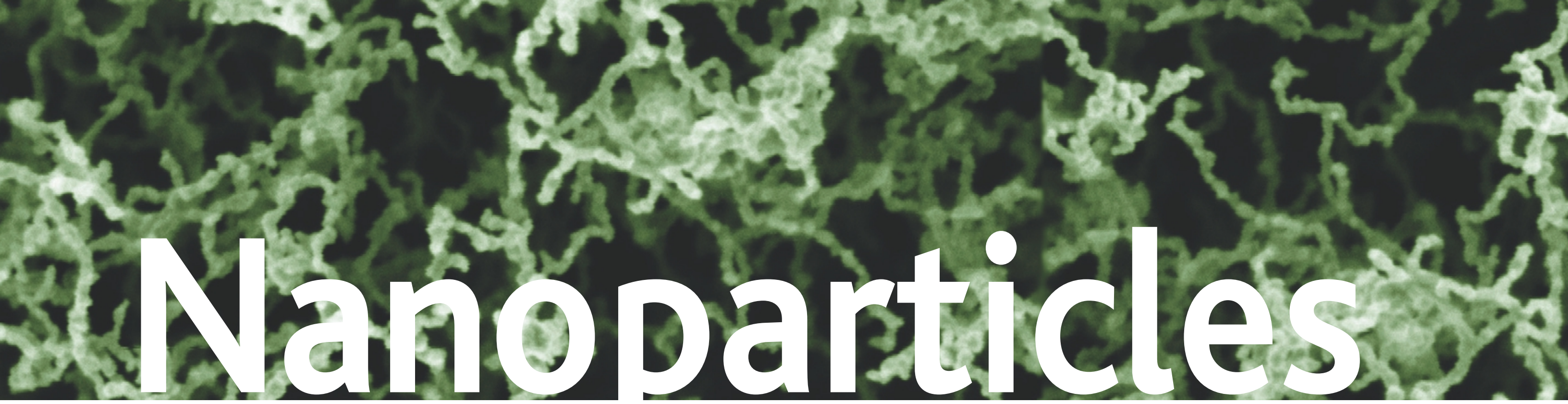

Nanoparticles as building blocks?

by Michael J. Pitkethly

Nanomaterials and, in particular, nanoparticles are at the forefront of the nanotechnology wave. Over recent years there has been a rapid increase in the range of available nanomaterials and the number of companies that supply them. A variety of production techniques is used, each with benefits and drawbacks, but these are being improved all the time. The current and potential applications for nanoparticles are growing and cover an extremely broad range of markets. Analysts have estimated that the size of the market will be $900 million in 2005 and $11 billion in 2010. This is causing a great deal of interest among companies, but there are still a number of hurdles to be overcome before the potential of nanoparticles is fully realized.

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The concept of the nanotechnology revolution has taken a grip on not only the scientific community but, increasingly, on the wider public as more and more articles appear that discuss what nanotechnology might provide in the future. But nanotechnology is not new and, although the term was first coined in the 1960s, it can be argued that material scientists and chemists have been working in nanotechnology since their disciplines started. In fact, nanoparticles were used over 2000 years ago in Roman glass, where clusters of Au nanoparticles were used to generate vivid colours.

The real move towards the use of nanoparticles did not occur until the early 20th century with the production of carbon black and, subsequently, fumed silica in the 1940s. However, it has only been with the development of high-speed computing, and hence modeling; advanced characterization techniques, such as atomic force microscopy and scanning tunneling microscopy; and synthesis routes, such as sol-gel processing, that it has been possible to design nanomaterials.

With these materials have come significant improvements in the performance of polymeric materials. However, this was achieved through an empirical approach – the materials were not designed but discovered.

It is this differentiation that distinguishes modern nanotechnology from previous activities in materials science and chemistry. As a recent European Union report[1] stated, “Nanotechnology is expected to create new materials with totally new, problem-solving properties.”

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Table 1 *Results of a survey of experts asked to define nanotechnology*[2].

