Nanotechnologies and nanomaterials in electrical and electronic goods: A review of uses and health concerns

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CONTENTS

Executive Summary

Nanotechnology refers to technologies that operate at the nanometer level (one billionth of a meter). Nanotechnology is a growing scientific field with applications in many different areas, including in electronics.

The production of electronic chips for mobile phones and computers that have lines etched on them only 65 or 90 nanometers wide has already been commercialised. Such uses of nanotechnology in electronics to miniaturise electronic components do not in themselves pose any threats to human health, although there may be additional concerns arising from novel processes and/or process chemicals necessary to carry out such nanoscale constructions (Walters *et al.* 2006).

Importantly however, there are uses of nanotechnology in electronics and electrical goods that do give rise directly to environmental and human health concerns. This is the use of synthetically produced nanoparticles in 'nanomaterials' to make electronic components or surface coatings for electrical goods. Nanomaterials are commonly defined as materials designed and produced to have structural features with at least one dimension of 100 nanometers or less. In electronics, a number of different nanomaterials are already being used commercially or are being used for research and development purposes. Some of the most commonly used nanomaterials for electronic and electrical equipment are carbon nanotubes and quantum dots and, in the case of surface coatings, nanoparticles of silver.

This report investigates some of the current uses of nanotechnology by the electronics industry and briefly explores what is known so far about the toxicity of relevant nanomaterials.

Some of the existing or emerging uses of nanomaterials in electronics include:

- the use of carbon nanotubes in semiconductor chips;
- research into the use of a variety of nanomaterials in lighting technologies (light emitting diodes or LEDs and organic light emitting diodes or OLEDs), with commercial use expected in the near future;
- use of 'quantum dots' in lasers, along with ongoing research into application of other nanomaterials in laser technology;
- a variety of nanomaterials used in lithium-ion batteries, or which are being researched for this use;
- potential use of carbon nanotubes and other nanomaterials in fuel cells and by the solar industry for use in photovoltaics.
- research into use of nanomaterials to produce lead-free solder, as well as the development of solder-free assembly technology.

In addition to the use of nanomaterials in electronics, some nanomaterials are also being used as surface coatings in certain electrical goods, primarily because they have anti-microbial properties. Products already marketed as having 'anti-microbial' nanomaterial coatings include refrigerators, vacuum cleaners, washing machines, mobile phones and computer mice.

Potential for Human Exposure and Environmental Contamination

Manufactured nanomaterials are likely to reach and contaminate the environment via disposal of manufacturing wastes, from product spillage during shipping or handling, as a result of wear and tear during use and when products enter the waste stream through recycling and/or disposal. Workers may be exposed to nanomaterials during the manufacturing process, especially if particles from nanomaterials become airborne and are inhaled. Exposure may also occur through skin contact or ingestion. Specifically with regard to electronics, the extent to which nanomaterials may leak out, be worn off over the period of use, leach out after disposal in landfills or become more widely distributed as a result of recycling or other disposal options is not yet known. Surface coatings with nanomaterials such as nano-silver may be of particular concern in this regard.

Toxicity

Concerns about the use of nanomaterials have been raised because engineered nanoparticles typically have very different properties (e.g. chemical, mechanical, electrical, biological) to the original (chemically identical) material. These properties may, in turn, lead to biological activity that differs from, and cannot be predicted from, knowledge of the original material. For instance, because of their size difference, nanoparticles have extremely high surface areas for their size compared to larger-scale materials, which means they have an increased potential for biological interaction with other substances. This in turn means that the toxicity of nanoparticles/nanomaterials needs to be assessed separately from the original material. Presently, study on the toxicity of nanomaterials is in its infancy, though the limited information which is available to date is already giving rise for concern (see bullet list below).

Some concerns regarding the use of nanomaterials have been brought to light because of what is already known about the health impacts of tiny particles present in air pollution, so-called ‘ultrafine’ particulate matter. These ultrafine particles are nano-sized and have been linked to respiratory illness and adverse cardiovascular effects in humans. Consequently, there is concern that if nanoparticles from nanomaterials become airborne, they too could also potentially be inhaled and have impacts on health. Yet another concern has arisen specifically about possible impacts of carbon nanotubes on human health. This is because carbon nanotubes are structurally similar to asbestos fibres, and asbestos fibres are known to cause serious impacts on health.

Research on the toxic impacts of nanomaterials has shown the following:

- **Carbon nanotubes** (nanomaterials with a tubular structure made from carbon): Exposure of rodents to single- and multi-wall carbon nanotubes caused inflammation, fibrosis and microscopic nodules (granulomas) in the lungs. The findings indicate that if air in a work environment contained respirable carbon nanotube particles in significant concentrations, prolonged exposures would likely cause serious lung diseases. However, it has been noted that further research is now needed to demonstrate whether airborne carbon nanotubes could be inhaled and actually reach the lungs because experiments to date have used a method of direct introduction to the windpipe.

- **Fullerenes** (Spherical fullerenes, often simply known as fullerenes, are also nanoparticles made from carbon): The large scale manufacture of fullerenes for different purposes including electronics means that they will inevitably eventually become environmental contaminants. It has already been shown that they can cause “significant damage in the brain” of largemouth bass, a species of fish. Fullerenes are also toxic to cultures of human cells.

- **Quantum dots** (Quantum dots vary in their chemical composition but are composed of metalloid crystalline core and a “cap” or “shell” that shields the core): Although the toxicity of each type of quantum dot needs to be assessed individually, a review of studies on different types of quantum dots has concluded that “they may pose risks to human health and the environment under certain conditions”.

- **Silver Nanoparticles:** It has long been known that silver is toxic to a wide range of microbes. Silver engineered into nanoparticles (‘nano-silver’) is being marketed for its anti-microbial effects. However, there is concern surrounding the widespread use of nano-silver with regard to the environment and human health because it is as likely to kill microbes that are beneficial to living beings and/or ecological processes as it is to kill harmful microbes. Nano-silver has also been shown to be toxic to certain mammalian cells in culture.

