Nanotechnologies – a New Branch of Chemistry?

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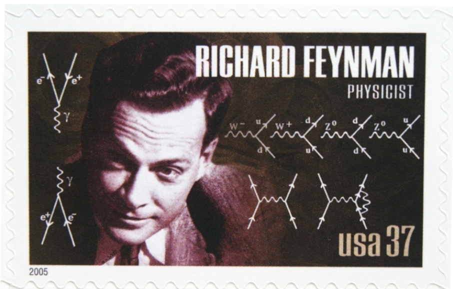
About the Author

Alan Smith's career began as a lecturer then he moved into industry and is now the managing director of AZ-TECH. He is the author of numerous papers on nanotechnology (often in IUPAC's *Chemistry International* and reprinted in these pages), and lectures worldwide on the topic to schoolchildren, the general public, international experts, and Heads of State. He is an advisor on nanotechnology for several governments and has facilitated over 50 technology roadmaps for establishments in many countries. His latest publication is a book on roadmapping emergent technologies; and a free booklet on nanotechnology for schools has been prepared for translation into a number of languages for ISESCO. Alan kindly agreed to provide an article for Vol. 75.

In 2005, the US Mail issued a stamp commemorating the contribution to science made by Richard Feynman, the 1965 Nobel Laureate in physics. He had worked on the Manhattan project in World War II, but his legacy was a talk at the California Institute of Technology in 1959 entitled *There's plenty of room at the bottom*.[1] In a nutshell, he was forecasting that if you went down to the nanoscale then you would see some interesting and exciting property changes. At that time it was not possible to work down at that scale, and we had to wait for Heinrich Rohrer and Gerd Binnig, two other Nobel Prize winners in physics (1986), to develop the scanning tunnelling microscope. It was only then that nanotechnology seemed to take off.



For most people it is difficult to appreciate how small a nanometre is, but a few well used examples bring it home. There are a billion (10^9) nanometres (nm) in a metre, which means that a human hair has a diameter of around 80,000 nanometres. If a gull lands on the deck of an aircraft carrier, the battleship sinks one nanometre lower in the water! A red blood cell is 7,000 nm across, a virus 150 nm, and a DNA strand 2 nm.

Size is not the key factor in potential property changes; the massive surface area increase is what provides those changes. To understand this, imagine a one metre cube of a chemical product; the surface area of the six-sided cube would be 6 m^2. If that cube of chemical was ground down into 1 millimetre cubes, there would be a billion of them and the surface area would be 6,000 m^2. If the chemical was ground down to 1 nm cubes, there would be 10^{27} particles and the surface area would be 6,000,000,000 m^2, that is 6,000 km^2. The whole of New Zealand occupies 268,000 km^2, and the Metropolitan area of Wellington is about 1,400 km^2!

For the chemist, benefits are clearly seen with recent work with gold, which is an excellent catalyst at the nanoscale but fairly inert as larger particles. Companies such as Johnson Matthey have realised that car catalysts are much more effective at the nanoscale, because of the massive increase in surface area.

Products

Actually, nanotechnologies are not something new, they have been with us all of our lives. As soon as we pop out the womb we have to rely on our own nanofluid; blood is a nanofluid. The next thing that happens is that we get a drink of milk; milk contains nanoparticulate casein. As we get older we are drinking from a bottle of beer; the plastic PET bottles incorporate nanotechnology to keep the flavour in and prevent UV light from degrading the product. Whisky contains nanoparticles; it may appear as a clear product but the nanoparticles are actually there. If you used a hair drier this morning, you would have produced tungsten nanoparticles, which are given off as the heating element warms up. So some nanotechnology-based products are natural and others have been deliberately engineered, often to enable nanotechnologies to provide beneficial properties.

