface topography at the micro and nano-level. The students will: (a) analyse different materials, including leaves, polymers, glass, etc., and analyse their wetting properties; (b) see and test functional nanomaterials that have been engineered at the nanoscale to be superhydrophobic: a porous silicon wafer fabricated at iNANO (analysis is done by watching a video) and a fabric (from Nano-Tex, Inc.).

FIELD OF NANOTECHNOLOGY APPLICATION: Energy and environment; Environmentally friendly materials

EXTRA TEACHER READING: Module 1, Chapter 2: Nanoscience in nature, and Chapter 5: Overview of nanomaterials,and Module 2, Chapter 2: Environment, and Chapter 3: Energy, in the NANOYOU Teachers Training Kit in Nanotechnologies

REQUIRED STUDENT PRE-KNOWLEDGE:

- Surface properties (hydrophilic, hydrophobic)
- Contact angle (use Appendix I if needed)

STUDENT READING:

- NANOYOU Student Background Reading — Experiment D: Superhydrophobic materials

EXPECTED OUTCOMES:

- Understanding of the effect of surface topography on contact angle, and the insurgence of superhydrophobicity
- Knowledge of novel advanced materials that have been engineered at the nanoscale to be superhydrophobic and their applications
- Analysis of a functional nanomaterial under research at iNANO, Aarhus University (through a video)
- Analysis and hands-on test of a superhydrophobic textile

STUDENT ASSESSMENT:

- NANOYOU Student Laboratory Worksheet — Experiment D: Superhydrophobic materials

BACKGROUND INFORMATION

1. Fundamentals of surface properties

The surface properties of a material are largely related to chemical species that are present at the surface. A very important surface property is its wetting behaviour (i.e. how water interacts with the surface). This property is related to the terminal groups of the molecules at the surface interface, which can be either hydrophilic (water-loving) or hydrophobic (water-hating).

TIP FOR TEACHERS: A very simple example to show in class is a drop of oil in water: oil is made of unsaturated fatty acids which have a chemical structure that makes them extremely water-repellent, so when oil is dropped in water, the oil molecules minimise their contact with water, forming a compact droplet. The instructor can start this part of the experiment by asking students to mention surfaces that are hydrophobic (plastic) or hydrophilic (glass).

One of the methods to quantify the wetting behaviour of a surface is to measure its contact angle (CA). The contact angle is the angle at which a liquid/vapour interface meets the solid surface as illustrated in **Figure 1**. The contact angle is the angle formed by the liquid and the three phase boundaries. The shape of the droplet is controlled by the three forces of interfacial tension, as shown in **Figure 1**. The contact angle provides **information on the interaction energy between the surface and the liquid** (an advanced description of the contact angle and its mathematical formulation are provided in **Appendix I to Experiment D**).

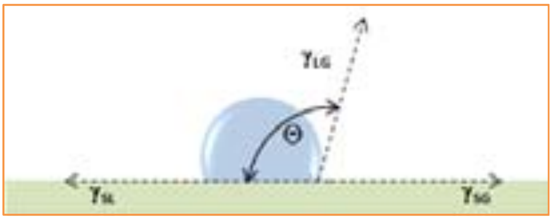

Figure 1: Static contact angle measurement of a droplet of water sitting on a flat solid surface

Image: iNANO, Aarhus University, Creative Commons Attribution Non-Commercial ShareAlike 3.0

The contact angle θ can be measured using an instrument called a contact angle **goniometer** (**Figure 2**). This gives a static measurement of contact angles. A droplet of water is deposited over the surface under investigation and the angle θ measured either manually or, in modern instruments, digitally, by capturing a digital image and using dedicated software.

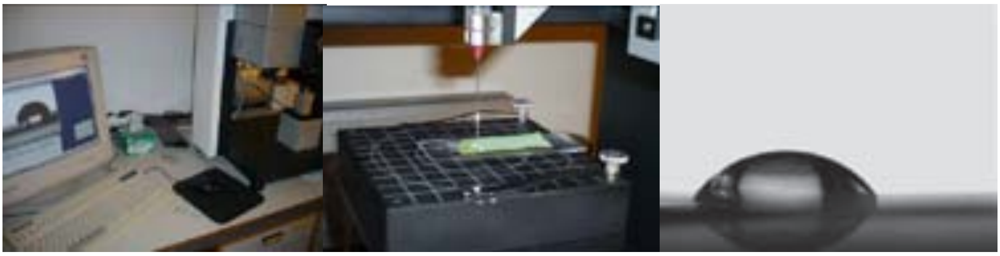

Figure 2: Contact angle goniometer with digital measurement capabilities

Images: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Surfaces can be classified depending on their contact angle as illustrated in the table below.

Contact angle value	Type of surface	Example
~ 0	Superhydrophilic	UV irradiated TiO_2
< 30	Hydrophilic	Glass
30–90	Intermediate (*)	Aluminium
90–140	Hydrophobic	Plastic
> 140	Superhydrophobic	Lotus leaf

(*) If the contact angle is towards 30, the material is defined as hydrophilic; if the contact angle is towards 90, the material is defined hydrophobic.

The larger the contact angle, the more hydrophobic a surface is. Consider what happens when water is put on a piece of glass: the water droplet will completely spread out across the glass and the contact angle will be close to 0°. The water droplet will be so flat that the measurement of the CA is actually difficult. On most hydrophilic surfaces, water droplets will exhibit contact angles between 0 and 30°. If a droplet is placed on less strongly hydrophilic solids, such as a piece of metal, it will have a contact angle up to 90° or larger depending on the material. Highly hydrophobic surfaces have water contact angles as high as 150° or even nearly 180°. These surfaces are **superhydrophobic**. On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent.

Surfaces with nanostructures tend to have very high contact angles, which can reach the superhydrophobic level. This can be understood by imagining that a surface with nano-roughness is formed of a series of very small pillars. When a droplet rests on this 'mat of pillars', it is in contact with a large fraction of air. Consider the ideal case of a single droplet of water in air, it will have a totally spherical shape ($\theta = 180°$). For a droplet of water on a surface with a large air fraction, the larger this fraction, the closer we get to this 'ideal' situation (for a mathematical description of this relationship, see Appendix I).

2. Learning from nature: the Lotus effect®

Materials scientists have long used different chemicals to change the surface properties of a certain surface; for example, silanes are routinely used to render glass hydrophobic.

TIP FOR TEACHERS: A simple example to show in class: metal kitchen utensils such as cooking pans where a layer of Teflon®, a type of plastic, is added to the metal surface of the pan to make it non-stick.

However, surface chemistry can only be used to make hydrophobic surfaces. To reach the superhydrophobic condition, it is necessary to insert topography into the surface, such as a micropattern (details are explained in Appendix I).

Superhydrophobicity is a surface property found in nature, for example in some leaves, such as the lotus leaf, and in some animals, such as in the leg of water striders (Figure 3).

Figure 3: Examples of natural materials that exhibit the Lotus effect®: (left) a water strider; (right) a lotus leaf

Images: (left) Izabela Raszkova, Wiki Commons, Creative Commons Attribution ShareAlike 3.0; (right) iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

The Lotus effect® is described in detail in **Module 1, Chapter 2: Nanoscience in Nature**.

The **superhydrophobic effect found in lotus leaves** has been extensively researched. The lotus plant (*Nelumbo nucifera*) is a native Asian plant which has the distinct property of rendering its leaves particularly clean even if its natural habitat is muddy. The leaves of the lotus plant have the outstanding characteristic of totally repelling water because they are superhydrophobic. The same effect is found in other leaves such as those of nasturtium (*Tropaeolum*) and some *Cannas* (**Figure 4**).

Figure 4: (left) Nasturtium plant; (right) water droplet resting on the surface of a nasturtium leaf

Images: Wiki Commons, Creative Commons Attribution ShareAlike3.0); (right) A. Otten and S. Herminghaus, Göttingen, Germany, NISE Network, reprinted under NISE Network Terms and Conditions

HOW IS THIS 'NANO'?

Detailed SEM analysis of leaves that display the Lotus effect® has revealed the presence of wax nanocrystals on the leaf surface. **These crystals provide a water-repellent layer, which is enhanced by the roughness of the surface, making it a superhydrophobic surface, with a contact angle of about 150°**. The result is that water droplets interfacing with such a leaf are in contact with a large fraction of air. This forces the water to bead and roll off. The images in **Figure 5** show the progressive magnification of a nasturtium leaf. In the last image on the right, **nanocrystals a few tens of nanometres** in size are shown.

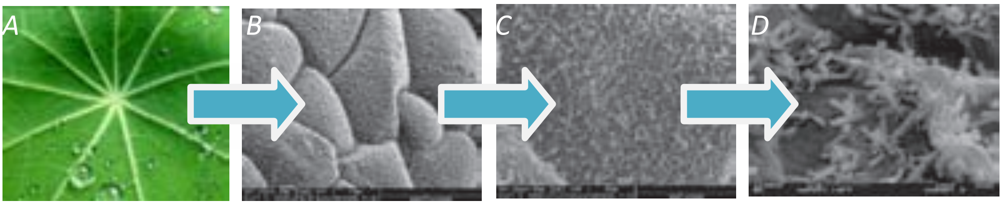

Figure 5: Close-up views at progressive magnification of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right)

Images: (A) A. Snyder, Exploratorium; (B, C) A. Marshall, StanfordUniversity, (D) A. Otten and S. Herminghaus, Göttingen, Germany; all images are material of the NISE Network (http://www.nisenet.org), reprinted under NISE Network Terms and Conditions

The consequence is that water droplets roll off the leaf surface and, in doing so, they drag dirt away, as shown in **Figure 6**. This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt.

Figure 6: Diagram summarising the connection between roughening and self-cleaning: (top) a droplet of water removes dirt from a surface as a result of the Lotus effect®; (bottom) graphical representation of contaminants and water droplets on a lotus leaf

Images: William Thielike, Wiki Commons, Creative Commons ShareAlike 3.0

Contaminants on the surface (generally larger than the cellular structure of the leaves) rest on the tips of the rough surface: when a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf.

3. Lotus-inspired innovative materials

The Lotus effect® has been an **inspiration for several innovative materials**, such as paints, coatings and textiles. The realisation that certain surface properties can induce water repellence is important in numerous applications. Materials scientists are now engineering numerous types of materials to render them superhydrophobic. The main areas of applications are summarised here.

- **Environmentally friendly coatings** and textiles that are dirt repellent and **require less cleaning**. This includes materials such as façade paints, textiles (including personal clothing) and sanitary coatings. In all of these materials, the added advantage is that less cleaning is needed (therefore, less detergent and waste water), with a consequent benefit for the environment.
- **Improving the performance of solar cells (energy application)**. One of the problems with this technology is that these cells are sited outside and therefore prone to becoming very dirty. This layer of dirt ‘masks’ the catalytic areas of the solar cells and therefore reduces their efficiency and lifetime. Coating the solar panel with a superhydrophobic coating keeps the panel considerably cleaner. Because of the nano-surface roughness, the coating is transparent to UV light, a necessity for these types of devices. The superhydrophobic coating is also durable, which further improves the solar panel lifetime.

Products examined in this exercise

1. NANO-TEX®

There are many instances where avoiding the wetting of a surface is an advantage, for example in **textiles**, which are routinely stained by liquids (juices, coffee, etc.) and solids (mustard, ketchup, etc.).

Some companies such as Nano-Tex, Inc. are now commercialising textiles that are engineered to confer superhydrophobic properties on their textiles (**Figure 7**). This effect is obtained by the presence of 'nano-sized whiskers' on the surface of the fibres that make up the fabric.

Figure 7: Liquid staining on a Nano-Tex® fabric

Image: Nano-Tex, Inc., © Nano-Tex, Inc.

In this experiment module, students will analyse and test a superhydrophobic textile from Nano-Tex, Inc. (Nano-Tex® Resist Spills fabric) and compare it with a real lotus leaf.

How does it work? Nano-Tex® Resist Spills fabric is engineered to mimic the Lotus effect®. This is achieved through a large number of very small 'pins', or 'whiskers' on the surface of the fibres. Therefore, the fabric does not contain a surface coating (which could be removed by washing or sweating), but rather the fibres are nano-engineered. The result is a material which is superhydrophobic, as illustrated by the contact angle measured and shown in **Figure 8**. A picture of the contact angle of a lotus leaf is shown for comparison.

Figure 8: (left) High resolution images of the Nano-Tex® fabric; (right) contact angle images of water droplets on Nano-Tex® fabric and lotus leaf

Images: (left) Nano-Tex, Inc., © Nano-Tex, Inc.; (right) iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

NOTE: Nano-Tex® Resist Spills fabric is used in a number of commercial products (see http://www.nano-tex.com for more information on the fabric and a list of brands that use this fabric in their products). Other companies are developing fabrics nano-engineered to resist spills and stains or with other improved properties. See the product inventory online (http://www.nanotechproject.org/inventories/consumer/) for more details.

2. POROUS SILICON

The second material analysed in this experiment is a material under research at iNANO which is made of **porous silicon**.

In this exercise, students cannot use a real piece of porous silicon. A video is provided to show in class (**NANOYOU Video 4 — Lotus effect® Part 2** (http://www.nanoyou.org).

As already mentioned, surfaces (or textiles) engineered to be superhydrophobic are made of very small 'pins', or 'whiskers' inspired from the microstructure of the lotus leaf. The **porosity and spacing of this fine structure determines the wetting properties of the material**. The material shown in the video has a contact angle of 167° (**Figure 9**).

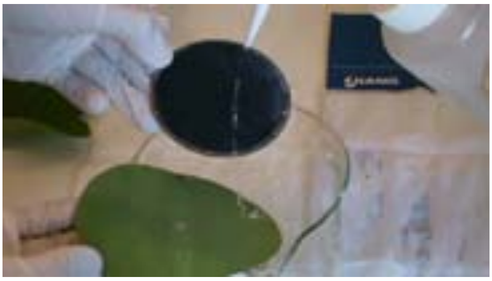

Figure 9: Image from the NANOYOU Video 4 — Lotus Effect®, Part 2 — showing a piece of porous silicon compared to a real lotus leaf

Image: L. Filipponi, iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

The superhydrophobic effect results from the peculiar micro/nanotexture of this surface.

How does it work?

