

Common nano-materials and their use in real world applications

ROBIN A. McINTYRE

ABSTRACT

Today engineered nano-materials have attracted a great deal of attention due to their important properties which have given birth to vast technological and economic growth in a number of industrial sectors. Nano-materials are indeed expected to become the cornerstone of a number of sectors such as micro-electronics, materials, textiles, energy, healthcare and cosmetic goods. Nano-technology applications will give rise to cleaner energy production, lighter and more durable materials, inexpensive clean water production and will benefit medical applications such as smart drugs and diagnostics.

However, one has to be mindful of the risks involved concerning potential toxicity and exposure route and the verdict is still out on a number of nano-materials as to the relative dangers to humans and the environment.

This brief review hopes to describe some of the main contenders and their real world applications but it should only be considered a snapshot of the industry and its relative potential.

Keywords: *nanotechnology, nano-materials, metal oxides, photocatalysis, fullerenes, carbon nanotubes, graphene, titanium dioxide, silica aerogels, nano-ceramics, quantum dots*



Dr Robin McIntyre is an Innovation Consultant at Pera Innovation, Melton Mowbray, Leicestershire, LE13 0PB, UK (E-mail: robin.mcintyre@pera.com) and a freelance science writer. He specialises in nanotechnology and renewable energy technologies. His main role is to develop concepts on behalf of clients and to prepare funding applications for submission to the EC and the TSB. He was awarded a PhD in Chemistry (2004), a Master's degree by Research (2001) and an MChem degree (1999) from the University of Warwick. He is also a Member of the Royal Society of Chemistry. He has previously worked for a nanotechnology company, Oxonica Ltd, where he specialised in the use of modified forms of nano-TiO₂ for application in cosmetics, plastics and coatings.

1. Introduction

The use of nano-materials in commercial products is rapidly increasing. In 2006, more than 300 commercial products on the market claimed to have enhanced properties due to incorporated nano-materials; this number had more than quadrupled by 2010¹. Silver is the most common nano-material used in products, followed by carbon-based nano-materials and metal oxides such as TiO₂.

Nanotechnology is going to pave the way for a revolution in materials, information and communication technology, medicine, genetics, *etc.* as commercialisation potential is driving innovation from the research laboratories into real world markets. The use of nano-materials can help to improve products and production processes with better characteristics or new functionalities. In coming years, products based on nanotechnology are expected to impact nearly all industrial sectors and will enter the consumer markets in large quantities. Due to the future potential of nanotechnology, many companies across the world are investing heavily in this sector.

According to the Nanotechnology Market Forecast to 2013 Report³ the global market for nanotechnologies is projected to grow at an annual growth rate (AGR) of around 20% until 2013. The report also projects that the market for nanotechnology incorporated in manufactured goods will be worth US\$ 1.6 Trillion, representing a CAGR of more than 49% in the forecast period (2009–2013). This growth will largely be driven by massive investment in nanotechnology R&D by both governments and corporates across the world.

According to the Project on Emerging Nanotechnologies (PEN)⁴ over 1,300 manufacturers have been identified who have nanotech-

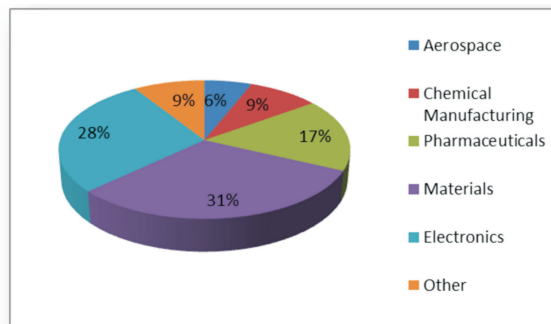


Figure 1 Estimates of the nanotechnology market 2010–2015² by market sector.

nology-enabled products which have entered the commercial marketplace around the world. The most recent update to the group's five-year-old inventory reflects the continuing use of the nanosized particles in everything from conventional products like non-stick cookware (based on nano-ceramic coatings) to more unique items such as self-cleaning window treatments (based on electrochromic nanosized metal oxides). Health and fitness items continue to dominate the market with over half of the known products relating to this sector.

This review seeks to explain some of the more commonly commercialised nanomaterial products and some of the main emerging application areas. It would not be possible to go into great detail about all of the applications and nano-materials available but it is intended as a snapshot of the current state of the art of some of the leading contenders.

2. Nano-silver

Silver has been used since ancient times for a range of purposes from jewellery to currency to more modern applications in photography and medicine where it has been used as an antiseptic in wound management. More recently interest has focused on the properties of silver at the nano-scale due to “unusually enhanced physicochemical properties and biological activities compared to the bulk parent materials or macro scaled counterparts⁵”.

Due to these properties there is great potential for the use of silver for numerous applications⁶ such as antimicrobial applications in medical devices and supplies and in various consumer products such as food packaging materials and food supplements, odour-resistant textiles, electronics and household appliances (*e.g.* Silver Nano[™] by Samsung⁷), cosmetics and medical devices, water disinfectants, and room sprays. Indeed, approximately 30% of such consumer products claim to contain silver nanoparticles. The estimated worldwide market size of nano-silver (for use in commercial products) was 320,000 kg/yr in 2009⁸ equating to a market value of \$290 million, although this is expected to expand rapidly to \$1.2 billion by 2016⁹. This volume may appear small, however, its toxicological burden might be 100 times, or even 10,000 times as great as this volume of bulk silver¹⁰.