Conclusions

Nanomaterials are already being used by the electronics industry and production is predicted to increase as research leads to an increasing number of uses. For example, with regard to carbon nanotubes, it has been predicted that “in time, millions of tonnes of nanotubes will be produced worldwide every year” (see Lam et al. 2006).

Large scale production of nanomaterials will bring with it the likelihood of widespread environmental contamination as well as possible exposure of manufacturing workers. Once released into the environment, the ultimate fate and effects of nanomaterials remain poorly understood and difficult to predict. Presently little is known about the environmental and health hazards of nanomaterials, though research on the toxicity of some nanomaterials already gives rise for concern.

Under these circumstances, where use of nanomaterials presents unknown but possibly detrimental environmental and human health hazards, it becomes logical to bring the precautionary principle into action. In this regard, Greenpeace is calling for an immediate moratorium on the release of all nanomaterials and nano-products. It is deemed necessary that evaluation/assessment of proposed nanomaterials is conducted on a precautionary basis such that the “burden of proof” is reversed. This means that all nanomaterials are assumed hazardous, and regulated accordingly, until such time as sufficient evidence becomes available that the nanomaterials present no potential for hazards to ecosystems or human health. Implementation of the precautionary principle also dictates that the onus should be placed on industry and regulators to establish whether a product meets health, safety and ecological criteria before being approved for use and release.

1. Introduction

The term ‘nano’ is used in science as a prefix meaning one billionth (using billion in its American sense of a one followed by nine zeros). A ‘nanometer’ therefore means one billionth of a meter and it is exceedingly small – about 10 atoms across. Nanotechnology refers to technologies that are working at the nanometer level (Whatmore 2006) and, as such, encompasses both a) techniques used to manufacture products with nano-scale characteristics and b) nanomaterials manufactured by whatever means. Both aspects have relevance in the field of modern electronics.

Nanoparticles can theoretically be produced artificially from nearly any chemical (Dreher 2004). Such engineered nanomaterials are commonly defined as materials designed and produced to have structural features with at least one dimension of 100 nanometers of less (Oberdörster *et al.* 2005b). Presently, most nanoparticles that are in use have been made from transition metals, silicon, carbon (carbon nanotubes, fullerenes) and metal oxides (zinc oxide and titanium dioxide). In some cases, engineered nanoparticles exist as nanocrystals composed of a number of compounds such as silicon and metals (as is the case for quantum dots) (Dreher 2004).

In electronics, the present method used in the manufacturing of electronic devices is called “top down” (i.e. manufacturing nanoscale components and materials from larger starting materials) though scientists are now also developing a new approach based on self-assembly of atoms and molecules, the so-called “bottom up” approach.

Top down nanotechnology has enabled the production of progressively smaller structures to be made using lithography and related techniques for the construction of electronic components and micro-electro-mechanical systems (MEMs) (Maruccio *et al.* 2004). Top down nanotechnology has, for example, led to the hugely successful semiconductor- and information-and-communications-technology- (ICT-) industries, as well as the manufacture of tiny micromechanical machines for sensing and actuation (MEMs) (see section 2 below).

Bottom-up technology is a promising alternative to top down, one which enables building of nanodevices and/or nanomachines starting from molecular building blocks instead of lithographically carving bigger pieces of matter into smaller and smaller pieces (Maruccio *et al.* 2004). The self-assembling properties of biological systems, such as DNA molecules, may be used to control the organisation of nanoparticles such as carbon nanotubes. This may lead to the ability to ‘grow’ parts of an integrated circuit, rather than relying on top down techniques (Whatmore 2006).

This report discusses the use of nanotechnology to produce smaller circuits (section 2), the use of nanoparticles in electronics (section 3) and the use of nanomaterial coatings in electronic and electrical equipment (section 4). Section 5 looks at the toxicology of nanomaterials which are currently used in electronics and electrical equipment.

2. Nanotechnology in Electronics Manufacture

Traditional electronic circuits are built by etching individual components into silicon wafers (Appell 2002). Commercialisation of integrated circuits (IC) and the creation of the microelectronics industry began in 1965 using silicon processing technology (Gargini 2004). Over time, there has been ever-increasing progress in the technology being used and, in parallel, a progressive reduction in size of circuits. Such rapid technological progress was first predicted in 1965 by Gordon Moore in the now famous ‘Moore’s Law’, which stated that integrated circuit density and performance would double every 18 months. This has broadly held true, the improvements being brought about by reduced transistor dimensions, increased transistor counts and increased operating frequencies (Bohr 2002).

Circuits have reduced in size over the years to such an extent that current generations of chips may carry circuits only 65 nm wide and more than a million transistors on a single piece of silicon a few millimetres across (Whatmore 2006). The field effect transistor (FET) was first scaled below 100 nm in the year 2000, inaugurating the era of silicon nanoelectronics (Gargini 2004). The term ‘nanoelectronics’ (circuit dimension less than 100 nm) can therefore now be used instead of ‘microelectronics’.

Presently 65nm and 90nm process technology is being used to manufacture chips (see list of products below). According to the company Intel, the next two process generations, 45 nm and 32 nm, are due to be produced in 2007 and 2009 respectively. Intel is now producing more than half of its mobile, desktop and server microprocessors using 65 nm process technology (Intel 2006).

According to research conducted by the Woodrow Wilson International Centre for Scholars in Washington DC, products on the market using 65 nm or 90 nm technology include:

- Intel Pentium D Processor, Intel Pentium 4 Processor, Intel Core Duo Processor and Intel StratFlash Cellular Memory by Intel;
- XBOX 360 by Microsoft;
- AMD Athlon 64 FX Processor and AMD Athlon 64 X2 Dual-Core Processor by AMD;
- IBM PowerPC 970FX/970MP Processor by IBM; and
- iMac G5 and IPod Nano by Apple Inc. (using memory chips from Samsung and Toshiba).