Surfaces engineered to be superhydrophobic are made of very small 'pins' inspired from the microstructure of the lotus leaf. The porosity and spacing of this fine structure determines the wetting properties of the material. To do so, scientists modify the surface of normal silicon (which is normally hydrophilic) by specialised methods: for example, electrochemical dissolution of crystalline silicon with HF ([17]). Surfaces engineered to be superhydrophobic have many applications (solar panel coatings, protein array surfaces, etc.). In this experiment, in **Video 4 — Lotus effect®, Part 2** (http://www.nanoyou.org) students will see a piece of porous silicon prepared by Dr Anton Ressine during his research at the Lund Institute of Technology (Sweden) and now under research at iNANO.

([17]) The interested reader can find more information in numerous reviewed papers, such asRessine, A. et al., *Analytical Chemistry*, 2003, 75, 6968–6974.

Figure 10 shows some samples of **porous silicon**, which can be engineered to be superhydrophobic. In this figure, sample A is normal silicon (untreated) and samples B, C and D are porous silicon samples obtained with different fabrication conditions. **Table 2** summarises the contact angle of each sample.

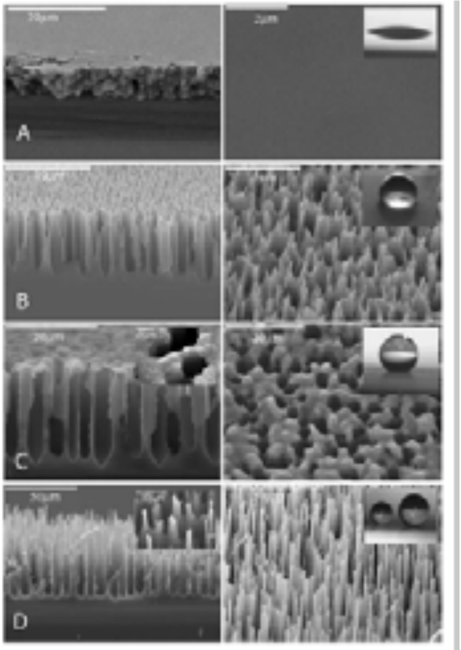

Figure 10: SEM Images of four different samples showing a change in contact angle from hydrophilic (A) to hydrophobic and superhydrophobic. Samples B to D are made of porous silicon, sample D is the one with the larger contact angle

Image: A. Ressine, 'Development of protein microarray chip technology', PhD thesis, 2005, reprinted with the permission of the author

Sample	Contact angle (°)
A	64
B	110
C	155
D	167

Table 2: Contact angles of samples in **Figure 10**

The sample of porous silicon shown **in the video is sample D**. As seen from Figure 10 and Table 2, it is the most superhydrophobic with a contact angle of 167°. What is interesting to note is that in sample B, the distance between the 'pillars' is smaller than in sample D, so the porosity (percentage of voids in the material) is lower. Therefore, in sample D, there is a larger 'fraction of air' to which the droplet is exposed, and the contact angle is larger. This examples shows that to engineer superhydrophobic surfaces, scientists need to find the right fabrication conditions to obtain the right balance of 'nano-pillars' and porosity within the silicon surface. It is this balance of micro and nanotexturing that leads to superhydrophobic materials.

The surface of the superhydrophobic porous silicon remarkably resembles that of a water strider, which also displays a micro/nanotextured surface. Notably, the contact angle of the water strider leg is also 167°.

THIS EXPERIMENT IN CLASS

Depending on the class level and time available, this experiment module can be used in different ways. The authors suggest the following.

1. Start with a general discussion on surface properties

- What property can be used to compare them?
- How does water interact with different surfaces?

2. Introducing the concepts of hydrophobicity and hydrophilicity

- Give definitions and some examples
- How can a hydrophilic surface (such as glass) be made hydrophobic? Students/teacher should discuss coatings and their effect on surfaces
- Define the contact angle as a surface characterisation method (depending on the level of the class, this can be less or more advanced; for an advanced class, refer to Appendix I).

3. Test different surfaces

Different materials should be tested for their wetting behaviour. The details are given in the next section. Materials that can be tested (from more hydrophilic to more hydrophobic) are: glass, coated wood, aluminium, plastic, parafilm.

- Ask the students to draw up a scale of hydrophobicity based on what they can see. Use the images provided in this kit (at the end of the **Student Laboratory Worksheet — Experiment D**).

4. Test a superhydrophobic surface: the lotus leaf

If available, a lotus leaf should be obtained from a botanical garden. If not available, alternative plants can be used, such as nasturtium.

- Discuss the Lotus effect® and how this is inspirational for new materials
- Watch the NANOYOU **Video 4 — Lotus effect®Part 2** (http://www.nanoyou.org) showing the Lotus effect® on a real lotus plant and the same effect on an artificially made surface (porous silicon, iNANO research labs)
- Let the students observe the effect on a real leaf and compare with other leaves

5. Test a superhydrophobic textile

- Test the Nano-Tex® textile for spills of liquids, solids, soil, etc.

6. Discuss applications and implications

- Nano-Tex® is an example of a practical application of nanotechnologies. Ask the students to think of other applications where the superhydrophobic effect might be useful.

MATERIALS

The material below is indicated assuming students will work in pairs.

Materials for the entire class (to be shared)

- Different stain agents to test (**amounts indicated are for the entire class**)
  - water
  - juice (1 l) or Coke (1 l)
  - balsamic vinegar or wine (1 glass)
  - cooking oil (1 glass)
  - ketchup (1 small container)
  - mustard (1 small container)
  - mayonnaise (1 small container)
  - organic soil (a couple of handfuls)

Materials for each student pair:

- Different surfaces to test
  - microscope glass slide
  - flat piece of plastic 10 x 10 cm (e.g. cut a piece out of a plastic sheet such as a plastic folder)
  - flat piece of aluminium foil 10 x 10 cm
  - piece of cloth 10 x 10 cm (ask students to bring from home or get remnants from fabric store)
  - two pieces of filter paper
  - pieces of textiles to compare (each about 10 x 10 cm): 4x Nano-Tex® Resist Spills fabric (18) and two other types (three samples of 100 % cotton and three samples of fabric made with synthetic fibre such as polyester or cotton/poly blend; in this protocol, we used a fabric with 70 % polyester, 30 % cotton)
- Different plant leaves (collect from school garden or bring from home)
  - common plant leaf such as ivy
  - piece of lotus leaf or nasturtium
- laboratory bottle filled with water
- 5x eyedroppers (or Pasteur pipettes) to apply the liquid stain agents
- plastic knives or spoons for applying the other stain agents
- bucket with laundry detergent and water (this can be shared by the entire class)
- 10 x 10 cm piece of sandpaper (a large sheet can be cut up)
- permanent marker
- several plastic cups to hold water and stain agents
- several plastic plates to put materials in when conducting the material testing
- paper, glue and scissors

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(18) We suggest purchasing a pair of trousers or a shirt made of the Nano-Tex® fabric (about EUR 40) and cutting it into pieces (see http://www.nano-tex.com for more information on the fabric and a list of brands that use this fabric in their products). A list of commercial products made of Nano-Tex® fabric can also be found online (http://www.google.co.uk/products?q=nano+tex&hl=en). Some products will be made of Nano-Tex® Resist Spills, or Nano-Tex® Resist Spills and Releases Stains. Both are fine for this experiment but might give slightly different results in terms of resistance to solids (see http://www.nano-tex.com for details on the technical difference between these two types of fabric).

SAFETY NOTE: This experiment does not use chemicals, simply common liquids and solids. Nevertheless, staining is possible so wash hands and surfaces thoroughly after handling. Use appropriate clothing protection, gloves and eye protection. Collect all liquids and washing water in glass/plastic containers and dispose of down the sink. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

TERMS OF USE OF IMAGES: Images in this experiment protocol are copyright of iNANO, Aarhus University unless otherwise specified differently. Permission is granted to share and distribute these images under the licence Creative Commons Attribute ShareAlike 3.0.

PROCEDURE

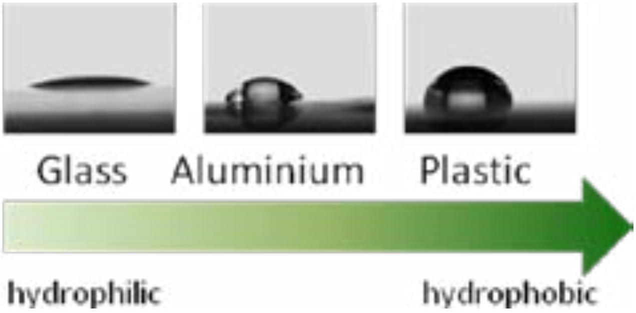
It is assumed that most schools will not have access to an instrument to measure contact angles, so this is not suggested and images are provided throughout the text on actual contact angle measurements conducted at iNANO. Images of contact angles on different surfaces are given in the Student Laboratory Worksheet —Experiment D: Superhydrophobic materials. However, if a teacher has access to this instrument, this experimental activity can include a session dedicated to contact angle measurements.

1. Understanding surface properties: hydrophilic and hydrophobic

Give students the different surfaces to test (as detailed in theMaterials section): glass slide, plastic, aluminium foil, wood, filter paper. Ask the students to place a couple of droplets of water on each material, recording their observations. Filter paper will absorb water very quickly.

Ask the students to order the materials starting from the most hydrophilic to the most hydrophobic based on their visual observation. Then ask the students to use the photos of water droplets provided in the Student Laboratory Worksheet — Experiment D: Superhydrophobic materials and match them to the scale they have just made.

Students should complete Q1 to Q4 of the student laboratory worksheet



2. Analysis of natural nanomaterials: the lotus leaf

- Collect some plant leaves with the students from the school garden, or ask them to bring a few from home (e.g. ivy).

TIP FOR TEACHERS: The collection of the leaves could be combined with a school visit to a botanical garden for a more general lesson on plants, their surface properties, etc. This would allow an interdisciplinary lesson that bridges natural sciences with chemistry.

If possible, collect a lotus leaf from a botanic garden in your town. If this is problematic, there are some alternative plants that can be used such as nasturtium (*Tropaeolum*).

TIP FOR TEACHERS: Nasturtium can be bought in the spring time as seeds and planted in a medium-sized pot. This way a school can have its 'lotus-like plant' to be used and tested as required at minimal cost! The entire plant can easily be bought at garden shops (in summer).

STEP 1

- **Ask the students to test the 'common' leaves they have collected (or brought from home) for their wetting behaviour.** Let them pour some water over the leaf and observe how it rolls off the surface. A bucket or other container should be used to collect the water. Paper towel should be to hand.

Students should complete Q5 and Q6 of the student laboratory worksheet

STEP 2

- **Now ask the students to test a lotus or nasturtium leaf**. Cut leaves into several pieces if you don't have enough for all the class.

Students should complete Q7 and Q13 of the student laboratory worksheet

STEP 3

- **After observing the Lotus effect®on a real plant, show the class the NANOYOU Video 4 — Lotus effect®Part 2** (http://www.nanoyou.org), which shows a surface engineered at iNANO (Aarhus University), with surface properties comparable to the lotus leaf (superhydrophobic).

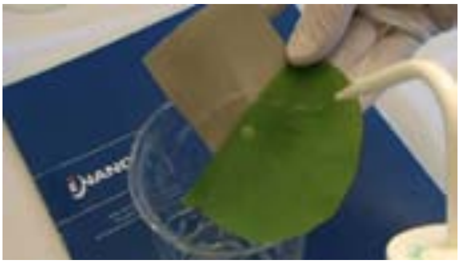
ALTERNATIVE: If the collection of leaves is problematic, this part of the experiment can be shown entirely through the video in the appendix (**Video 3 — Lotus effect®, Part 1** (http://www.nanoyou.org): natural plants showing the Lotus effect®; **Video 3 — Lotus effect®, Part 2** (http://www.nanoyou.org): the wetting properties of lotus leaves compared with conventional leaves, with the wetting behaviour of an advanced material investigated at iNANO, and with a piece of Nano-Tex® fabric. A direct comparison between a lotus leaf and these advanced materials is shown). The questions listed in the Student Laboratory Worksheet — Experiment D: Superhydrophobic materials should be available while watching these videos to encourage class discussion.

3. Analysis of a functional nanomaterial

In this part of the experiment, students analyse a textile that has been engineered to replicate the Lotus effect® and has self-cleaning properties.

STEP 1

- Give each student **a piece of Nano-Tex® and a piece of a normal cotton fabric**. Place both in a plastic plate and let them pour water over it. If possible, have a lotus or nasturtium leaf available in class for comparison (the leaf can be cut into pieces if necessary and shared in class).



NB: If lotus or nasturtium leaves are not available, use the **Video 3 Lotus effect®, Part 2** (http://www.nanoyou.org).

Students should complete Q15 of the student laboratory worksheet

STEP 2

Now students should test the Nano-Tex® fabric and compare it tonormal cotton and a semi-synthetic fabric. In this step, liquid stains should be used (Coke, vinegar, oil, etc.).

- Each student should have a piece of cotton fabric, a piece of a semi-synthetic fabric, and a piece of Nano-Tex®.
- Give each student four plastic cups, each containing one of the liquids to be tested (juice, Coke, vinegar, oil, etc.).
- Let the students place a droplet of each liquid to be tested (juice, Coke, vinegar or wine, and oil) on each of the fabrics, with the aid of a pipette.

- Students should leave the solutions on the **three types of fabrics at the same time and for a fixed duration**.

TIP FOR TEACHERS: A good idea would be to assign different 'testing times' to different students or small groups of students. This way, students could test the effect of the liquid staining on the fabric (in particular the Nano-Tex®) for 5 minutes, 10 minutes, 20 minutes, etc. Of course, each student could do all the tests but then more pieces of fabrics will be needed.

- After the set time, ask the students to remove each liquid gently from the fabric using a piece of paper towel.

Students should complete Q16 and Q17 of the student laboratory worksheet

STEP 3

Now students should test the Nano-Tex® fabric and compare it tonormal cotton and a semi-synthetic fabric. In this step, semi-solid stains should be used (mayonnaise, mustard, etc.).

- Each student should have a piece of cotton fabric, a piece of a semi-synthetic fabric, and a piece of Nano-Tex®.
- Give each pair of students a plastic plate with some of the semi-solids to test (mayonnaise, ketchup, mustard, etc.). Also provide a permanent marker. **Students should have paper towel or a damp cloth to hand.**
- Now ask the students to test the three types of fabrics with the 'solids' chosen — ketchup, mustard, mayonnaise. On the fourth area available, ask them to mark it with a permanent marker or a pen.
- After a set time (e.g. 5 minutes), ask the students to try to remove the solids from the fabrics, using a damp cloth or paper towel. Students should be careful not to mix the different solids. Observations on how the fabrics stain should be recorded.

