

## Chapter 1

# Nanoparticles: Building Blocks for Nanotechnology

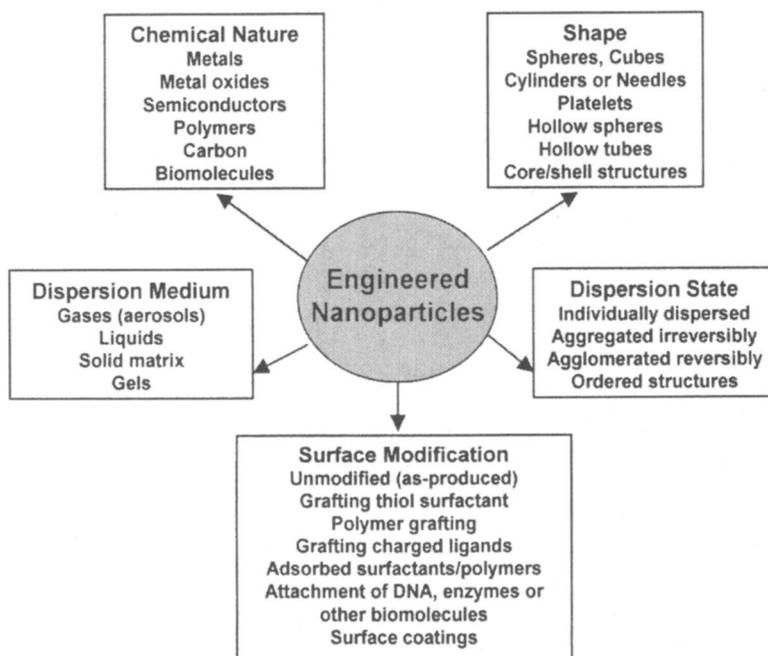
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Nanoparticles are defined as particles with size in the range of 1 to 100 nm at least in one of the three dimensions. Because of this very small size scale, they possess an immense surface area per unit volume, a high proportion of atoms in the surface and near surface layers, and the ability to exhibit quantum effects. The resulting unique properties of nanoparticles cannot be anticipated from a simple extrapolation of the properties of bulk materials. Nanoparticles exist with great chemical diversity in the form of metals, metal oxides, semiconductors, polymers, carbon materials, organics or biological. They also exhibit great morphological diversity with shapes such as spheres, cylinders, disks, platelets, hollow spheres and tubes, etc. Nanoparticles can be generated via a number of synthetic routes based on gas, liquid or solid phase approaches. The synthesized nanoparticles have to be surface modified in most cases, in order to passivate and stabilize them since their nanoscale renders them chemically very reactive and/or physically aggregative. The nanoparticles are also surface functionalized in order to meet the needs of specific applications. Nanoparticles serve as the fundamental building blocks for various nanotechnology applications.

## Introduction

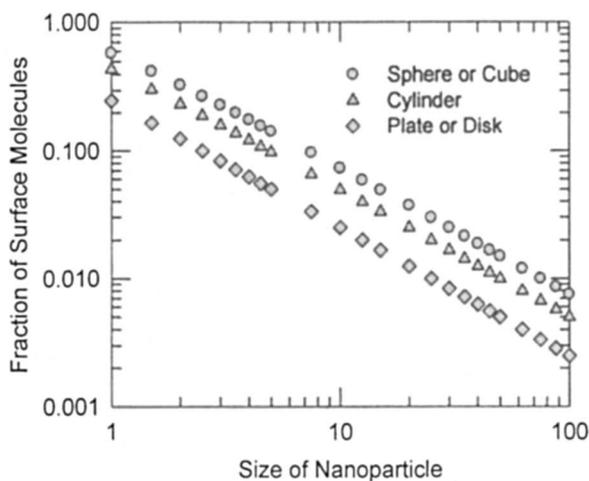
The term 'nanoparticle' is used to describe a particle with size in the range of 1 to 100 nm, at least in one of the three possible dimensions. In this size range, the physical, chemical and biological properties of the nanoparticle change in fundamental ways from the properties of both individual atoms/molecules and of the corresponding bulk material. Nanoparticles can be made of materials of diverse chemical nature, the most common being metals, metal oxides, silicates, non-oxide ceramics, polymers, organics, carbon and biomolecules. Nanoparticles exist in several different morphologies such as spheres, cylinders, platelets, tubes, etc. Generally, they are designed with surface modifications tailored to meet the needs of specific applications they are going to be used for. The enormous diversity of the nanoparticles (Figure 1) arising from their wide chemical nature, shapes and morphologies, the medium in which the particles are present, the state of dispersion of the particles and most importantly, the numerous possible surface modifications the nanoparticles can be subjected to make this an important active field of science.