(Woodrow Wilson International Centre for Scholars 2006)

The same study also noted that many current flash memory chips are based on 90 nm fabrication technology.

3. Nanomaterials in Electronics

While the manufacture of chips described above uses nanotechnology, it does not use nanomaterials in the sense of free or bound nanoparticles. However, such nanomaterials are also being used in electronics. Some of the most common nanomaterials being investigated and used are carbon nanotubes and quantum dots, a description of each of which is given below.

Carbon Nanotubes and Fullerenes

Fullerenes are a family of substances made of carbon in the form of a hollow sphere, ellipsoid or tube. Spherical fullerenes are commonly known simply as fullerenes (C_{60}) or now less frequently as ‘Bucky balls’ (after Richard Buckminster Fuller who popularised in architecture the geodesic dome structures which these molecules resemble) and have been researched for use in electronics and other applications.

Tubular fullerenes, generally called carbon nanotubes, are considered as possibly the most famous objects in nanotechnology and possess extraordinary properties arising from their nanoscopic dimensions. They were discovered in 1991 in the insoluble material of arc-burned graphite rods. Carbon nanotubes are molecules which are composed only of carbon atoms and are markedly different from bulk graphite. They can be viewed as a graphene sheet rolled into a cylinder and seamlessly welded together. Carbon nanotubes exist in either of two forms, single-wall carbon nanotubes and multi-wall carbon nanotubes. Single-wall nanotubes consist of a single graphene layer while multi-wall nanotubes consist of multiple concentric layers (Gröning 2005).

In addition to the synthetic production of carbon nanotubes for research and commercial purposes, it has recently been discovered that multi-wall carbon nanotubes were present in particulate matter collected from propane or natural gas kitchen stoves. Multi-wall carbon nanotubes were also found in particulate matter collected in outdoor air, with one possible source being car exhaust fumes (Lam *et al.* 2006).

Carbon nanotubes can be either ‘metallic’ or semi-conducting depending on the actual way in which the carbon atoms are assembled in the tube. The metallic forms possess electrical conductivities 1000 times greater than copper and are now being mixed with polymers to make conducting composite materials for applications such as electromagnetic shielding in mobile phones and static electricity reduction in cars. Their use has been demonstrated in super-capacitors for energy storage, field emission devices for flat panel displays and nanometer-sized transistors (see further below) (Whatmore 2006).

Quantum Dots

Quantum dots are semiconductor nanocrystals (2-100 nm) which have unique optical and electrical properties. In structure, quantum dots consist of a metalloid crystalline core and a ‘cap’ or ‘shell’ that shields the core. Quantum dot cores can be formed from a variety of metal conductors such as semiconductors, noble metals and magnetic transition metals. The shells are also formed of a variety of materials. Therefore, not all quantum dots are alike and they cannot be considered to be a uniform group of substances (Hardman 2006).

With regard to the cores of quantum dots, group III-V series quantum dots are composed of mixtures of compounds such as indium phosphate (InP), indium arsenate (InAs), gallium arsenate (GaAs) and gallium nitride (GaN). Group II-IV series of quantum dots are composed of mixtures of compounds such as zinc sulfide (ZnS), zinc-selenium (Zn-Se), cadmium-selenium (CdSe) and cadmium-tellurium cores (CdTe) (Hardman 2006).

3.1 Use of Nanomaterials in Chips

The company Nantero Inc. announced in November 2006 that it has developed the technology to produce semiconductors using carbon nanotubes on silicon wafers and has been issued patents on the process (Nantero 2006a). Nantero is developing a high density nonvolatile random access memory chip called NRAM (Nanotube-based/Non-volatile random access memory) chip. Carbon nanotubes are used as active memory elements and integrated with traditional semiconductor technology. NRAM is slated to replace DRAM (dynamic RAM), SRAM (static RAM), flash memory and ultimately hard disk storage. In other words, according to the manufacturers, NRAM is a universal memory chip suitable for countless existing and new applications in the field of electronics (Nantero 2006b).

IBM has developed carbon nanotube transistors. They are working towards the development of chips using nanotubes, and have announced in 2006 that they had succeeded in building a complete electronic integrated circuit around a single carbon nanotube molecule. This was built using standard semiconductor processes and was described as “a critical step toward the integration of the technology with existing chip-making techniques” (IBM 2006).

Intel is looking at the possible replacement of copper wires inside semiconductors using carbon nanotubes. However, due to difficulties with the technology they say that use of nanotube interconnects in commercial chips is likely to be several years away (Kunellos 2006).

Other nanomaterials currently being researched for nanocrystal memories are the ferroelectric oxides barium titanate [$BaTiO_3$], lead zirconate titanate [$Pb(Zr,Ti)O_3$] and barium-strontium titanate [$(Ba,Sr)\text{-}TiO_3$] for transducers, actuators, and high-k dielectrics (Matsui 2005). The use of quantum dots in flash memory applications is also under investigation (eg. Corso *et al.* 2003, Liu *et al.* 2006).

3.2 Use of Nanomaterials in Lighting/Displays

Solid state lighting (SSL) encompasses technology to make lighting technologies more energy efficient, longer lasting and cheaper. Instead of using inert gases or vacuum tubes, it relies on light being emitted from a semiconductor. Two of the main technologies involved are light-emitting diodes (LEDs) in which the emissive layer is inorganic, and organic light-emitting diodes (OLED) in which the emissive layer is an organic material. In some cases, the use of nanomaterials for these lighting technologies is being investigated. For instance, nanocrystals of cadmium selenide (CdSe) have been developed which could be used in LED or OLED lighting devices (Office of Technology Transfer and Enterprise Development 2006). The company Norel has advertised itself as the first company to use nanostructured fullerenes in its OLED (Norel 2005).