Lobby groups in some countries appear to be anti-science and against progress. Recently we have seen their attention directed to GM foods; and they predicted that the Hadron Collider at CERN on the Swiss/French border would see us all disappearing into a black hole. Stem cells have also been in the limelight, and nanotechnologies have had more attention than they deserve. Nanotechnologies cut across all market sectors: it is difficult to define what is meant by nanotechnologies since they encompass ultrafine particles, emulsions, and thin films, and are both natural and produced by us. Some of the lobby groups are even asking for a moratorium on anything *nano*. Toxicologists are also making hay while the sun shines with a plethora of studies looking especially at what are being called engineered nanoparticles. However, at an international conference (Nanotoxicology 2010) held in Edinburgh, the main speaker, Prof. Gunter Oberdörster (University of Rochester), argued that most studies are of limited value to a risk assessment as they have been performed at unrealistic exposure doses. Unlike chemists, lobby groups and few toxicologists seem to have an understanding of risk assessment. A chemical as simple as hydrogen peroxide can serve as a mouthwash but also as a rocket fuel!

Major technologies seem to come along in waves, with solid state physics in the fifties leading on to microelectronics that provide the electronic devices we now accept as commonplace. In the seventies, biological science produced biotechnology which has had such an impact on healthcare, but now we are seeing the start of nanoscience and nanotechnology developing new functional materials which are listed as being used in over 1,000 new products in many sectors (Fig. 1).[2] As with most new developments, it is the high profit areas that are the first to accept and promote new products, but already nanotechnology is encroaching into most industry sectors. The potential markets for nanotechnology-based products have been estimated as $US1 trillion by 2015 in a much quoted report from the US National Science Foundation in 2000.

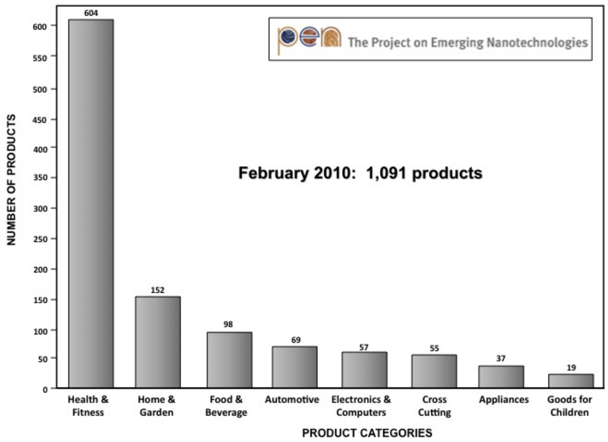


Fig. 1. Nanotechnology-based consumer products inventory

Already it is clear that the benefits provided by nanotechnology-based products far outweigh any potential problems. The nano-components being used come in different forms, thin films, nanotubes, and nano-particles, as illustrated in Fig. 2.

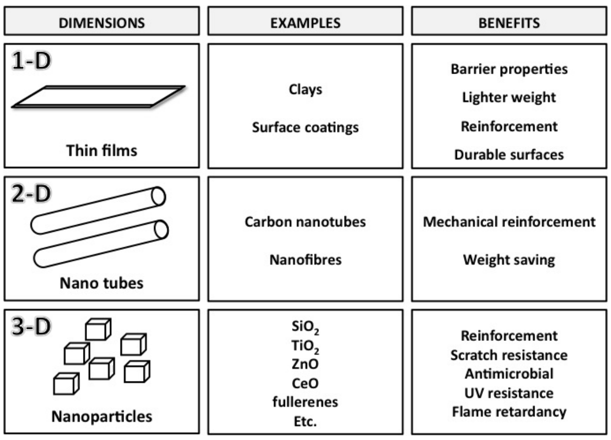


Fig.2. Types of nanotechnologies

Sports and Leisure

The sports and leisure sector often leads with the introduction of new products, because it can cope with higher costs through greater margins. For example, Formula One motor sport pioneers new developments before we see them on our own cars. Plastic panels have replaced metal panels in most cars and today the polymer is *reinforced* with nano-sized platelets, thereby providing reduced weight and improved strength. These platelets come from bentonite clays; the same clays that are used for thickening water-based non-drip paints. Each 8 μm grain of clay contains over a million platelets and, a bit like reinforcing concrete, the platelets strengthen the polymer when incorporated at around 15%. However, the platelets have to be well dispersed to give the increased strength, so the inorganic clay has to be compatibilized using quaternary ammonium salts to encourage it to be mixed into the polymer.

