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# Nanomaterials for practical functional uses

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**Abstract**

The term nanotechnology, which enjoys wide public use, is a concept that covers a wide range of developments in the field of nanoscale electronic components, along with its decades-old application in nanocarbon-black particles or silicates manufactured using the sol–gel process. When we refer to nanotechnology today, the term is limited to dealing with particles or assemblies whose dimensions range in size from a few nanometres up to around 100 nm. Intensive development work is now being carried out in new fields in many industrial and university research facilities, with the help of nanoscale particles or subassemblies. Along with the already familiar items, this applications-oriented research has covered such new developments as carbon nanotubes or electronic circuits. All materials are composed of grains, which consist of many atoms. Grains of conventional materials vary in size from tens of microns to one or more millimetres. Nanomaterials are no longer merely a laboratory curiosity and have now reached the stage of commercialization being lead by activity, often government supported, in the USA, UK, Japan, Singapore, Malaysia, Taiwan, Korea, Germany and in recent years China and Australia. This is the opening of a whole new science in some respects, and the usefulness to our everyday lives will become increasingly apparent. The potential of nanominerals, as just one sector of nanomaterials technology have some very real and useful outcomes:

- Production of materials and products with new properties.
- Contribution to solutions of environmental problems.
- Improvement of existing technologies and development of new applications.
- Optimisation of primary conditions for practical applications.

These materials are revolutionizing the functionality of material systems. Due to the materials very small size, they have some remarkable, and in some cases, novel properties. Significant enhancement of optical, mechanical, electrical, structural and magnetic properties are commonly found with these materials. Some key attributes include:

- Grain size on the order of $10^{-9}$ m (1–100 nm).
- Extremely large specific surface area.
- Manifest fascinating and useful properties.
- Structural and non-structural applications.
- Stronger, more ductile materials.
- Chemically very active materials.

*Production of nanomaterials*. There are various widely known methods to produce nanomaterials other than by direct atom manipulation. In *plasma arcing*, the very high temperatures associated with the formation of an arc or plasma is used to effectively separate the atomic species of feedstock, which quickly recombine outside the plasma to form nanosized particles, which may have novel compositions. In the case of *chemical vapour deposition*, feed gases are reacted in a chamber and the resulting species attracted to a substrate. Once again the reaction products can be controlled and not only in terms of composition but also in terms of how they are deposited. The substrate effectively provides a template from where the deposited coating can grow in a very well controlled manner. *Electro-deposition* involves a similar process; however the controlled coating is deposited from solution by the application of an electric field. *Sol–gel synthesis* uses chemical means to produce intimately mixed compounds that are hydrolysed into gels. The gels can be deposited on any surface and shape at well controlled thicknesses and on subsequent heating, decompose

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to leave a thin layer of the desired coating. This technique is well suited to coating large surface areas with very well defined nanometre scale compounds. In *high intensity ball milling*, as the name suggested, high impact collisions are used to reduce macrocrystalline materials down into nano-crystalline structures without chemical change. A relatively new technique termed Mechanochemical Processing (MCP) technology, being developed by Advanced Nanotechnologies based in Perth, is a novel, solid-state process for the manufacture of a wide range of nanopowders. Dry milling is used to induce chemical reactions through ball-powder collisions that result in nanoparticles formed within a salt matrix. Particle size is defined by the chemistry of the reactant mix, milling and heat treatment conditions. Particle agglomeration is minimized by the salt matrix, which is then removed by a simple washing procedure.