Quantum dots have been investigated as building blocks for tuneable optical devices such as light emitting devices and lasers. Zinc oxide (ZnO) nanoparticles are under investigation for various optoelectronic devices, and galium nitride (GaN) likewise for LEDs (Matsui 2005). For example, the use of ZnO nanowires in LEDs may ultimately enable the development of large-area lighting on flexible substrates (Burgess 2006).

In June 2006, one company announced that it had succeeded in making the world’s first quantum dot display (EuroAsia Semiconductor 2006). The display features a layer of quantum dot material sandwiched between two semiconductor regions. The display has the potential to deliver what the company calls a ‘super visual experience’, of an apparently higher quality than liquid crystal displays, by producing brighter, richer and more accurate colours while consuming less power. The company says that the quantum dot displays are more reliable and simple to manufacture than new display technologies based on organic light-emitting devices (OLEDs).

According to a review of a report by the Semiconductor Equipment and Materials International (SEMI) on the current and future use of nanotechnology in the electronics industry, the display industry is expected to use nanomaterials commercially in the near future. Carbon nanotubes are expected to be commercialised in the near term for backlights and field emission displays, along with polymer and transmission films that also use nanomaterials (Photonics Spectra 2006).

Carbon nanotubes are already being used in the development of new flat screen displays. In 2005, Motorola reported the development of a 5-inch Nano Emissive Display (NED) prototype. This first of its kind prototype was created through a proprietary method of growing carbon nanotubes directly on glass to provide superior electron emissions that yield an energy-efficient, high definition display. According to the manufacturers, the technology can be used to make large, flat panel displays with superior quality and longer lifetimes at significantly lower costs than current displays (Motorola 2005). Motorola is in discussions with large display manufacturers to license the technology for commercialization (Personal Communication with Motorola, January 2007).

The company Eikos Inc. has developed a transparent conductive coating technology branded “Invisicon” using carbon nanotube inks. It has potential applications in flat panel displays and OLED lighting and solar cells (Eikos 2006). It is not yet used on OLED lighting or solar cells commercially, though it is used commercially in the Japanese market for electrostatic control in a variety of products (personal communication with Eikos Inc.).

The company Nanofilm has developed ultra-thin self-assembling films that act as a protective layer for displays, such as computer displays, cell phone windows, ATMs and PDAs (Nanofilm 2006). However, at the time of writing this was at the research stage and not currently commercialized (personal communication from Nanofilm).

3.3 Use of Nanomaterials in Lasers

Research is being conducted on making laser devices from arrays of semiconductor nano-dots and nanowires. If successful, this technology is expected to bring about miniaturisation and power efficiency improvements compared to other laser devices (Ball 2003, European Commission 2005, Simonite 2006).

The company Fujitsu, in combination with the University of Tokyo, has developed and commercialised a quantum dot laser. The company say that quantum dot lasers are significantly superior to conventional semiconductor lasers and it is anticipated that they will become a core technology to realize high-performance light sources for optical telecommunication (Fujitsu 2006).

3.4 Use of Nanomaterials in Batteries

The properties of carbon nanotubes make them potentially useful as an anode material or as an additive in lithium-ion (Li-ion) battery systems (Endo *et al.* 2006). In 2005, one article noted that the anode of Li-ion batteries is primarily made from various carbonaceous materials but that carbon nanotubes promise to boost this rate of growth, either by themselves or when incorporated into appropriate composite material (Carbon Nanotubes Monthly 2005). Gröning (2005) wrote that the predominant part of commercially produced carbon nanotubes is used for the manufacturing of porous conductive electrodes for Li-ion batteries.

In 2005, Toshiba launched a rechargeable Li-ion battery which used ‘nano-particles’ (Toshiba 2005), although it is not clear whether carbon nanotubes or another nano-material is used. Altair Nanotechnologies Inc. developed a nano-titanate material which it uses commercially in Li-ion batteries (personal communication). A123 has developed and commercialised Li-ion batteries based on nanophosphate technology (A123 2006). Other nanomaterials under investigation for use in Li-ion batteries are nanoparticles of vanadium, manganese and cobalt compounds (Matsui 2005).

According to Endo *et al.* (2006), the use of carbon nanotubes is also being investigated in the application of additives to electrodes of lead-acid batteries.

3.5 Use of Nanomaterials in Fuel Cells and Photovoltaic Cells

According to an article in Carbon Nanotubes Monthly (2005), the use of nanotubes in fuel cells and photovoltaic cells is expected to hit the market within a decade. With regard to fuel cells, the structure of carbon nanotubes shows some promise for hydrogen storage. It is anticipated that carbon nanotube technology will contribute to the development of fuel cells, as a catalyst support, and also as a main component of bipolar systems (Endo *et al*. 2006). Motorola is one company involved in research into fuel cells using carbon nanotubes (Motorola 2006). Sony has been developing fuel cell technology using fullerenes. Other nanomaterials under investigation for use in fuel cells are nanoparticles of platinum and platinium alloys (Matsui 2005). Recent research on quantum dots suggested that they may also be used in fuel cells in the future (Weiss 2006).

In the case of photovoltaics, there is interest from the solar cell industry in using carbon nanotubes, due to their excellent conductive properties (Carbon Nanotube Monthly 2005). In August 2006, the company NanoHorizons signed a licensing agreement with Solarity, a developer and manufacturer of photovoltaic cells. The licensed technology utilizes a nanoscale-engineered structure to absorb and collect solar energy (NanoHorizons 2006). The technology, which is still in the research stage, involves design centred on a ‘nanocomposite’ material, which may use carbon or metal ‘nanorods’. The invention is also applicable to development of an OLED but is currently not licensed for pursuit of that use (personal communication with NanoHorizons).

Matsui (2005) noted that titanium dioxide (TiO_2) and cadmium selenide (CdSe) nanoparticles are being investigated for use in photovoltaic devices. Recent research using quantum dots suggested that they may be able to increase the efficiency of solar cells (Weiss 2006).

3.6 Use of Nanomaterials in Electric double-layer capacitors (EDLC)

The EDLC is applicable as a hybrid energy source for electric vehicles and portable electric devices. Research to improve EDLC using carbon nanotubes is already underway (Endo *et al.* 2005). Few further details are available at this stage.