Students should complete Q18 and Q19 of the student laboratory worksheet

NOTE: The Nano-Tex® will appear considerably less stained than the other fabrics, but some traces of solids might be left (depending on what is used), which can be easily removed with the fingers. The permanent marker stain will not be removed with this method (it needs soap and water). The fabric may appear nearly perfectly clean, but not totally. **Point this out to the students, as it is important to keep in mind that 'nano is not magic', and even this fabric will need some cleaning, but this will require much less effort and detergent.**

- The same piece of Nano-Tex® can be reused so students can be encouraged to test it to the limit, by vigorously rubbing the solids to the fabric and see what happens!

STEP 4

Now students should test the Nano-Tex® fabric and compare it to normal cotton and a semi-synthetic fabric. In this step, organic soil is used.

- Each student should have a piece of cotton fabric, a piece of a semi-synthetic fabric, and a piece of Nano-Tex®. Give each pair of students some organic soil in a plastic plate.
- Place some organic soil in the middle of each fabric, fold the fabric and ask the students to rub it in. Then open each piece of fabric, remove the soil in each, and observe. Did all the fabrics get dirty? In the same way? Some soil will be visible even on the Nano-Tex® fabric.

- Now ask the students to try to **clean the fabrics with their hands**: while the cotton and semi-synthetic fabric will remain somewhat dirty (the soil seems to be lodged inside the fibres of the fabric), the Nano-Tex® fabric will appear considerably cleaner. In the images provided, the Nano-Tex® fabric is shown after it has been rubbed with some soil (left), and how it appears after the dirt has been wiped off just by using the fingers (right).

Students should complete Q20 to Q26 of the student laboratory worksheet

STEP 5

Test the Nano-Tex® with sandpaper.

- Each student should have a new piece of Nano-Tex® and a piece of sandpaper.
- This can be tested to see **how durable the fabric is**. Ask the students to observe how water rolls off this fabric first. Then give them a piece of sandpaper, and ask them to rub it over the fabric. Does this affect the fabric? Test the fabric to its limit! **NB:** The use of heat is not recommended.

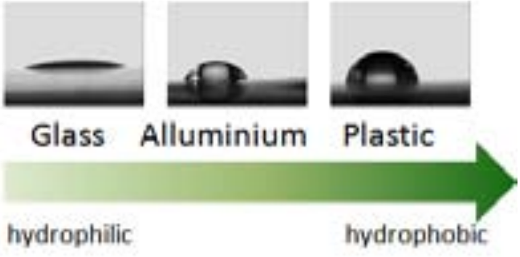
Students should complete question Q27 of the student laboratory worksheet

ANSWERS TO QUESTIONS

Q1: Filter paper absorbs water, so it is very hard to estimate the contact angle. Furthermore, because water is absorbed by this material, the contact angle would not be the right tool to assess its surface properties.

Q2: It should be glass, aluminium, plastic. Glass should be on the side of 'very hydrophilic' but plastic should not be classed as 'very hydrophobic'.

Q3: None of the material is very hydrophobic, as shown by the shape of the droplet.



Q4: The photos should be as in the image here displayed.

Q5: Water will wet common leaves.

Q6: Water droplets slide over the leaf but don't roll.

Q7: Water doesn't wet the surface of the leaf.

Q8: Water droplets roll off the leaf, they look like beads.

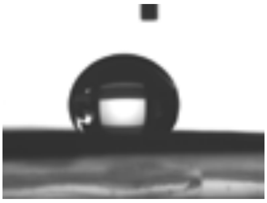
Q9: Water droplets bounce off the leaf like beads.

Q10: It is very hard to get a water droplet to rest on the leaf: it behaves like a bead, and is very unstable. This means the surface is extremely hydrophobic.

Q11: No, even if the leaf is kept under running water, when you stop the water it is completely dry.

Q12: It is much more hydrophobic than plastic.

Q13: The picture should be placed on the far right of the scale. The correct picture is displayed here.



Q14: The porous silicon material behaves very similarly to the lotus leaf.

Q15: Yes, it does.

Q16: Yes, there is. All liquids seem to rest on the surface of Nano-Tex® and form little beads, whereas in the other fabrics liquids quickly spread.

Q17: Liquid stains are easily removed from the fabric simply by absorbing them with paper towel. Almost no trace is left. Cleaning is very simple.

Q18: When solids are placed on Nano-Tex®, the effect is not as clearly visible as with liquid stains.

Q19: Removal of solid stains is easy but a little bit of the stain remains. This can be easily taken away by simply brushing the fabric with the hands.

Q20: All solids can be removed using a wet cloth. The only solid that cannot be removed with this method is the permanent marker stain.

Q21: All fabrics except Nano-Tex® seem to 'absorb' the dirt, in the sense that it clearly penetrates the fabric. In the case of Nano-Tex®, dirt seems to remain on the surface, and overall this fabric is stained less.

Q22: No, even Nano-Tex® shows a little staining, although much less than the other fabrics.

Q23: Nano-Tex®.

Q24: The only fabric that becomes clean as new is the piece of Nano-Tex® tested with dirt. All others show a little staining, particularly from the permanent marker.

Q25: Nano-Tex®.

Q26: The stain that is hardest to remove from Nano-Tex® is the permanent marker. This contains some chemicals that are deliberately very hard to remove.

Q27: Even after sanding, the piece of Nano-Tex® retains its properties. The material is very durable. **NB:** The answer here also depends on the degree of damage done by the students, how long they sand it, etc.

CREDITS: This experiment is partly adapted from the Applications Activity: Nano-Tex(*http://mrsec.wisc.edu/Edetc/IPSE/educators/nanoTex.html*).

We would like to thank Nano-Tex, Inc. for their courtesy in providing a piece of their Nano-Tex® textile (Resists Spills), and for providing images of this material.

The author wishes to thank Anton Ressine (iNANO, Aarhus University) for providing the porous silicon sample shown in the videos of this experiment.

REFERENCES

Barthlott, W., Neinhuis, C., 'Purity of the sacred lotus, or escape from contamination in biological surfaces', *Planta*, 1997, 202: 1–8.

Eiji Hosono, Shinobu Fujihara, Itaru Honma, and Haoshen Zhou, 'Superhydrophobic Perpendicular Nanopin Film by the Bottom-Up Process', *Journal of the American Chemical Society*, 2005; 127(39) pp. 13458–9.

Cheng, Y. T., Rodak, D. E., Wong, C. A., Hayden, C. A., 'Effects of micro and nano-structures on the self-cleaning behaviour of lotus leaves', *Nanotechnology*, 2006, 17:1359–62.

Ressine, A. et al., 'Macro-/Nanoporous Silicon as a Support for High-Performance Protein Microarrays', *Analytical Chemistry*, 2003, 75: 6968–6974.

APPENDIX FOR TEACHERS

SUPERHYDROPHOBIC MATERIALS

Extra resources for teachers on contact angle

The concept can be illustrated with a small liquid droplet on a flat horizontal solid surface (**Figure 1**). The contact angle is the angle formed by the liquid and the three phase boundaries. The shape of the droplet is controlled by the three forces of interfacial tension, as shown in **Figure 1**. The contact angle provides information on the interaction energy between the surface and the liquid.

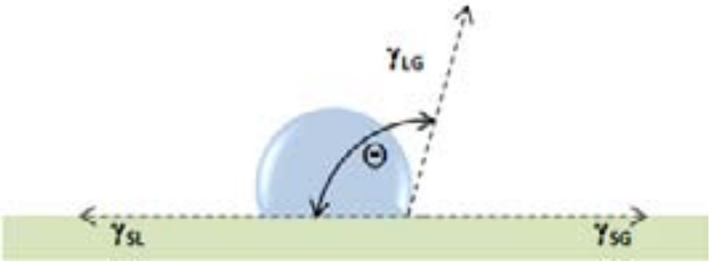


Figure 1: Static contact angle measurement of a droplet of water sitting on a flat solid surface

In 1805, Thomas Young defined the contact angle θ by analysing the forces acting on a fluid droplet resting on a solid surface surrounded by a gas:

$$\gamma_{SG} = \gamma_{SL} + \cos\theta^{*}\gamma_{LG} \quad \textbf{(Eq. 1)}$$

where:

γ_{SG} = interfacial tension between the solid and gas

γ_{SL} = interfacial tension between the solid and liquid

γ_{LG} = interfacial tension between the liquid and gas

Young's equation represents an idealistic situation where it is assumed that the surface is planar (without any roughness) and chemically homogeneous. 'Real' surfaces are not like this: they will display a degree of surface heterogeneity and roughness.

Consider a droplet of water on a surface which is not chemically heterogeneous, but has 'patches' of different chemistries (**Figure 2**):

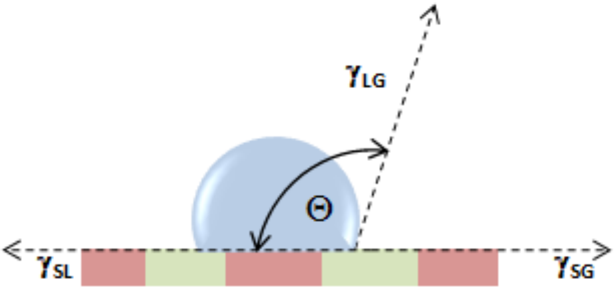


Figure 2: Contact angle measurement of a water droplet on a flat heterogeneous surface having two different surface chemistries

Young's equation can be rewritten for the case of a heterogeneous surface composed of two fractions φ_1 and φ_2 each having its planar contact angle θ_1 and θ_2, producing a total effective contact angle θ^* equal to:

$$\cos\theta^* = \varphi_1\cos\theta_1 + \varphi_2\cos\theta_2 \qquad \textbf{(Eq. 2)}$$

Now consider a surface with a surface roughness. The water droplet resting on such a surface will be alternately in contact with air and with areas of solid surface (Cassie-Baxter model):

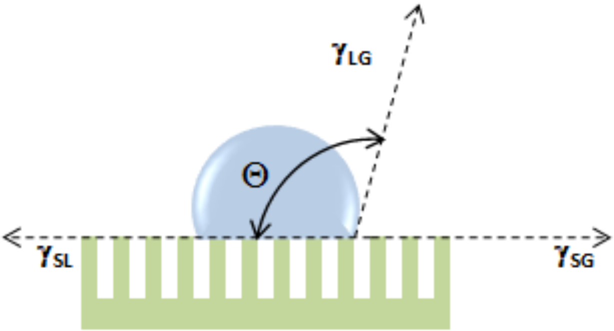


Figure 3: Cassie-Baxter model of contact angle measurement of a water droplet sitting on a surface with topographical features.

For an ideal surface that impedes total wetting, there is no contact with the surface, so there is no contact angle and $\theta_2 = 180°$. In this case, Young's equation can be rewritten as in (**Eq. 1**) but the surface can be described as an alternating air and solid interface. This means that for the 'air fraction' $\theta = 180°$ and **Eq. 2** becomes:

$$\cos\theta^* = \varphi_1\cos\theta_1 + \varphi_2\cos 180$$

since cos 180 = 1 then:

$$\cos\theta^* = \varphi_1\cos\theta_1 + \varphi_2 \qquad \textbf{(Eq. 3)}$$

In the extreme case where the droplet is in contact only with air, $\theta = 180°$. Therefore, the bigger the air fraction of the surface roughness, the bigger is the contribution to Eq. 3, and the higher the resulting contact angle. **For this reason, it is predicted that a surface with nanoscale surface roughness will give rise to surfaces with very high contact angle values (superhydrophobic). Figure 4** exemplifies this concept.

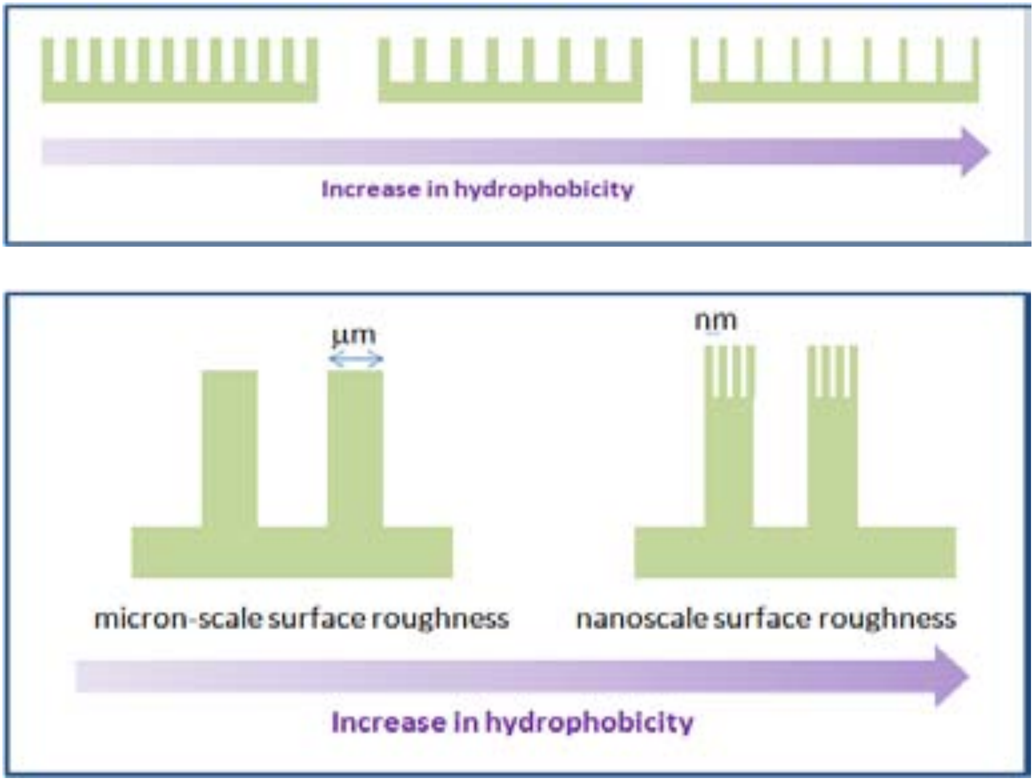


Figure 4: Schematic representations showing the effect of changing porosity (top) and size of the topography (bottom) on surface hydrophobicity

STUDENT BACKGROUND READING

SUPERHYDROPHOBIC MATERIALS

The aim of this experiment is to analyse some innovative materials that are highly water repellent, stain less and require less cleaning as a result of their surface nano-engineering. These materials have been developed using nature as an inspiration, since some plant leaves have exceptional properties due to their surface composition. The property considered here is the superhydrophobic effect found in some leaves, such as the lotus leaf. The effect is due to **interplay of surface chemistry and surface topography at the micro and nano-level**.

