Environmental Effects of Novel Materials

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My main areas of research are in nanoparticles, both their synthesis and study of their physicochemical properties, and in nanostructures. In what follows, I will limit my replies to these specific areas. The description of the current state of the field and the corresponding references in this report is not exhaustive and only attempts to show some of the current issues under discussion.

Theme 1. What are new materials and what developments are likely over the next 5-10 years.

1**. What is a novel material**?

1.1 Are nanoparticles new?

Nanoparticles have been known and used for a long time although without recognition of their structure. Over 150 years ago, Faraday was the first to carry out the synthesis of gold nanoparticles that were stable in solution and some of his preparations are still in the Royal Institution! Gold nanoparticles are responsible for the unusual optical effects that can be seen on reflection or transmission in the Roman Lycurgus cup (4th century AD), in the British Museum. Other common examples are the use of nanosized carbon particles in the manufacture of tyres and the use of dispersed metals in catalysis.

The changes that have occurred in the last 10-15 years are in relation to the possibility of synthesising stabilised nanoparticles that could be treated as simple chemical compounds. Although the initial synthesis for metals[1] produced stable materials that had a gold metallic core and a ligand shell that used thiols to attach stabilising hydrocarbon residues to the metal cluster, many other metals and ligands were investigated worldwide. There has been an intense interest in these novel materials and the initial paper (Ref. 1) has attracted now some 1600 citations. Metals have not been the only subjects of intense attention and many ligand stabilised semiconducting particles have also been developed. This type of nanoparticles falls within the category of new materials since the decrease in size results in new properties and at the same time, the presence of a stabilising organic ligand shell makes them ideal to include organic ligands that allow further functionalisation chemistry.

1.2 Why there has been so much interest in ligand stabilised metal nanoparticles?

The interest in these new materials is in relation to the great chemical flexibility offered by the ligand shell. This has been particularly important for developments in their use as building blocks for the chemical construction of nanostructures.

3. What sort of materials and technologies are being developed over the next 2, 5, and 10 years?

See reply to question 8.

5. Impact on resource depletion
For nanoparticles, this is minimal

6. Issues of re-use and recycling
Very little consideration has been given to these questions since the area is very new and the number of applications is not that large. An example where re-use might be important is in the use of silver nanoparticles-ceramic composites for water purification. Re-use might be important here but the market for these experimental devices is very small at present. Recycling of precious metals in industrial catalysts has been carried out for many years and there is nothing very new here. For example, the re-use of car exhaust converters that employ metal nanoparticles is well known.

7. Waste generation
It is difficult to predict the amount of additional waste that will be generated by the large-scale application of nanoparticles and nanostructures. This will depend very much on the way the industrial applications of synthetic nanoscale objects develop. For example, if the development of magnetic media for data storage is not replaced by other methods, e.g., optical storage, the requirements of the computer industry will increase the demand of nanostructured materials and for example, chemical synthetic methods requiring magnetic materials such as cobalt and specialised magnetic alloys can give rise to waste disposal concerns.

The other area of development, biological applications and analyses is unlikely to give rise to waste disposal problems.

Theme 2. Environmental and health impact of novel materials

8. Important impacts on the environment and human health
As I mentioned in the introduction, I will only refer to possible impacts of nanoparticles and nanostructured materials. In order to comments on these (and other issues in the requested written evidence), it is important to discuss the areas where nanoparticles and nanostructures could have a large industrial and societal impact and then analyse the effect that these developments could have on environmental questions. The analysis presented below is not a fully comprehensive description of all the possibilities but a description of some applications, both present and future, which in my view have emerged in the last 5-10 years.

8.1 Magnetic nanoparticles
There are two main areas of interest: (a) Magnetic recoding media and (b) Bioassays.

The requirements of modern computers for data storage has followed a continued increase and these have resulted in new technological requirements for magnetic materials. Figure 1 illustrates the growth of areal density (Number of bits stored