3.7 Use of Nanomaterials in Lead-free solder

The phenomenon of melting point depression of nano-scale metal particles has been studied since the 1960s. Presently, research is being conducted with the application of nanotechnology to suppress lead-free solder reflow temperature (iNEMI 2005). The company Motorola is leading a low temperature lead-free nano-solder initiative for the International Electronic Manufacturing Initiative (iNEMI) (Motorola 2005).

In another iNEMI initiative, Motorola are also looking at mechanically adhesive nano-hooks which could allow for solder-free assembly (Motorola 2005). iNEMI (2006) note that “this research project is designed to identify and demonstrate electronic assembly using only mechanical means. For example, research activity into dry adhesives has recently accelerated with the newfound understanding of the mechanisms behind the strong adhesive force generated by the gecko. “Adhesive forces 200 times higher than those of a gecko have been observed at the nanoscale level with carbon nanotube surfaces”.

4. Nanotechnology Coatings

Coatings containing nano-particles are already being used in some electrical products.

Coatings developed for anti-microbial properties generally contain silver nano-particles. Silver has natural anti-bacterial and anti-fungal properties and silver engineered into nano-particle size increases the surface area in contact with micro-organisms which, in turn, improves its bacterial and fungicidal effectiveness (Nanotech Plc 2006). Products using silver nano-particle coatings include:

- Daewoo refrigerator – using “Nano Silver Poly technology”, in which particles of silver are mixed in plastic resin. It is applied to major parts of the refrigerator in order to restrain the growth and increase of a wide variety of bacteria and to suppress odours (Daewoo 2006).

- Daewoo vacuum cleaner – the vacuum cleaner has a nanosilver-coated ‘cyclone canister’ that allegedly has the effect of removing bacteria and a plethora of dust particles, inhibiting odour, allergy-inducing spores, and other harmful debris (Daewoo 2006).

- Daewoo washing machine – again uses Nano Poly Technology by which, according to the manufacturer, “many hurtful bacteria in clothes shall be sterilized perfectly” (Daewoo 2006).

- Antibacterial mobile phones – LG Electronics use a Nano Silver antibacterial coating on their mobile phone (Woodrow Wilson International Centre for Scholars 2006). The Motorola i870 mobile phone has an anti-bacterial coating made from silver zeolite nano-particles (Motorola 2005).

- Germ free wireless laser mouse by IOGEAR Inc. - coated with a titanium dioxide and silver nanoparticle compound (Woodrow Wilson International Centre for Scholars 2006). According to the manufacturer, “the special coating protects users from bacteria and germs by neutralizing the harmful microbes on the mouse”.

Besides using silver nanoparticles as coatings, Samsung have developed techniques for using them in the wash cycle – the so called ‘silver wash’ technology which is designed to improve the washing of clothes. According to Samsung, their ‘silver wash’ system:-

“…is an advanced washing technology with superb bacteria killing capabilities. Imagine 400 billion silver ions dissolved in water to make a super cleaning solution that affects your clothes at an almost molecular level. Its sterilizing ability of 99.99% and lasting antibacterial action will redefine your idea of purity. SILVER WASH utilizes 99.99% pure silver for a lasting investment for your health and garments…

“SILVER WASH uses nano technology to electrolyze pure silver during wash and rinse cycles. Over 400 billion silver ions are released and penetrate deep into fabric for effective sanitization…”

“Silver Nano particles are dispensed in the washing and rinsing cycles. These silver particles can sanitize and disinfect fabrics throughout the life of the washing machine... And not only does its effect protect your fabrics, it also disinfects your drum and all its internal parts”

(Samsung 2006).

The commercialization of the silver wash by Samsung has led to concerns regarding toxicity risks to the environment and human health. Concerns have led to the withdrawal of Samsung’s silver washing machine from Sweden. Friends of the Earth are calling for its withdrawal from the market in Germany and Australia. The US EPA has announced it will move to introduce the world’s first nanotechnology-specific regulations. Under the EPA proposal, products which contain nano silver and claim to provide ‘anti-bacterial’ properties will be regulated as pesticides (Washington Post 2006). However, the EPA's decision may not be effective, critics point out, because if the company deletes from its advertising the assertion that silver can kill bacteria, it won't have to register the washer. Consequently, the Natural Resources Defence Council have urged the EPA to review all consumer products containing nanosilver and require manufacturers to register such products as a pesticide (Christen 2007).

5. Exposure to, and Toxicity of, Nanomaterials

Consideration of the possible health risks of nanotechnology falls into two categories, those where the structure itself is a free particle and those where the nanostructure is an integral feature of a larger object (EC 2006). In consideration of health risks, the latter case would not be considered to pose immediate risks to human health or the environment from the nanotechnology itself. For instance, in electronics, the use of nanotechnology to build smaller circuits down to the nanoscale, that is, using 65nm and 90nm process technology in the manufacture chips, may not be considered in itself to present substantial risks to the environment or human health, although there may be additional concerns arising from novel processes and/or process chemicals necessary to facilitate such nanoscale constructions.

Conversely however, the manufacture, use and disposal of materials comprising or containing free or bound nanoparticles, for the production of nanomaterials such as carbon nanotubes or nano-silver, does give rise directly to human health and environmental concerns. This is because nanoscale materials typically have markedly different properties (e.g. chemical, mechanical, electrical, magnetic, biological) to the original (chemically identical) material at larger scales. These properties may in turn lead to biological activity that differs from, and cannot be predicted from, the bulk properties of the constituent chemicals and compounds (Oberdörster *et al.* 2005b). The assessment of the toxicity of nanomaterials (‘nanotoxicology’) and their environmental fate remains very much in its infancy, well behind the commercial development and ongoing use of such materials in applications (including hundreds of consumer products) which ultimately result in releases of free nanoparticles to the environment. Indeed, as Braydich-Stolle *et al.* (2005) noted, despite the wide application of nanomaterials, there is a serious lack of information concerning their impact on human health and the environment.

