Chapter 2: Applications of Nanotechnologies – 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 burning of oil, coal and gas. Only a small portion comes from natural processes such as volcanic action and 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, being either in a solid, liquid or gas form. The small size of nanomaterials, together with their high surface-to-volume ratio, can lead to very sensitive detection.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

These properties will allow developing highly miniaturise, 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 to discuss 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 pre-treatment process and removal of the contaminated area is often required, with a consequent disturbance of the ecosystem. Nanotechnology allows 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, thanks to its ability to manipulate matter at a molecular level, nanoscience can be used to develop remediation tools that are specific for 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

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

methods that allow 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 investigated for remediation include iron and bi-metallic nanoparticles, semiconductor nanoparticles, magnetic nanoparticles and dendrimers. Below are some detailed examples

Remediation using metal nanoparticles

The use of zero-valent (Fe0) 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 (in rocks, soil, water, etc.), some industries have started using an "iron powder" to clean up their new industrial wastes. However, the "iron powder" (that is, 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.

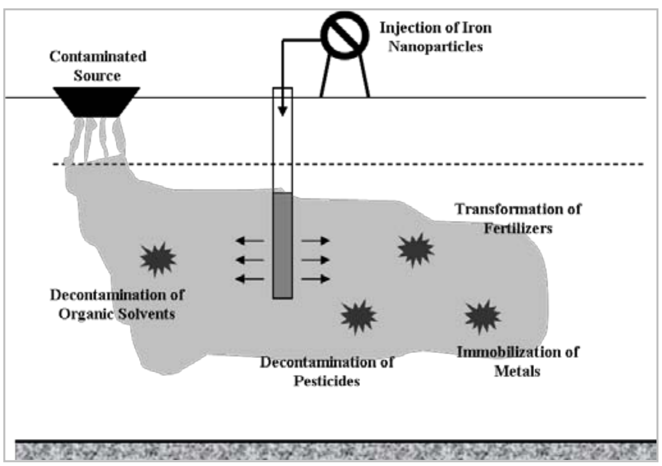
Another matter of concern is the decrease in reactivity of iron powders over time, possibly due to the formation of passivation layers over their surface.

Nanotechnology has offered a solution to this remediation technology in the form of iron nanoparticles. These nanoparticles are 10 to 1000 times more reactive then 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 to 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

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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.

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. Thanks to 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 nonaqueous 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.

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

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 TiO2 and ZnO are capable of transferring

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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 sun radiation. There is evidence that those 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 forms:

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 instance silica-titania nanocomposites are being investigated for 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 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.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Remediation using magnetic nanoparticles

Another class of nanoparticles that have environmental applications is magnetic nanoparticles. For instance, 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 one 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 be also precipitated using nano-scale zero-valent iron ($Fe0$) 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 $Fe0$. 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 & 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,

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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 oil material. Another method that is 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 area so they can absorb sixteen 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. A company called 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 above, 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 programs. 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.

Nano-membranes and nano-filters

Nanotechnology can also be employed for the fabrication of nano-filters, nano-adsorbents and nano-membranes 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 for the fabrication of these products.

In principle, **"nano-traps"** designed for a certain contaminant can be produced, for instance having a specific pore size and surface reactivity. An example is given by the work carried out at Rice's CBEN,

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

where researchers are developing reactive iron oxide ceramic membranes (ferroxane membranes) that are capable of remediating organic waste in water (**Figure 2**).

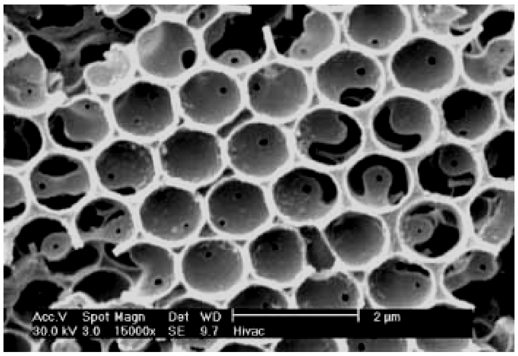


Figure 2. A ceramic nano-membrane. Photo courtesy of Professor M. Wiesner, Wiesner Laboratory, Duke University.

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 instance, researchers at the University of Tennessee are investigating a new type of nano-fibre for the removal of micro-organisms via filtration that can also kill them on contact.

An interesting application of nano-membranes has been developed by researchers from 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 nanosize of the holes forming the membrane, which are "tunnels" accessible only to the water molecules. Another distinctive feature of this nano-membrane is its ability to repel organics and bacteria, thanks to the chemical composition of the nanoparticles embedded in the membrane. Compared with conventional RO membrane, these are thus less prone to clogging, which increases the membrane lifetime with an obvious economic benefit.