Wilson Sports have used clay platelets in tennis balls. At Wimbledon, the cry of *new balls please* echoes across the courts, because the players strike the ball so hard nowadays, forcing the air out after only a few games. The new Wilson balls have clay platelets dispersed in the butyl rubber, and the millions of tiny platelets provide a very tortuous route for any gas molecules trying to escape. The balls therefore hold their pressure for far longer than conventional balls.

There are even better developments for weight saving on the horizon, by using carbon nanotubes (CNTs) that are minute whiskers with a diameter of about 1 nm. These CNTs have only been identified in the last 20 years but they are formed when just about anything is burned. If you burned your toast this morning, you produced about 10^{-12} kg of CNTs! However, the chemists have come up with a more efficient route to their manufacture, and they are beginning to find application in several sports and leisure applications.

Roger Federer and the Williams ladies use Wilson racquets which contain about 3% CNTs in the plastic material used for the racquets. Rafa Nadal now uses Babolat racquets which have also gone *nano*. Floyd Landis won the Tour de France a few years ago, being the first to use a bike which had a CNT-plastic frame. The SOLO crossover alternative energy car from California-based Velozzi has CNTs for all its body panels, and achieves 100 miles per gallon.

There is an additional property that CNTs provide which is also being seen in new products. This makes use of the ability of CNTs to conduct electricity and also heat. Metal fuel lines in cars are being replaced by CNT-plastic tubes, and the fuel pumps on the Audi A4 and A5 models are no longer metal but are CNT-plastics.

As will be discussed later, there have been suggestions that CNTs could have toxicity issues, but more recent developments are indicating that graphene, single tiny sheets of graphite, have similar properties to CNT; potentially at much reduced cost. The 2010 Nobel Prize for physics was awarded to Andre Geim and Konstantin Novoselov, at the University of Manchester, for their pioneering work on graphene.

Textiles

Some of the earliest applications for nanotechnology have been in the field of textiles, overcoming the problems of coating fabrics by conventional means, which make them feel stiff and uncomfortable. A US-based company, Nano-Tex, is leading in this area, with nanotechnology coatings being used in many leading suppliers' favourite brands. Nano-Tex uses this revolutionary technology to enhance fabrics at a molecular level; producing material that resists spills, repels stains, wicks away moisture, and resists static, without sacrificing comfort. These coatings are now finding application not just in apparel, but in home textiles, and commercial interiors, providing fabrics that retain their natural softness and which are more durable. As well as shirts and trousers, it is now possible to buy curtains, carpets and upholstery that have been treated with nano-scale surface materials.

For stain resistance, the fibres are coated with a thin layer of a super hydrophobic material that mimics the water repellancy of lotus leaves, which have quite a bumpy surface when viewed at close to nano-scale. A drop of water landing on the leaf runs off because of a cushion of air that is under the droplet; a bit like how a hovercraft moves along. As it runs off, it gathers dirt and provides a cleaner surface. Nano-Tex's *Coolest Comfort* provides breakthrough moisture wicking, where, fundamentally, each fibre has been transformed by nanotechnology to give a fabric which balances body temperature, and allows it to breathe. The next development from Nano-Tex is likely to be cotton that is made to permanently feel like silk, again based on very thin nanotechnology coatings.

In addition, it is also possible to purchase socks and under-garments that are odour resistant. For these, the fibres either have had silver nanoparticles incorporated into them, or they have been coated with silver nanoparticles. Silver has a long history of use as an antimicrobial - the Assyrians around 2,500 BC carried their water in silver containers, and even today the Bedouins put a silver coin in their leather water carriers knowing that the water will stay fresh for longer. At nanoparticulate scale, silver is an excellent anti-microbial and, more recently, it has been found that nanoparticulate copper also offers anti-microbial properties.