Deliberately manufactured nano-materials are likely to enter the environment from manufacturing effluent or from spillage during shipping or handling. Within products such as electronics, the extent to which nano-materials may leak out or be worn off over the period of use is not known as no research has been done on this subject. It is possible that nano-materials from electronics may also reach the environment when they are disposed of, during recycling, disposal in landfills or by other methods (Oberdörster *et al.* 2005). With regard to human exposure, occupational exposure during manufacturing process may arise from particles in nano-materials becoming airborne and then being inhaled. Research into the potential occupational health risks associated with inhaling engineered nano-structured particles is only just beginning (Maynard and Kuempel 2005). Inhalation may be the major route of occupational exposure but ingestion and dermal exposures during manufacture, use and disposal of engineered nanomaterials also needs to be considered (Oberdörster *et al.* 2005).

Particular concern regarding exposure and potential health impacts of nanomaterials has arisen due to past knowledge of the hazards of exposure to nano-sized particles generated unintentionally as a component of air pollution, either in the work place or in the urban environment. Exposure to these so called ‘ultrafine’ particles (defined as particles <100 nm) can cause inflammatory responses in the lungs in laboratory animals and has been associated with adverse respiratory and cardiovascular effects in humans resulting in illness and mortality in susceptible sub-groups within the human population (Oberdörster *et al.* 2005). In animals, such particles have been shown to be deposited in the lungs after inhalation and can enter the blood and lymph circulation to reach other organs of the body such as the bone marrow, spleen, lymph nodes and heart (Oberdörster *et al.* 2005). It has been noted that, because nanoparticles can pass through biological membranes, they could affect the physiology of any cell in an animal body (Braydich-Stolle *et al.* 2005). Recently it was found that multi-wall carbon nanotubes were present in samples of particulate matter from outdoor air, with one possible source being vehicle exhaust fumes. Given their toxicological properties, it has been suggested that multi-wall carbon nanotubes could contribute to the adverse respiratory and cardiovascular effects of particulate air pollution, although this will require further study (Lam *et al.* 2006).

Other research that has given rise to concerns in relation to nanomaterials, specifically to fibre-shaped materials such as carbon nanotubes, is the substantive body of information regarding asbestos. The concern arises from the fact that there are structural similarities between nanotubes and asbestos fibres. Both are long, durable and have potential to reside in the lungs for long periods of time (Greenpeace Environmental Trust 2003). Fibre-shaped nanomaterials may represent a unique inhalation hazard and their pulmonary (lung) toxicity should therefore be evaluated as a matter of urgency (Maynard 2006). Inhalation of asbestos can lead to increased risks of both non-malignant (asbestosis) and malignant lung diseases (lung cancer and mesothelioma) (Maynard and Kuemel 2005). The Royal Society noted in their 2004 report on nanotechnology that “given previous experience with asbestos, we believe that nanotubes deserve special toxicological attention” (Royal Society 2004).

The size of a particle and its surface area are important characteristics of a material with regard to its toxic potential, and nowhere more so than at nanoscales. As the size of a particle decreases, its surface area increases in relation to its mass and this allows a greater proportion of atoms or molecules to be displayed on the surface rather than the interior of the material (Nel *et al.* 2006). The increased number of active sites at the surface gives increased potential for biological interaction (Oberdörster *et al.* 2005b) and the intrinsic toxicity of the particle surface will be emphasized (Donaldson *et al.* 2004). Therefore, an engineered nanoparticle may have very different properties and toxicological potential than its original macro-scale counterpart, despite being chemically identical. Even two nanoparticles made of the same elements but of different sizes or chemical architecture may have drastically different properties (Service 2005). Therefore, the toxicity of a substance, such as pure carbon, is likely to differ from an engineered carbon nanomaterial such as carbon nanotubes.

Because of their unique properties, including their possible toxicity, the hazards of nanomaterials must be assessed separately. The safety evaluation of nanomaterials cannot rely on the toxicological and ecotoxicological profile of the bulk material that has been determined historically using conventional toxicology. Since each engineered nanomaterial may have different toxicological properties, the safety assessment for engineered nanomaterials must be performed on a case by case basis (EC 2006). Studies assessing toxicity of nanomaterials used in electronics/electrical equipment, namely carbon nanotubes, fullerenes, quantum dots and nanoparticles of silver are discussed below.

5.1 Carbon Nanotubes

Airborne exposure and dermal exposure to single wall carbon nanotubes has been assessed where workers handled unrefined material. Dermal exposure was assessed using glove deposits, and estimated at 0.2 to 6 mg per hand, while airborne exposure was estimated at 0.7 to 53 $\mu g/m^3$ (study reviewed by EC 2006). Although airborne exposures were very low, Oberdörster *et al.* (2005) noted that even very low concentrations of nano-sized materials in the air represent very high particle number concentrations. For example, a low concentration of 10 $\mu g/m^3$ of unit density 20-nm particles translates into 1 x 10^6 particles/cm^3. Existing mass concentration-based exposure limits may therefore have very limited application to nanoparticle safety. Furthermore, even if only a tiny fraction of all nanoparticles inhaled over a given time are retained in lung or other tissues, the cumulative impacts from repeated low concentration exposures could well be significant.