In this experiment you will:

- study and **test the properties of a lotus leaf** (or another type, the nasturtium leaf, which has similar properties);
- learn about functional nanomaterials that have been engineered at the nanoscale to be superhydrophobic: a **porous silicon wafer** under study at iNANO (by watching a video); and a fabric (from Nano-Tex, Inc.) — you will **test Nano-Tex®** fabric to see how it performs compared to a normal piece of cotton fabric and compared to a lotus leaf.

In this document, background information for the experiment is provided: we will review some fundamental concepts of surface properties, and then see how natural materials can become inspirational to some new advanced materials that totally repel water!

1. SURFACE PROPERTIES

The surface properties of a material are largely related to **chemical species that are present at the surface**. A very important surface property is its wetting behaviour (i.e. how water interacts with the surface). This property is related to the terminal groups of the molecules at the surface interface, which can be either hydrophilic (water-loving) or hydrophobic (water-hating). Think of what happens when you put oil in water — the oil will tend to agglomerate and form one big droplet and rest on the surface of the water. This is because water is hydrophilic, but oil is hydrophobic. The two liquids try to minimise their contact.

One of the methods to quantify the wetting behaviour of a surface is to measure its contact angle (CA). The contact angle is the angle at which a liquid/vapour interface meets the solid surface as illustrated in **Figure 1**. The contact angle provides **information on the interaction energy between the surface and the liquid**.

The contact angle θ can be measured using an instrument called a contact angle **goniometer** (**Figure 2**). This gives a static measurement of contact angles. A droplet of water is deposited over the surface under investigation and the angle θ measured either manually or, in modern instruments, digitally, by capturing a digital image and using dedicated software.

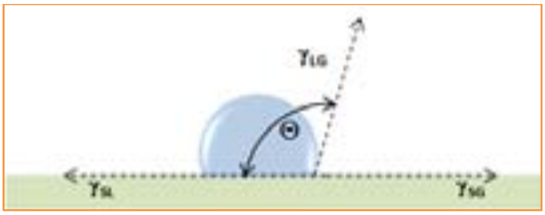


Figure 1: Static contact angle measurement of a droplet of water sitting on a flat solid surface

Image: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Figure 2: Contact angle goniometer with digital measurement capabilities

Images: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

Surfaces can be classified depending on their contact angle as illustrated in the table below.

Contact angle value	Type of surface	Example
~ 0	Superhydrophilic	UV irradiated TiO_2
< 30	Hydrophilic	Glass
30–90	Intermediate (*)	Aluminium
90–140	Hydrophobic	Plastic
> 140	Superhydrophobic	Lotus leaf

(*) If the contact angle is towards 30, the material is defined as hydrophilic; if the contact angle is towards 90, the material is defined hydrophobic.

Hydrophilic means 'water-loving', and hydrophobic means 'water-hating'. The larger the contact angle, the more hydrophobic a surface is. Consider what happens when you put water on a piece of glass: the water droplet will spread out all over the glass and the contact angle will be close to 0°. The water droplet will be so flat that the measurement of the CA is actually difficult.

On most hydrophilic surfaces, water droplets will exhibit contact angles between 0 and 30°. If the droplet is placed on less strongly hydrophilic solids, such as a piece of metal, it will have a contact angle up to 90° or larger depending on the material. Highly hydrophobic surfaces have water contact angles as high as 150° or even nearly 180°. **These surfaces are 'superhydrophobic'. On these surfaces, water droplets simply rest on the surface, without actually wetting it to any significant extent.**

Surfaces with nanostructures tend to have very high contact angles, which can reach the superhydrophobic level. This can be understood by imagining that a surface with nano-roughness is formed of a series of very small pillars. When a droplet rests on this 'mat of pillars' it is in contact with a **large fraction of air**. Consider the ideal case of a single droplet of water in air, it will have a totally spherical shape ($\theta = 180°$). For a droplet of water on a surface with a large air fraction, the larger this fraction, the closer we get to this 'ideal' situation.

2. LEARNING FROM NATURE: THE LOTUS EFFECT®

Materials scientists have long used different chemicals to change the properties of various surfaces. Think of metal kitchen utensils such as cooking pan: a layer of Teflon®, which is a type of plastic, is added to the metal surface of the pan to make it non-stick.

Surface chemistry can, however, only be used to make hydrophobic surfaces. **To reach the super-hydro-phobic condition, it is necessary to insert topography into the surface, such as a micro or nanopattern.**

Superhydrophobicity is a surface property found in nature, for example in some leaves, such as the lotus leaf, and in some animals, as in the legs of water striders (Figure 3).

Figure 3: Examples of natural materials that exhibit the Lotus effect®: (left) a water strider; (right) a lotus leaf

Images: (left) Izabela Raszkova, Wiki Commons, Creative Commons Attribution ShareAlike 3.0; (right) iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

How does it work? The lotus plant (*Nelumbo nucifera*) is a native Asian plant which has the distinctive property of rendering its leaves particularly clean even if its natural habitat is muddy. For this reason, it is regarded as a symbol of purity. The leaves of the lotus plant have the outstanding characteristic of **totally repelling water because they are superhydrophobic.** The consequence is that water droplets roll off the leaf surface and, in doing so, drag dirt away from it. This effect, 'self-cleaning', renders the lotus leaf clean and resistant to dirt. The **same effect is found in other leaves** such as those of nasturtium and some *Cannas* (**Figure 4**).

Figure 4: (left) Nasturtium plant; (right) water droplet resting on the surface of a nasturtium leaf

Images: (left) Wiki Commons, Creative Commons Attribution ShareAlike 3.0; (right) A. Otten and S. Herminghaus, Göttingen, Germany, NISE Network, reprinted under NISE Network Terms and Conditions

How is this 'nano'?

Detailed SEM analysis of leaves that display the Lotus effect® has revealed the presence of wax nanocrystals on the leaf surface. **These crystals provide a water-repellent layer, which is enhanced by the roughness of the surface, making it a superhydrophobic surface, with a contact angle of about 150°**. The result is that water droplets interfacing with such a leaf are in contact with a large fraction of air. This forces the water to bead and roll off. **Figure 5** shows the progressive magnification of a nasturtium leaf. In the last image on the right, **nanocrystals few tens of nanometres** in size are shown.

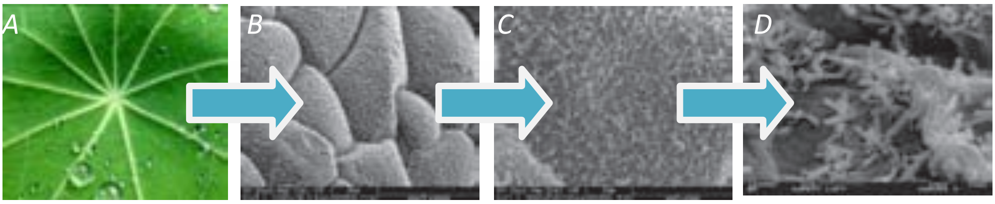


Figure 5: Close-up views at progressive magnification of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right)

Images: (A) A. Snyder, Exploratorium; (B, C) A. Marshall, Stanford University; (D) A. Otten and S. Herminghaus, Göttingen, Germany; all images are material of the NISE Network, reprinted under NISE Network Terms and Conditions

Contaminants on the surface (generally larger than the cellular structure of the leaves) rest on the tips of the rough surface. When a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf (**Figure 6**).

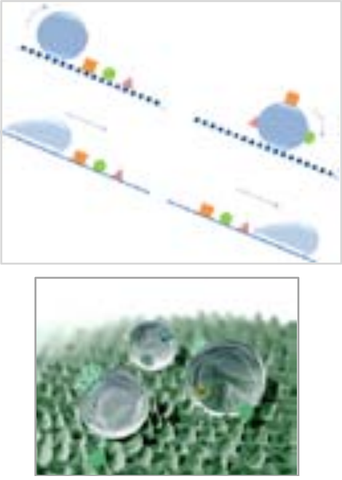


Figure 6: Diagram summarising the connection between roughening and self-cleaning: (top) a droplet of water removes dirt from a surface due to the Lotus effect®; (bottom) graphical representation of contaminants and water droplets on a lotus leaf

Images: by William Thielike, Wiki Commons, Creative Commons ShareAlike 3.0

NEW ADVANCED MATERIALS AND THEIR APPLICATIONS

The Lotus effect® has been an **inspiration for several innovative materials**, such as paints, coatings, and textiles. The realisation that certain surface properties can induce water repellence is important in numerous applications. Materials scientists are now engineering numerous types of materials to render them superhydrophobic. The **main areas of applications are summarised here.**

- **Environmentally friendly coatings** and textiles that are dirt repellent and **require less cleaning**. This includes materials such as façade paints, textiles (including personal clothing) and sanitary coatings. In all of these materials, the added advantage is that less cleaning is needed (therefore, less detergent and waste water), with a consequent benefit for the environment.
- **Improving the performance of solar cells (energy application)**. One of the problems with this technology is that they are sited outside and therefore can become very dirty. This layer of dirt 'masks' the catalytic areas of the solar cells and therefore reduces their efficiency and lifetime. Coating the solar panel with a superhydrophobic coating keeps the panel considerably cleaner. Because of the nano-surface roughness, the coating is transparent to UV light, a necessity for these types of devices. The superhydrophobic coating is also durable, which further improves the solar panel lifetime.

These are not the only areas of applications. Another important area is the **nanomedicine** sector where nano-engineered superhydrophobic surfaces are used to improve **microarray technology**.

PRODUCTS EXAMINED IN THIS LABORATORY EXERCISE

1. NANO-TEX®

There are many instances where avoiding the wetting of a surface is an advantage, for example in **textiles**, which are routinely stained by liquids (juices, coffee, etc.) and solids (mustard, ketchup, etc.). Some companies such as Nano-Tex, Inc. are now commercialising textiles that are engineered to confer superhydrophobic properties on their textiles (**Figure 7**). This effect is obtained by the presence of ‘nano-sized whiskers’ on the surface of the fibres that make up the fabric.

Figure 7: Liquid staining on a Nano-Tex® fabric

Image: Nano-Tex, Inc., © Nano-Tex, Inc.

In this experiment, you will analyse and test a superhydrophobic textile from Nano-Tex, Inc. and compare it toa real lotus leaf. You will stain a piece of fabric using liquids and solids (such as ketchup, mustard, etc.).

How does it work? Nano-Tex® Resist Spills fabric is engineered to mimic the Lotus effect®. This is achieved through a large number of very small ‘pins’ or ‘whiskers’ on the surface of the fibres. Therefore, the fabric does not contain a surface coating (which could be removed by washing or sweating), but rather the fibres are nano-engineered. The result is a material which is superhydrophobic, as illustrated by the contact angle measured and shown in the **Figure 8**. A picture of the contact angle of a lotus leaf is shown for comparison.

Figure 8: (left) High resolution images of the Nano-Tex® fabric; (right) contact angle images of water droplets on Nano-Tex® fabric and lotus leaf

Images: (left) Nano-Tex, Inc., © Nano-Tex, Inc.; (right) iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

2. POROUS SILICON

The second material to be analysed in this experiment is a material under research at iNANO in collaboration with Lund University which is made of **porous silicon**. **You will see the behaviour of this material in a video.**

As already mentioned, surfaces (or textiles) engineered to be superhydrophobic are made of very small 'pins' or 'whiskers' inspired by the microstructure of the lotus leaf. The **porosity and spacing of this fine structure determines the wetting properties of the material**. The material shown in the video has a contact angle of 167°.

The superhydrophobic effect results from the particular micro/nanotexture of this surface.

In this experiment, you will see how porous silicon compares with a real lotus leaf in terms of wetting in a video.

Figure 9: Images from NANOYOU Video 4 — Lotus effect®, Part 2 — showing the wetting properties of a piece of porous silicon (left) and how this material compares with a real lotus leaf (right)

Images: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0

How does it work?

Surfaces engineered to be superhydrophobic are made of very small 'pins' inspired by the microstructure of the lotus leaf. The porosity and spacing of this fine structure determines the wetting properties of the material. To do so, scientists modify the surface of normal silicon (which is normally hydrophilic) by specialised methods.

Figure 10 shows some samples of **porous silicon**, which can be engineered to be superhydrophobic. In this figure, sample A is normal silicon (untreated) and samples B, C and D are porous silicon samples obtained with different fabrication conditions. **Table 2** summarises the contact angles of each sample.

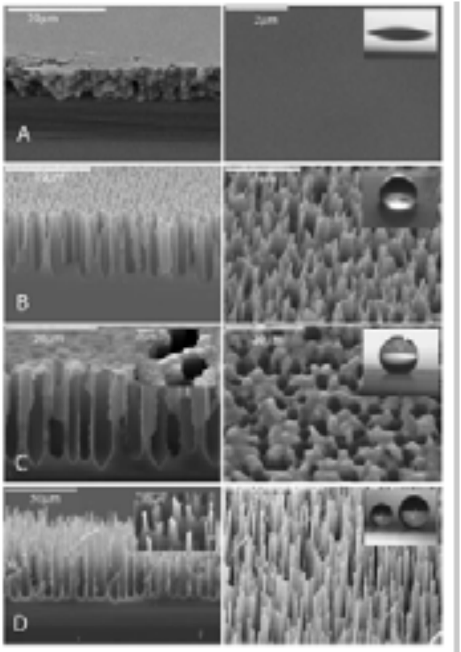


Figure 10: SEM images of four different samples showing a change in contact angle from hydrophilic (A) to hydrophobic and superhydrophobic. Samples B to D are made of porous silicon, sample D is the one with the larger contact angle

Image: A. Ressine, 'Development of protein microarray chip technology', PhD thesis, 2005, reprinted with the permission of the author

Sample	Contact Angle (°)
A	64
B	110
C	155
D	167

Table 2: Contact angles of samples in **Figure 10**

The sample of porous silicon shown **in the video is sample D**. As seen from Figure 10 and Table 2, this is the most superhydrophobic with a contact angle of 167°. What is interesting to note is that in sample B, the distance between the 'pillars' is smaller than in sample D, so the porosity (percentage of voids in the material) is lower. Therefore, in sample D, there is a larger 'fraction of air' to which the droplet is exposed, and the contact angle is larger. This examples shows that to engineer superhydrophobic surfaces scientists need to find the right fabrication conditions to obtain the right balance of 'nano-pillars' and porosity within the silicon surface. It is this balance of micro and nanotexturing that leads to superhydrophobic materials.

