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Nanotechnology and the environment: A European perspective

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Abstract

The potential positive and negative effects of nanotechnology on the environment are discussed. Advances in nanotechnology may be able to provide more sensitive detection systems for air and water quality monitoring, allowing the simultaneous measurement of multiple parameters and real time response capability. Metal oxide nanocatalysts are being developed for the prevention of pollution due to industrial emissions and the photocatalytic properties of titanium dioxide nanoparticles can be exploited to create self-cleaning surfaces that reduce existing pollution. However, while nanotechnology might provide solutions for certain environmental problems, relatively little is known at present about the environmental impact of nanoparticles, though in some cases chemical composition, size and shape have been shown to contribute to toxicological effects. Nanotechnology can assist resource saving through the use of lightweight, high strength materials based on carbon nanotubes and metal oxide frameworks as hydrogen storage materials. Other energy related applications include nanostructured electrode materials for improving the performance of lithium ion batteries and nanoporous silicon and titanium dioxide in advanced photovoltaic cells. It is important to develop an efficient strategy for the recycling and recovery of nanomaterials and methods are needed to assess whether the potential benefits of nanotechnology outweigh the risks. Life cycle analysis will be a useful tool for assessing the true environmental impacts.

Keywords: Gas sensors; Biosensors; Nanowires; Nanomaterials; Nanotoxicology; Catalysis; Photovoltaics; Hydrogen storage; Lithium batteries; Sustainability

1. Introduction

Applications of nanoscience and nanotechnology can be expected to have a significant impact on sustainable development, influencing virtually all industrial sectors including healthcare, agrifood, transport, energy, materials, and information and communications technologies (ICT). Our present reliance on fossil fuels for energy and transport, and the by-products and waste from manufacturing industries have a major impact on the environment, leaving areas of land and bodies of water unsuitable for other use, and in the worst cases destroying whole ecosystems. Nanotechnology can contribute to resource saving through improvements in the efficiency of renewable energy sources, reduced consumption of materials, and the possibility of substituting alternative, more abundant materials for those that have limited availability. It also holds promise for improving the environment, by reducing waste and our dependence on non-renewable natural resources, and in cleaning up existing pollution [1]. The ability to detect and quantify the presence of toxic agents in the environment is a first step towards taking remedial action and nanotechnology can help provide improved systems for environmental monitoring.

In contrast to the United States [2–4], the European Union (EU) does not at present have a specific research initiative on nanotechnology and the environment. However, some major European research projects are already underway in this area and it has been generally recognised that nanotechnology offers significant opportunities for improving the environment. A European Commission—Nanoforum joint workshop was recently organised to examine the potential impacts of nanotechnology on the environment [5]. Its purpose was to discuss ways in which nanotechnology could be used for the benefit of the

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environment, while at the same time remaining aware of the potential risks. The application areas considered were: (i) monitoring; (ii) remediation and pollution; (iii) resource saving. This paper reviews a number of relevant research activities, with emphasis on projects funded by the European Commission during the Sixth Framework Programme. It considers both the potential positive and negative implications of nanotechnology for the environment, and draws conclusions regarding future priorities for the research needed to ensure its safe and responsible technological development.

2. Environmental monitoring

Present day monitoring systems for air pollution consist of large, fixed stations situated in urban areas at geographically separated locations that fail to meet the need for monitoring localised "hot spot" pollution peaks. Solid state gas sensors based on nanocrystalline metal oxide thin films can provide faster response with real-time analysis capability, higher spatial resolution, simplified operation and lower running costs compared with conventional methods such as chemiluminescence and infra-red spectrometry. Their sensitivity and selectivity are dependent on operating temperature, film thickness, porosity and grain size and can be increased by doping with a platinum catalyst [6–8]. Micro-machined multi-element sensors have been fabricated [9] that can reversibly and selectively detect carbon monoxide and nitrogen dioxide (NO_2), by measuring the changes in electrical conductivity due to chemisorption of gas molecules. Detection of CO at concentrations less than 1 ppm and NO_2 below 10^{-1} ppm, corresponding to levels at or below the existing EU legal limits, has been achieved.

By combining solid-state gas sensors with a global positioning system (GPS), and connecting them via an intelligent sensor network [10] data can be transmitted from remote locations to a central service site to allow real-time analysis and fast response. The objective of the Advanced Distribution Architecture (ADA) for Telemonitoring project is to develop and implement innovative network architecture, embedded in the existing communications infrastructure, for air quality monitoring applications. Integration of metal oxide thin film technology with CMOS compatible device fabrication makes possible the selective detection of low concentrations of CO, NO_2 and CH_4 in a cost-effective manner [11].