How would you define nanotechnology?	(% of respondents agreeing with each definition)
Technology that works with elements up to 100 nm in size	45
Technology that works with elements on a sub-micron level	17
Technology that operates under new laws of physics	5
Technology that operates at the level of atoms and molecules	23
Other/no response	10

What are nanoparticles?

Although nanotechnology is widely talked about, there is little consensus about where the nano domain begins. In a recent report[2] published by 3i in association with the Economist Intelligence Unit and the Institute of Nanotechnology, around one hundred nanotechnology experts were surveyed and, as can be seen from Table 1, gave widely differing views on the definition.

For the purposes of this article, I have arbitrarily taken nanoparticles to be discrete particles that have a diameter of 250 nm or less. Trying to convey what this means in terms of scale has lead to some awe-inspiring statistics. For example, 2 g of 100 nm Al nanoparticles contains a sufficient number of particles to give every human on the planet 300 000 particles each, while nanosilicates have an interfacial area that is equivalent to cramming a soccer field within a raindrop. This still leaves a hugely diverse range of materials: polymers, metals, and ceramics. Nanoparticles can also be formed in a wide number of morphologies, from spheres through flakes and platelets to dendritic structures. Fig. 1 shows three examples.

Why are nanoparticles interesting?

Just because these materials can be made into very small particles does not immediately mean that they have any practical use. However, the fact that these materials can be made at this scale gives them the potential to exhibit some very interesting properties. Materials with particle sizes on the nanoscale between 1 nm and 250 nm lie in the domain between the quantum effects of atoms and molecules and the bulk properties of materials. It is, therefore, in this no-man's land that many physical properties of materials are controlled by phenomena that have critical dimensions on the nanoscale.

The ability to fabricate and control the structure of nanoparticles allows the scientist and engineer to influence the resulting properties and, ultimately, design materials to give the desired properties. There is an extremely wide range of applications where the physical size of the particle can provide enhanced properties that are of benefit, for example: the small size allows finer polishing and smoother surfaces; where the grain size is too small for dislocations, high-strength, high-hardness metals can be made; and the high

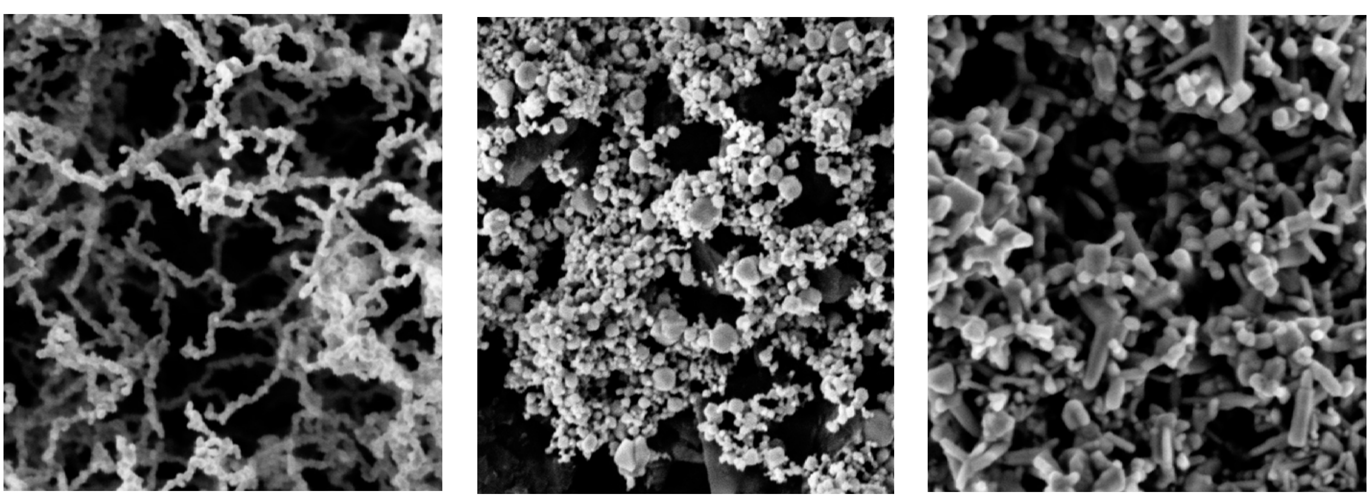

Fig. 1 Micrographs showing three examples of nanoparticle morphologies.