The potential leaching of silver nanoparticles from products has resulted in unprecedented attention from regulatory bodies of national governments and public pressure groups¹¹. An example of this is the addition of silver nanoparticles to socks (*e.g.* AgActive

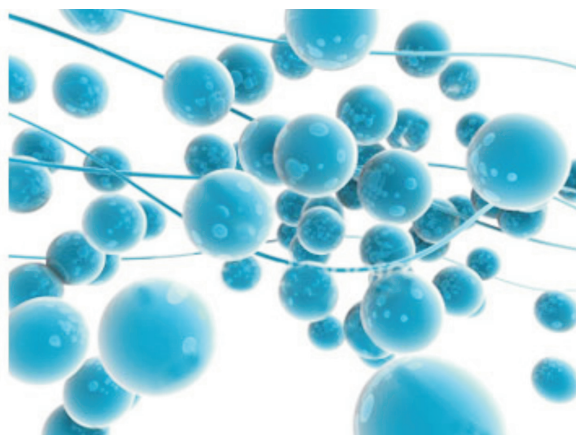


Figure 2 Showing nano-silver particles attached to fibres.

or SmartSilver[®]) for the purposes of neutralising the bacteria associated with foot odour.

A recent study¹², however, revealed that the silver can easily leak into waste water during washing cycles, thus potentially disrupting helpful bacteria used in waste-water treatment facilities, or endangering aquatic organisms in lakes and streams. It was reported that some brands of socks lose nearly 100% of their silver content within four washings, while two other brands lost less than 1% over the same number of washings.

Nano-silver has also been incorporated into washing machines (manufactured by companies such as Daewoo or Samsung) for enhanced antimicrobial activity¹³. This has also provoked a response from the Swedish Environmental Protection Agency which has protested against this particular application due to the potential risk of nano-silver leaching into the waste water stream.

Despite the rapidly growing market for nano-silver-containing products, there is still some way to go in the development and acquisition of knowledge in relation to the possible risks of exposure to these types of nanoparticles so one must exercise caution in their application and use for now.

Another potential application for nano-silver, which is currently being researched by academics (research projects such as FP7 project CLIP¹⁴ and HIFLEX¹⁵) and a number of industrial companies which would benefit the consumer electronics industry, is its potential replacement for indium tin oxide (ITO) which is a commonly used transparent conductive oxide employed in display devices and photovoltaic cells.



Figure 3 Image of non-ITO based flexible organic PV cell (Image from Hiflex project).

It is worth noting that transparent conductive coatings and films have attracted both considerable end user interest and investment in the past two years. From a commercial viewpoint the market for this technology is worth \$2.9 billion now and is expected to grow to around \$4.9 billion by 2014¹⁶. The market up until now has been dominated by ITO, but this material is in relatively short supply and is expensive to deposit due to complex processing requirements. It is also relatively fragile when deposited in films. So the ‘holy grail’ for the electronics industry is to develop a better alternative as one cannot rely upon the suitability of ITO for the rapidly growing display touch-sensor market indefinitely.

Currently the transparent properties of nano-silver films are nearing those of ITO although ITO can probably still prevail over nano-silver in this regard which prevents the material from being used in the high-end LCD business in the short term. However, producing thinner layers of nano-silver, or incremental improvements in nano-structures, may result in reaching acceptable values. Even today, nano-silver is the most effective alternative to ITO when considering conductivity.

3. Carbon-based nano-materials

3.1 Carbon nanotubes

Among the various nano-scale materials, carbon nanotubes (CNTs) exhibit the most extraordinary mechanical and electrical properties. CNTs are the strongest and most flexible molecular material, which is due to the C—C covalent bonding and seamless hexagonal

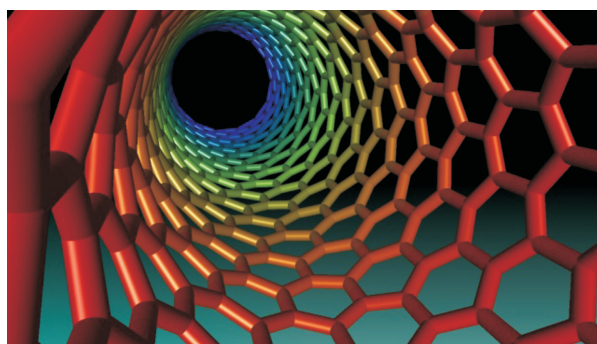


Figure 4 Image of a carbon nanotube.

network. CNTs also possess electrical conductivity (semiconductivity) and high thermal conductivity in the axial direction¹⁷.

CNTs are essentially sheets of graphite rolled in tubular form. The dimensions are variable (down to 0.4 nm in diameter) and can exist also as nanotubes within nanotubes, leading to a distinction between multi-walled and single-walled carbon nanotubes (MWCNT and SWCNT). Apart from their remarkable tensile strength, nanotubes exhibit varying electrical properties (depending on the way the graphite structure spirals around the tube and other factors) and so they can be insulating, semiconducting or conducting.

Structural and electrical characteristics of CNTs make them promising candidates for the development of smart composite materials. Composites can be prepared of carbon nanotubes and polymers which have high electrical conductivity, with applications in a conventional cold cathode or a polymer LED. They can also introduce electrical conductivity to materials which additionally indicate an improved mechanical performance. Incorporated into a polymer matrix, CNTs can produce composites with a very high strength and high elastic modulus which may lead to the development of ultra-resistant materials for use as reinforcement fibres.