Marks and Spencer have been carrying out a trial in the UK with pyjamas impregnated with these antimicrobial properties, which are claimed to be clinically proven to reduce the risk of MRSA (Methicillin-resistant *Staphylococcus aureus* that is also called multidrug-resistant *Staphylococcus aureus*), the bacterium responsible for several difficult-to-treat infections in humans. Rohan market silver-impregnated underpants that are antimicrobial, and more recently the US space programme has employed similar technology. Koichi Wakata, a Japanese astronaut has recently returned from a trip on board the shuttle Endeavour having visited the International Space Station. On his return, he admitted that he had been wearing the same pair of underpants for a month. The underpants are part of a trial for when astronauts visit Mars. They are antistatic, flame retardant, odour-eating, antimicrobial, and water absorbent, and appeared to stand up well during the 57 million mile journey. The clothing was designed by the Japanese Space Agency and is known as J-Wear. It is made of cotton and polyester but with what is described as a futuristic silver coating that gives it the special properties. There are also socks, T-shirts, trousers and leggings in the range.

Food and Drink

The Helmut Kaiser Consultancy[3] estimated that worldwide sales of nanotechnology in the food sector would rise to over $US20 billion by 2010, with nanotechnology products for food and beverage packaging having reached $US860 million in 2004.

There are several areas where different nanotechnologies will have a marked impact in the food area:

- Packaging, *e.g.* lighter weight; novel barrier materials; sensor technology for food traceability and shelf-life
- Food safety, *e.g.* antimicrobials; rapid food spoilage detection, analysis of other contaminants
- Functional coatings, *e.g.* antimicrobial surfaces; easy clean surfaces, food processing equipment
- Nutrition, *e.g.* enhanced bioavailablity of nutrients and vitamins; controlled release of fat from products
- Texture, taste and health improvement, *e.g.* lower fat, salt or sugar products; *cleaner* labels by improved ingredient functionality.

Alcoa have been active in promoting lighter weight packaging materials, with clay-based nanocomposite materials, but they also provide barrier properties to retain the flavour of foodstuffs and prevent the ingression of oxygen, water, and unwanted odours that are detrimental to the flavours. Bayer have developed a new plastic film, Durethan® KU 2-2601, based on polyamide and clay platelets that are impervious to gases and provide enhanced gloss to the film.[4] They say that these new films will *make sure that the smell of Swiss cheese will not mix with that of salami in the refrigerator at the grocery store*. There are also major opportunities for nanotechnologies in *track and trace* messaging on packaging which are already under development.

Food safety is a major issue in most countries, and with silver being such an excellent antimicrobial, it is being used in a variety of plastics for refrigerators, food packaging and many other food contact areas. FresherLonger™ food storage containers, infused with silver nanoparticles, give clear examples of how the storage time for foods can be extended[5] with 24 hour growth of bacteria being reduced by over 98% compared with conventional containers.

Not surprisingly, all this new product activity has attracted the attention of lobbying groups, including activists who have demanded that the Environmental Protection Agency in the States stops the sale of over 200 nanosilver products[6] that they say are potentially dangerous. However, FERA (previously known as the Central Science Laboratory) has carried out leaching tests for the UK's Department of Environment, Food and Rural Affairs (DEFRA) to determine whether the clays or silver nanoparticles can escape from the polymers into which they have been dispersed. Even under extreme damage conditions, only background traces of silver were detected and no clay material was extracted, which suggests that that there is no need for concern if the nanomaterials are locked into plastics.

The size of particles hitting the tongue affects the taste and texture, as well as the bioavailability of foodstuffs. By controlling the size in foods these properties can be altered to the benefit of the consumer. There are some who are concerned about the addition of nano particles to foods, but it is not widely recognised that many natural and processed foods are already structured at the nanoscale as well as having a proportion of nano particles present. Salt also has been shown to have a faster taste perception when the size is reduced, and one of the projects of Eminate,[7] a wholly owned subsidiary of the University of Nottingham, is the production of ultrafine salt, which enables certain products to be formulated with less salt because of the greater taste sensation from much smaller salt granules.

Transport

A sugar cube has around one in ten million atoms on its surface whereas a one nanometre cube of sugar has 80% of its atoms on the surface. The huge surface area achievable at the nanoscale is a feature of car catalyst developments. As well as the weight saving and increased modulus provided for plastics by clays and carbon nanotubes, metal engine covers have been replaced by polymeric materials. The Mitsubishi Shogun model was one of the early examples using silica nanoparticle-based plastics to repel the heat which would cause a conventional plastic to melt.