*Figure 1. Various features contributing to the diversity of engineered nanoparticles. The same chemical can generate a wide variety of nanoparticles.*

## Nanoscale Properties and Relevance

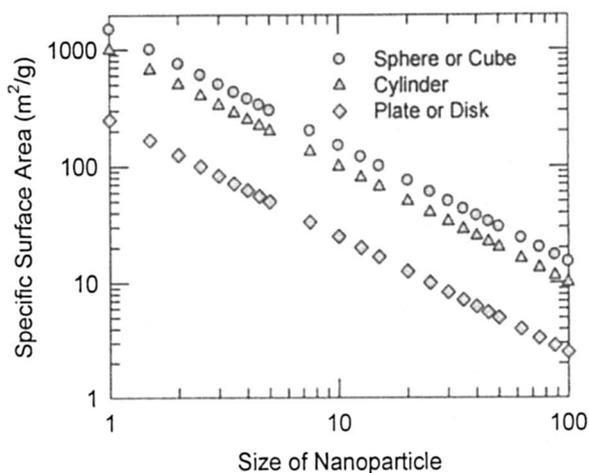
The most significant consequences of the nanoscale are the presence of a high fraction of atoms/molecules constituting the nanoparticle on the particle surface rather than in the particle interior (Figure 2) and the immense surface area available per unit volume of the material (Figure 3). Both of these properties increase in magnitude with a decreasing particle size. The unique physical, chemical and biological properties of nanomaterials originate from these two features. In some nanoscale materials quantum effects are exhibited allowing for a number of interesting applications. Further, unusual morphologies such as carbon nanotubes (CNT) and dendrimers contribute to morphology dependent novel applications.



*Figure 2. Calculated fraction of molecules at the surface as a function of nanoparticle size for particles of various shapes. The assumed atomic/molecular size is 0.5 nm. The size of nanoparticle refers to the diameter in the case of a sphere and a cylinder, the side for a cube and the thickness for a plate and a disk. The sphere and cube have all three dimensions in the nanoscale, the cylinder has two dimensions in the nanoscale and the plate and disk have one dimension in the nanoscale.*

The small particle size leads to many unique properties of nanoparticles. Nanoparticles display interesting optical properties since the absorption and/or emission wavelengths can be controlled by particle size and surface functionalization. If the nanoparticle size is below the critical wavelength of

light, then transparency can be attained. The chemical nature and the size of the nanoparticle control the ionic potential or the electron affinity and thereby the electron transport properties. For metals, with decreasing size of nanoparticles, the sintering and melting temperatures decrease. Nanoparticles may be incorporated into a solid matrix to provide better thermal conduction. For some metals and metal oxides, the decrease of the particle size results in improved magnetic behavior. Individual metallic magnetic nanoparticles can exhibit superparamagnetic behavior.



*Figure 3. Calculated surface area per unit volume as a function of nanoparticle size for particles of various shapes. The assumed atomic/molecular size is 0.5 nm and the particle density is 1 g/cm<sup>3</sup>.*