Due to their large surface area, CNTs are interesting media for electrical energy storage¹⁸ and they are still under investigation as a hydrogen storage medium¹⁹. CNTs show good properties in electron emission which could result in large area display applications²⁰.

The IR vibration of nanotubes is being investigated for the possibility of using IR radiation to enable the manipulation of carbon nanotubes. Their use as molecular pincers in actuators is also under investigation²¹.

The excellent electrical and mechanical properties of carbon nanotubes like electrical conductivity, heat transmission capacity, heat stability, high strength or low density, makes them candidates for use as fillers and many other applications.

Recently, CNTs were used as needles to bring active agents into living cells (Kanzius RF Therapy). This process could be applied, *e.g.* as a new way to a therapy against cancer.

Other medical uses involve CNTs in polymer nanocomposites as scaffold materials for bone cell proliferation²² and bone formation²³.

Other potential applications of interest which involve this unique nanomaterial are: novel battery technologies²⁴, photovoltaics²⁵ and nano-based transistors or carbon nanotube field effect transistors (CNTFETs)²⁶.

According to Frost and Sullivan²⁷ the global addressable market for carbon nanotube-based composites was \$18.79 billion in 2008, projected to grow at 3–7% per annum. Significant growth has been attributed to growing interest from aerospace, defence, automotive and construction industries owing presumably to the added strength and flexible properties gained from inclusion of CNTs in a composite structure.

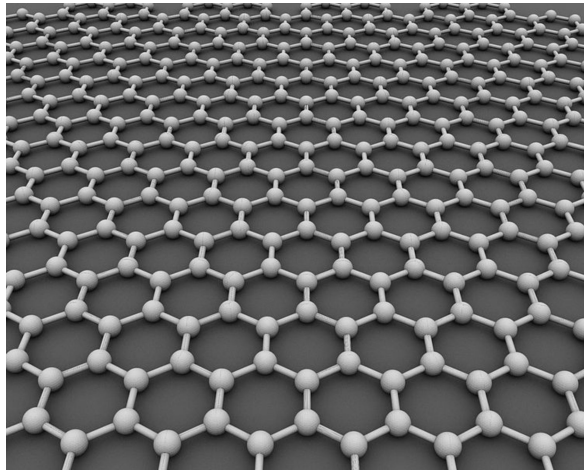
3.2 Graphene

Another popular carbon-based nanomaterial which has emerged over the past few years is that of graphene which has been pioneered by Professors Geim and Novoselov²⁸, who won the Nobel Prize for Physics in 2010 and later gained both a knighthood for their work in this field²⁹.

Graphene is an allotrope of carbon whose structure is one-atom thick planar sheets of sp^2 bonded carbon atoms. These planar sheets are densely packed in a honeycomb crystal lattice. Graphene is therefore one of the thinnest materials in the universe as well forming a highly uniform crystal lattice with no vacancies nor dislocations in the structure. For this reason graphene has intriguing properties and has yielded new physics.

Graphene's most notable property is that its conducting electrons arrange themselves into quasi-particles that behave more like neutrinos or electrons moving close to the speed of light³⁰.

The most obvious applications for graphene will be to replace silicon chips as this mature technology is fast reaching its fundamental limits $< 10 \text{ nm}^3$ ³¹. It has been proposed that graphene wafers could be used for electronic applications as well as for high



*Figure 5 Crystalline structure of graphene in a hexagonal grid.
Reference: <http://en.wikipedia.org/wiki/File:Graphen.jpg>*

frequency transistors (THz range) and miniature circuit boards. However, a number of barriers exist to be able to accomplish this including scale up of graphene sheet production to that required for application in large scale industrial sectors.

Graphene is currently being utilised in the same manner as carbon nanotubes as a filler material in composites for strength reasons. The projected market size for graphene used in this way is \$59 million by 2015³².

It is also being researched as a potential alternative to transparent conductive oxides such as indium tin oxide (ITO) as it can better this material in terms of mechanical strength and flexibility. This offers potential for large area organic electronics as it can be deposited from solution over large areas³³.

Other potential applications include photovoltaics³⁴, ultra-capacitors³⁵, bio-devices³⁶ (diagnosis and detection) and anti-bacterial surfaces³⁷.

4. Nano titanium dioxide

Nano-TiO₂ can be used in a wide variety of applications such as self-cleaning surfaces and textiles, UV-resistant coatings and paints, disinfectant sprays, sunscreens, water treatment agents, anticancer treatments. TiO₂ is indeed one of the most widely used nano-scale materials with market revenues for nano-TiO₂ powder alone

estimated to be \$360 million in 2009 which is projected to grow to \$1.4 billion by 2017³⁸.

Amongst the multiple uses of nano-TiO₂, three major applications will be highlighted here, namely photocatalytic, cosmetics and photovoltaics.

4.1 Photocatalysis

One of its other main uses, other than as a pigment in paints, plastics and coatings is as a photocatalyst. Titanium dioxide (TiO₂) is a semiconductor which was initially investigated by Honda and Fujishima in the early 1970s³⁹. In the presence of water and UV light, TiO₂ generates free hydroxyl radicals, which are able to undergo secondary reactions with organic matter, leading to its complete degradation to final products CO₂ and H₂O. These processes are called advanced oxidation processes (AOPs).