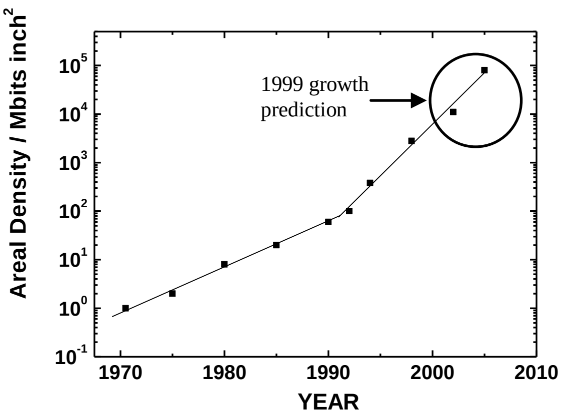

Figure 1. Growth of information density for magnetic materials in computer hard disks. Data from Dennis E. Speliotis, *J. Magnetism and Magnetic Mat.*, 1999, **193**, 29-35.

per square inch of hard disk) for data storage devices since 1970. The predictions in 1999 were that an areal density of 100 Gbits/inch^2 would be reached by 2010. The very rapid pace of development in data storage for computers can be seen when considering that Seagate had already developed a hard disk with and areal density of 250 Gbits/inch^2 by 2006.[2] This is an area of great interest and much efforts is being put into the development of the corresponding new materials and the development of self assembly techniques necessary for the construction of the required nanostructures.[3] Magnetic nanoparticles have been proposed for the construction of very high-density hard disks since their small size allows the achievement of high areal densities for information storage media.

Bioassays in which magnetic nanoparticles are used as a medium that allows concentration from their solution by magnetic focussing are being actively investigated. The basis of these methods is to allow the ligand shell of the nanoparticles to react with the analyte of interest, followed by magnetic separation from the solution. The analyte can be, for instance, a bacterium present at low concentrations in water. The type of magnetic separations described allows, for example, the rapid screening of bacteriological water purity and magnetic focussing represents a powerful concentration method.

Environmental and health issues for these materials are related to manufacture (See Section 7), recycling and disposal, in particular considering the large and regular increase in the use of computers. The latter will be a common problem with materials that employ nanoparticulate matter and when simple recycling methods are employed. For example, crushing as a first step in the extraction of valuable metals has to be carried out under controlled and regulated conditions since nanoparticles can be carried in air and their effect on human health is still not well understood.

8.2 Bioassays and analytical applications

The strong absorbance of gold and silver nanoparticles (the so-called surface plasmon band) has been used in analytical applications. Synthesis, fabrication, and characterisation methods for nanomaterials now allow the control of their size, shape, and composition. The ability to carefully tailor the physical and chemical properties of nanoparticles has been important for their application in bioanalyses.[4,5] Different analytical formats require control of participle size and geometry e.g., for Raman spectroscopy, which requires control of light-scattering properties. Nanoparticles can now be synthesised to produce materials of greatly enhanced Raman scattering cross section that allow detection of analytes even at the single molecule level.

Another application that is becoming important is DNA detection using the unusual optical properties of gold and silver nanoparticles based on proximity effects for nanoparticle recognition. Isolated metal particles have a strong absorbance (the so-called plasmon band) caused by the collective oscillations of the free electrons within the metal cores. This plasmon band absorbance is profoundly altered when two nanoparticles are placed in close proximity to each other due to the electrostatic coupling of the two oscillating dipoles resulting from the absorption of electromagnetic radiation. When this happens, a new band appears at wavelengths longer than that of the main plasmon band (The so-called longitudinal plasmon band). This new absorption is due to the coupling of two vicinal nanoparticles. The presence of this new band is an indication that a recognition event has taken place used for analyses and can be easily visualised by the change in colour of the nanoparticle dispersion. An example of possible applications is the use of nanoparticles plasmon coupling for DNA recognition as schematically shown in Figure 2.

Another application of nanoparticles plasmons is to make use of their unusual light scattering properties. Plasmons can be excited with white light but the energy is re-emitted at the wavelength corresponding to the plasmon band. This process is quite different from classical