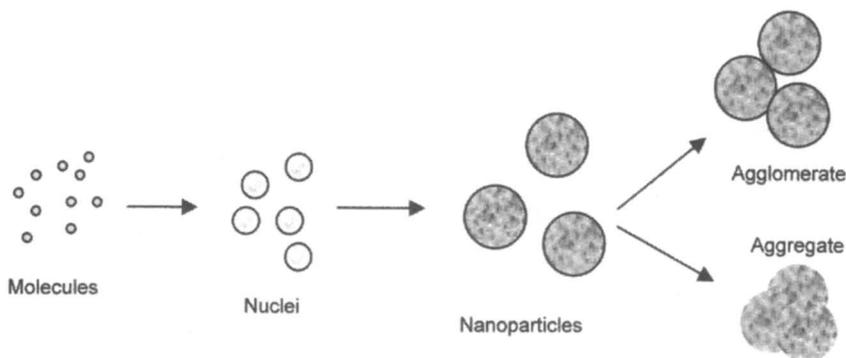
The large specific surface area of nanoparticles is the origin of a number of their unique applications. Catalysis is enhanced by high surface area per unit volume and the homogenous distribution of nanoparticles. High surface areas give strong interactions between the nanoparticles and the solid matrix in which they may be incorporated. In composites, depending on the chemistry of the nanoparticle, its aspect ratio, extent of dispersion and interfacial interactions with the polymer matrix (which can be modified by surface functionalization), it is possible to obtain different levels of mechanical properties for the final composites. In particular, a high elastic modulus can be achieved without a proportional loss in impact strength that is commonly observed when larger particles are used. The platelet morphology and large specific surface areas of silicate particles enhance the barrier properties of polymer membranes by vastly increasing the pathway for molecular transport of permeating substances.

Nanoparticles can also influence the flammability of polymers by increasing the glass transition temperature and the heat deflection temperature.

## Nanoparticle Synthesis Methods

Nanoparticles can be synthesized by a variety of methods using gas, liquid or solid phase processes. These include gas phase processes of flame pyrolysis, high temperature evaporation, and plasma synthesis; microwave irradiation; physical and chemical vapor deposition synthesis; colloidal or liquid phase methods in which chemical reactions in solvents lead to the formation of colloids; molecular self-assembly; and, mechanical processes of size reduction including grinding, milling and alloying.

Gas phase synthesis approaches are based on homogeneous nucleation of a supersaturated vapor and subsequent particle growth by condensation, coagulation and capture (Figure 4).



*Figure 4. Mechanism of nanoparticle production using vapor phase or liquid phase/ colloidal methods. The methods differ in the way the starting molecules are generated by vaporization or by chemical reaction/precipitation. The nuclei may be amorphous or crystalline and lead to amorphous or crystalline nanoparticles. Because of their intrinsic instability, the nanoparticles may form agglomerates that can be easily redispersed or form non-dispersible aggregate clusters.*

The supersaturated vapor can be generated in many ways depending on the chemical nature of the material, but typically by heating a solid and evaporating it into a carrier gas phase. The supersaturation is achieved by cooling or by chemical reaction or by some combination of these. The supersaturated vapor

can nucleate homogeneously in the gas phase and also heterogeneously by contact with surfaces. The nuclei grow by collision and condensation to give rise to a distribution of particle sizes and morphologies. Depending on the heating and cooling processes used, a wide range of gas phase methods such as flame pyrolysis (fumed silica,  $\text{TiO}_2$ ), furnace flow reactors (Ag, Ga, Al, PbS, Pb, Si, Ge), laser induced vaporization and pyrolysis (silica and iron), thermal and microwave plasmas (metals and metal oxides), sputtering (metals), and laser ablation have been employed.

Vapor deposition methods are based on forming a vapor by pyrolysis, followed by reduction, oxidation and allowing the deposition of the vapor on a surface. Starting from initial nuclei existing as islands on a surface, the growth is controlled by various ways to produce nanoparticles ( $\text{TiO}_2$ , ZnO, SiC). An important example of this approach is the production of carbon nanotubes.

Colloidal methods are based on precipitation processes in solutions. For example, solutions of different ions can be mixed under controlled conditions of temperature and pressure to form insoluble precipitates. By controlling the nucleation and growth kinetics, particles of various sizes and morphologies can be produced. The method has been implemented in bulk solutions and also in confined systems such as reverse micelles. To control the process of nucleation, ultrasonic or sonochemical effects have also been employed. A wide range of metal, metal oxide and organic nanoparticles have been produced by colloidal wet chemical approach.

