NANOYOU Teachers Training Kit in Nanotechnologies

Chapter 2 – Environment

MODULE 2- Application of Nanotechnologies
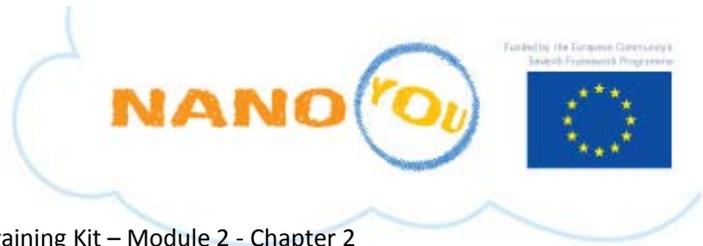
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Chapter 2: Applications of Nanotechnologies – Environment

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.

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

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

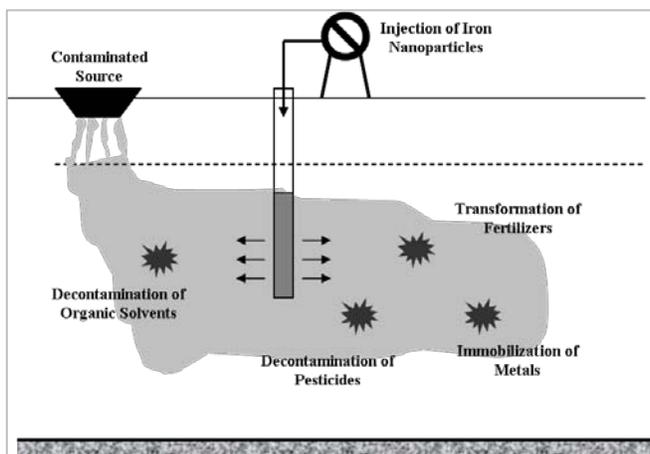### Remediation using metal nanoparticles

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

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 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.

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,

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,

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

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.

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

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.

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**).
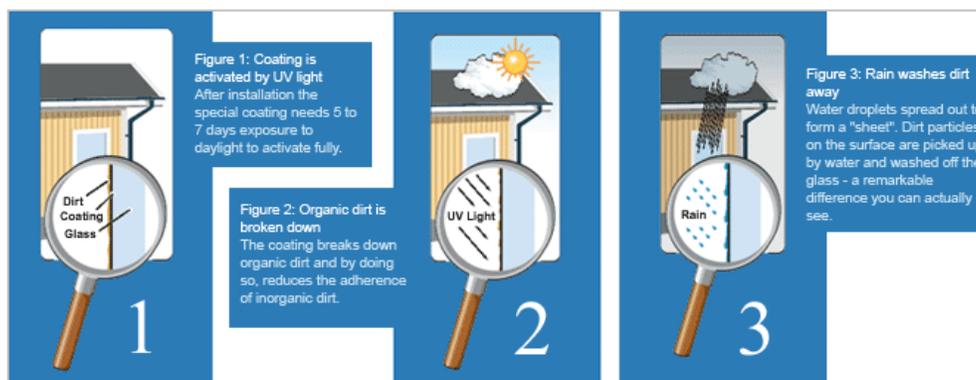

Figure 3. Explanation on how the Pilkington Activ™ Self Cleaning Glass works as described by the manufacturer (www.pilkington.com).

The 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.)

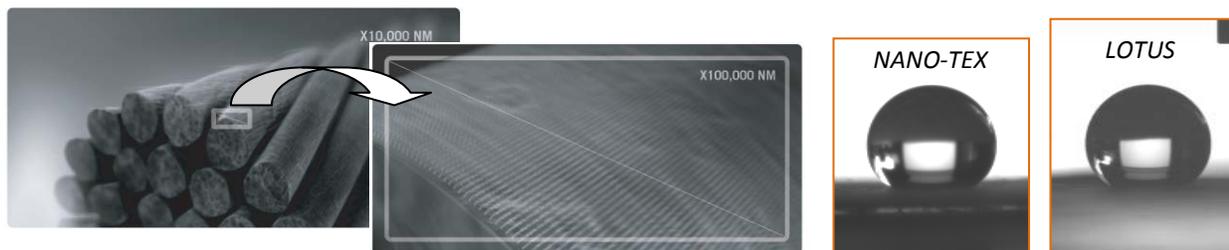is obtained by the presence of "nano-sized whiskers" on the surface of the fibres that compose the fabric.