The catalytic effect is based on the hole-electron-pair generation in the semiconductor by irradiation with UV light facilitating redox reactions through the formation of absorbed radicals on the catalyst surface. Despite its larger band gap (3.2 eV), requiring light activation at shorter wavelength and therefore higher energy, the anatase modification of TiO₂ shows significantly higher photocatalytic activity compared to the common rutile modification (3.0 eV), due to the difference in their conduction band position.

In coatings technology, TiO₂ and ZnO are usually embedded into organic binder systems, which have to be protected against photo-degradation. Historically, this has been achieved by passivating the TiO₂ and ZnO particles, for its use as white pigment, by encapsulating the particles in an impervious barrier coating of alumina or silica, resulting in highly stabilized pigment grades for exterior coatings.

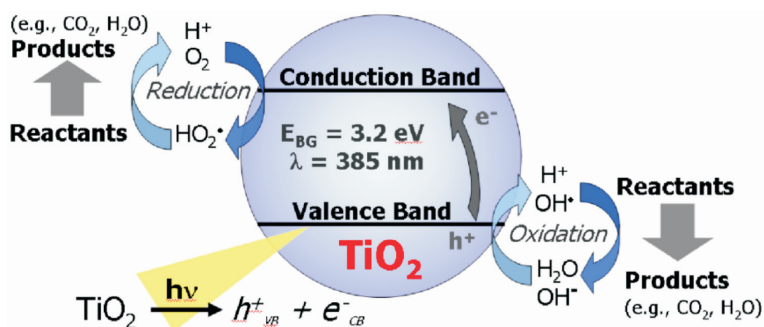


Figure 6 Showing the TiO₂-assisted photocatalytic breakdown of pollutants.

Applications using the photocatalytic activity of TiO₂ (especially Degussa P25 which has been studied in photocatalysis for a number of years) for degradation of organic pollutants and dirt have been developed on inorganic substrates like ceramics, glass, concrete and gypsum plaster, which are stable against photodegradation. Some applications on such substrates, like self-cleaning building glass facades⁴⁰ and wastewater treatment use TiO₂ in its anatase form⁴¹.

Recent research activities have utilised active forms of nano-TiO₂ with high photocatalytic activity, to photo-degrade organic pollutants, soiling and microbiological fouling. A key issue for researchers, however, is still the effectiveness of self-cleaning systems and the stability of the matrices against photodegradation, *e.g.* self-degradation, chalking, *etc.*

In the past 20 years, significant efforts have been made to decrease environmental pollution by applying sustainable methods. Photocatalysis has been identified as a promising approach to address this issue. Photocatalytic depollution is highly efficient at ambient temperatures and a complete breakdown of pollutants and contaminants to non-toxic products can be achieved by exposing to sunlight. As a result, over 1800 patents per year dealing with the topic “photocatalysis” have been registered over the last 7 years showing the importance of this topic for science and industry.

Currently, the photocatalytic effect is mainly applied in the construction sector, for example in exterior wall paints to decrease air pollution generated by *e.g.* automobile emissions. Water remediation is still an important issue in Europe but is even more important in non-developed, remote regions in Asia, Africa and South-America. Photocatalytic systems have advantages in terms of use in South East Asia and other developing global regions as they are highly cost-effective, as well as suitable for the specific climate conditions of these areas.

Photocatalytically active surfaces, based on nanosized TiO₂ and zinc oxide (ZnO), are known to have great potential in the field of depollution and decontamination. This is due to their light-induced capability to produce effectively freeradicals, which cause the degradation of the organic pollutants and microbial organisms. This property will be employed as an extremely energy effective method for the depollution and decontamination of air and water, especially in remote areas where there are no other sources of power. More specifically, we focus on the potential of photocatalysis for application in paints and filter systems.

Remediation of polluted water is important for dealing with environmental disasters, such as oil spillages, and also for enabling

access to clean drinking water especially in remote areas. Both of these issues can be dealt with by using photocatalytic technology applied to a water filter system. The principal use of filter devices based on the photocatalytic effects is already known. However, effectiveness will be increased through the novel design of the devices and by the development of photocatalytic substances with increased light absorption in the visible region.

TiO₂ has been studied and used as a photocatalyst in numerous commercially available products such as air depolluting roofing systems⁴², facade coatings with de-soiling and de-polluting properties⁴³, air filtration⁴⁴ systems, hygienic surfaces⁴⁵ *etc.* However, a large proportion of the products have been developed to differing levels of efficiency.

Significant band-gap engineering R&D efforts have been undertaken toward the development of narrow band-gap photo-catalysts⁴⁶ which are activated by visible light for interior applications (such as wall paints) where the availability of the solar influx is lower than for external applications. The breakthrough was achieved with doped TiO₂ and ZnO catalysts which offer a cut-off wave length in the visible region of sun light. This kind of catalysis is named Advanced Oxidation Process (AOP). In principle such products are coloured which is a challenge for formulation of white paints. Although commercially available photocatalytic paints exist^{47,48} which provide some degree of catalytic effect, there is still a requirement to develop significantly the technology for efficient usage.

4.2 TiO₂ in cosmetics

Nanosized TiO₂ and ZnO have been used in cosmetic products for some time, in particular as an active ingredient in sunscreens. In 2005 Oxonica Ltd⁴⁹ (now licensed by Croda plc) patented a revolutionary new UV filter called Optisol[®] which was based on nanosized TiO₂ doped with manganese oxide which was sold and marketed as an additive in Boots' Soltan Facial Sun Defence Cream.