The surface of the superhydrophobic porous silicon remarkably resembles that of a water strider, which also displays a micro-/nanotextured surface. Notably, the contact angle of the water strider leg is also 167°.

CREDITS: This experiment was partly adapted from the Application Activity: Nano-Tex, (*http://mrsec.wisc.edu/Edetc/IPSE/educators/nanoTex.html*).

We would like to thank Nano-Tex, Inc. for their courtesy in providing a piece of their Nano-Tex® textile (Resists Spills), and for providing images of this material.

The author wishes to thank Anton Ressine (iNANO, Aarhus University) for providing the porous silicon sample shown in the videos of this experiment.

STUDENT LABORATORY WORKSHEET

SUPERHYDROPHOBIC MATERIALS

Student name:.........................

Date:.......................................

AIM:

- Understanding of the presence of nanostructures on the composition of a natural material and how these affect its properties
- Novel advanced materials that have been engineered at the nanoscale to be superhydrophobic and their applications
- Analysis of a functional nanomaterial under research at iNANO (video)
- Analysis and hands-on test of a superhydrophobic textile

BEFORE YOU FILL IN THIS WORKSHEET

- Read STUDENT BACKGROUND READING — EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS
- Ask your teacher any questions you have

MATERIALS

- different surfaces to test:
  - microscope glass slide
  - flat piece of plastic 10 x 10 cm (e.g. cut a piece out of a plastic sheet such as a plastic folder)
  - flat piece of aluminium foil 10 x 10 cm
  - two pieces of filter paper
  - pieces of textiles to compare (about 10x10 cm):
    - four of Nano-Tex® and two other types
    - three samples of 100 % cotton
    - three samples of fabric made with synthetic fibre such as polyester or cotton/poly blend (in this protocol we used a fabric with 70 % polyester, and 30 % cotton)
- different stain agents to test
  - glass of water, glass of juice and/or glass of Coke
  - balsamic vinegar or wine (1 glass)
  - cooking oil (1 glass)
  - ketchup (1 spoonful)
  - mustard (1 spoonful)
  - mayonnaise (1 spoonful)
  - organic soil (a couple of handfuls)

- different plant leaves (collect from school garden or bring from home)
  - common plant leaf such as ivy
  - piece of lotus leaf or nasturtium
- laboratory bottle filled with water
- five eyedroppers (or Pasteur pipettes) to apply the liquid stain agents — plastic knives or spoons for applying the other stain agents
- bucket of laundry detergent and water (you might need to share this with the entire class)
- 10 x 10 cm piece of sandpaper
- permanent marker
- several plastic cups to hold water and stain agents
- several plastic plates to put materials on when conducting the material testing
- paper, glue and scissors

SAFETY NOTE: This experiment does not use chemicals, simply common liquids and solids. Nevertheless, staining is possible so wash hands and surfaces thoroughly after handling. Use appropriate clothing protection, gloves and eye protection. Collect all liquids and washing water in glass/plastic containers and dispose of down the sink. All experiments are carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of carrying out the experiments described.

PROCEDURE

You will now test a series of materials, starting with common materials and moving on to more advanced materials. When you test the materials with water or other liquids/solids, do so by placing the material on a plastic plate in order to collect the water neatly. **Dispose of the collected water between tests!**

1. Understanding surface properties: hydrophilic orhydrophobic?

- Take the four surfaces to test: a glass slide, a piece of plastic, aluminium foil, wood and filter paper. Place a couple of droplets of water on each material, and record your observations in the table provided.

Material	Hydrophilic or hydrophobic?	Comments
Aluminium		
Plastic		
Filter paper		
Glass		

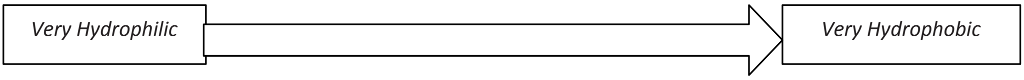
Based on your visual observation, classify the materials as hydrophilic or hydrophobic (fill in the table provided).

Q1: Did filter paper behave like the other materials? If not, why?

…………………………………………………

Q2: Put the **aluminium, plastic and glass** in order, starting from the most hydrophilic to the most hydrophobic, based on your visual observation.

……



Q3: Would you define any of the material tested so far as ‘very hydrophobic’? Why?

…………………………………………………………

Q4: Now cut out the photos on the last page of this document, and paste them below to recreate the same scale you have just made in Q2. Write under each photo which material you think it is.

STEP 1

- **Put in one plastic plate a leaf of common plant you have collected** (e.g. ivy). If you have more than one, test each independently.

2. Analysis of natural nanomaterials: lotus leaf (or nasturtium)

STEP 1

- **Put in one plastic plate a leaf of common plant you have collected** (e.g. ivy). If you have more than one, test each independently.
- **Pour some water over each leaf** and observe how water rolls off the surface. A bucket or other container should be used to collect the water. You should have a paper towel to hand.

Q5: Do the water droplets wet the surface of the leaf (i.e. is water left on the leaves once you stop pouring water)? Give an answer for each type of leaf you have tested.

……………………………………………………………

Q6: Do the water droplets roll or slide over the leaf?

....

STEP 2

- **Now, in a second plastic plate place a leaf (or a piece of leaf) of lotus or nasturtium** (depending on what your teacher gave you).

Q7: Do the water droplets wet the surface of the leaf (i.e. is water left on the leaves once you stop pouring water)? Give an answer for each type of leaf you have tested.

....

Q8: Do the water droplets roll or slide over the leaf?

....

Q9: What happens if you place the leaf horizontally on the bench and splash it with water?

....

Q10: Can you get a droplet to remain motionless on the surface? Is it easy or difficult? What does this tell you about the surface properties of the leaf?...

- **Place the lotus or nasturtium leaf under running water.**

Q11: Even after running the leaf under water, does it become wet?

....

Q12: Based on your observation, is the lotus (or nasturtium) leaf more or less hydrophobic than plastic?

....

Q13: Where would you place the photo of the contact angle of a lotus leaf (provided at the end of this document) in the order in Q4? Cut out all the photos again and make a new scale below, writing under each the type of material.

STEP 3

- Watch the **NANOYOU Video 4 — Lotus effect®, Part 2**, which shows a surface engineered at iNANO (Aarhus University), which has surface properties comparable to those of the lotus leaf (superhydrophobic).

Q14: How does the porous silicon material shown in the video compare with the lotus leaf in terms of surface properties?

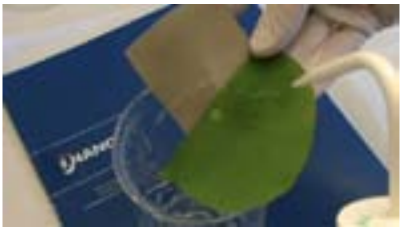
…………………………………………………………………

…………………………………………………………………

…………………………………………………………………

3. Analysis of a functional nanomaterial

In this part of the experiment, you will analyse a textile that has been engineered to replicate the Lotus effect® and have self-cleaning properties.



- **Take a piece of Nano-Tex® and a piece of a normal cotton fabric**. Place each in a plastic plate.
- Pour some water over them. If possible, use a lotus or nasturtium leaf for comparison.

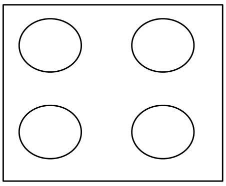
Q15: Does the Nano-Tex® fabric behave like the Lotus effect® in terms of how water wets it?

…………………………………………………………

- **Now you will test the Nano-Tex® fabric and compare it to normal cotton and a semi-synthetic fibre.** For this you need **in total** three pieces of cotton fabric, three pieces of a semi-synthetic fabric, and four pieces of Nano-Tex® (each about 10 x 10 cm). **Follow the steps below**.

STEP 1

Now you should test the Nano-Tex® fabric and compare it tonormal cotton and a semi-synthetic fibre. In this step, liquid stains should be used (Coke, vinegar, oil, etc.).



- Get a glass of each of the liquids you will test (juice, Coke, vinegar or wine, and oil).
- Place your three pieces of different fabrics in a row: left, cotton; middle, semi-synthetic; right, Nano-Tex®. Write on a piece a paper the type of fabric and place it under each fabric (as in the image). Decide in which order you will test the liquids and write it here:

- Using a pipette, **place a droplet of each liquid to be tested on each fabric**. You should leave the solutions on the three types of fabrics for a fixed amount of time. Indicate this in the table provided. Perform this test sequentially, one liquid and one fabric at a time.

- After the set time, gently remove the liquid from after fabric using a piece of paper towel.

Record your observations in the table provided. Write down whether the liquid was absorbed, whether it remained on the fabric surface, whether it stained the fabric, and whether you could remove it with the paper towel. Add any further comments you have.

Time of liquid staining: … seconds (complete)				
Material	Juice	Coke	Vinegar or wine	Oil
Cotton fabric				
Semi-synthetic fabric				
Nano-Tex®				

Q16: Was there a clear difference between the Nano-Tex® fabric and the other fabrics? Describe.

………………………………………………

Q17: How easy was it to remove the liquid stains from the Nano-Tex® fabric? Did all the liquid stains come off?

………………………………………………

STEP 2

Now you should test the Nano-Tex® fabric and compare it tonormal cotton and a semi-synthetic fibre. In this step, solid stains should be used (mayonnaise, mustard, etc.)

- **Now test the three types of fabrics with the 'solids' chosen**: ketchup, mustard, mayonnaise. Have some paper towel to hand.

  Take three new pieces of fabric, one of each type. Place some of each solid on each fabric. Use a spoon or spatula to place the solid on the fabric. In one area, mark it with a permanent marker (see Figure). To compare the fabrics, you must define a set time for staining for this experiment (e.g. 5 min).

- After the set time (e.g. 5 min), remove the solids from the fabrics, using a **wet cloth**.

NOTE: Be careful not to mix the different solids!

In the table provided, record your observations on how each solid stains the fabrics.

Time of solid staining: … seconds (complete)				
Material	Ketchup	Mustard	Mayonnaise	Permanent marker
Cotton fabric				
Semi-synthetic fabric				
Nano-Tex®				

Q18: Was there a clear difference between the Nano-Tex® fabric and the other fabrics? Describe.

……………………………………………

……………………………………………

Q19: How easy was it to remove the solid stains from the Nano-Tex® fabric? Did all the solid stains come off?

……………………………………………

……………………………………………

STEP 3

Now you should test the Nano-Tex® fabric for resistance to dirt and compare it to normal cotton and a semi-synthetic fibre. In this step, organic soil is used.

- **Take three new pieces of fabric, one of each type.**
- Place some organic soil in the middle of each piece, fold the fabric and rub it. Then open each piece of fabric, remove the soil, and observe.

Q20: Did all the fabrics get dirty? In the same way? Describe.

………………………………………………………………………………

………………………………………………………………………………

- **Now try to clean the fabrics used in STEP 3 with your hands.**

Q21: Could you clean the fabrics? Is there a clear difference between them? Describe.

……………………………………………………………

Q22: Was there a fabric that could be totally cleaned and appear as new?

……………………………………………………………

Q23: Which type of fabric could be cleaned more easily?

……………………………………………………………

- **Now try to clean the three fabrics used in ALL STEPS with cold water and soap.**

Q24: Do all the fabrics become clean? If not, which one does?

……………………………………………………………

Q25: Which type of fabric could be cleaned more easily?

………………………………………………………………

Q26: Is there a type (or more) of stain that doesn't come off the Nano-Tex® samples? Which one? Why do you think this is so?

………………………………………………………………

STEP 4

Test the Nano-Tex® with sandpaper.

- Take a new piece of Nano-Tex® and a piece of sandpaper.
- Test to see **how durable the fabric is**. First, observe how water rolls off this fabric. Cut the piece in two, take a piece of sandpaper, and rub it over the surface of one of the two pieces. Test the fabric to its limit!

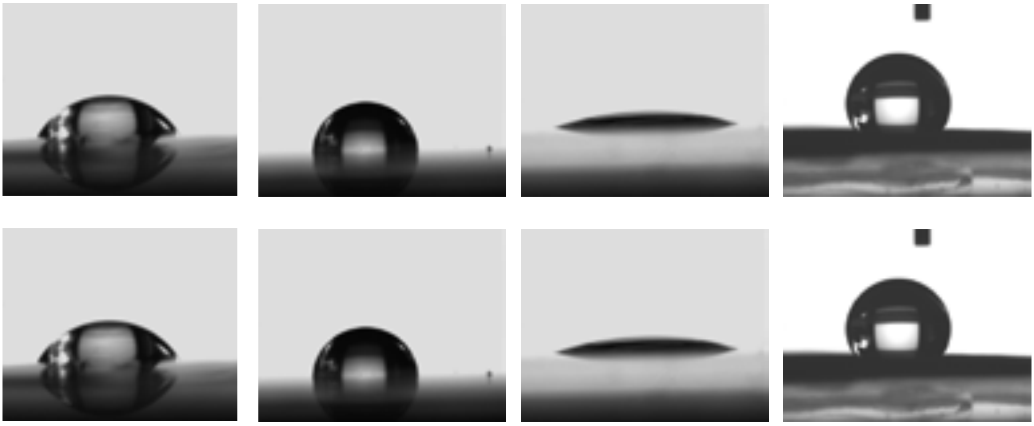
  NB: The use of heat is not recommended.

Q27: Did the treatment with sandpaper alter the properties of the Nano-Tex® fabric? How does this affect the fabric?

…………………………………………………

……………………………………………………………………………………

USE THESE IMAGES TO COMPLETE Q4 and Q13



CREDITS: This experiment was partly adapted from the Application Activity: Nano-Tex, (http://mrsec.wisc.edu/Edetc/IPSE/educators/nanoTex.html).