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 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.

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.

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.

*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

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

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.
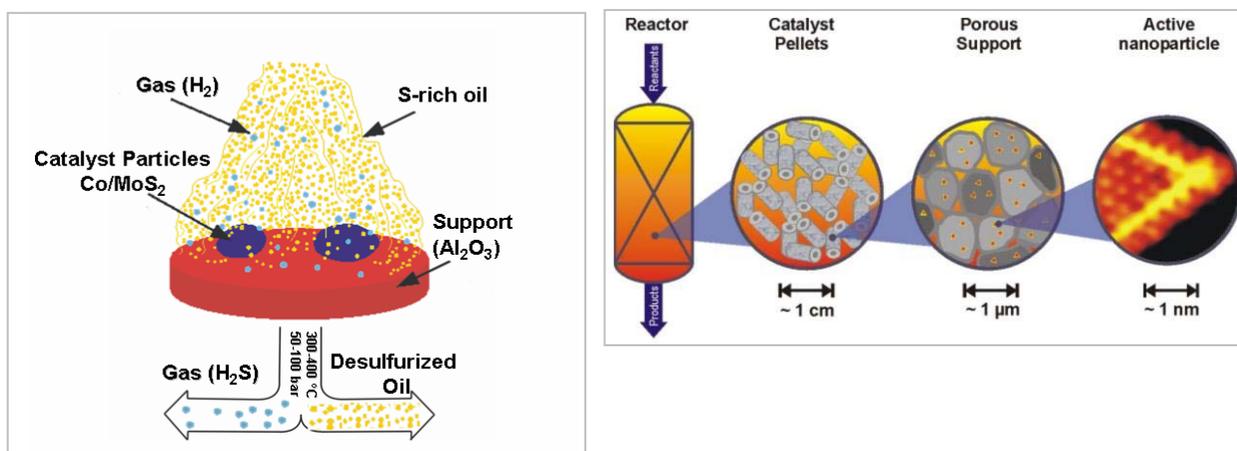

Figure 6. (Left) Overview of the hydrodesulphurisation (HDS) catalytic reaction. (Right). Schematic representation showing how nanoparticles could be included in the catalyst material of a desulphurising fuel reactor. The image on the far right is a real Scanning Tunnelling Microscope (STM) image of 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.

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 Pt and Pd, which are extremely expensive. There is a great need Alternatives are in great 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 CO 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 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 40% times more than commercially available materials. Considering that there are over 14 million light-duty diesel vehicles worldwide, and 2 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.
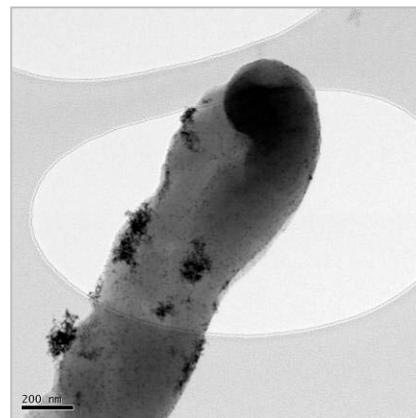

Figure 7. An SEM image of Desulfovibrio desulfuricans, a Gram negative bacterium after Pd recycling. Pd is produced as nanoparticles (black particles in the image) located on the cell surface and in the periplasmic space of the bacterium. (Image courtesy of Rikke Lousie Myer, iNANO. Copyright iNANO).

The hope is to use bacteria to recover catalytically active Pd from industrial waste, and to use recovered Pd for other catalytic processes.