Table 2 *Characteristic lengths in solid-state science model, based on* [3].

Field	Property	Scale length
Electronic	Electronic wavelength Inelastic mean free path Tunneling	10-100 nm 1-100 nm 1-10 nm
Magnetic	Domain wall Spin-flip scattering length	10-100 nm 1-100 nm
Optic	Quantum well Evanescent wave decay length Metallic skin depth	1-100 nm 10-100 nm 10-100 nm
Superconductivity	Cooper pair coherence length Meissner penetration depth	0.1-100 nm 1-100 nm
Mechanics	Dislocation interaction Grain boundaries Crack tip radii Nucleation/growth defect Surface corrugation	1-1000 nm 1-10 nm 1-100 nm 0.1-10 nm 1-10 nm
Catalysis	Surface topology	1-10 nm
Supramolecules	Kuhn length Secondary structure Tertiary structure	1-100 nm 1-10 nm 10-1000 nm
Immunology	Molecular recognition	1-10 nm

surface area enables the production of more efficient catalysts and more energetic materials (Table 2).

How are they made?

The manufacture of nanoparticles can be achieved through a wide variety of different routes. Some have been in existence for many years; others are far more recent.

In essence, there are four generic routes to make nanoparticles: wet chemical; mechanical; form-in-place; and gas phase synthesis. It is worth exploring each of these, as the resultant materials can have significantly different properties, depending on the fabrication route that is chosen. Also, some routes are more suited to the fabrication of certain classes of materials than others.

- ***Wet chemical processes*** These include colloidal chemistry, hydrothermal methods, sol-gels, and other precipitation processes. Essentially, solutions of different ions are mixed in well defined quantities and under controlled conditions of heat, temperature, and pressure to promote the formation of insoluble compounds that precipitate out of the solution. These precipitates are then collected through filtering and/or spray drying to produce a dry powder. The advantage of these wet chemical processes is that a large variety of compounds can be fabricated, including inorganics and organics, as well as some metals, in essentially cheap equipment and significant quantities. Another important factor is the ability to control particle size closely and to produce highly monodisperse materials. However, there are limitations on the range of compounds that are feasible: bound water molecules can be a problem and, for sol-gel processing in particular, yields can be quite low. So, for bulk production, large quantities of starting materials may be required, which could be expensive.
- ***Mechanical processes*** These include grinding, milling, and mechanical alloying techniques. Provided that one can produce a coarse powder as a feedstock, these processes use the age-old technique of physically pounding coarse powders into finer and finer powders, similar to flour mills. Today, the most common processes are either planetary or rotating ball mills. The advantages of these techniques are that they are simple, require low-cost equipment, and, provided that a coarse feedstock powder can be made, many materials are capable of being processed. However, there can be difficulties, such as agglomeration of the powders, broad particle size distributions, contamination from the process equipment itself, and the achievement of very fine particle sizes. Commonly, these methods are used for inorganics and metals, but not organic materials.
- ***Form-in-place processes*** These include lithography, vacuum deposition (physical vapor deposition and chemical vapor deposition), and spray coatings. These processes are more geared to the production of nanostructured layers and coatings, but can be used to fabricate nanoparticles by scraping the deposits from the collector. However, they tend to be quite inefficient and are generally not used for the fabrication of dry powders, although some companies are beginning to exploit these processes.
- ***Gas phase synthesis*** This includes flame pyrolysis, electroexplosion, laser ablation, high-temperature evaporation, and plasma synthesis techniques. Flame pyrolysis has been used for many years in the fabrication of simple materials such as carbon black and fumed silica, and is being used in the fabrication of many other compounds. Laser ablation is capable of making almost any nanomaterial, since it utilizes a mix of physical erosion and evaporation, but the production rates are extremely slow and most suited to research use. Both RF (radio frequency) and DC (direct current) plasmas are being used successfully to make a wide range of materials. The heat source is very clean and controllable, and the temperatures

in the plasmas can reach in excess of 9000°C, which means that even highly refractory materials can be processed. However, this also means that these methods are not suitable for processing organic materials.