If a moth had not evolved with anti-reflective eyes, a bat or owl would be able to pick it off quite easily. The Audi TT Roadster has copied the moths' eyes anti-reflective nanoscale patterns for its instrument panel so that it can be seen clearly in sunny conditions.

Bowling balls were the first objects to have anti-scratch surfaces achieved through a final lacquer containing alumina nanoparticles. This technology is now used for the final coating on Mercedes cars.

A spin out from Oxford University, Oxonica, has developed cerium oxide nanoparticles which are used at part per million levels in diesel fuel for cars. They catalyze the burn of the fuel, giving around 15% more miles per gallon, and because of a more efficient burn, there are less exhaust fumes. Unfortunately, the company ran into patent problems.

The Audi Le Mans Quattro (R8 model) has shock absorbers based on magnetic nanoparticles suspended in a fluid. Although there are many new applications in the automotive sector, the largest use of nanoparticles has been in tyres in the form of carbon black nanoparticles. This has been used for nearly a hundred years and currently the market size is in excess of 6 million tonnes per annum.

In the aerospace sector, the potential for weight saving is enormous. The new Airbus A380 is made up of around 17% composite materials based on carbon fibres, whereas the Boeing 787 Dreamliner, with composite wings, comprises about 50% composites. CNTs offer even more weight saving, so we can expect the next generation aircraft to be even lighter in weight (Fig. 3). Another feature of the Dreamliner is that it has special silver nanofilters which, in flight, maintain high quality air, killing 99.7% of influenza viruses.

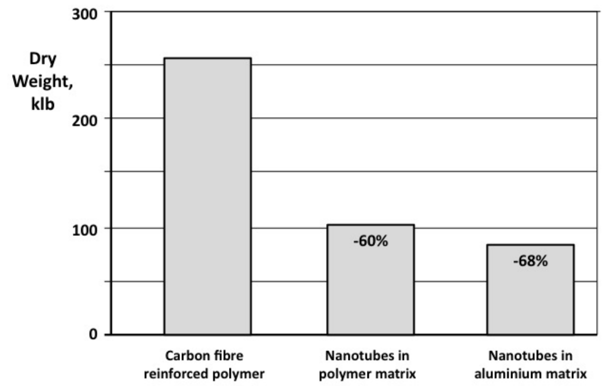


Fig. 3. Weight reduction with carbon nanotubes

Super hydrophobic surfaces, like those used for textiles, have the potential to be used on aircraft to repel moisture that should mean that de-icing planes will become something of the past. Other nano-thick functional coatings have been designed to be much harder wearing ones, and others provide stealth coatings for military aircraft. In the US, the Department of the Air Force are researching biomimetic coatings; trying to copy the pearl layers of an oyster shell which manages to produce these ceramics without the use of very high temperatures.

Construction

The construction sector has not adopted nanotechnology as rapidly as it might, but there are clear opportunities in weight saving and functional surfaces. There is also some work going on to reduce the weight of concrete by forming nanostructured material, and other nanostructured products are being developed to insulate buildings (as well as cars and planes) from noise and heat. However, one application that has seen good growth is the use of a 35 nm thick layer of titanium dioxide on glass. Pilkington Glass has developed this technology over the last 20 years, with the coating going onto the outside of the glass during the float glass process. When photons from the sun hit the glass the titanium dioxide catalyses the breakdown of the dirt on the pane, and the next time it rains the residue is washed off (Fig. 4). Very applicable when it comes to cleaning the windows in a glass skyscraper! Using the same technology, an EU-funded project has developed coatings of nanoparticulate titanium dioxide for buildings so that environmental pollution, in the form of nitrogen and sulfur oxides, is broken down. The first building to apply this technology was the new Jubilee Church in Rome; one is left wondering whether this could help solve the pollution problems in many big cities.