In laboratory studies, exposure to single wall carbon nanotubes via the trachea (wind pipe) caused significant inflammatory pulmonary effects that were transient in rats (Warheit *et al.* 2004) and were more persistent in mice (Lam *et al.* 2004). In mice, exposure to single wall carbon nanotubes for 7 days or 90 days caused granulomas (microscopic nodules) and, in some cases, inflammation, whereas exposure to a non-nanoscale carbonaceous material (a relatively low-toxicity dust called carbon black) did not affect the lungs. Exposure of the mice to quartz on an equal-weight basis caused mild to moderate inflammation while carbon nanotubes resulted in much greater toxicity. This is of concern with regard to carbon nanotubes because quartz is considered to be a serious occupational health hazard in chronic inhalation exposures (Lam *et al.* 2004). In mice that were exposed for 90 days, fibrosis was also evident (a condition causing scarring of the lung in which the air sacs of the lungs become replaced by fibrotic tissue). In a review of the toxicology of carbon nanotubes by Lam *et al.* (2006) it was noted that another study, published in 2005 by Shvedova *et al.*, also showed that exposure of mice to single wall carbon nanotubes caused inflammation, granulomas and fibrosis. Furthermore, significant damage had also been recorded in that study to lung cells. The same toxicological effects of inflammation, granulomas and fibrosis in the lungs were also found in rats that were exposed to multi-wall carbon nanotubes (see Lam *et al.* 2006). However, the animal studies exposed rodents to carbon nanotubes directly through the wind pipe and not via the normal inhalation of air contaminated with carbon nanotubes. Lam *et al.* (2006) therefore suggested that it is now imperative that inhalation toxicity studies should be carried out to demonstrate whether carbon nanotube particles can reach the lung and produce lung lesions.

In current practice, single wall carbon nanotubes are classified as a new form of graphite on material safety data sheets provided by the manufacturers of these nanoparticles. However, the study by Lam *et al.* (2004) suggested that extrapolations from graphite-based permissible exposures limits may not be protective for exposure to nanotubes due to their pulmonary toxicity (Dreher 2004). If workers were chronically exposed to respirable carbon nanotubes at the permissible exposure limit concentration for synthetic graphite, they would likely develop serious lung lesions (Lam et al. 2006). Therefore, Lam *et al.* (2004) noted that this regulation limit should not be used to protect workers from carbon nanotubes. Lam *et al.* (2006) also noted another study by Shvedova *et al.* which showed that carbon nanotubes were intrinsically toxic, and hence cautioned that exposure of workers to respirable single wall carbon nanotubes particles may pose a risk that they will develop lung lesions.

Several *in vitro* studies using cells in culture have been carried out to test the toxicity of carbon nanotubes and, like the above *in vivo* studies, they reported significant effects. For example, Jia *et al.* (2005) investigated effects of single- and multi-wall carbon nanotubes on alveolar macrophages, cells which constitute the first line of immunological defence in the lung. Both types of nanotube were toxic to the cells and impaired phagocytosis (the major function of alveolar macrophages), with single-wall nanotubes exerting toxic impacts at lower doses than multi-wall nanotubes. Oberdörster *et al.* (2005) reviewed two studies on keratinocytes (skin cells) and bronchial epithelial cells which showed that exposure to single-wall carbon nanotubes resulted in oxidative stress. Monteiro-Riviere *et al.* (2005) reported that multi-wall carbon nanotubes caused an irritation response in epidermal kerationcytes (skin cells). However, this study does not provide information as to whether carbon nanotubes are an occupational risk because the keratinocytes lack the added protection of the stratum corneum, the surface layer of cells on skin. Nevertheless, the study suggested that the toxicology of nanotubes should be carefully assessed before widespread public exposure.

Two *in vitro* studies reported that carbon nanotubes induced apoptosis (programmed cell death). A study by Cui *et al.* (2005) showed that single-wall carbon nanotubes inhibited growth of HEK293 cells (human embryo kidney cells) by inducing apoptosis and decreasing cellular adhesion ability. A study by Bottini *et al.* (2006) on human T lymphocytes (immune system cells) reported loss of cell viability through apoptosis after exposure to multi-wall carbon nanotubes.

5.2 Fullerenes

The current manufacture of fullerenes in large quantities (not just for electronics but other applications also) means that they will eventually contaminate the environment in measurable concentrations. One study was performed to assess toxicity to fish in the aquatic environment (Oberdörster 2004). It should be noted that fullerenes may be coated before use with a range of different materials, but it is unknown how long such coatings would persist in the environment and breakdown could be possible. The study therefore assessed the toxicity of uncoated fullerenes. Under experimental conditions, fullerenes caused oxidative stress (a sign of inflammation) in the brains of largemouth bass suggesting, according to the authors, “significant damage in the brain” (Hood 2004). The results indicated that nanomaterials can have adverse effects on aquatic organisms (Oberdörster 2004); it is possible that effects in fish may also predict potential effects in humans.

Another study investigated the acute toxicity of fullerenes to two freshwater crustaceans, a marine copepod crustacean and two freshwater fish (Oberdörster *et al.* 2006). Fullerenes were not acutely toxic to these species. However, in *Daphnia magna*, a freshwater crustacean, fullerenes caused mortality, delays in moulting and reduced ability to produce offspring in concentrations as low as 2.5 ppm. Such a concentration would be considered high in the environment, although data on environmental levels are not available. It was noted that the adverse effects observed in *Daphnia* could cause considerable population level effects.

A study on human immune system cells (monocyte macrophages) showed that fullerenes were internalised in the cells and located at several unexpected sites within the cell, in particular along the nuclear membrane and within the nucleus. This indicates that fullerenes may exert toxic effects on cells via a number of pathways (Porter *et al.* 2006). A study on the toxicity of pure crystalline fullerene (C_{60}) *in vitro* reported that it was toxic and caused cell death, and results on the nature of the toxicity were in keeping with results of the above study on largemouth bass (Isakovic *et al.* 2006). A study on human skin cells *in vitro* exposed cells to fullerene-based amino acid solutions and reported that exposure decreased cell viability and initiated a pro-inflammatory response, and indicator of toxicity (Rouse *et al.* 2006).

A study on immune cells of the lung (alveolar macrophages) showed that carbon nanotubes were toxic to the cells (see above), although in this study no significant toxicity was observed with fullerenes (Jia *et al.* 2005).