We would like to thank Nano-Tex, Inc. for their courtesy in providing a piece of their Nano-Tex® textile (Resists Spills), and for providing images of this material.

The author wishes to thank Anton Ressine (iNANO, Aarhus University) for providing the porous silicon sample shown in the videos of this experiment.

SUPPORTING INFORMATION FOR EXPERIMENT PACKAGE

Videos cited in the Experiment Package can be found in the Nano Lab section of the NANOYOU website (www.nanoyou.eu). All student background reading and student laboratory sheets are available in different languages, translations can be found in the same webpage. A simplified version of each experiment for the 11-13 year group is also available.

See section on Copyrights at the end of the book, from page 407 onwards, for references on credits.

CONCLUSIONS

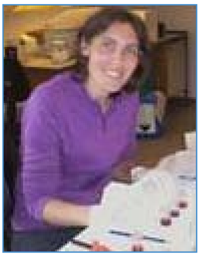
The aim of this training kit was to provide educators and teachers with relevant, accurate and updated material that will help them inform, motivate and inspire young people about nanotechnologies and their applications. In doing so, it allowed educators and teachers to develop a balanced syllabus containing both theory and experimental components to suit the various student levels and educational approaches of participating schools. To facilitate this, materials were organised in self-contained modules that offered increased flexibility throughout the development of the course: a case study approach provided educators and teachers with practical applications and examples to discuss nanotechnologies in the classroom.

Over its three modules, this book addressed the fundamental concepts, the main application areas and selected hands-on experiments to explain nanotechnology. Furthermore, this book presented background materials, literature reviews, specific case studies and ideas on how to integrate nanoscience and the concepts of nanotechnologies into science curricula, complete with topics on the ethical, societal, legal and safety aspects to encourage class debates.

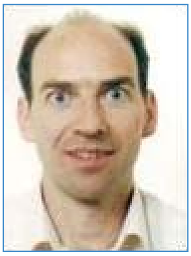
We are confident that a panoply of readers will appreciate this effort, as nanotechnology is one of the very frontiers of science today, likely to affect us all in our daily life. In this book, the scientific and technological background and prospects, as well as the opportunities, risks and uncertainties associated with nanotechnologies have been extensively and deeply addressed: this will allow various audiences, be they young people, teachers, businesses, organisations or the general public, to become increasingly aware of the scientific and societal implications of nanotechnology, calling on them to become increasingly involved in the dialogue being framed by various initiatives at European, national and local levels.

Good governance at EC level is also promoted by this exercise through the development of inclusive policy debates. As a result of this book, European citizens will be more able to see and understand how all this new frontier science and technology could influence their lives; this book also represents a true ‘first’ from this point of view, contributing to the setting up of an extensive, accurate and deep knowledge base, stemming from school level, to develop a science-grounded societal dialogue on the future benefits and risks that nanotechnology could offer in the future.

ABOUT THE AUTHORS



Luisa Filipponi (b 1976) has worked in the area of nanotechnology communication and education since 2007. She has experience in science writing and communication, especially for the non-technical audience including topics related to Ethical, Legal and Social Aspects (ELSA). Her expertise includes developing experiments for schools and teacher training on nanotechnology. She has worked for iNANO (Aarhus University) at various FP7 projects on nanotechnology communication and outreach (NANOCAP, NANOYOU, and currently NANOPINION). In January 2011 she established her own freelance activity on nanotechnology communication (www.inscience.it) and worked as scientific consultant to the NANOCHANNELS project and for the scientific radio program Moebius Scienza (Radio24). Luisa holds a BSc in Chemistry and a PhD in Nano- and Microtechnology and before becoming a science communicator she was a researcher in the area of protein micro- and nanoarrays through a project involving Nanotechnology Victoria (Nanovic, Australia). Luisa is the author of a review for the Wiley Encyclopedia of Biomedical Engineering, (John Wiley & Sons, Inc., 2006), co-author of a chapter in `Microarray Technology and its Applications' (Springer & Verlag 2005), author and co-author of various scientific publications and co-inventor of two patents.



Duncan Sutherland (b 1970) has worked in the area of nanotechnology for life science since 1995 with a focus on Self assembly nanofabrication routes, nanostructured biomaterials and nanoscale biosensors. After completing his Ph.D in Physics at the University of Bristol he moved to Chalmers in Sweden where he became a project leader in the Chemical Physics Group of the Department of Applied Physics. During his time in Sweden he developed self-assembly based engineering approaches to nanofabrication utilising colloidal particles systems and applied them to the study of nanostructured interfaces in different physical and life science applications. In March 2006 he moved his group to the iNANO center at the University of Aarhus taking up an Associate Professor faculty position. The Nanobiointerfaces group has research interests in biomaterials, biosensors, biofouling, nanotoxicology as well as the fundamentals of plasmonic interactions at metal nanostructures. In addition to his research activities, teaching and industrial collaborations, A/Prof. Sutherland is also involved in outreach activities, including communicating fundamental concepts, benefits and applications of nanotechnologies to NGOs, trade union representatives, industry members and the general public.

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We are also very grateful to the pilot schools from 20 EU Member and Associated States, which initiated, launched, tested and provided feedback to the lessons, discussion on applications and experiments composing the present compendium listed below (more details at http://nanoyou.eu/en/nano-educators/pilot-schools.html?view=alphacontent)

Austria (BRG/BG Klusemann, Graz; Borg 3 , Vienna); Belgium (Institut Don Bosco, Brussels); Cyprus (St. Theodoros Gymnasium, Pafos); Czech Republic (Střední průmyslová škola, Třebíč; Mendelova střední škola, příspěvková organizace, Nový Jičín, Šenov u Nového Jičína); Denmark (Aabenraa Statsskole, Billund; Teknisk Gymnasium Christiansbjerg, Aarhus); Finland (Maunulan yhteiskoulu ja Helsingin matematiikkalukio, Helsinki); France (St Louis, Chateaulin); Germany (Jakob-Fugger-Gymnasium, Augsburg; Tannenbusch-Gymnasium, Bonn; Phaenovum, Lörrach; Jakob-Fugger-Gymnasium, Augsburg); Greece (4th Lyceum Stavroupolis, Thessaloniki); Hungary (Bánki Donát Műszaki Középiskola, Nyíregyháza; Kossuth Lajos Secondary Grammar School, Mosonmagyaróvár); Italy (Istituto Istruzione Superiore G.Carducci, Ferrara; ISISS “Piana di Lucca” - Liceo Scientifico “E. Majorana”, Capannori; ITIS Marconi, Verona; IISS “G. Peano – C. Rosa, Nereto; ISIS Cavazzi Sorbelli Liceo Scientifico, Pavullo); Latvia (Riga Purvciems Secondary School, Riga); Lithuania (“Ausra” Secondary School, Birzai); Portugal (Escola Secundária com 3º Ciclo Madeira Torres, Torres Vedras; Agrupamento de Escolas Eugenio de Andrade, Porto; Escola Secundária Francisco Simões, Almada; Escola Básica e Secundária de Santa Maria; Vila do Porto, Azores); Romania (Dimitrie Ghica School, Comanesti Bacau; “Dimitrie Anghel” School; COLEGIUL NATIONAL NICOLAE TITULESCU, Pucioasa; Liceul Teoretic Piatra, Piatra; “CALISTRAT HOGAS“ National College, Piatra_Neamt; Secondary School nr.2 along with Children’s Club Zimnicea, Zimnicea); Slovakia (Secondary Technical School Of Transport Kosice, Kosice; Spojená škola Martin, Martin; Gymnazium Janka Jesenského, Bánovce nad Bebravou); Spain (I.E.S. Manuel de Falla, Cadiz; Colegio Pedro Poveda, Jaén; Escola Gavina SCV, Picanya; Valencia; IES Sant Just Desvern, Barcelona, Catalunya); Sweden (Buråsskolan, Gothenburg); Turkey (UPS Haluk Undeger High School, Istanbul; TED Afyon Koleji Özel İlköğretim Okulu, AFYONKARAHİSAR); UK (The Glasgow Academy, Glasgow; Smithycroft Secondary School, Glasgow; Eastbrook School, London; Upton Hall School, Merseyside; Battle Abbey School, Battle).

BIBLIOGRAPHY AND EXTRA READING FOR STUDENTS AND TEACHERS

Chapter 1: Medicine and Healthcare

Public documents (no subscription required)

European Technology Platform (2006), *Nanomedicine — Nanotechnology for health* (ftp://ftp.cordis.europa.eu/pub/nanotechnology/docs/nanomedicine_bat_en.pdf).

Nanomedicine — An European Science Foundation-European Medical Research Councils (EMRC) Forward Look Report, 2005 (http://www.esf.org/research-areas/medical-sciences/publications.html).

ObservatoryNANO Focus Report (2010), *Nanotechnology and regenerative medicine* (http://www.observatorynano.eu) (includes a market report).

ObservatoryNANO Focus Report (2010), *Nanotechnology and therapeutic delivery* (http://www.observatorynano.eu) (includes a market report).

ObservatoryNANO Project Reports, *Scientific and technological trends: medicine, healthcare and nanobio* (http://www.observatorynano.eu/project/catalogue/2HM/), 2009; the following subtopics are covered: cosmetics; diagnostics; novel bionanostructures; implants; surgery and coatings; theurapeutics; regenerative medicine.

Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies (2007), *NanoFrontiers — On the Horizons of Medicine and Healthcare* (http://www.nanotechproject.org/process/assets/files/2702/188_nanofrontiers_newsletter.pdf).

Reviews from journals (paid subscription required)

Duncan, R., ‘Polymer conjugates as anticancer nanomedicines’, *Nature Reviews*, 2006, 6, 688–701.

Duncan, R., ‘The dawning era of polymer therapeutics’, *Nature Reviews*, 2003, 2, 347–360.

Farokhzad, O. C., Langer, R., ‘Nanomedicine: Developing smarter therapeutic and diagnostic modalities’, *Advanced Drug Delivery Reviews,* 2006, 58(14), 1456–1459.

Filipponi, L., Nicolau, D. V., ‘Cell Patterning’, *Wiley Encyclopedia of Biomedical Engineering*, John Wiley & Sons, Inc., 2006.

Kubik, T. Bogunia-Kubik, K., Sugisaka, M., ‘Nanotechnology on duty in medical applications’, *Current Pharmaceutical Biotechnology*, 2005, 6, 17–33.

Medina, C., Santos-Martinez, M. J., Radomski, A., Corrigan, O. I., Radomski, M.W., ‘Nanoparticles: pharmacological and toxicological significance’, *British Journal of Pharmacology*, 2007, 1–7.

Ratner, B. D., Bryant, S. J., ‘Biomaterials: where we have been and where we are going’, *Annual Reviews in Biomedical Engineering*, 2004, 6, 41–75.

Sakiyama-Elbert, S. E., Hubbell, J. A., ‘Functional biomaterials: design of novel biomaterials’, *Annual Reviews in Materials Research*, 2001, 31, 183–201.

S. C. Jakeway, A.J de Mello, E. L. Russell, Miniaturised total analysis systems for biological analysis (Review), *Fresenius Journal of Analytical Chemistry*, 2000, 366, 525–539.

Silva, G. A., ‘Neuroscience nanotechnology: progress, opportunities and challenges’, *Nature Reviews*, 2006, 7, 65–74.

Wagner, V., Dullaart, A., Bock, A.-K., Zweck, A., ‘The emerging nanomedicine landscape’, *Nature Biotechnology*, 2006, 24(10), 1211–1217.

Wickline, S. A., Lanza, G.M., ‘Nanotechnology for Molecular Imaging and Targeted Therapy’, *Circulation*, 2003, 107, 1092–1095.

Vo-Dinh, T., Cullum, B., ‘Biosensors and biochips: advances in biological and medical diagnostics’ (Review), *Fresenius Journal of Analytical Chemistry*, 2000, 366, 540–551.

Books

Kumar, S. S. R. C, Hormones, J., Leuschner, C. (eds), *Nanofabrication towards biomedical applications-techniques, tools and impact*, Wiley-VCH Verlag GmbH & Co., 2005.

Müller, U. R., Nicolau, D. V. (eds), *Microarray technology and its applications*, Springer-Verlag (2005).

Articles from journals (paid subscription required)

These specific references have been used in writing this chapter.

Collins, P. G., Bradley, K., Ishigami, M. Zettl, A., ‘Extreme oxygen sensitivity of electronic properties of carbon nanotubes’, *Science*, 2000, 287(5459), 1801–1804.

Cui, Y. Wei, Q. Park, H., Lieber, C. M., ‘Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species’, *Science*, 2001, 293(5533), 1289–1292.

Flacke, S., Fischer, S., Scott, M. J., Fuhrhop, R. J., Allen, J. S., McLean, M., Winter, P., Sicard, G. A., Gaffney, P. J., Wickline, S. A., Lanza, G. M., ‘Novel MRI Contrast Agent for Molecular Imaging of Fibril Implications for Detecting Vulnerable Plaques’, *Circulation*, 2001, 104, 1282–1285.

Han, M. Gao, X., Su, J. Z., Nie, S., ‘Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules’, *Nature Biotechnology?* 2001, 19, 631–635.

http://www.magforce.com

Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G., Peng, K., Cjo, K., Dailt, H., ‘Nanotube molecular wires as chemical sensors, *Science*, 2000, 287 (5453), 622–625.

Nam, J.-M., Thaxton, C. S., Mirkin, C. A., ‘Nanoparticle-based bio-barcodes for the ultrasensitive detection of proteins’, *Science*, 2003, 301, 1884–1886.

O’Neal, D. P., Hirsch, L. R., Halas, N. J., Payne, J. D., West, J. L., ‘Photo-thermal tumor ablation in mice using near infrared-adsorbing nanoparticles’, *Cancer Letters*, 2004, 209, 171–176.

Patolsky, F. Zheng, G., Lieber, C. M., ‘Nanowire-based biosensors’, *Analytical Chemistry*, 2006, 4261–4269.

Staples, M., Daniel, K., Cima, M. J., Langer, R., ‘Application of micro- and nano-electromechanical devices to drug delivery’, *Pharmaceutical Research*, 2006, 23(5), 847–863.

Storhoff, J. J., Marla, S. S., Garimella, V., Mirkin, C. H.; ‘Labels and detection methods’, Müller, U. R., Nicolau, D. V. (eds), *Microarray technology and its applications*, Springer-Verlag (2005).