Optisol[®] offered benefits over existing filters for sunscreens in that, in addition to protecting against UVB, the traditional focus of sun protection, it offers enhanced protection against UVA light (also responsible for skin damage).

The material itself is based on nanosized TiO₂, a commonly used ingredient in sunscreens which acts to absorb UV light. A tiny amount of manganese is incorporated within the titanium dioxide



Figure 7 Image showing use of sunscreen containing nanoTiO₂.

lattice which provides major benefits; the manganese absorbs extra UVA giving a higher level of protection and also acts to stop the formation of free radicals in the titanium dioxide. These effects give an enhanced performance which is extremely photo-stable ensuring that the product's ability to protect isn't broken down by the sun.

Concerns over the use of nano-materials within cosmetic formulations including sunscreens have been ongoing for some time but drawing on the best evidence available it has been reported that nano-particulates used in this manner do not pose a significant risk⁵⁰. However, similar to the exposure risks of other nanomaterial-based products, more research and testing is required in order to gain a full understanding of the risks involved.

It is also worth mentioning here that nano-TiO₂ has also been investigated for use in other polymer formulations other than cosmetic formulations, such as thermoplastics and paints, by a large group of researchers to varying degrees of success. As this field is vast and well researched it will not be covered here in this review but for interest one would look towards the work done by Professor Norman Allen at Manchester University⁵¹ as a good place to start.

4.3 Nano TiO₂ used in photovoltaics⁵²

The dye-sensitized solar cell (DSSC), pioneered by Grätzel *et al.*^{53,54} are principally organically based whose operating principles bear similarities to photosynthesis. DSSC technology could provide a technically and economically credible alternative to present day p-n junction photovoltaic devices.

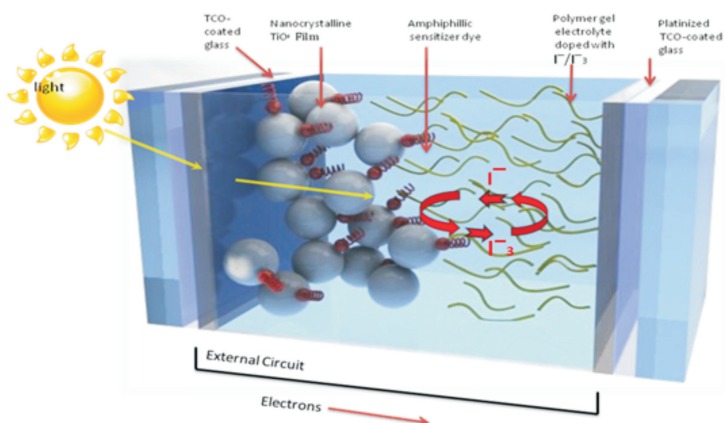


Figure 8 Schematic of a dye sensitised solar cell.

In contrast to the conventional silicon systems, where the semiconductor assumes both the task of light absorber and charge carrier, the two functions are separated here. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band gap metal oxide semiconductor, which is usually nano-particulate titanium dioxide (TiO_2) as it is relatively abundant and inexpensive. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the metal oxide. Carriers are transported in the conduction band of the semiconductor to the charge collector.

The use of sensitizers having a broad absorption band in conjunction with metal oxide films of nano-crystalline morphology can facilitate the harvesting of a larger fraction of sunlight.

The dye-sensitised solar cell consists of a transparent conducting glass electrode coated with porous nano-crystalline TiO_2 , dye molecules attached to the surface of the TiO_2 , an electrolyte containing a redox couple such as I^-/I_3^- and a catalyst-coated counter electrode. Upon illumination, the cell produces voltage over, and current through, an external load connected to the electrodes.

The different steps of the photo-conversion process can best be described in conjunction with the schematic structure of a DSSC (Figure 8).

Presently, the highest cell efficiency values are of the order of $\sim 11.0\%$ for small scale laboratory cells (0.25 cm^2) and $\sim 8.2\%$ on larger cells (2.36 cm^2). Recent progress of researchers at the Energy Research Centre of the Netherlands (ECN) in device manufacturing

indicates that this technology is approaching maturity for market introduction.

The key to efficient light harvesting is the high surface area of the nano-porous TiO₂ film. While a single monolayer of dye molecules on a flat TiO₂ film can typically absorb not more than a negligible amount of incoming light, the nanostructured TiO₂ films provide enough surface area for more than 1000 dye monolayers, allowing for considerable light harvesting over a broad range of the dye absorption spectra. The open porosity of the film allows liquid electrolyte to fill all pores of the film, resulting in the required contact of every dye molecule to both the TiO₂ and the electrolyte phase.

The key problems of dye-sensitised solar cells, similar to those of organic photovoltaics or OPV, amount to low efficiency, low stability and low scalability. The low efficiency is linked to the absorption spectrum of the dyes used in the cells which does not extend far enough into the near infrared region of the optical spectrum and undesirable back-transfer of injected electrons to the redox electrolyte.

5. Nano-ceramics

Over the last decade, nano-ceramics have been revolutionizing conventional materials design in many applications by tailoring their properties through structural control at the atomic scale. Most commercially important nano-ceramic materials are simple metal oxides such as silica and titania (already mentioned), alumina (for propellants, particularly in the space industry), iron oxide (magnetic storage technology), zinc oxide (sunscreens), ceria (fuel catalysts, used in coatings industry) and zirconia (thermal barrier materials and oxygen sensors). Also of increasing importance are mixed metal oxides such as indium tin oxide (ITO used in displays and solar cells), antimony oxide (flame retardant and opacifying agent) and barium titanate (capacitors). In terms of market size of nano-scale ceramic powders, it is worth in the region of \$528 million in 2010. This should increase at a CAGR of 16.4% to reach \$1.2 billion in 2016, equating to 24% market share of the entire ceramic powders market⁵⁵.