The Nano-structured Solid-State Gas Sensors with Superior Performance project (NANOS4) is applying advanced micro- and nano-technologies for the development of metal oxide gas sensors of increased sensitivity. Fabrication techniques include vapour phase transport process crystal growth and optical, ion and electron beam nanolithography for the selective removal of material. Tin, indium, zinc or tungsten oxides are synthesised in the form of nanowires, nanobelts and nanocombs [12,13]. These morphologies increase the effective surface area of the metal oxide exposed to the gas and will be applied in fabricating the next generation of selective and stable mesoscopic gas sensors.

The implementation of the EU Water Framework Directive requires monitoring of organic substances down to nanogram per liter levels There is therefore a need for fast, sensitive, cost-effective, and easy-to-use analytical systems capable of measuring various organic molecules in aqueous samples. The Automated Water Analyser Computer Supported System (AWACSS) project has developed a remote biosensor station [14] that is able to measure real-time data on levels of pollutants (pesticides, antibiotics, natural toxins, carcinogens, industrial waste etc.) and transmit them to a central computer [15]. This device utilises an integrated optical chip based on an immunoassay technique [16] that can detect and provide information on up to 32 different analytes within 18 min. No prior sample treatment is needed other than a single pre-filtration stage to remove particulate matter. The minimum detection limits are below the EU recommended safe levels for most critical compounds, and the chip can be reused up to approximately 500 times before the surface chemistry requires regeneration.

While there have been notable advances in detecting pollutant molecules in air and water, there still remains a need for inexpensive and portable instrumentation for the detection and measurement of nanoparticles. The toxicity of nanoparticles is dependent on surface area and shape as well as chemical composition and size. No systems are currently available that can accurately and routinely determine all these parameters simultaneously. The potential applications for instrumentation of this type include analysis of ultrafine particles generated by combustion processes and workplace monitoring for industries manufacturing engineered nanoparticles.

3. Remediation and pollution

Filtration and purification plants used to supply clean drinking water in many cases have limited success due to the inefficiency of the active materials. As a result of their much larger specific surface area nanoparticles are significantly more active than larger particles of the same material. This property has been exploited in the use of iron oxide nanoparticles for removing arsenic from groundwater [17]. Iron oxide nanoparticles are able to bind irreversibly arsenic five to ten times more effectively than micron-sized particles and, because of their superparamagnetic properties, can be separated from the purified water by the application of a magnetic field. The nanoparticles can afterwards be retrieved by deactivating the magnetic field with negligible risk of their being released into the environment. Laboratory tests have indicated that in excess of 99% of arsenic in water samples can be removed using 12 nm diameter iron oxide nanoparticles.

Metal oxide catalysts play an essential role in the production of petrochemicals, as well as in energy applications and for environmental protection. The Co-ordination of Nanostructured Catalytic Oxides Research and Development in Europe (CONCORDE) project is developing nanostructured metal oxide catalysts for applications in remediation or prevention of pollution and to contribute to a more efficient use of energy and materials. The research activities comprise advanced preparation methods, development of new catalysts, surface chemistry of metal oxides, improvement of catalyst performance, studies of catalytic reactions and catalyst engineering. Many applications involve mixed catalysts consisting of different oxides or noble metals [18–20], so that the catalytic activity is determined not only by the constituent atoms, but also by the neighbouring crystal or surface structures. It is therefore necessary to control precisely the synthesis of the nanostructured catalysts and to understand the chemical reactivity of the catalytic active centre and how this is affected by the reaction conditions. The applications include $DeNO_x$ catalysts for the removal of nitrogen oxides from fossil fuel power plant emission gases and titanium dioxide photocatalysis for degradation of volatile organic compounds (VOCs).

Nanoparticles can be incorporated into paints and coatings to increase their functionality and durability and create "self-cleaning" surfaces. The field of self-cleaning coatings has been surveyed in a recent review [21] covering the principal materials employed in commercial applications and summarising the current research activities. Hydrophobic coatings have been used to manufacture liquid-repellent surfaces and self-cleaning glasses have recently become available that exploit the photocatalytic action of a thin layer of TiO_2 deposited on the surface. The Photocatalytic Innovative Coverings Applications for Depollution Assessment (PICADA) project is investigating the application of titanium dioxide nanoparticles for use in architectural coatings with de-soiling and de-polluting properties. Titanium dioxide is a potent oxidising agent when exposed to UV radiation and is able to break down VOCs, nitrous oxides and other pollutants into less harmful species. Irradiation with photons of energy >3.2 eV generates electron pairs and hole pairs that cause redox actions with oxygen and water molecules [22], forming oxygenated free radicals that react with the compounds adsorbed on the surface, leading to their degradation [23].