As can be seen, a multitude of different methods can be employed to manufacture nanoparticles. All of them are being used commercially and each has its own merits and drawbacks. However, it is difficult to generalize as to which methods will dominate, since it is the demand for specific materials that will drive the adoption of a particular manufacturing process.

The market for nanoparticles

Adding particulate materials to a matrix has been a common technique for changing the properties of materials almost since the first synthetic materials were developed. However, the size of the additives was usually larger than the nanoscale. The first industrial production of a nanomaterial occurred with the production of carbon black early in the 20th century and, subsequently, fumed silica in the 1940s. These materials are still produced and used in vast quantities, and some well known companies such as Degussa and Cabot base their business on these materials.

However, it was not until the latter half of the last century that the scientific understanding of materials incorporating ultrafine particulates really developed and it was realized that significant improvements to properties could be achieved. During the 1960s, 1970s, and early-1980s there was a gradual expansion as large multinational companies established subsidiaries. But the real burst in the commercialization of nanoparticle production has occurred over the last ten years or so.

Where the data[4-10] are available, one can see this rapid growth in Fig. 2. The number of companies doubled in the 1990s, and the current rate of formation looks set to match if not exceed this in the coming years. The vast majority of this recent growth has come through the establishment of new, small start-up companies that have been spun-out of universities, government laboratories, or set up by entrepreneurs. Currently, it is estimated that over half of all nanomaterial companies fall into this category. This phenomenon has been fueled, to a certain extent, by the growth in venture capital as a source of funding[11], particularly in the US where a significant proportion of these companies are situated.

Although accurate data is difficult to obtain, there are probably in excess of 320 companies producing nanomaterials in various forms in the world today, of which about 200 are nanoparticle producers. The split between types of material is shown in Table 3.

However, not all these companies sell the nanomaterials that they make and many are geared up to generate and license intellectual property based on the use of their nanomaterials. In addition to these companies, there are others that make nanomaterials for use in their own products.

The question that arises is, what are the markets for nanomaterials that have driven this rapid growth in the number of companies in the field? To a certain extent, the markets already exist. There are many applications where the possibilities of re-engineering existing materials down to the nanoscale can improve performance and hence open up new products. Examples include: pyrotechnics and explosives, where nanoscale Al provides a greater energy release rate;

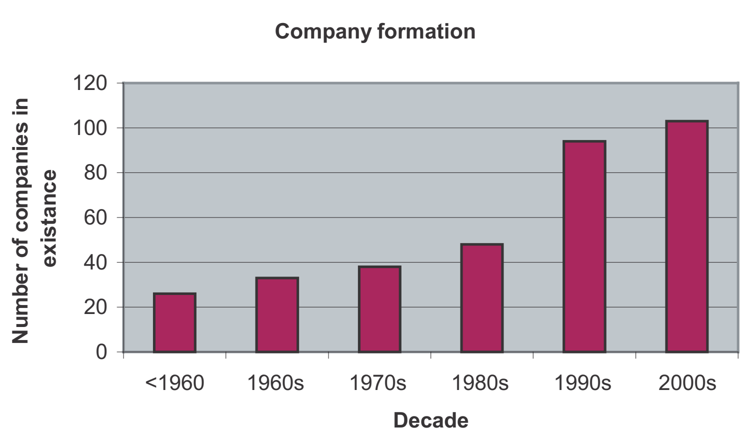

Fig. 2 The growth in the number of nanomaterials companies[4-6].