Some of the advantages of nano-ceramics include the development of ceramic coatings for greater biocompatibility in medical and dental implants, using ceramic nanoparticles as drug carriers for site specific drug delivery, and improving the quality and perfor-



Figure 9 Wear resistant nano-ceramic coating on a metal component.

mance characteristics of composites (hardness, fracture toughness and wear resistance).

As conventional ceramic materials are hard, brittle and difficult to machine, nano-crystalline ceramics (*e.g.* silicon nitride and silicon carbide) can be easily formed and machined to produce products for the automotive sector, such as ball bearings. They can also be pressed into complex net shapes and sintered at significantly lower temperatures than conventional ceramics, thus reducing energy requirements and increasing manufacturing throughput time.

5.1 Wear resistance and lubrication

Nanostructured coatings offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings. In many applications it is far more cost-effective to apply wear-resistant materials as a coating than to manufacture an entire part out of the ceramic.

For example, the application of nano-composite coatings can extend the life of any steel-based substrate that can benefit from improved wear resistance, resulting in reduced maintenance and material replacement costs. The resulting cost savings in the form of increased productivity will be significant, as will the energy savings and reduced carbon emissions.

5.2 Medical and dentistry

The use of nano-ceramic materials for medical applications includes biomimetic composite materials such as nano-scale calcium phosphate crystallites which are similar to hydroxyapatite (natural

nanocomposites formed in the body, mainly composed of collagen) as they show good biological properties as they have the capacity to form a chemically bonded interface with bone. Nano-ceramic materials are typically used for coatings on implants⁵⁶ (where better wear resistance and biocompatibility are favourable properties) and for bone graft/repair⁵⁷.

Organically modified ceramics (for enhanced dispersion) and nano-ceramic fillers are being utilised in modern dentistry for enhanced biocompatibility and high fracture toughness. Materials such as Ceram.X[™] are being used as a restorative material due to their simplification of the procedure by being easier to handle and work with and offering the patient better restorative treatment with less time spent in treatment.

5.3 Energy-efficient coatings

Progress in the development of energy-efficient coatings on glass has led to the study of ‘smart-glass’ with special functional coatings that can regulate solar energy in response to an external stimulus⁵⁸. Thermochromic smart windows are considered attractive because they are visibly transparent and can intelligently control the amount of solar heat (mainly in the near-infrared region) in response to changes in ambient temperature.

Vanadium oxide⁵⁹ or VO₂ is the most promising thermochromic ceramic candidate material. However, related materials



Figure 10 Showing a VO₂ coated glass panel termed “smart window”
Reference: <http://blogs.rsc.org/ee/>

have not been commercialised due to the expensive production techniques employed, relative stability of the formed product and lifetime.

Presently, gas-phase deposition methods, such as sputtering and chemical vapour deposition (CVD), are the most common methods for the fabrication of VO₂ films onto substrates, yet these methods are still dependent on innovative technologies to meet the requirements of practical large area applications such as glass in the building envelope.

6. Silica aerogel

Aerogels were first made by Kistler⁶⁰ in the early 1930s and can be characterised as materials with the lowest density of any known solid. Aerogels are a heterogeneous class of porous, solid materials which exhibit a number of extreme properties. They are predominantly known for their extremely low densities ranging from 0.0011 to $\sim 0.5 \text{ g cm}^{-3}$. Silica aerogel in particular is only three times heavier than air. Typically aerogels consist of 95–99% air or vacuum in volume.

Essentially, an aerogel is a dry, low density, open-porous, solid framework of a gel with pore diameters in the range of 1 to 100 nm in diameter. As a consequence of the pore size, distribution and porosity, they have very low thermal conductivity ($\lambda \sim 4 \text{ mW/mK}$) if they are used as the filler in a vacuum insulation panel. The reason for low thermal conductivity is that



Figure 11 Image showing a section of aerogel material.

the Knudsen number is >1 and conductive heat transfer through the gas is suppressed. The drying process is critical because the build-up of tensile stresses within the polymeric network, as the vapour-liquid interface recedes, tends to cause it to collapse. This problem has been overcome by performing the drying operation under supercritical conditions (*i.e.* by using liquid CO_2) which suppresses the formation of a liquid vapour interface. Unfortunately, in turn, supercritical drying involves the heating and evacuation of highly flammable solvents such as alcohols which are hazardous at high temperatures (250°C).

An alternative is to replace alcohol with liquid carbon dioxide which has the advantage that only low temperatures (35°C) are required. Aerogels are strong in compression, but their structure results in an inherently brittle material making handling difficult.

A significant advantage of aerogels is that the temperature dependence of their thermal conductivity is lower than that of other materials and, as such, researchers and industrialists are investigating their incorporation into insulation materials for enhanced energy management⁶¹. The biggest disadvantage of aerogels is their extremely high cost due to the need for supercritical drying during the manufacture (approx. $\text{€}2,000/\text{m}^3$). Attempts to produce lower cost aerogel blankets have taken some novel approaches, such as the use of cheap water glass as a silica source and glass wool modified by alumina sol⁶².