Super-hydrophilic filters

In many circumstances access to clean and safe water is a problem. Nano-filters allow filtering water from contaminants such as arsenic and other heavy metals. One commercial reality is the LifeSaver® Bottle that has a super-hydrophilic filter inside that can block material up to 15nm in size, which includes viruses and bacteria. The filter is inserted in a plastic bottle and allows cleaning contaminated water on-site.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Pollution Prevention

Nanotechnologies offer many innovative strategies to reduce the production of pollution in numerous processes. These include: reduction of waste in manufacturing processes; reduction of the use of harmful chemicals; reduced emission of greenhouse-effect gases in fuel combustions; 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 to produce advanced materials that pollute less, or as a method to increase the efficiency of certain industrial processes (e.g. catalytic process).

Materials

Materials that are more environment-friendly fabricated 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 in the range of 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**).

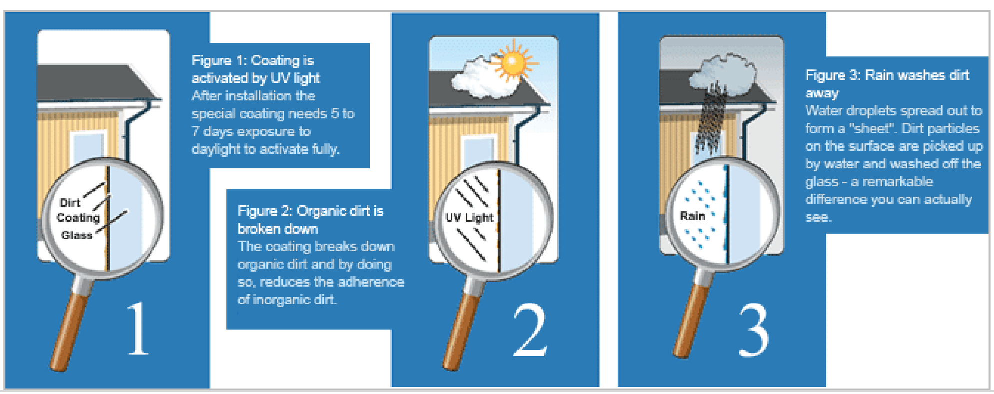


Figure 3. Explanation on how the Pilkington Activ™ Self Cleaning Glass works as described by the manufacturer (www.pilkington.com).

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

The coating is hydrophilic (water contact angle (CA) is 20 compared to conventional soda glass for which CA is 40). Upon dirt deposition, 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

At times 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 **Chapter 2 of Module 1 "Natural Nanomaterials"**). 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 roll-off 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. Material 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 are now commercialising textiles that are engineered to confer superhydrophobic properties on their textiles (**Figure 4 and Figure 5**). This effect

Figure 4. Liquid staining on a Nano-Tex® fabric. (Image credit: image courtesy of Nano-Tex, Inc., Copyright Nano-Tex. Inc.)

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

is obtained by the presence of "nano-sized whiskers" on the surface of the fibres that compose the fabric.

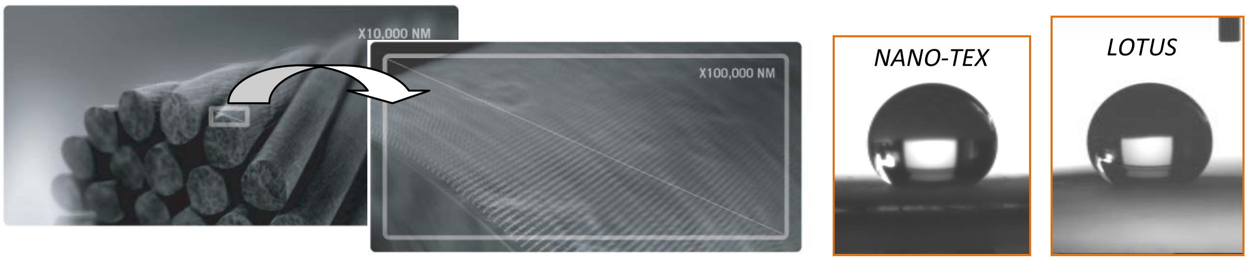


Figure 5. High resolution images of the Nano-Tex® fabric (Images courtesy of Nano-Tex, Inc., Copyright Nano-Tex. Inc). (Right:) contact angle images of water droplets on Nano-Tex® fabric and lotus leaf (Images: iNANO; Aarhus University, Creative Commons Attribution ShareAlike 3.0).


EXPERIMENT

Experiment D in the Experiment Module deals with studying the lotus effect and learning 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 of the need for cleaning**. Currently there are various products commercialised or under research that make use of this principle, for instance Lotusan®, an exterior paint from the firm Sto launched in 1999. The application of this exterior paint reduces the attack of dirt to the façade it is applied to, 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 the cleaning it needs, with a reduction of water usage and obvious environmental benefit.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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 instance to protect medical surfaces and tools, or to reduce microbial attack in the hull of boats. Sprays and coatings for this aim 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. Anti-fouling surfaces are investigated for coating of medical utensils and instruments, for coating household appliances, as well as for coating boats. A nanomaterial that is becoming widely used is silver nanoparticles.