Table 3 *The primary material product type and market focus of nanomaterials companies*[4-6].

Type of product	Number
Nanoparticles	160
Nanotubes	55
Nanoporous materials	22
Fullerenes	21
Quantum dots	19
Nanostructured materials	16
Nanofibers	9
Nanocapsules	8
Nanowires	6
Dendrimers	5
Total	321
Primary market	**Focus %**
Medical/pharma	30%
Chemicals and advanced materials	29%
ITC	21%
Energy	10%
Automotive	5%
Aerospace	2%
Textiles	2%
Agriculture	1%

lapping and polishing compounds, where track dimensions on Si chips are approaching 150 nm and the polishing media need to be significantly less than this to keep defects small compared to the track dimensions; and magnetic recording media, where higher-density storage is driven by finer particle and grain sizes as storage media approach terabyte capacities.

This type of evolutionary progression to nanoscale materials will continue as the benefits are realized. However, the growth in interest cannot be explained entirely by such evolutionary development. As more research effort is directed towards investigating nanoscale materials, the ability to make a step-change in performance is being found all the time. This is opening up totally new applications and the possibility of making products that have been hypothesized for many years, such as targeted drug delivery methods, new optoelectronic devices, and smaller, more efficient energy devices. This has given rise to some widely differing estimates of the size of the nanotechnology market and the nanomaterials subset of this. Nanotechnology as a whole is estimated to represent a market of $11 trillion by 2010, with nanomaterials growing from $490 million today to $900 million in 2005 and $11 billion in 2010[1,6,12]. However, the impact of nanomaterials will extend well beyond the immediate value of the materials themselves.

One estimate has been made that nanostructured materials and processes could have an impact of over $340 billion by 2010[13].

Looking at the major markets for functional nanomaterials today, the largest by volume are automotive catalysts, chemical mechanical planarization (CMP), magnetic recording media, and sunscreens, at 11 500 tonnes, 9400 tonnes, 3100 tonnes, and 1500 tonnes, respectively[4]. However, the value of the market is dependent upon the materials that are used, as well as the actual use. This means that although the market for catalysts has a much larger volume than that for sunscreens, the value is very similar. The extreme end of the spectrum is biodetection and labeling materials, where a small amount goes a long way and, although only a few kilos are sold, the price per kilo is many orders of magnitude greater than that for CMP materials, for example.

There is a myriad of applications utilizing nanoparticles either on the market or under development, and Table 4 identifies some of the key applications that currently use nanoparticles, as well as others being developed, which rely on nanoparticles. The scope and number of applications for nanoparticles[14-19] continues to grow, and companies are finding more and more uses for these materials.

What does the future hold for nanoparticles and their manufacturers?

The use of nanoparticles is set to escalate and the market has the potential to increase dramatically over the next ten years as more uses for these materials are developed and commercialized.

A major impact will be in the medical and pharmaceutical markets as new treatments relying on nanoparticles obtain licenses for use. However, there are many other applications where the time-to-market is considerably less than for the pharmaceutical and medical sector, particularly for consumer goods. As mentioned above, there should be a market expansion from $490 million today to $900 million in 2005 and $11 billion in 2010. But there are still many challenges facing nanomaterials companies that need to be overcome before this potential can be fully realized, including:

- How to produce materials in volume production at viable prices – many current techniques cannot scale-up sufficiently to produce the cost reductions required to target volume markets.