Moreover, besides the low thermal conductivity, a high solar energy and daylight transmittance can be achieved by using this material. All these characteristics make monolithic silica aerogel a very interesting material for use in highly energy-efficient windows. The compression strength of aerogel is sufficient to take up the atmospheric pressure if evacuated but the tensile strength is very low, which makes the material fragile, *i.e.* if in contact with liquid water the surface tension in the pores would demolish the aerogel structure.

Therefore, the application of aerogels for window glazing⁶³ requires the aerogel to be protected against water and tensile stress. This can be achieved by placing the aerogel between two layers of glass and apply a gas- and vapour-tight rim seal. When evacuated to a rough vacuum only compression stresses will be present in the aerogel due to the external atmospheric pressure.

7. Quantum dots (QDs)⁶⁴

7.1 QDs in photovoltaics

Recently there has been some interest in utilising materials with tunable bandgaps to maximise the conversion by extending the light harvesting range through the use of intermediate band materials. Intermediate band materials reside within the band gap of a semiconductor and can accept valence band electrons or holes at different energies (corresponding to different wavelengths of light) and help to maximise solar energy harvesting. Examples of an intermediate band material are quantum dots which offer significant advantages.

Quantum dots or nanoparticles are semi-conducting crystals of nanometre (a billionth of a metre) dimensions. They have quantum optical properties that are absent in the bulk material due to the confinement of electron-hole pairs (called excitons) on the particle, in a region of a few nanometres.

Two approaches have been considered based on semiconductor quantum dots and quantum dot arrays that could lead to ultrahigh efficiencies through enhanced photocurrent and are detailed as:

1. Using high energy photons in the solar spectrum to create multiple electron–hole pairs from single photons.
2. Formation of an intermediate band (IB) within the semiconductor bandgap to enable absorption of a second sub-bandgap photon to excite the electrons in the IB to the conduction band.

7.2 QDs in diagnostics

Quantum dots are semiconductor nanoparticles that have unique optical and electrical properties. When exposed to light, these nanoparticles emit distinctly different colours depending on their size (the smaller the quantum dots, the brighter the colour, see Figure 12). Although fluorescent dyes have been used for decades in the human body for biomedical imaging (to track the effects of cancer drugs, for instance), they are often imprecise and only visible for short time periods.

Fluorescent quantum dots can provide an alternative dye as they are brighter, more precise, and have better lifetimes. Quantum dots have the advantage that they can be injected directly into cells or attached to proteins in order to track, tag, or identify specific biomolecules, and these offer ultimate detection sensitivity.

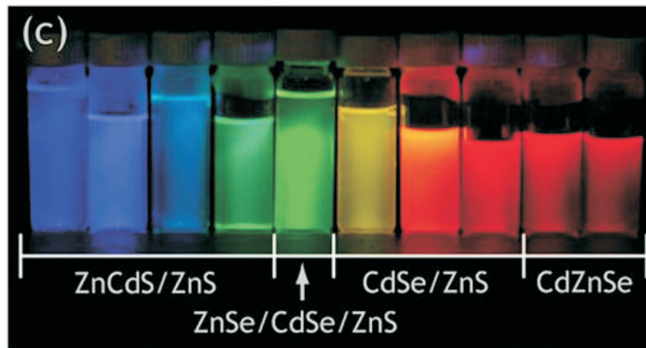


Figure 12 Photograph of the photoluminescence of chloroform solutions of different QD types.

Reference: http://en.wikipedia.org/wiki/File:QD_coloration.jpg

8. Conclusions

The future of nano-materials is very promising with the emergence of novel materials with unique properties that can change the way industry designs and manufactures products from transportation to medical devices. For example the ability to be able to fabricate items which are stronger and lighter will benefit the automotive and aerospace sectors and will help to reduce fuel usage in the coming years where demand for oil will increase.

I have tried to detail the main nano-materials that are currently being used in industry but it has not been possible to describe the entire market for these unique materials. I hope I have provided a snapshot of the current state of the art of the most promising candidates.

As a final note it is worth noting that although nano-materials can offer numerous advantages over their micro-sized counterparts, researchers and industrialists must still spend resource and time examining the safety and environmental implications of using these materials to prove they do more good than harm.