*Keywords:* Nanoparticles; Nanomaterials; Nanominerals; Nanotechnology; Plasma arcing; Chemical vapour deposition; Electro-deposition; Sol–gel synthesis

## 1. Introduction

Nanotechnology is a word mentioned in the press virtually everyday. With nanotechnology it is possible to create materials from building blocks the size of atom clusters, which exhibit enhanced electronic, magnetic, optical and chemical properties. The enhanced properties extend far beyond and offer far greater potential than just the inherent 'economy of geometry' of miniaturization. Nanomaterials are powders and materials optimised at the nanoscale (1–100 nm). At the nanosize the theories of classical and quantum mechanics are no longer valid and a rich variety of unexpected properties are possible. New applications for materials can be created with novel or significantly enhanced properties. Such properties include transparency, hydrophobicity, photoluminescence, toughness and hardness, chemical sensing and bioavailability. Products produced from these materials exhibit unique properties and have a wide range of high value commercial applications in rapidly expanding markets. The key characteristics demanded of nanoparticles to capture high value markets include: small particle size, narrow size distribution, low levels of agglomeration and high dispersibility.

The strong interest in nanotechnology stems from the concept that structures may be designed and built that exhibit superior electrical, mechanical, chemical or optical properties compared to the materials we know today. Traditionally, products are constructed by etching away at materials to make them smaller, while nanotechnology takes something at the molecular scale and builds by adding one atom or molecule at a time. Nanoparticles are produced in two main ways. The traditional way of producing tiny particles has been "top-down" referring to the reduction through attrition and various methods of communition in the traditional sense. During the past few years and increasingly, methods of production using "bottom up" techniques are being increasingly utilised. Research into self-assembling, smart materials with many and varied applications are producing performance potential greater than we have seen previously.

The unique properties of nanomaterials and structures on the nanometer scale have sparked the attention of materials developers. Incremental shifts in product performance using these materials for example, as fillers in plastics, as coatings on surfaces, and as UV-protectants in cosmetics are already occurring. The technology holds more promise for the future, though, and is expected to bring more disruptive changes to both products and markets.

Nanotechnology is entering many industry sectors including medicine, plastics, energy, electronics, and aerospace. Carbon nanotubes have been demonstrated to be 100 times stronger than steel, yet have only one-sixth the weight. They can be made in structures that are as electrically conductive as copper or structures that act as semiconductors. The array of nanomaterial is very wide so a selection follows but is by no means exhaustive. New applications for nanomaterials are being worked on in hundreds of laboratories around the globe. Some will find useful applications that will revolutionise much of how we will live in the years ahead.

## 2. Examples of where nanotechnology is becoming used

### 2.1. Functional polymer fillers

The need for plastic products to improve their basic viscoplastic characteristics, in order to allow them to compete with traditional materials, is being fulfilled by the development of composite materials. This is being done by incorporating such inorganic fillers as glass fibre, talcum or kaolin. Mineral-based reinforcement additives in dosage quantities of between about 20 and 60% are mixed into these polymers to give them their required characteristics. A disadvantage is the associated increase in the density of these composite materials. At the end of the 1980s, Toyota developed a totally new concept, with the help of nanoclays, for optimising the characteristics of plastics destined for use in the car industry. This development relies on bentonite, a layered clay material that has been in industrial use for over a century. Functional polymers are far more versatile than classic construction materials. Besides improving the performance of systems in medical technology, telecommunication or optoelectronic, functional polymers are also found in everyday products like paint and concrete. Traditionally functional polymers are produced from special monomers or by carefully controlling the polymer architecture. Even tiny amounts of functional polymers can have a dramatic impact. At Degussa, for instance, such systems are used to disperse pigments or to agglomerate extremely fine particles. The crucial factor in these systems is the specific interaction between the macro-molecules and the particles at the interface. Consequently, properties like flow behaviour of concrete can be significantly improved by adding small amounts of special comb like polymers. These polymers are highly effective because of the well-dosed coordination of the functional groups of the lateral chains responsible for regulating viscosity. By covering the surface of the cement