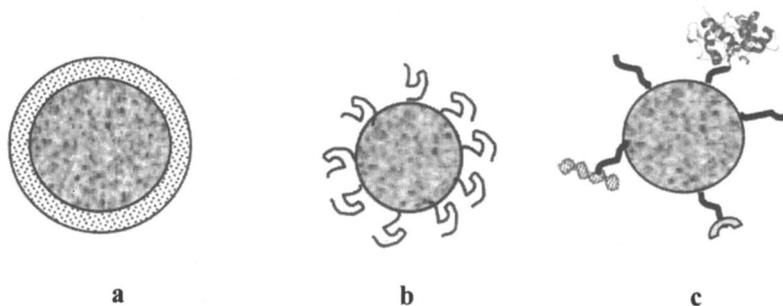
The molecular self assembly method is a spontaneous process by which nanoparticles are created starting from molecules. This is a particularly effective method for the production of polymeric nanoparticles starting from amphiphilic block copolymer molecules. An added advantage of this approach is the ability to produce thermodynamically stable nanoparticles whose size and shape can be controlled by the choice of the block copolymer (type, block composition and molecular weight) and the choice of the solvent and self-assembly conditions.

In addition to the nanoparticle synthesis approaches in gas or liquid phases, it is also possible to use solid substrates as heterogeneous nucleating sites to build up nanoparticles at solid-liquid interfaces. Indeed, by using patterned surfaces, one may be able to control the nucleation and growth processes thereby affecting the nature of nanoparticles produced.

All of the above synthesis approaches start at the molecular level to build up or create the nanoparticles. In the opposite direction, mechanical size reduction methods such as grinding and milling have also been employed to generate nanoparticles. These methods are the traditional approaches to produce fine particles and they have been able to generate nanoparticles from minerals such as clay, coal and metals. To avoid particle aggregation in the course of the size reduction process, the grinding and milling operations are often carried out with colloidal stabilizers.

## Surface Modification of Nanoparticles

Once the nanoparticles are produced and purified to a satisfactory level it is often necessary to introduce surface modifications. The surface modifications can be for the purposes of (a) passivating a very reactive nanoparticle, (b) stabilizing a very aggregative nanoparticle in a medium (which may be a solvent or a polymer melt) where the nanoparticles are to be dispersed, (c) functionalizing the nanoparticle for applications such as molecular recognition, or (d) promoting the assembly of nanoparticles (Figure 5). Most commonly used surface modification methods include grafting thiolated surfactants or polymers, adsorption of charged surfactants, charged ligands or polymer brushes, attachment of biological molecules such as DNA, peptides, proteins, antigens, streptavidin or coating a continuous polymer film on nanoparticles.

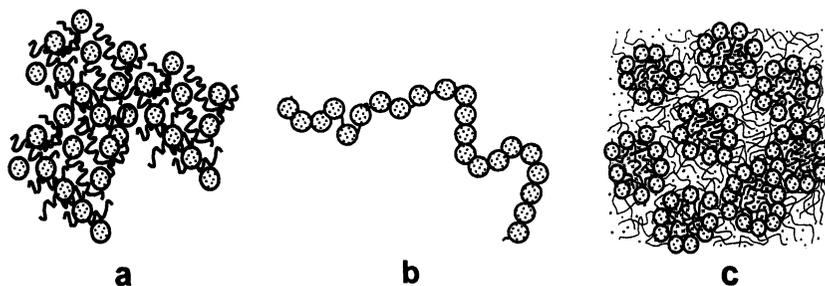


*Figure 5. Different approaches to surface modifications. (a) Surface treatment to make the interfacial tension at the nanoparticle-medium interface close to zero allowing for thermodynamic stability of the nanoparticle dispersion. The treatment could be the charging of the surface or coating with ligands. (b) Surface adsorption of a surfactant or a block copolymer to provide interparticle electrostatic and/or steric repulsions that would provide kinetic stability of the nanoparticle dispersion. (c) Surface modification to make the nanoparticle functional in one of many ways including hydrophobic or hydrophilic, the ability to bind to specific molecular recognition elements, DNA, enzymes, bridge to other nanoparticles, etc. The surface modification may involve a linker molecule.*

Much of this book is devoted to a description of various types of surface modifications performed on metal, metal oxide, semiconductor, polymer, carbon, organic and biological nanoparticles and specific examples can be found in the different book chapters.

## Assembling Nanoparticles

For most practical applications, the nanoparticles have to be assembled in one, two or three dimensions, similar to how atoms and molecules are assembled into matter. For example, a sensing device may require that nanoparticles be arranged with specified inter-particle separation. An optoelectronic device may require the nanoparticles to be assembled to create a patterned surface. In general, it will be necessary to place the nanoparticles in specified locations on a substrate so that addressing and connecting them to the macroscopic outside world will be possible.