Wang, H., Branton, D., ‘Nanopores with a spark for single-molecule detection’, *Nature Biotechnology*, 2001, 19, 622–623.

Chapter 2: Environment

Public documents (no subscription required)

Emerging challenges — nanotechnology and the environment, United Nations Environment Programme (UNEP) (http://www.unep.org/yearbook/2007/PDF/7_Emerging_Challenges72dpi.pdf).

Green Nanotechnology: It’s Easier Than You Think (PEN8), Woodrow Wilson Center International Center for Scholars (http://www.nanotechproject.org/events/archive/green_nanotechnology_its_easier_than/).

Overview and Comparison of Conventional and Nano-Based Water Treatment Technologies, Meridian Institute (http://www.merid.org/nano/watertechpaper/).

Rickerby, D., Morrison, M. (eds), *Report from the Workshop on Nanotechnologies for Environmental Remediation*, JRC Ispra, 16 and 17 April 2007 (http://www.nanoforum.org).

Silver Nanotechnologies and the Environment (PEN 15), Wooodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies, April 2008 (http://www.nanotechproject.org/publications/archive/silver/).

US Environmental Protection Agency, White Paper *Nanotechnology*, 2007 (http://www.epa.gov/osa/nanotech.htm).

Reviews from journals (paid subscription required)

Masciangioli T., Zhang, W., ‘Environmental technologies at the nanoscale’, *Environmental Science & Technology*, 2003, 102A–108A.

Zhang, W., ‘Nanoscale iron particles for environmental remediation: An overview’, *Journal of Nanoparticle Research*, 2003, 5, 323–332.

Articles from journals (paid subscription required)

These specific references have been used in writing this chapter.

Acosta, E. J. et al., 'Linker-based biocompatible microemulsions', *Environmental Science & Technology*, 2005, 39, 1275–1282.

Appell, D., 'Wired for success', *Nature*, 2002, 419, 553–555.

Cortalezzi, M. M., Colvin, V., Mark R. Wiesner, 'Controlling submicron-particle template morphology: effect of solvent chemistry', *Journal of Colloid and Interface Science*, 2005, 283, 366–372.

Cortalezzi, M. M. et al., 'Ceramic membranes derived from ferroxane nanoparticles: a new route for the fabrication of iron oxide ultrafiltration membranes', *Journal of Membrane Science*, 2003, 227, 207–217.

Cui, Y., Park, H., Lieber, C. M., 'Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species', *Science*, 2001, 293, 1289–1292.

Diallo, M. S., Christie, S., Swaminathan, P., Johnson Jr., J. H., Goddard, W. A., 'Dendrimer enhanced ultrafiltration — 1. Recovery of Cu(II) from aqueous solutions using PAMAM dendrimers with ethylene diamine core and terminal NH_2 groups', *Environmental Science & Technology*, 2005, 39, 1366–1377.

Elliott, D. W., Zhang, W., 'Field assessment of nanoscale bimetallic particles for groundwater treatment', *Environmental Science & Technology*, 2001, 35(24), 4922–4926.

Forzani, E. S., Zhang, H., Chen, W., Tao, N., 'Detection of heavy metal ions drinking water using a high-resolution differential surface plasmon resonance sensor', *Environmental Science & Technology*, 2005, 39, 1257–1262.

Gemming, S., Seifert, G., 'Catalysts on the edge', *Nature*, 2007, 2, 21–22.

Gu, H., Xu, K., Xu, B., 'Biofunctional magnetic nanoparticles for protein separation and pathogen detection', *Chemical Communications*, 2006, 941–949.

Kamat, P. V., Huehn, R., Nicolaescu, R., 'A sense and shoot approach for photocatalytic degradation of organic contaminants in water', *Journal of Physical Chemistry* B, 2002, 106, 788–794.

Kanel, S. R., Manning, B., Charlet, L., Choi, H., 'Removal of arsenic(III) from groundwater by nanoscale zero-valent iron', *Environmental Science & Technology*, 2005, 39, 1291–1298.

Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G. Peng, S., Cho, K., Dai, H., 'Nanotube molecular wires as chemical sensors', *Science*, 2000, 287, 622–625.

Liu, L. Yan, Heiden, P., Laks, P., 'Use of nanoparticles for controlled release of biocides in solid wood', *Journal of Applied Polymer Sciences*, 2001, 79, 458–465.

Mueller, N. C., Nowack, B., 'Exposure modelling of engineered nanoparticles in the environment', *Environmental Science & Technology*, 2008, 42, 4447–4453.

Oxonica (http://www.oxonica.com/energy/energy_envirox_casestudy.php).

Oyama, T., Aoshima, S., Horikoshi, S., Hidaka, H., Zhao, J., Serpone, N., ‘Solar photocatalysis, photodegradation of a commercial detergent in aqueous TiO_2 dispersions under sunlight radiation’, *Solar Energy*, 2002, 77, 525–532.

Patolsky, F., Lieber, C. M., ‘Nanowire nanosensors’, *Materials Today*, 2005, 20–28.

Pitoniak, E., Wu, C., Mazyck, D. W., Powers, K. W.,Sigmund, W., ‘Adsorption enhancement mechanisms of silica-titania nanocomposites for elemental mercury vapour removal’, *Environmental Science & Technology*, 2005, 39, 1269–1274.

Shao, M., Shan,Y., Wong, N., Lee, S., ‘Silicon nanowire sensors for bioanalytical applications: glucose and hydrogen peroxide detection’, *Advanced Functional Materials*, 2005, 15, 1478–1482.

Subramanian, V., Wolf, E., Kamat, P. V., ‘Semiconductor-metal composite nanostructures — To what extent do metal nanoparticles improve the photocatalytic activity of TiO_2 films?’, *Journal of Physical Chemistry* B, 2001, 105, 11439–11446.

Yavuz, C. T. et al., ‘Low-field magnetic separation of monodisperse Fe_3O_4 nanocrystals’, *Science*, 2006, 314, 964–967.

Wang, C.-B., Zhang, W., ‘Synthesizing nanoscale iron particles for rapid and complete decholorination of TCE and PCBs’, *Environmental Science & Technology*, 1997, 31(7), 2154–2156.

Chapter 3: Energy

Public documents (no subscription required)

Hessian Ministry of Economy, Transport, Urban and development (2008), *Application of nano-technologies in the Energy Sector* (http://www.hessen-nanotech.de/mm/NanoEnergy_web.pdf).

Nanoforum, European Nanotechnology Gateway (2004), *Nanotechnology Helps Saving the World’s Energy Problems* (http://www.nanoforum.org).

Nanoscience Research for Energy Needs, National Nanotechnology Initiative 2004 (https://public.ornl.gov/conf/nanosummit2004/energy_needs.pdf).

Nanotechnology: Energizing the Future, Nanofrontiers Newsletter Fall 2008, Wooodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies (http://www.nanotechproject.org/publications/archive/nanotechnology_energizing_future/).

ObservatoryNANO Focus Report, *Nanotechnology in batteries*, April 2010
(http://www.observatorynano.eu) (includes a market evaluation report).

ObservatoryNANO Focus Report, *Nanotechnology in batteries for electric vehicles*, April 2010
(http://www.observatorynano.eu) (includes a market evaluation report).

ObservatoryNANO Focus Report, *Nanotechnology in photovoltaics*, April 2010 (http://www.observatorynano.eu) (includes a market evaluation report).

ObservatoryNANO Project Reports, *Scientific and technological trends: Energy* (http://www.observatorynano.eu/project/catalogue/2EN/); the following subtopics are covered: photovoltaics; thermoelectricity; fuels cells and hydrogen production and storage; batteries and supercapacitors; fossil fuel and nuclear energy; energy harvesting.

Reviews from journals (paid subscription required)

Grätzel, M., 'Photoelectrochemical cells', *Nature*, 2001, 414, 338–44.

Pandolfo, A. G., Hollenkamp, A. F., 'Review: Carbon properties and their role in supercapacitors', *Journal of Power Sources*, 2006, 157, 11–27.

Smalley, R. E., 'Future Global Energy Prosperity: The Terawatt Challenge', *Materials Matters Bulletin*, Vol. 30, June 2005, 412–417; a comprehensive overview of the 'Energy challenge' discussed by Professor R. E. Smalley is available online (http://smalley.rice.edu) (free access).

Zäch, M., Hägglund, C., Chakarov, D., Kasemo, B., 'Nanoscience and nanotechnology for advanced energy systems', *Current Opinion in Solid State and Materials Science*, 10 (2006) 132–143.

Articles from journals (paid subscription required)

These specific references have been used in writing this chapter.

Boukai, A. I., Bunimovich, Y., Tahir-Kheli, J., Yu, J.-K., Goddard, W. A., Heath, J. R., 'Silicon nanowires as efficient thermoelectric materials', *Nature*, 2008, 451, 168–171.

Bowers II, M. J., McBride, J. R., Rosenthal, S., 'White-Light Emission from Magic-Sized Cadmium Selenide Nanocrystals', *Journal of the American Chemical Society*, 2005, 127, 15378–15379.

Du, C., Pan, N., 'High power density supercapacitor electrodes of carbon nanotube films by electrophoretic deposition', *Nanotechnology*, 2006, 17, 5314–5318.

Lauritsen, J. V., Bollinger, M. V., Lægsgaard, E., Jacobsen, K. W., Nørskov, J. K., Clausen, B. S., Topsøe, H., Besenbacher, F., 'Atomic-scale insight into structure and morphology changes of MoS2 nanoclusters in hydrotreating catalysts', *Journal of Catalysis*, 2004, 221, pp. 510–522.

Lauritsen, J. V., Nyberg, M., Nørskov, J. K., Clausen, B. S., Topsøe, H., Lægsgaard, E., Besenbacher, F., 'Hydrodesulfurization reaction pathways on MoS_2 nanoclusters revealed by scanning tunneling microscopy', *Journal of Catalysis*, 2004, 224, pp. 94–106.

Lauritsen,J. V., Nyberg, M., Vang, R. T., Bollinger, M. V., Clausen, B. S., Topsøe, H., Jacobsen, K. W., Lægsgaard, E., Nørskov, J. K., Besenbacher, F., 'Chemistry of one-dimensional metallic edge states in MoS_2 nanoclusters', *Nanotechnology*, 2003, 14, pp. 385–389.

Pushparaj, V. L., Shaijumon, M. M., Kumar, A., Murugesan, S., Ci, L., Vajtai, R., Linhardt,R. J., Nalamasu, O., Ajayan, P. M., ‘Flexible energy storage devices based on nanocomposite paper’, *Proceedings of the National Academy of Sciences* (USA) 2007, 104 (34), 13574–13577.

Pushparaj, V. L., Shaijumon, M. M., Kumar, A., Murugesan, S., Ci, L., Vajtai, R., Linhardt, R. J., Nalamasu, O., Ajayan, P. M., ‘Flexible energy storage devices based on nanocomposite paper’, *Proceedings of the National Academy of Sciences* (USA), 2007, 104 (34), 13574–13577.

Raja, K. S., Mahajan, V. K., Misra, M., ‘Determination of photo conversion efficiency of nanotubular titanium oxide photoelectrochemical cell for solar hydrogen generation’, *Journal of Power Sources*, 2006, 159,1258–1265.

Schaller, R. D., Klimov, V. I., ‘High efficiency carrier multiplication in PbSe nanocrystals: Implications for solar energy conversion’, *Physical Review Letters*, 2004, 92, 186601–1 to 186601–4.

Schlapbach, L., Züttel, A., ‘Hydrogen-storage materials for mobile applications’, *Nature*, 2001, 414, 353–358.

Taberna,P. L., Mitra, S., Poizot, P., Simon, P., Tarascon, J.-M., ‘High rate capabilities Fe_3O_4 -based Cu nanoarchitectured electrodes for lithium-ion battery applications’, *Nature Materials*, 2006, 5, 567–573.

Chapter 4: Information and Communication Technologies

Public documents (no subscription required)

Ermolov, V. et al., ‘Significance of nanotechnology for future wireless devices and communications’, Nokia Research Center, *Proceedings 18th IEEE International Symposium on Personal, Indoor and Mobile Radio Communications* (PIMRC’07) (http://research.nokia.com/files/PIMRC07-1169.pdf).

Meoli, D., May-Plumlee, T., ‘Interactive electronic textile development’, *Journal of Textile and Apparel Technology and Management*, 2002, Vol. 2, Issue 2, pp. 1–12 (http://www.tx.ncsu.edu/jtatm/volume2issue2/articles/meoli/meoli_full.pdf).

ObservatoryNANO Project Reports, Economic Data-Market Reports: Information and communication, *Market Study of Nanotechnology for ICT Applications* (http://www.observatorynano.eu/project/document/2537/).

ObservatoryNANo Project Reports, *Scientific and technological trends: information and communication* (http://www.observatorynano.eu/project/catalogue/2IC/); the following subtopics are covered: integrated circuits, displays, memory, power, photonics, beyond CMOS.

‘The evolution of interactive textiles’, *Speciality Fabrics review* (http://specialtyfabricsreview.com/articles/0910_f2_interactive_textiles.html).

Videos

SmartHand project (http://www.youtube.com/watch?v=IKMqM7th1hA).

Book chapter

van den Hoven, J., 'The Tangled Web of Tiny Things: Privacy Implications of Nano-electronics', *Nanotechnology and Society*, 2009, III, 147–162, doi:10.1007/978-1-4020-6209-4_8.

Articles from journals (paid subscription required)

These specific references have been used in writing this chapter.

Lindwer, M. et al., 'Ambient intelligence visions and achievements: linking abstracts ideas to real-world concepts', *Proceedings of the Design, Automation and Test in Europe Conference and Exhibition* (2003) (http://doi.ieeecomputersociety.org/10.1109/DATE.2003.10173).

McCray, W. P., 'How spintronics went from the lab to the iPod', *Nature Nanotechnology*, 2009, 4:2–4.

Moodera, J. S., LeClair, P., 'Spin electronic: a quantum leap', *Nature Materials*, 2003, 2: 707–708.

RESOURCES FOR TEACHERS

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ABOUT THIS DOCUMENT

Below is a list of online resources, textbooks, books, DVDs, movies, magazines and journals where you can find information about nanotechnology and ELSA and safety topics related to it. There are also listed resources developed specifically for teachers. This information will be also available on the NANOYOU project website (http://www.nanoyou.eu), which is constantly updated.