Silver is a metal that has a long history of being used for its anti-bacterial 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, silver nitrate 1 % 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 **anti-bacterial 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 skin. The few cases of death due to silver intoxication have been related to very high concentrations of silver.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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, bedding items (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 of 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 are also raised concerning silver nanoparticle uptake by plant 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 benign bacteria used to remove ammonia in waste water. The concern is that if large quantities of consumable products (like socks, toothbrushes, jackets, etc.) are used, large amounts of silver ions, silver nanoparticles or their aggregate forms could be released into rivers and lakes and damage the eco-system. Many agencies are calling for stricter safety testing of nano-based products and for research on the safety of these products.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

NANOYOU DILEMMA The example of silver nanoparticles in a consumer product (socks) is one of the NANOYOU dilemmas included in the ***NANOYOU Role Play Card Game- Antibacterial Socks*** *(see www.nanoyou.eu/en/decide). In this dilemma students consider the case of* ***socks having 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 eco-toxicity of nanosilver, students are encouraged to reflect on this product through a benefit vs. 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****, like tooth-brush, is debated the* ***NANOYOU NT Virtual Dilemma- Nano toothbrush*** *(see nanoyou.eu/en/decide). Here the question we ask is if the prolonged use of the tooth brush 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 microorganisms to the surface of the boat, which otherwise reduce its speed. In time the coating can degrade, so we ask students to think if this could have an unwanted environmental effect.* *See also page 23 of this document.*

Other coatings

A number of products are appearing on the market that can infer 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 game. Students need to match the nanomaterial, to its application, connecting it to a specific need. The game can be found at: http://nanoyou.eu/en/play-nano.html

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Fertilisers and wood treatment products

Another area where nanotechnologies are making a contribution is the development of fertilisers and wood treatment products that are more stable and leach less into the environment. For instance, researchers at Michigan State University have incorporated biocides for wood treatment inside polymeric nanoparticles. Their small size allows them to travel efficiently inside the very fine, sieve-like structure of wood. 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 (**Chapter 2 and Chapter 5 in Module 1**). One example is biomimetic water-harvesting materials. Some plants and insects have the ability to capture water from fog. For instance 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. Thanks to this fine nanostructure, as droplets accumulate in size, they roll from the tops to the waxy channels to a place in the beetle's back that supplies its mouth. A company called QinetiQ, LtD from UK has developed sheets that capture water vapour from cooling towers and industrial condensers based on the nanostructure of the beetle wing. These materials can capture ten times more water than conventional technology.

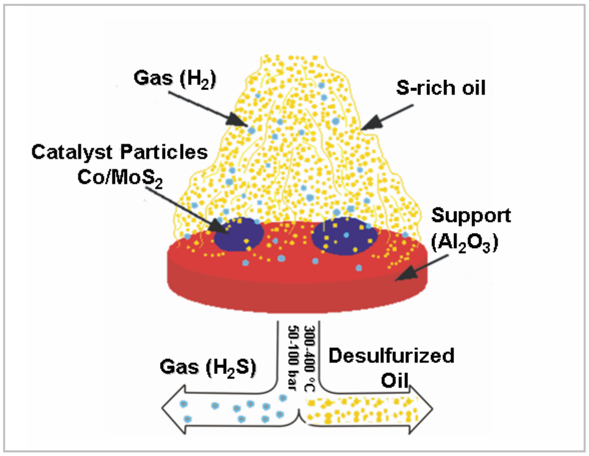
Nanocatalysis

A catalyst is a substance that increases a chemical reaction rate 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 higher 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.

In the environmental field, nanocatalysis is being investigated for instance for **desulphurising fuels**, with the aim of developing "clean" fuels containing very low sulphur products (produced in the fuel during its

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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.



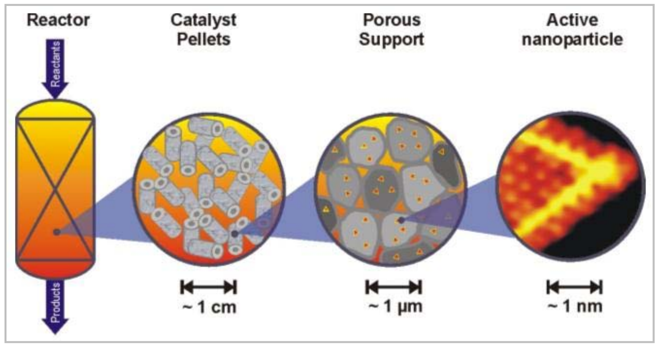


Figure 6. (Left) Overview of the hydrodesulphurisation (HDS) catalytic reaction. (Right). Schematic representation showing how nanoparticles could be included in the catalyst material of a desulphurising fuel reactor. The image on the far right is a real Scanning Tunnelling Microscope (STM) image of an MoS_2 nanocrystal on Au(111) showing peculiar atomic distribution at the edges of the crystal. (Image credit: courtesy of F. Besenbacher, iNANO, Aarhus University.)

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 UK (another 500 buses were tracked as control). It was found that the test buses used 5% less fuel then the controls and that the fuel savings more than paid for the additive.

Nanoscale catalysts are also promising for **improving air quality** and for treating particularly challenging **contaminants in water** that must be reduced to a very low level.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433