There is considerable progress being made with photovoltaic cells. The conventional use of silicon, which has become increasingly expensive, is also the subject of nanotechnology-based research. Thin nano-films of silicon, and other materials, such as cadmium telluride and copper indium gallium selenide, are being developed, but there is also attention on what nature manages to do. Plants grow, by using chlorophyll catalysts to convert water and carbon dioxide into their energy contributor and oxygen, and solar cells are now being developed that try to copy that process. These have been developed by Prof. Michael Grätzel, (Ecole Polytechnique de Lausanne) and use dye catalysts coated on nanoparticles to provide a large surface area to capture photons. Other work in the field of photovoltaics is examining organic polymers.

Fig. 4. Nano coated glass-fronted building.

Household Products

Although numerous household products have always had nano-features, there is now much more effort being placed in using the properties that nanotechnology brings. Just about anything that has been ground down will have a proportion of nanoparticles in it. Even the miller in the Middle Ages knew that when he was grinding his flour, he would get a varied particle size distribution. The larger lumps would be no good for making decent bread, but he would certainly have been producing some nanoparticulate material!

Hydroxyapatite nanoparticles are being used in many toothpaste applications. Using this natural material builds up minute cracks in the enamel which prevent people eating very cold ice cream. Many of the more expensive sunscreen and anti-ageing products contain nanoparticulate titanium dioxide which is much more effective as a barrier against harmful UV light than the conventional micro particles and does not appear white, like Aussie cricketers' noses, when rubbed on the skin. Despite lobby groups saying that these nanoparticles are harmful, tests have not shown any indication that they are harmful, even on damaged skin, probably because the particles tend to flocculate, but still retain a large, effective surface area. Many emulsion-based products are down at the nanoscale. Some of the hair shampoos that also contain conditioners are designed so that the conditioner is released when the hair is finally rinsed.

Nanotechnology-based products are particularly diverse in the home. There has been an EU project called PolyCond, which has produced a prototype electrical plug that has replaced brass with CNT-plastic for the pins. This gives 82% weight saving at one fifth the cost of a brass pin, and gives an overall saving of 40% for the finished plug. Drill bits are coated with thin nano-layers so that they last longer, and similarly some Wilkinson Sword razors have the cutting blades coated with nano-layers of diamond. There are products for waterproofing stoneware so that it is not eroded; the Firth of Forth Railway Bridge in Scotland, the first steel bridge in the world, was painted in 1890 and since then it has been painted continuously ever since. At last they will not have to paint it again! For the past 25 years the painters have been using nano-based paints that are much more effective at controlling corrosion.

Ten years ago, if you impatiently removed paper from your computer printer, you finished up with ink all over your fingers. This does not happen now, because some of the inks are nanoparticulate and the paper has nanoparticles on it. The increase in surface area means that the solvents evaporate much more rapidly and give instant drying.

Healthcare

Healthcare is where nanotechnology will probably make the most impact, with the development of novel drug delivery systems specifically targeting the location of the problem. At the nanoscale, particles are more soluble, so there are companies looking at using nanoparticulate pharmaceuticals at lower than conventional doses, thereby having fewer side effects. At the nanoscale things happen more rapidly and more sensitively, and already we are beginning to see nanosensors that are aimed at detecting the disease before it has a hold on the body. Some of these sensors are able to detect just a few molecules; not dissimilar to a dog being able to smell a pheasant 100 yards away.

Nanoparticulate imaging products are also being used to give finer definition of where problems might be occurring. Flocculating nanoparticles, which exhibit colour depending on their ability to diffract light, can change colour, and this type of indicator is used in pregnancy test kits for example. The whole healthcare field is likely to see major changes - certainly a sector to watch.

Energy and the Environment

Undoubtedly, the energy sector will benefit from nanotechnologies through developments that have already been discussed in this article. In addition to the nanotechnology research on photovoltaics, there is much research on new batteries to provide longer life, easier recharging, and also storage of energy.[8] Lighter weight blades for wind turbines are being promoted with CNT technology by Bayer. The larger the blade diameter, the more power is generated (Fig. 5), but large heavy blades are either slow to move in the wind or need electricity to get them started, and occasionally break under the strain. Nanotechnology offers stronger and lighter weight blades.