Table 1
Comparison of the main reinforcement additives and their respective parameters

| Additive | Morphology | Particle dim. (μm) | L/D | Density (g/cm$^3$) |
|---|---|---|---|---|
| Glass sphere | Spherical | Ø 2.5 | 1 | 2.5 |
| Calcium carbonate | Cube | 0.2–10 | 1 | 1.7 |
| Kaolin | Lamella | 0.5 × 5 | 3–10 | 2.6 |
| Talc | Lamella | 0.5 × 5 | 3–10 | 2.8 |
| Glass fibre | Fibre | 10 × 200 | 20 | 2.5 |
| Carbon fibre | Fibre | 7 × 200 | 30 | 1.6 |
| Montmorillonite | Lamella | 0.001 × 0.2 | 100–500 | 2.4 |

*Source*: Sud Chemie.

grains the macro-molecules prevent premature fusion of the particles (Tables 1 and 2).

### 2.2. Nanowire and nanotube arrays for EMI shielding

Composite materials with superior thermal, electrical and mechanical properties, metal and semiconductor nanowires as tags for bioassays, etc. Carbon nanotubes, seamless tubes of graphite sheets of nanosized diameter, include single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT). In some cases, the ends of the nanotubes are open, whereas in other cases they are closed off with full fullerene caps. Depending on sheet direction and diameter a nanotube may be either metallic or semi-conducting. Compared with all other kinds of natural materials, carbon nanotubes have the highest theoretical strength, although their specific gravity is only one-sixth of steel. Carbon nanotubes provide special advantages in shielding and absorbing electromagnetic radiation, field emission, thermal conductivity, hydrogen storage, adsorption, catalyzing, etc.

### 2.3. Chemical gas sensing

Robust low power microsensors and microsensor arrays with high sensitivity and selectivity, such as humidity sensors, solid-state resistive sensors, combustible gas sensors, etc.

### 2.4. Ceramic MEMS

2D and 3D microcomponents and microelectromechanical devices for harsh application environments, high aspect ratio MEMS, microchannel plates, etc.

### 2.5. Energy conversion

Photo-voltaics, radiation detection, electroluminescent and lasing materials and devices, components for mesoscopic energy sources, etc.

### 2.6. Electronics and related fields

Scanning probes and scanning microscopy standards, storage media and Terabit memory, flat panel displays, vacuum microelectronics for harsh environments, field emission cathodes, photonic band gap materials and devices, etc.

### 2.7. Marine anti-fouling

Due to the small size of the nanomaterials, the particles are held in the coating lattice and are not readily leached out of the coating by the marine environment, while slowly releasing ions to help provide longer-term anti-fouling character. The need for longevity of antimicrobial activity in marine environments is widely recognized.

### 2.8. Textile fibres

Nanoparticles have been incorporated into products such as nylon, polypropylene and other polymers to provide long-term antimicrobial character even in harsh environments and after extensive thermal cycling. The need for minimizing or eliminating microbial growth on a variety of textile-based substrates has become a major challenge.

Nanosized zinc oxide and copper oxide due to the small particle size can be readily incorporated into synthetic fibres such as nylon prior to extrusion through spinnerets to impart antimicro-

Table 2
Nanocomposite properties indicating dramatically improved properties

| Polymer | Nanofiller (%) | Module; of elasticity (MPa) | Elongation at break (%) | Yield stress (MPa) | $H_2O$ permeation (120 μm film) (g/m$^2$/d) | HDT-A (°C) |
|---|---|---|---|---|---|---|
| Properties of polyamid 6 and 6.6 nanocomposites | | | | | | |
| PA 6 | 0 | 3400 | 90 | 83 | 15 | 80 |
| PA 6 | 3% Nanofil 919 | 4100 | 70 | 90 | 5 | 105 |
| PA 6 | 5% Nanofil 919 | 4500 | 5 | 94 | 6 | 110 |
| PA 6.6 | 0 | 3000 | 50 | 78 | 4 | 85 |
| PA 6.6 | 3% Nanofil 919 | 3700 | 5 | 88 | 3,3 | 95 |
| PA 6.6 | 5% Nanofil 919 | 4100 | 2 | 86 | 3,0 | 100 |

Processing—Twin Screw Extruder, ZSK25, Coperion L: D 40. Temperature—PA 6: 230–250 °C; PA 6.6: 270–290 °C, 300 rpm, 5 kg/h. *Source*: Sud Chemie.

bial activity with minimal effects on colour and clarity, surface gloss, physical properties and melt flow properties. Applications include carpet fibres, water filters of various types, fabrics for use in healthcare facilities and various institutions, apparel, home furnishings and a variety other end uses.