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 (for instance, 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 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"; these include, for instance: bottom-up atomic-level synthesis for developing improved catalysts; inserting information into molecules to build new materials (such as DNA) through highly specific synthetic routes; scaling down material usage during chemical reaction 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 having 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 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 upon 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. First, 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 packing more detection sites 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 includes various areas, like 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 few nanometres. When the electrodes are exposed to a solution of water containing metal ions, these deposit inside the nano-gap in 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"
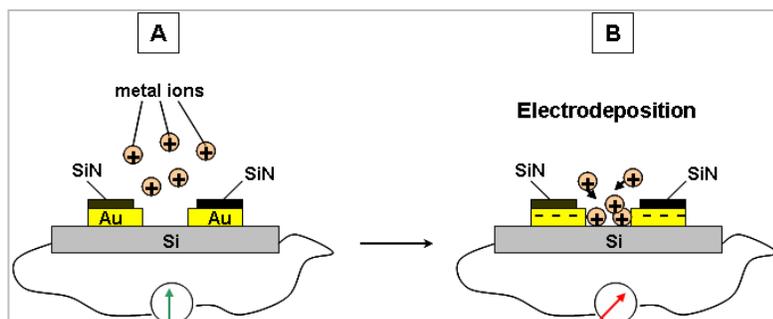
Figure 8. Schematic representation of a nanocontact sensor. (A) A drop of sample solution containing metal ions is placed onto a pair of nanoelectrodes separated with an atomic scale gap on a silicon chip. (B) Holding the nanoelectrodes at a negative potential, electrochemical deposition of a single 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 credit: adapted from: Proceedings of Nanotechnology and Environment: Applications and Implications, Progress Review Workshop III (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 instance towards gaseous molecules (such as NO_2 and NH_3) than that of existing solid-state sensors. In this case, direct binding of the gaseous molecule to the surface of the SWNT is the mechanism involved in sensing, 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 to 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 limit their development. First, existing synthetic methods produce a mixture of metallic and semiconducting NTs, 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 NTs needs to be modified to have specific functionalities to bind those species. Flexible methods to modify the surface of NTs to bind a large variety of analytes are not yet well established. Conversely, nanowires of semiconductors such as Si 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 in real-time a wide range of analytes could be used to develop sensors for detecting 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 in the nanoscale regime. 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.
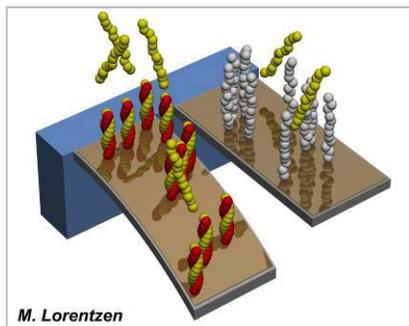

Figure 9. Schematic diagram of a cantilever based biosensor. The yellow molecules bind specifically to the red molecules on the right hand cantilever and are detected by the bending of the cantilever. (Image courtesy of M. Lorentzen (iNANO, University of Aarhus). Copyright © Lorentzen).

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 instance the mission of the NanoFOOD consortium at iNANO (Aarhus University). One project in particular focuses on the characterization and exploitation of **proteins immobilised on surfaces**. Immobilization 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, health care 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 be phased out by 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 application 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 biofilm 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 specific chemical, like 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 like 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 area, so they are very reactive, and can be functionalised to be very sensitive to detect a specific chemical specie, like oxygen, and provide a fast response. In a similar way

nanoparticles could be used to detect other chemicals that indicate food spoilage, like ethanol, or even the presence of bacteria. This nanosensor could be even be engineered to continuously wireless communicate the status of the product it contains to the manufacture.

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*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 Play Card Game- Nanotechnology in food packaging** (see 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 mean time, should these materials be disposed 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?"*

*Nanotechnology in food packaging, is debated also in the **NANOYOU NT Virtual Dilemma- Nanotechnology in food packaging** (see nanoyou.eu/en/decide).*