*Figure 6. Assembling nanoparticles for applications. (a) Nanoparticles with stabilizing polymer molecules around them in a random three dimensional arrangement to create a porous nanoparticle system for catalytic or adsorption applications. (b) Nanoparticles assembled on a polyelectrolyte or a DNA molecule to serve as a nanoelectrical wire. (c) Nanoparticles assembled on a block copolymer patterned surface with nanoparticles located at the domain boundaries for a sensor application. (Adapted from reference 1.)*

A number of approaches have been developed to accomplish this objective. For example, surface patterning has been used to direct polymer and silica nanoparticles to specific surface locations. Self-assembled surfactant and block copolymer nanostructures have been used as templates to direct the nanoparticle assembly of metal oxide particles to generate mesoporous materials. Cationic (or anionic) polyelectrolytes have been used to direct the assembly of oppositely charged nanoparticles such as negatively charged gold particles or silica particles. Nanoparticles can also self-assemble into nano-crystalline materials. A variety of molecular recognition methods such as antigen-antibody interactions have been used to direct the assembly of nanoparticles that have the recognition molecules bound to their surfaces. The binding of DNA to the nanoparticle surface has been used to create particle assemblies dictated by nucleic acid interactions. Nanoparticles have also been self-assembled at air-liquid and

liquid-liquid interfaces taking advantage of surface tension effects. Also the dewetting of a solid surface by a polymer solution has been exploited to attain nanoparticle self-assembly. Biological nanoparticles such as viruses can self-assemble to yield ordered nanoparticle assemblies in one, two or three dimensions.

## **Nanoparticle Commercial Applications**

Existing and potential applications involving nanoparticles are almost endless. The following list from Ref.(2), with additions, provides examples in various fields of technology. The amount of nanoparticles usage in different applications may vary significantly.

The Project on Emerging Nanotechnologies (3) lists more than 470 products in May 2007, that are verified to include some form of nanotechnology, the number being double that was reported the same time in 2006. Many of the products address consumer needs in health care and fitness, home and garden, electronics and computers, food and beverage, automotive, appliances and products for children. The positive view with which the nanoproducts are being greeted is reflected in the explicit choice of the term 'nano' in the names of many commercial products, for example, Nano & UV Artificial Teeth Cleaner, Nano Air Filter, Nano Anti Aging Cream, Nano B-12 Vitamin Spray, Nano Bag, Nano Breast Cream, Nano Cold Catalyst Air Purifier, Nano Pacifier, Nano Trousers, Nanoceuticals Artichoke Nanoclusters, Nanodesu X Bowling Ball. The preponderant nanomaterials in these 470 commercial products are shown on Figure 7.

In 2005, over US \$32 billion of products sold claimed to have incorporated some nanotechnology (3). The global investment in nanotechnology research and development is approximately US \$9 billion. There are more than 4,000 US Patents filed to-date. The growing interest in nanoparticles and their importance can also be measured by the increase in the number of scientific publications (Figure 8).

## **Conclusions**

Nanoparticles constitute the building blocks for nanotechnology and thus for numerous potential applications in energy and power, health and biomedicine, electronics and computers, environmental applications, new engineering materials, consumer goods, personal care products, food and transportation. To perform these functions nanoparticles have to be synthesized, passivated to control their chemical reactivity, stabilized against particle aggregation, and functionalized to achieve specific performance goals. The individual nano-