### 2.9. Permanent coatings

Long-term antimicrobial activity can be imparted in many coating formulations through the incorporation of nanomaterials. The desire for permanent coatings to impart long-term antimicrobial or bacteria-stat properties to coated products has been expressed in a variety of industries, including healthcare, industrial and institutional cleaning, food processing, food service, and general paints and coatings. NanoTek® zinc oxide, copper oxide or doped zinc oxides can be fully dispersed into a wide variety of coating formulations, including urethanes, acrylics and vinyl acetates and have shown utility in UV curable and thermosetting coatings as well as in water-based coating systems.

### 2.10. Catalysts

The use of nanomaterials based on rare earth metal oxides allows for the preparation of thinner active layers, which can mean less precious metal usage. These nanomaterials also allow for the preparation of higher solids dispersions that are very stable, minimizing the number of coating steps and losses due to flocculated dispersions. Automotive catalytic converters are a key focus area for catalyst performance. One way to achieve lower emissions in a cost effective manner is to utilize co-catalysts that provide good oxygen storage capability and thermal stability in thinner layers. Nanoceria and mixed rare earth metal oxides meet the criteria necessary to enhance catalytic converter performance when properly incorporated into a catalyst system, and because they are dense, single phase individual crystals, there is nothing to collapse during thermal cycling.

### 2.11. Fuel cells

This is likely to be increasingly important as traditional energy sources continue to escalate in cost. It has been reported that the use of rare earth metal oxides has utility in various aspects of fuel cell design, but especially as components in electrodes and as low-temperature electrolytes in solid oxide fuel cells (SOFC). Nanoceria and mixed rare earth metal oxides have shown promise in testing for such applications.

### 2.12. Sunscreen formulations

Nanomaterials can act as sun blockers to protect human skin in formulations that go on smooth, silky and clear. Eliminating unnecessary exposure to the harmful UV rays of the sun has increasingly become a key health concern.

### 2.13. Semiconductor polishing

As the semiconductor industry continues to move forward to smaller chip architecture, the need for advanced CMP slurries becomes a requirement that cannot be met by the slurries provided in the past. Currently fumed silica and colloidal silica are being used. Both of these are nanoparticles used for several decades already. New types are being developed now including ceria, mixed rare earth metal oxides and alumina dispersions which are on the forefront of providing high planarity surfaces and efficient removal rates. The unique surface chemistry of these nanomaterials allows formulation of highly concentrated dispersions at a variety of pH. Cabot is another leader developing products for this market.

## 3. Conclusions

Nanoparticles are being developed by many companies both large and small. Universities are helping drive many of the new areas of research forward. Perhaps the most commonly used nanoparticle products in use today include: fumed silica, colloidal silica, nanosized zinc oxide, copper oxide and alumina. A rapidly growth market, possibly the largest in volume at this time is the production of nanoclays, made from montmorillonite (main constituent of bentonite) and used in flame-resistant cables and in automotive parts. Advancing nanoscience from the laboratory into a technology suitable for product applications has been the goal of many small start-up companies. Moving nanomaterials into products and the commercial arena is now the objective of major chemical and materials firms. This is occurring through internal programs and through investments in small technology companies to find materials, processes, and applications.

## Further reading

[1] Azom.com website for news and research findings.
[2] Cientifica Ltd., Technology and Market Reports. Madrid, Spain.
[3] Sud Chemie Company Nanofil© literature.
[4] Nanophase Technologies Inc. company literature.
[5] CSIRO literature.