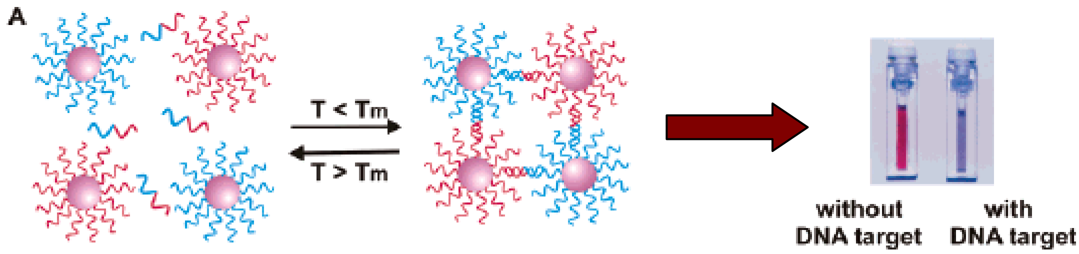

Figure 2 Schematic description of attachment of complementary single stranded DNA containing attached gold nanoparticles. Hybridisation results in forcing the clusters close to each other and hence a change in the absorbance due to the appearance of a longitudinal plasmon band. Melting the structures reverts the colour from blue to the original red corresponding to the free particles in solution.[4]

fluorescence and is akin to light scattering. The greatest difference with fluorescence is the absence of quenching of the excited state of the fluorophore. In addition, large quantum efficiencies can be achieved. This observation can be used in a variety of ways in analysis, for example, for the direct replacement of fluorophores as recognition probes or as proximity probes, since the presence of longitudinal plasmons results in the emission of light al longer wavelength than those of the primary plasmon band. In analytical science, light emission has great advantages in sensitivity over absorbance measurements since single photon counting is possible. In addition, wavelength discrimination provides a powerful tool for advanced analytical determinations.

It is likely that these applications will become common for analysis. From the point of view of the health impact of these new materials, the applications of these developments can have a large influence in fast throughput bioanalytical chemistry. The environmental impact of these materials is likely to be minor since the quantities employed are very small and in additions, the use of biological samples implies very controlled laboratory conditions.

8.3 Consumer goods

8.3.1 Antibacterial coatings

Silver has been known for a long time, to be a very efficient antimicrobial agent of low toxicity. In some important cases such as the treatment of severe burns, the use of silver salts of very low solubility has been particularly effective as a potent bactericide due to the slow release of silver from fabrics. These materials are easily prepared by reduction of silver salts by the aldehyde terminal groups on cotton fabric. The nanoparticles are stabilised by the fabric itself.[6] Synthetic textiles, such as polypropylene have also been prepared and shown to posses strong antibacterial properties.[7] The ease of manufacturing has led to the use of silver nanoparticles as delivery systems and some companies are already advertising the so called “nano socks” with a strong antibacterial and / or deodorization power resulting from the incorporation of silver nanoparticles in textiles and in toothbrushes. In addition, antibacterial paints for household products have been proposed.

The difference between these products and others that use silver is that, although the antibacterial agent is the same, the nanoparticles are brought into close contact with the skin. The stability of chemically stabilised nanoparticles is remarkable[1] and we do not know at present their biological effects if incorporated within a living cell. There should be a question mark on the marketing of these products until proper toxicological tests are carried out, similar to those required for the acceptance of any chemical product for general use by the public. It has to be made clear that this is not due to any peculiarity of nanoparticles that can have an unpredictable effect but is a simple precaution that has to be taken with any chemical compound that can be incorporated in living organisms.

The problems in regulating the use of nanoparticles in the consumer market have been recently highlighted by Van Noorden[8] in relation to the need of separating environmental risks due to the chemicals involved from those specifically related to the nanoparticles that result form the possibility of their incorporation in the cells of living organisms due to their small size.

8.3.2 Sunscreen protection creams

The use of nanoparticles of TiO_2 in sunscreens has been the matter of some debate with the FDA. The advantage of nanoparticles is the high absorbance to UV. Recent products by Oxonica Materials Ltd, UK appear to have eliminated the potential risks of formation of radicals due to hole-electron pair formation resulting from light absorption. Concerns about the use of these materials have been expressed regarding the possibility of incorporation of the oxide nanoparticles in the bloodstream.

*8.4 Nanoparticles currently sold as chemical*s

Nanoparticles are beginning to appear in catalogues of chemicals. Some examples of this new development are given below.