References

1. Maynard, A.D., Aitken, R.J., Butz, T., Colvin, V., Donaldson, K., Oberdorster, G., Philbert, M.A., Ryan, J., Seaton, A., Stone, V., Tinkle, S.S., Tran, L., Walker, N.J. and Warheit, D.B. (2006) *Nature*, **444**, 267–269.
2. Nano Business Alliance.
3. “Nanotechnology Market Forecast to 2013” Report by ResearchandMarkets available at http://www.researchandmarkets.com/research/2012b4/nanotechnology_mar
4. <http://www.nanotechproject.org/>
5. Espulgar, W.V., Nonato, G. and Santos, C. (2011) *Int. J. Scien. Eng. Res.*, **2**(8), 1.
6. Wijnhoven, S.W.P. *et al.* (2009) *Nanotoxicology*, **3**(2), 109–138.
7. <http://www.samsung.com/sg/consumer/learningresources/silvernano/site.html>
8. Gottschalk, F. *et al.* (2010) *Environ. Toxicol. Chem.*, 1036–1048.
9. *NanoSilver Markets 2011*, Nanomarkets, Glen Allen, VA 23058.
10. Maynard, A. (2006) *Nanotechnology: A research strategy for addressing risk*. PEN 3, Washington: Woodrow Wilson International Centre for Scholars.
11. “*Silver Soils*”, Birch, H. (2012) *Chem. World*, February 2012, 36–39.
12. Benn, T.M. and Westerhoff, P. (2008). *Environ. Sci. Technol.*, **42**, 4133–4139; Erratum, **42**, 7025–7026.
13. Vigneshwaran, N., Kathe, A.A., Varadarajan, P.V., Nachane, R.P. and Balasubramanya, R.H.J. (2007) *Nanosci. Nanotechnol.*, **7**, 1893, 1897.
14. <http://www.clip-fp7.eu/>
15. <http://www.hiflexopv.eu/index.php>
16. *Silver-Based Transparent Conductor Markets–2011*. NanoMarkets LC.
17. <http://www.cnanotech.com/>
18. Dillon, A.C. (2010) *Chem. Rev.*, **110**(11), 6856–6872.
19. Benard, P. *et al.* (2007) *J. Alloys Compounds*, **446–447**, 380–384.
20. <http://www.igm.uni-stuttgart.de/forschung/arbeitsgebiete/cnt/index.en.html>
21. <http://nanotechnologytoday.blogspot.com/2011/08/newly-synthesized-polymer-fitted-with.html>
22. Zanello, L.P., Zhao, B., Hu, H. and Haddon, R.C. (2006) *Nano Lett.*, **6**(3), 562–567.
23. <http://www.wired.com/medtech/health/news/2005/08/68512>
24. http://www.eurekalert.org/pub_releases/2007-08/rpi-bbs080907.php
25. <http://www.sciencedaily.com/releases/2007/07/070719011151.htm>
26. Postma, H.W.Ch., Teepen, T., Yao, Z., Grifoni, M. and Dekker, C. (2001) *Science*, **293**(5527), 76–79.
27. *Frost & Sullivan’s study on potential market for carbon nanomaterials applications*, February 2011.
28. Geim, A.K. and Novoselov, K.S. (2007) *Nature Mater.*, **6**, 183–191.
29. <http://www.bbc.co.uk/news/science-environment-16362899>
30. <http://www.aps.org/publications/apsnews/200910/physicshistory.cfm>
31. http://www.nsf.gov/news/news_summ.jsp?cntn_id=111341&org=NSF&from=news
32. <http://www.azonano.com/news.aspx?newsID=10592>
33. Wang, X., Zhi, L. and Mullen, K. (2008) *Nano Lett.*, **8**(1), 323–327.
34. <http://www.sciencedaily.com/releases/2010/07/100723095430.htm>
35. Ruoff, R.S. *et al.* (2008) *Nano Lett.*, **8**(10), 3498–3502.

36. Xu, M., Fujita, D. and Hanagata, N. (2009) *Small*, **5**(23), 2638–2649.
37. Fan, C. *et al.* (2010) *ACS Nano*, **4**(7), 4317–4323.
38. [http://vacuumcoating.info/nano-TiO₂-for-dsscs-optimization-production-and-market-2](http://vacuumcoating.info/nano-TiO2-for-dsscs-optimization-production-and-market-2)
39. Fujishima, A. and Honda, K. (1972) *Nature*, **238**, 37–38.
40. <http://www.prlog.org/10105760-self-cleaning-nanotechnology-solution-for-todays-pollution.html>
41. Wang, J. *et al.* (2008) *Environ. Prog.*, **27**(2), 242–249.
42. www.siplast-international.com
43. PICADA EC funded project.
44. www.Stadlerformusa.com
45. ObservatoryNANO paper Briefing No. 10 *Chemistry & materials–applications of photocatalysis*.
46. Kemp, T.J. and McIntyre, R.A. (2006) *Polymer degradation and stability journal*, **91**(1), 165–194.
47. Then, D. and Weinhold, P. *Farbe Lack*, **112**(4), 39–43.
48. STO Informationen 2011: http://www.sto.de/97421_DE-StoColor_Climasan-Kisch.htm
49. www.oxonica.com
50. *A review of the scientific literature on the safety of nanoparticulate titanium dioxide or zinc oxide in sunscreens* (2009) Report commissioned by Australian Government, Department of Health and Ageing.
51. http://www.chem-mats.mmu.ac.uk/home_page.htm
52. McIntyre, R.A. (2010) *Sci. Prog.*, **94**(4), 361–392.
53. O'Regan, B. and Grätzel, M. (1991) *Nature*, **335**, 737.
54. Grätzel, M. (2001) *Nature*, **414**, 338–344.
55. *Advanced ceramics and nanoceramic powders* (2011) BCC Research report.
56. Ma, J., Wong, H., Kong, L.B. and Peng, K.W. (2003) *Nanotechnology*, **14**, 619–623.
57. <http://www.emdt.co.uk/article/new-developments-bioceramic-implant-materials>
58. Gao, Y. *et al.* (2012) Nanoceramic VO₂ thermochromic smartglass: A review on progress in solution processing, Nano Energy.
59. Mlyuka, N.R. *et al.* (2009) *Solar Energy Mater. Solar Cells*, **93**, 1685–1687.
60. <http://eetd.lbl.gov/ecs/aerogels/kistler-early.html>
61. <http://www.aerowolle.de/>,
62. Chandradass, J., Sung Kang and Dong-sik Bae (2008) *J. Non-Crystall. Solids*, **354**, 4115–4119.
63. <http://www.airglass.se/>
64. Luque, A., Marti, A. and Nozik, A.J. (2007) *MRS Bull.*, **32**, 236–241.