Nanotechnology will surely have a major effect on the environment. More durable materials and surfaces will produce longer life products - and we are currently only seeing the tip of the iceberg in terms of exciting developments.

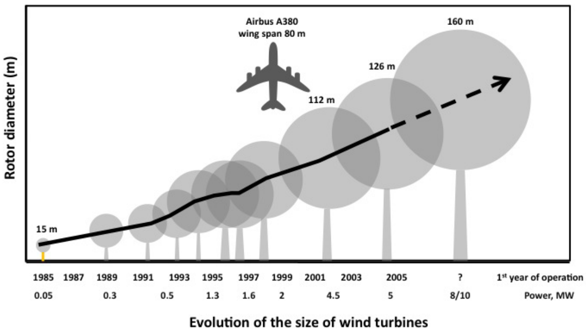


Fig. 5. Relationship between power output and wind turbine diameter

As well as the airborne pollution, previously mentioned, there is also the potential to clean up ground pollution. Work is being carried out with suspended iron nanoparticles being pumped into contaminated ground where they can catalyse the breakdown of a variety of pollutants. They are then sucked out of the ground once they have been effective.

Societal Issues

There has been considerable hype associated with nanotechnology, from industrialists and academics wanting more government funding, from lobby groups needing more membership subscriptions, and from toxicologists who seek more funding for toxicity testing. In reality, we are seeing more anti-science being reported in the press, often nowadays directed at nanotechnology. In a world recession, lobby groups and the media should show more responsibility and base their thoughts more on fact. A report from Cientifica stated: *For policy makers who are not scientific experts (and few are) speculative concerns are given equal weighting with scientific results*. An interesting report from Oxford Economics in the UK said that for every 5 GBP earned in the UK 1 GBP came from chemists, and in a population of 61 million, 5.1 million jobs are dependent on chemists. Clearly, we need more backing for technology developments, starting with politicians; that is what provides growth.

In some countries, however, nanotechnology is not regarded as a problem and *nano* is added to products as a marketing tool to indicate that it is something innovative and exciting. You can purchase Nano-water in China, which has nothing nano about it; in Thailand you can purchase Nano Breast Serum, which if you rub it in the right places stops your breasts sagging. The Nano iPod and the Tata Nano car may have some circuitry down at the nanoscale, but there is nothing really nano about them, other than them being a bit small. However, in the US, many companies that were proud to add *nano* into their name when they were launched are now changing their names just to avoid unwanted hassle.

An issue is that nanotechnologies are particularly broad and cut across all market sectors, and there is no good definition describing what it is or even which parts of it might potentially be a problem. The recent definition of a nanomaterial by the OECD describes it as: *Nanomaterials intentionally produced to have specific properties or specific composition, a size range typically between 1 nm and 100 nm and material which is either a nano-object,* i.e. *that is confined in one, two, or three dimensions at the nanoscale, or is nanostructured,* i.e. *having an internal or surface structure at the nanoscale.*

The very act of boiling an egg means that it is a nanomaterial since boiling it produces a nanostructured material! Furthermore, a report[9] produced by OECD and Allianz, states that in a normal room there are 10,000 nanoparticles in a single square centimetre, and this increases dramatically as one goes into a forest or into a street. This means that with every breath, you are inhaling a cocktail of around 5 million nanoparticles. Much of the work on formulating nanoparticles into products is all about stopping them flocculating, so that might be happening in the atmosphere. However, nanoparticulate atmospheric pollution causes the colours of sunsets, which is mostly the result of volcanic action; after Krakatoa exploded in 1883, there were decades of bright red sunsets.

There is also great potential for nanotechnologies to be having an impact on the developing world, particularly through healthcare, solar energy, and water purification. The latter has not been mentioned previously, but there are now nano-membranes which will remove bacteria and viruses, and other contaminants, from polluted water.

For the chemist, nanotechnologies present opportunities in cleaner processing, improved formulations, and many new product opportunities. As a White House press release said:[10] *Nanotechnology is the next industrial revolution.*

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