There is a need to develop a better understanding of the short and long term implications of nanotechnology for health and the environment. Two complementary European projects are addressing this issue. The aim of the Improving the Understanding of the Impact of Nanoparticles on Human Health and the Environment (IMPART) project is to foster communication regarding the potential health and environmental effects of nanoparticles at regional, national and international level in order to reduce duplication of effort, pool expertise and facilitate co-operation. The Investigative Support for the Elucidation of the Toxicological Impact of Nanoparticles on Human Health and the Environment (NANOTOX) focuses on potential routes of dispersion and contamination by nanoparticles. A major concern is that nanoparticles may not be detectable after release into the environment, creating difficulties for remediation. A comprehensive set of guidelines and recommendations is currently being developed for use by European legislators, regulators and policymakers for their safe production and use.

There are four distinct classes of nanoparticles that humans can be potentially exposed to: combustion derivatives; bulk manufactured nanoparticles; free engineered nanoparticles; medically administered nanoparticles. Elevated levels of PM_{10} are known to be associated with increased morbidity and mortality due to respiratory and cardiovascular disease [24–26] and inhalation of particulate matter in this size range has been shown to cause inflammation of the lungs and endothelial dysfunction. Both the surface area and the chemical nature of the particles have a significant influence on the physiological outcomes. There is also increasing evidence that inhaled nanoparticles, as a result of their small size, are able to penetrate the lung epithelium, allowing translocation to the liver, spleen, brain and other organs [27].

The surface chemistry of nanoparticles is a principal determinant of their toxic properties. While C_{60} fullerene particles are cytotoxic, for example, the hydroxylated form, $C_{60}(OH)_{24}$, is found to be of low toxicity to cultured cell lines, as are functionalized single-walled carbon nanotubes [28,29]. Although aggregates can generally be considered to be less dangerous than individual nanoparticles, disaggregation tends to occur after inhalation on contact with surfactants present on the lining of the lung. Risk assessment for nanoparticles has to take into account the toxicological hazard, the probability of exposure and the environmental and biological fate, transport, persistence, transformation into the finished product and recycling. One way of reducing the likelihood of exposure is to encapsulate the nanomaterials within an inert barrier (e.g. silicon can be used to coat quantum dots). Another is to create immobile nanostructures on a surface that have a similar activity to free nanoparticles without the risks inherent in dispersion.

The Safe Production and Use of Nanomaterials (NANOSAFE2) project is developing and validating a risk assessment and hazard management strategy, including methods for detection, traceability and characterisation, for the safe industrial production of nanoparticles. This takes into account the whole life cycle including production, storage, transportation, and transformation into the final product, as well as during use and final disposal at the end of product life. Advanced technological solutions are being studied to design safe production equipment, handling and confinement systems, individual protection devices and filters to limit both exposure to nanoparticles and their release into to the environment.

4. Resource saving

Sustainable development is the basis for economic growth while ensuring protection of the environment. Nanotechnology is an essential component of innovation in the chemical industry and other materials-based industries, while environmental concerns will influence future product development. Carbon nanotubes have many potential applications, including high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and radiation sources, hydrogen storage media, and nanometre-sized semiconductor devices, probes and interconnects [30]. Metal organic frameworks (MOFs) have the highest specific surface area ($3500\,m^2/g$) of any manufactured nanomaterial and a hydrogen capacity at room temperature comparable to that of carbon nanotubes at cryogenic temperatures [31]. The production costs represent a significant barrier to the application of many nanomaterials but the development of innovative process can be expected to reduce these. A decrease in the cost of single-walled nanotubes from the present €1000/kg to less than €50/kg would make their widespread use economically viable.