Table 4 *A selection of current and future applications utilizing nanoparticles.*

Area	Under development	On the market	Well established
Power/Energy	Nanocrystalline Ni and metal hydrides for batteries Dye-sensitized solar cells using TiO_2 Hydrogen storage using metal hydrides Improved anode and cathode materials for solid oxide fuel cells Thermal control fluids using Cu	Environmental catalysts, ceria in diesel	Automotive catalysts
Healthcare/medical	Nanocrystalline drugs for easier absorption Inhalable insulin Nanospheres for inhaling drugs currently injected using biocompatible Si Bone growth promoters Virus detection using quantum dots Anticancer treatments Coatings for implants such as hydroxyapatite	Sunscreens using ZnO and TiO_2 Molecular tagging: quantum dots, CdSe Carriers for drugs with low water solubility	Ag antibacterial wound dressings, ZnO fungicide Au for biolabeling and detection MRI contrast agents using super-paramagnetic iron oxide
Engineering	Cutting tool bits: WC, TaC, TIC, Co Spark plugs using nanoscale metal and ceramic powders Nanoporous silica based on aerogels for high-efficiency insulators Controlled delivery of herbicides and pesticides Chemical sensors Molecular sieves	Abrasion-resistant coatings using alumina, $Y\text{-}Zr_2O_3$ Nanoclay-reinforced polymer composites Lubricant/hydraulic additives: Cu MoS_2 Pigments Self-cleaning glass using TiO_2 Propellants using Al	Structural enhancement of polymers and composites Thermal spray coatings based on TiO_2, TiC-Co, etc. Inks: conducting, magnetic, etc. using metal powders
Consumer goods		Anti-counterfeit devices	Packaging using silicates Ski wax White goods Glass coatings for anti-glare, anti-misting mirrors using TiO_2 Sports goods: tennis balls, rackets using nanoclays Water- and stain-repellent textiles
Environmental		Alumina fibers for water treatment Self-cleaning glass using TiO_2 based nanostructured coatings Photo-catalyst water treatments using TiO_2 Anti-reflection coatings	Tiles coated using alumina and others Sanitary ware Soil remediation using Fe
Electronics	Nanoscale magnetic particles for high-density data storage EMI shielding using conducting and magnetic materials Electronic circuits, NRAM, using Cu, Al Display technologies including field-emission devices using conducting oxides	Ferro-fluids using magnetic materials Optoelectonics devices such as switches using rare-earth-doped ceramics Conductive coatings and fabrics using rare-earth-doped ceramics	CMP alumina, ceria Coatings and joining materials for optical fibers based in Si

- How to supply the materials in a form suitable for inclusion in manufacturing processes – understanding the surface chemistry and how particles can be dispersed in a wide variety of media will be key to the adoption of many materials.
- Consistency and reliability in volume production –

tolerances on size and composition can be achieved reliably for simple compounds such as binary oxides and for more complex materials in small batch production, but doing this for complex materials in volume manufacture is not so easy.

- Characterization – it is possible to characterize materials to a great extent. However, many of the techniques are appropriate for the research laboratory, but not for the production environment. What is required are rapid, bulk, and, preferably, on-line techniques to monitor properties such as particle size distribution.
- The need to focus in a very broad market will determine the survival of many nanomaterials companies in the short term as they start to build revenues.
- Adding and retaining value will be key to the longer-term viability of companies as volumes and the pressure to reduce prices and margins increase. The approach being adopted by many is that of securing intellectual property to provide a longer-term income stream.
- Health, safety, and environment – the profile of nanotechnology has increased in recent months, with a focus on the potential long-term effects of nanotechnology and, more immediately, of nanomaterials on humans and the environment[20-22]. As with any high-profile technology, questions will be asked, but some nanomaterials have been with us for many years without causing concerns. However, it is very important to the success of this industry that any concerns are addressed. The key aspect is: are there any detrimental effects, over and above those already identified for the materials, that occur purely from the fact that these materials are in the nano-form? It is also highly unlikely that nanomaterials will be used without being incorporated into some other media, such as a composite or liquid. Research is under way into the effects of nanomaterials and it is difficult to draw any firm conclusions to date, but there is evidence that there may be positive benefits from these types of materials, both for humans and the environment[22,23].

Conclusion

Nanoparticles and nanomaterials represent an evolving technology that has the potential to have an impact on an incredibly wide number of industries and markets. The challenge for nanomaterials companies in seeing this potential come to fruition will be to provide materials in volume, with the desired quality, in an economic manner. NT

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