Examples form the Strem Chemicals, Inc. catalogueCobalt nanoparticles 10-12 nm
Cobalt nanoparticles, toluene wet 10-12 nm
Iron-cobalt nanoparticles 5-8 nm.
Platinum/tetra-n-octylammonium chloride colloid, purified (70-85% Pt) 2.8 ± 0.5 nm.
Rhodium/tetra-n-octylammonium chloride colloid, purified (70-75% Rh) 2.0 ± 0.5 nm..
Nickel/tetra-n-octylammonium chloride colloid, purified (65-70% Ni) 2.8 nm (average).
Gold/tetra-n-octylammonium chloride colloid 2.6 ± 1.1 nm.
Platinum-ruthenium/tetra-n-octylammonium chloride colloid (~7 wt% Pt, ~3.5 wt% Ru) 1.7 nm ± 0.5 nm.
Platinum colloid (polyethyleneglycol-dodecylether hydrosol) (~10 wt% Pt) 1.2 ± 0.3nm.
Rhodium colloid (polyethyleneglycol-dodecylether hydrosol) (~9 wt% Rh) ~2 nm.
Platinum-ruthenium colloid (polyethyleneglycol-dodecylether hydrosol) 1.3 nm.
Examples form the Aldrich Chemicals catalogue Cat No 660434. Dodecanethiol functionalized gold nanoparticles solution 2 % (w/v) in toluene (Nanoelectronic grade)
Cat No G1402. Gold colloid ~0.01% $HAuCl_4$, ~0.75 A520 units/mL, 4-5 nm mean particle size (monodisperse)The safety assessment for the latter is non-specific covering almost all possible hazards, most likely due to the lack of specific information about the toxicity of these materials. These examples are given to indicate that nanoparticles have ceased to be a laboratory curiosity and due to the many applications that are being found, are becoming widely accessible.

9. Potential for solving environmental problems.

Fuel cells employ nanostructured materials dispersed on carbon. Although new alloy materials are being developed, the use of nanoparticles in fuel cells is not new. This is an example, however, of how the further development of materials already available can have a large environmental impact by decreasing emissions from vehicles.

10. Monitoring and effect on human health
The toxicology of nanoparticles has not been extensively investigated. As mentioned in Section 8.3.1, a distinction has to be made between the chemistry of the nanoparticles constituents and the toxicology of the nanoparticle as a whole. The size of some of these materials is sufficiently small to allow their penetration across cell walls. Whether this is possible or not depends on the chemical nature of the stabilising coating. Indeed, the wide range of ligands that can be employed allows the design of capping ligands that would specifically penetrate the cell wall.

Theme 3 How to manage novel materials in society

22. Relationship to other technologies, e.g. genetically modified organisms
No, nanoparticles are very different from genetically modified organisms. Of course, they cannot reproduce or enter into biological functions like say, a virus. Nanoparticles must be treated as complex chemical compounds and their toxicology must be assessed in the same way as that of a chemical.

23. Balance between regulatory systems and the management of uncertainty
Again, the same methods used for the control of the risk of new chemical should apply in the case of nanoparticles. HSE has a great deal of experience in these problems.

26. Question of need, control and consequences.
This is a very complex general question. In the case of nanoparticles, the experience in the US is very instructive. There is a huge investment to try to understand first what are the nature, the physical, chemical and biological properties and the potential applications of these new materials. In my view, for these novel materials, the question of control is not very relevant at present, except in ensuring that consumer goods incorporating nanoparticles comply with general toxicology requirements already in place. It is more important to encourage investment in basic research before entering a detailed discussion of these issues since otherwise we run the risk of trying to establish controls about something that we do not understand. This, of course, does not mean that there should not be any control over products that are reaching commercialisation at present; in my view, the precautions that have to be taken are those commonly employed for new chemical compounds. There are in place sufficiently robust regulatory instruments to defend the public interest. What need to be understood are issues of the consequences of incorporation of nanoparticles within human cells (See below comments under Recommendations).

Recommendations in relation to environmental and health issues
An effort should be made to encourage a comprehensive toxicological investigation of a) the physical chemistry of transport of nanoparticles across biological membranes in relation to the structure and chemistry of their capping ligands and b) the biological effects of nanoparticles when incorporated within living cells (DNA damage, cell viability). These studies should integrate the different expertises required and should avoid fragmentation of the problem according to individual professional interests and should be in coordination with those from other authorities such as the U.S. Food & Drug Administration. For information about the latter, see, for example the following important reports:

http://ntp.niehs.nih.gov/files/Nano_Testing_Consortium_Cole_051007.pdf
and
http://ntp.niehs.nih.gov/ntp/htdocs/Chem_Background/ExSumPdf/Nanoscale_materials.pdf

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