Nanotechnology can also provide resource savings through improvements in efficiency for renewable energy sources and energy storage devices. The ALISTORE European Network of Excellence on Advanced Lithium Energy Storage Systems is aiming to increase the power output of rechargeable lithium batteries from the present 200 to 300 Wh/kg by using nanostructured electrode materials [32–35]. Electron production per electrode atom has been increased from 0.6 to 2 with nanostructured lithium cobalt oxide, formed in situ during the first charge cycle so no free nanoparticles are generated. Alternatively, iron fluoride, cobalt chloride, rubidium oxide and nickel phosphide can be used and are equally or even more effective (up to 6 electrons/metal atom). The use of nanostructured electrodes increases charge/discharge rates by shortening the diffusion paths of lithium ions and electrons and can better accommodate the migration of lithium ions during charge cycling, so that the batteries are also intrinsically safer. It has been shown that electrode integrity is not affected after more than 1000 charge/discharge cycles.

Nanoporous silicon has advantages as a material for solar cells, including its anti-reflection, light trapping and surface passivation properties, the reduced thickness of the active layer due to the lower diffusion length for efficient charge collection, and a higher attainable voltage [34]. Its porous structure leads to quantum confinement and an increase in the bandgap, while the increased light absorption results in higher internal quantum efficiency (IQE). The deposition of nanocrystalline Si thin films by low energy plasma enhanced chemical vapour deposition (LEPECVD) reactor is being investigated by the Nanocrystalline Silicon Films for Photovoltaic and Optoelectronic Applications (NANOPHOTO) project [36]. As an alternative to Si photovoltaics, organic solar cells have been developed using TiO_2 nanoparticles coated with an organic dye to convert light into energy by a process analogous to photosynthesis [37,38]. Absorption of photons by the TiO_2 causes electrons to be injected into the conduction band and the particles to diffuse towards the positive electrode; iodine ions in the electrolyte collect electrons at the negative electrode, causing a current to flow. Although the conversion efficiency is only around 10%, this type of cell can be manufactured from inexpensive, low purity materials using simple methods. Solid state dye sensitized solar cells, in which the liquid electrolyte is replaced by a metal, are also under development [39].

Nanotechnologies offer remarkable possibilities for increasing the efficient use of natural resources and energy. While the EU as a whole has stabilised its consumption of raw materials over recent years, its reliance on imports has greatly increased. Many of the key materials used in advanced technologies are in extremely finite supply. Platinum, for example, is obtained from only four sites worldwide that have a total annual production of 200 tonnes, while only 350 tonnes of indium are mined annually from just six sites. Both these materials are indispensable components for critical technologies (e.g. platinum for catalytic converters and indium in LCD screens and solar cells). Without an effective recycling and recovery strategy, the dispersion of these strategic resources in the environment will eventually create severe shortages of raw materials for economically important industries. It is therefore essential to examine closely the material requirements of new technologies, and invest in those that are sustainable, either because they use abundant materials or allow optimisation of material usage to limit the dispersion of rare materials and facilitate recycling [40,41].

In carrying out an environmental impact assessment for nanomaterials the whole life cycle needs to be considered, not just the production phase. Life-cycle analysis (LCA) is a useful technique for the calculation of the energy and raw material requirements for a product's manufacture, use and final disposal or re-use. To minimise the environmental impact and achieve sustainability, material loops must be closed and it is essential to obtain an accurate estimate of the full environmental impact [42]. This can be illustrated by considering the case of ICT [43,44], which was initially expected to reduce significantly the consumption of energy and materials. While this has been achieved to an extent, the overall savings are considerably smaller than originally projected and each processor requires a substantial quantity of raw material for its production (approximately 20 kg to manufacture a 90 g chip) as well as the consumption of a considerable amount of energy during use.

5. Conclusions and recommendations

- Due to their high spatial resolution and sensitivity, sensor systems can complement and improve the effectiveness of conventional analytical instruments for environmental monitoring.

- Analysis methods need to be developed to detect nanoparticles in the environment that accurately determine nanoparticle shape and surface area.
- Nanoparticles can be beneficial in catalytic and remediation applications; however their dispersion in the environment could make it almost impossible to take remediative action if there were ensuing safety issues.
- Fundamental studies of structure–function relationships are required for nanoparticles; it is important to relate both surface area and chemistry to functionality and toxicity.
- Full risk assessments should be performed on new nanomaterials that present a real risk of exposure during manufacture or use.
- The use of nanomaterials and nanoparticles can lead to significant savings in resources and increases of efficiency in manufacturing and energy related applications.
- A longer term outlook regarding material use needs to be adopted, including analysis of sustainability and, wherever possible, the use of abundant materials. Where the use of scarce materials is unavoidable an effective strategy for recycling/recovery is required.
- Life-cycle analysis should be carried out for new nanotechnology products, including different usage scenarios.

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