ONLINE RESOURCES (Information on nanotech)

- **The Project on Emerging Nanotechnologies** (http://www.nanotechproject.org)
  This is a project by the Woodrow Wilson International Center for Scholars and is probably one of the best places online to find information about nanotechnologies, including safety and ELSA issues. This project has created a number of very good reports (under 'publications') that can be downloaded (or you can request a print copy). Here, you will find presentations, videos, webcasts, etc., of very interesting meetings and panels. There is also a Consumer Product Inventory of all products commercialised that claim to contain some form of 'nano'.

- **Science 2020** (http://www.2020science.org)
  This is the personal blog of Andrew Maynard, Chief Science Adviser at the Woodrow Wilson International Center for Scholars' Project on Emerging Nanotechnologies. This is a brilliant blog, with a lot of interesting posts about nano-related articles and debates. You can also ask questions or comment directly and Andrew is quick to reply!

- **The Royal Society** website (http://www.nanotec.org.uk)
  Here, you find the report (free to download) *Nanoscience and nanotechnologies: opportunities and uncertainties*, by The Royal Society and The Royal Academy of Engineering (2004). This is the report that kick-started all the debate about the safety of nanotech.

- **Nanotechnology in the European Commission** (http://cordis.europa.eu/nanotechnology/)
  Specific documents of interest are *Towards a European strategy for nanotechnology* (COM(2004) 338 final of 12 May 2004), and Nanoscience and nanotechnologies: *An action plan for Europe 2005-2009* (COM(2005) 243 final of 7 June 2005).

- **National nanotechnology Initiative** (NNI) (http://www.nano.gov)
  The NNI is the biggest US initiative on nanotech, funded by the government. Teaching resources are available (http://www.nano.gov/html/edu/eduteach.html).

ONLINE RESOURCES (Material for teachers/trainers)

- **Nanosense project** (http://www.nanosense.org)
  This is probably the biggest project oriented at materials for teachers. There are some very good PDFs (free to download) that cover aspects such as teaching nanoscience in school, ideas on how to integrate nanoscience in chemistry or physics curricula, as well as background documents, PPTs, exercises, etc. This project was founded by the National Science Foundation (NSF).

- **Educational portal of the University of Wisconsin-Madison** (http://mrsec.wisc.edu/Edetc/)
  The biggest educational portal in terms of material, lesson plans, lab exercises, etc., put together by scientists and experts in communication precisely about nanoscience. It has some material for teachers. This educational portal of the University of Wisconsin-Madison receives funding from the National Science Foundation (NSF).

- **NISE** (Nanoscience Informal Education Network) network (http://www.nisenet.org)
  This is one of the best network of informal educators and it has material for schools as well as science exhibits, nano-days, etc. Members of the network can share ideas etc. Some of the material has been reviewed by the teachers and their comments are reported (very good). The experiments are mostly a refined version of those developed by the Wisconsin-Madison University (above). Funded by the NSF.

- **AccessNano** (http://www.accessnano.org)
  This is an Australian educational resource for secondary schools. Lots of material and very well done. It has an industry-application focus. AcessNano is an Australian government initiative funded through the Australian Office of Nanotechnology, under the Department of Innovation, Industry, Science and Research in working with the Department of Education, Employment and Workplace Relations. AccessNano has been produced by foresight and science communications consultancy Bridge8 Pty Ltd. The material was developed in close collaboration with industry, academia and science teachers across Australia. Partners include Nanotechnology Victoria Ltd (http://www.ausnano.net/index.php?page=groups&group=5150/): Nanotechnology Victoria Ltd (Nanovic) is a venture for delivering nanotechnology research outcomes to Victorian industry. It is a venture involving three major universities, and also receives funding from the Australian Government.

- **Nano Education Portal** (http://www.nanoed.org/)
  This is a big web educational portal with educational resources, news, seminars, etc., on teaching nano at school (all levels). Funded by the NSF.

- **Nano what?** (http://www.nanowhat.co.uk/teach/)
  Educational portal developed by the University of Nottingham with materials for teachers and videos.

- **Nano School Box** (http://www.nanobionet.de/publications.htm)
  This box was developed during the FP6 European project Nano2 Life between academic and industry partners. It was produced by a private company that was part of the project called NanoBioNet (http://www.nanobionet.de/eng.htm). It costs EUR 235 plus VAT.

- **Nano-lessons in a box**
  (http://www.nano-cemms.uiuc.edu/content/education/education_kits/index.php)
  An educational kit developed with funding from the NSF and Motorola. Teachers can borrow the kit free, use it, but it must be returned within two weeks.

- **NanoBits Education Kit**
  (http://www.nanovic.com.au/index.php?a=education.resources%20 for%20schools.nanobits%20kit&p=361)
  This is an educational kit for teenagers and young adults, developed by nanotechnology Victoria. It is sold by a private company (http://www.nanogoodsandservices.com/products.html) and costs ASD 120.

ONLINE (Specifically about nanotech and ELSA & safety)

- **NANOCAP Project** (http://www.nanocap.eu)
  This is an FP6 project (now completed) that dealt with nanotech and ELSA and safety and workers' issues. On the nanacap.eu website you can find and 'ethics portfolio' which was written specifically for NT. On this website, you can find several references on nanoethics.

- **ObservatoryNANO** (http://www.observatorynano.eu/project/)
  This an FP7 project where you can find some reports on nanotech (applications) which are easy to read and relatively comprehensive. Under the heading 'societal issues', there is a section dedicated to nanoethics and a very good 'ethics toolkit'.

- **2020 Science** (http://www.2020science.org)
  Here you find a blog with the list of the best 10 places where to find information about nanotechnology safety and ELSA — to be recommended! See http://2020science.org/2009/09/14/nanotechnology-safety-ten-useful-resources/

- **nano & me** (http://www.nanoandme.org)
  A new and brilliant website, easy to ready, practical info about applications of nanotech, safety and impact on society (ELSA).

TEXTBOOKS (19)

- Hornyak, Gabor L., Joydeep, Dutta, Tibbals, Harry F., Roa, Anil K., ***Introduction to Nanoscience.***
  This is an excellent textbook written for undergraduate (university) level. It is detailed and very well written. It focuses on nanoscience, not much on its application.

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(19) All books and textbooks are available at www.amazon.com

- Hornyak, Gabor L., Moore, John J., Tibbals, Harry F., Joydeep, Dutta, ***Fundamentals of Nanotechnology.***
  This textbook is ideally the continuation to Introduction to Nanoscience but it is not necessary to buy both. This book focuses more on the application of nanotech (rather than the basic science). Brilliant, well written, very comprehensive. Does not cover safety and ELSA.

READING BOOKS (Short)

- Wilson, Mick; Kannangara, Kamali; Smith, Geoff; Simmons, Michelle; Raguse, Burkhard; ***Nanotechnology: Basic Science and Emerging Technologies.***
  This book is for those who need an introduction to the basic concepts of nanoscience and nanotech. It is easy to read, not too specialised, and offers many examples of real nanotech research.

- Ratner, Mark A., Ratner, D., ***Nanotechnology: A Gentle Introduction to the Next Big Idea.***
  This book is a little bit more technical than *Nanotechnology: Basic Science and Emerging Technologies* but it is easy to read and, again, has many examples of real nanotech research.

MOVIES AND DVDs

- **Talking NANO 6-DVD Video Set**
  This is a fantastic DVD set providing a basic introduction to nanotechnology, potential applications, implications, and impacts. Designed for classroom, informal, and professional development use, the videos are tightly edited with close-ups and illustrations. The set is available at cost (UDS 34.99) online (http://www.talkingnano.net) along with detailed content information, clips and reviews.

- **NanoInLife**
  This is a recent movie by the Directorate-General for Research and Innovation. It is good, easy to understand, covers basics and applications. Watch it online for free (http://www.athenaweb.org/programs/summary/nanotechnology-nanofilters-chip-oled-nanomedicine-1001004.html). NB: The site htt://www.athenaweb.org has numerous (free) videos about nano, very good. Just put ‘nano’ in the search field and you will find many of them!

MAGAZINES, JOURNALS

- **NANO magazine** (http://www.nanomagazine.co.uk/)
  A good magazine in which to find easy-to-read articles about nanotech. It is low on hype and also covers controversial aspects such as regulation, toxicity, ELSA, etc. Some articles are available online, for some you need a subscription.

- **Nature Nanotechnology and others**
  Nature Nanotech is a peer-reviewed journal with excellent articles about nanotech (specialised reading). Other very good journals include *Science, Nature, Small, Advanced Materials, Nano Today*, and there are many more. A subscription is needed.

- **ACS Nanotation** (http://community.acs.org/nanotation/Home/tabid/36/Default.aspx)
  A good website to find latest information on research published in ACS (American Chemical Society) journals. It has also a community area, ‘ask a scientist’ etc.

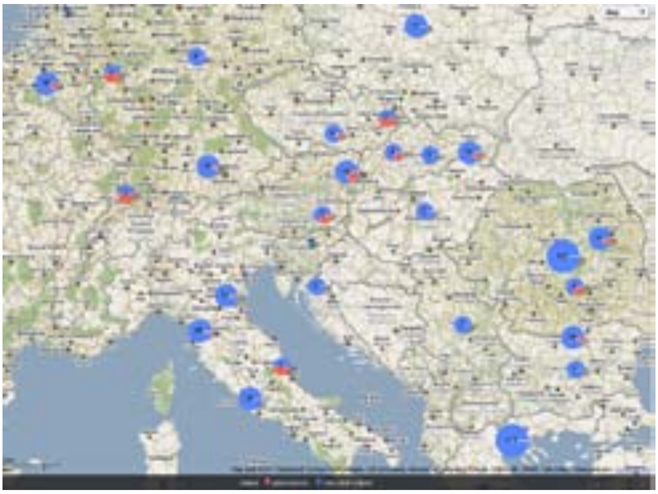
ANNEX

The components of this compendium, its lessons, discussions on applications and experiments have been tested by hundreds of teachers, professors and educators from 956 schools which participated to this experience in 20 European countries in two phases from 2010 to 2011. We call it the “NANOYOU experience”: it reached 35.825 initially registered students, about 40.000 students including late arrivals in Austria, Belgium, Cyprus, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Italy, Latvia, Lithuania, Portugal, Romania, Slovakia, Sweden, Spain, Turkey and the UK. Fifty pilot schools were particularly active in testing and providing feedback, inputs and contributions to the compendium, while 906 ancillary non-pilot schools have essentially been testing it. Overall figures are provided in the attached table.

	Pilot schools	Ancillary non-pilot schools	Total participating schools	Students initially registered in the ‘NANOYOU experience’	Countries in EU Member and Associated States
Stage one: 2009-10	24	479	503	11,673	15
Stage two: 2010-11	26	426	452	24,152	20
Total	**50**	**908**	**958**	**35,825**	**20**

Overview of schools and students from EU Member and Associated States initially registered as participants in the “NANOYOU experience”.

Map of schools from EU Member and Associated States registered as participants in the “NANOYOU experience”.
The blue part of the pie charts corresponds to the share of ancillary non-pilot schools in that geographical area and the red part represents the share of pilot schools. A well balanced geographical repartition of the schools is apparent all over Europe and selected Associated States. A geographical triangle of participation is also evident: Italy-Greece and Romania seem to have been the cornerstones of the distribution of participating schools. A fine-tuned focus on Germany and Romania shows the well balanced repartition is present at both large scale and regional level.



Map of schools from the EU participating in the NANOYOU experience: focus on Germany and Romania.
The lists of pilots schools involved in this experience in the first and second stage can be found on the Nanoyou website: http://nanoyou.eu/en/nano-educators/pilot-schools.html?view=alphacontent .

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Uyar, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, © 2008; Image p.101: *Nature Biotechnology*, 2001, 19:631–35, reprinted with the permission of Macmillan Publishers Ltd, © 2001; Image p.103: Xu et al., *Journal of the American Chemical Society*, 2008, 130:14958–14959, reprinted with the permission of the American Chemical Society, © 2008; Image p.105-106: Wikimedia Commons, image for public domain; Image p.107 (top): Wiki Commons, Creative Commons Attribution Non-Commercial Share Alike 3.0; Image p 107 (bottom): Michael Ströc, GNU Free Documentation Licence; Image p.108: M. A. H. Hyder, Master Thesis, Technical University of Hamburg-Harburg, Germany, reprinted with the permission of the author, © M. A. H. 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Jensen, 'Hydrogen Fuel Cells', Aktuel Naturvidenskab, 2004 (http://www.ird.dk), reprinted with the permission of the author; Image p. 212: T. R. Jensen, 'Hydrogen Fuel Cells', *Aktuel Naturvidenskab*, 2004 (http://www.ird.dk), Naturvidenskab 2004; Image p. 213: Wiki Commons, Public image; Image p. 215: iNANO, Aarhus University; Image p. 217: P. L. Taberna et al., 'High rate capabilities Fe3O4-based Cu nano-architectured electrodes for lithium-ion battery applications',*Nature Materials*, 2006, 5:567–573, reprinted with the permission of Macmillan Publishers Ltd, © 2006; Image p. 220: Qin et al., 'Microfibre-nanowire hybrid structure for energy scavenging', *Nature*, 2008, 451:809–13, reprinted with the permission of Macmillan Publishers Ltd, © 2008; Image p. 226: http://commons.wikimedia.org/wiki/User:Wgsimon, Creative Commons Attribution Non-Commercial Share Alike 3.0; Image p. 236: A. 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EXPERIMENT B (pages 275 to 303): this experiment was adapted from the activity 'Preparation of Cholesteryl Ester Liquid Crystals' (http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/ index.htm)and the 'Exploring materials: Crystal Liquids' activity developed by the NISE (Nanoscale Informal Science Education) Network (Creative Commons Attribution Non-Commercial Share Alike 3.0). The activity was developed for the NISE Network with funding from the National Science Foundation under Cooperative Agreement #ESI-0532536. Any opinions, findings, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Foundation

EXPERIMENT C (pages 305 to 339): this exercise was partly adapted from the experiment reported in 'Color my nanoworld', *Journal of Chemical Education*, 2004, 81(4), and the experiment 'Citrate synthesis of gold nanoparticles', University of Wisconsin-Madison (http://www.mrsec.wisc.edu/Edetc/curriculum/index.html); a more detailed description of the synthesis of colloid gold is given by Keating et al., *Journal of Chemical Education*, 1999, 76(7):949–955

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