5.3 Quantum Dots

As stressed above, quantum dots vary greatly in their chemical composition and cannot be considered to be a uniform group of substances. Each individual type of quantum dot possesses its own unique physiochemical properties which, in turn, may be expected to influence its potential toxicity. Nevertheless, a recent review of studies assessing the toxicity of quantum dots suggested, in general terms, that “they may pose risks to human health and the environment under certain conditions” (Hardman 2006).

Little information is available on routes of exposure to quantum dots, their stability, aerosolization, and how they partition into different environmental compartments (*e.g.* soil, sediment, water, air, biota). Potential routes of human exposure include *inter alia* indirect environmental exposure and occupational exposure via the workplace for employees such as engineers and researchers. Workplace exposures may occur through routes of inhalation, dermal contact or ingestion. As discussed above, it is already well established that human exposure to ultrafine particles can occur commonly as a result of air contamination and has toxicological implications. For quantum dots, Hardman (2006) noted that inhalation exposures may pose potential risks given that quantum dots have been shown to be incorporated into a variety of cells experimentally and remain there for weeks to months.

Environmental exposures could result from, for example, leakages and spillage during manufacturing and transport. This is of concern primarily because many quantum dot core metals, such as cadmium, lead and selenium are known to be toxic to vertebrates at relatively low concentrations (parts per million). Cadmium and selenium are two of the most widely used constituent metals in quantum dots and these are of considerable human health and environmental concern (Hardman 2006). The toxicological properties of these metals in the form of nanoparticles may differ substantially from the bulk materials, but are clearly of concern nonetheless.

Hardman (2006) reviewed studies on the toxicity of quantum dots in cell culture systems (*in vitro*). While some studies have shown that quantum dots were not toxic to cells, others have shown they can have toxic effects. In some cases, toxicity was attributed to oxidative and photolytic conditions which resulted in degradation of the core-shell coatings of the quantum dots. In turn, this resulted in exposure of cells to potentially toxic ‘capping’ material or intact core metalloid complexes.

There are few *in vivo* studies so far available on quantum dots, but three studies have shown that the quantum dots can accumulate in a variety of organs and tissues in rodents. Overall, the studies showed that toxicity depends on many factors, including the physiochemical properties of quantum dots and environmental conditions. For instance, influencing factors included quantum dot size, electrical charge, concentration, outer coating bioactivity and stability (Hardman 2006).

5.4 Nanoparticles of Silver

It has long been known that silver exhibits toxicity to a wide range of micro-organisms. Consequently silver-based compounds have been widely used in bactericidal applications, such as preservatives, and in preparations use to treat burns and a variety of infections (Morones *et al.* 2005).

Recently, silver has been engineered into nanoparticles (often termed ‘nano-silver’). Recent applications of nano-silver include the ‘anti-bacterial’ coatings in some electrical goods and Samsung’s ‘silver wash’ technology (see above). However, important concerns have been raised as to the possible toxic effects of nano-silver to the environment and to human health. In this regard there is legitimate concern that nano-silver does not discriminate between different strains of bacteria and is likely to kill bacteria which are beneficial to other organisms and/or ecological processes.

Another concern relating to nano-silver is its possible toxicity to animal and human health. While only a few studies have been performed in this regard, they nevertheless raise fundamental questions about the wisdom widespread and increasing use of nano-silver in consumer goods. For example, a study was performed to investigate the potential toxicity of silver nanoparticles on developing embryos of chickens. While whole embryo development did not appear to be influenced by the silver nanoparticles, there was an impact on development of the lymphatic system (Grodzik and Sawosz (2006)

Hussain *et al.* (2005) investigated the *in vitro* toxicity of silver nanoparticles in rat liver cells. A number of tests on the exposed cells showed that silver nanoparticles were highly toxic to the cells, with results suggesting that the likely underlying mechanism was oxidative stress. Similarly, studies on a neural cell line (Hussain *et al.* 2006) and on mouse stem cells (undifferentiated male reproductive cells) (Braydich-Stolle *et al.* 2005) identified cytotoxicity of silver nanoparticles, in the latter case apparently by drastically reducing mitochondrial function and causing increased leakage of ions through cell membranes.

Amid growing concerns over the use of nano-silver, the US EPA announced in November 2006 its intention to regulate consumer items made with nanoparticles of silver if the products advertise that they kill bacteria. In such cases, the silver nanoparticles will be regulated as a pesticide (Washington Post 2006).

6. Conclusions

The brief synthesis of data provided here indicates that nanomaterials are already receiving diverse and extensive usage by the electronics industry. Production is predicted to increase as research and innovation increases further the range of application on electrical and electronic equipment, as well as in many other commercial, medical and industrial products.

Large scale production of nanomaterials will bring with it the likelihood of widespread environmental contamination as well as possible exposure of manufacturing workers. Once released into the environment, the ultimate fate and effects of nanomaterials remain poorly understood and difficult to predict. Presently little is known about the environmental and health hazards of nanomaterials, though the research on the toxicity of some nanomaterials as reviewed briefly above already gives rise for concern.

Under these circumstances, where use of nanomaterials presents unknown but possibly detrimental environmental and human health hazards, it becomes logical to bring the precautionary principle into action. In this regard, Greenpeace is calling for an immediate moratorium on the release of all nanomaterials and nano-products. It is deemed necessary that evaluation/assessment of proposed nanomaterials is conducted on a precautionary basis such that the “burden of proof” is reversed. This means that all nanomaterials are assumed hazardous, and regulated accordingly, until such time as sufficient evidence becomes available that the nanomaterials present no potential for hazards to ecosystems or human health. Implementation of the precautionary principle places the responsibility on industry and regulators to establish whether a product meets health, safety and ecological criteria before being approved for use and release.

In the light of the ‘late lessons’ learned in the last decade from the failures in management of hazardous chemicals, the continued widespread commercial development and deployment of nanomaterials in electronics (as in other sectors) without effective regulatory controls and in advance of completion of fundamental research and the development of essential assessment techniques can only be seen as an unjustifiable and irresponsible approach.

7. References

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