**Table 1. Examples of Present and Potential Applications of Nanoparticles**

Biomedicine	<ul style="list-style-type: none"> <li>• Antibacterial creams and powders (Ag)</li> <li>• Biocompatible coatings for implants</li> <li>• Biolabeling and detection (Au, Ag, Quantum dots)</li> <li>• Biosensors (metal oxide, polymer nanoparticles, CNT)</li> <li>• Bone growth promoters (hydroxyapatite ceramics)</li> <li>• Cancer diagnostics and targeted drug delivery (magnetic nanoparticles)</li> <li>• Cell, receptor, antigen, enzyme imaging (Quantum dots)</li> <li>• Fungicides (ZnO, Cu<sub>2</sub>O)</li> <li>• Gene delivery (CNT)</li> <li>• MRI contrast agents (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>)</li> <li>• Dental composites</li> </ul>
Consumer Goods and Personal Care Products	<ul style="list-style-type: none"> <li>• Anti-bleaching, scratch resistance additives in paints</li> <li>• Anti-scratch coated tiles (alumina)</li> <li>• Barrier packaging (silicates)</li> <li>• Glass coatings for anti-glare, anti-misting mirrors (TiO<sub>2</sub>)</li> <li>• Skin creams with antioxidant vitamins (nanocapsules)</li> <li>• Sunscreens (ZnO and TiO<sub>2</sub>)</li> <li>• Tennis balls, rackets (nanoclays, carbon nanotubes))</li> <li>• Water- and stain-repellent textiles</li> </ul>
Electronics and Computers	<ul style="list-style-type: none"> <li>• Chemical mechanical planarization (alumina, silica, ceria)</li> <li>• Coatings and joining materials for optical fibers (Si)</li> <li>• Conductive coatings/fabrics (rare-earth-doped ceramics)</li> <li>• Display technologies (conducting oxides)</li> <li>• Electronic circuits (Cu, Al)</li> <li>• EMI shielding using conducting and magnetic materials</li> <li>• Ferro-fluids (Fe, FeCo, Fe<sub>3</sub>O<sub>4</sub>)</li> <li>• Magnetic particles for high-density data storage (Fe)</li> <li>• Optoelectronics devices (Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> doped with rare-earth metals)</li> </ul>
Engineering Materials	<ul style="list-style-type: none"> <li>• Anti-scattering layers in photographic film</li> <li>• Chemical sensors</li> <li>• Conducting/magnetic inks (metal powders)</li> <li>• Cutting tool bits (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, WC, TaC)</li> <li>• Thermal spray coating techniques (TiO<sub>2</sub>, TiC-Co)</li> <li>• Flame retardant polymer formulations (nanoclay)</li> <li>• Lubricants and sealants/hydraulic additives (Cu MoS<sub>2</sub>)</li> <li>• Molecular sieves</li> <li>• Pigments (metals and metal oxides)</li> <li>• Polymer composites (nanoclays, TiO<sub>2</sub>, SiO<sub>2</sub>)</li> <li>• Spark plugs (metal and ceramic powders)</li> <li>• Wear/abrasion-resistant coatings (alumina, Y-Zr<sub>2</sub>O<sub>3</sub>)</li> </ul>

*Continued on next page.*

**Table 1. Continued.**

Environmental	<ul style="list-style-type: none"> <li>• Controlled delivery of herbicides and pesticides</li> <li>• Self-cleaning glass (TiO<sub>2</sub> based coatings)</li> <li>• Soil remediation (Fe)</li> <li>• Water treatment (photo-catalyst treatments, TiO<sub>2</sub>)</li> </ul>
Food	<ul style="list-style-type: none"> <li>• Flavors and colors in food and beverages (nanocapsules)</li> <li>• Frying oil refining catalysis (ceramics)</li> <li>• Food packaging materials (nanoclays, SiO<sub>2</sub>, TiO<sub>2</sub>, Ag)</li> <li>• Nutraceutical delivery (liposomes, block copolymer micelles)</li> <li>• Food pathogen sensing</li> </ul>
Power and Energy	<ul style="list-style-type: none"> <li>• Anode and cathode materials for solid oxide fuel cells (nanoclays, CNT)</li> <li>• Catalysts for various fuel technologies (metals and metal oxides)</li> <li>• Conducting polymers for bipolar plates in fuel cells</li> <li>• Dye-sensitized solar cells (TiO<sub>2</sub>, ZnO, Au)</li> <li>• Environmental catalysts (TiO<sub>2</sub>, CeO<sub>2</sub> as diesel additive)</li> <li>• Fuel cell catalysts (Pt in PEM cells)</li> <li>• Hydrogen storage (metal hydrides)</li> <li>• Improved electrodes in batteries and supercapacitors</li> <li>• Thermal control fluids (Cu)</li> </ul>
Transportation	<ul style="list-style-type: none"> <li>• Automated highways</li> <li>• Battery technology</li> <li>• High strength, light weight composites for increasing fuel efficiency</li> <li>• High temperature sensors</li> <li>• Improved displays</li> <li>• Thermal barrier and wear resistant coatings</li> <li>• Wear-resistant tires</li> </ul>

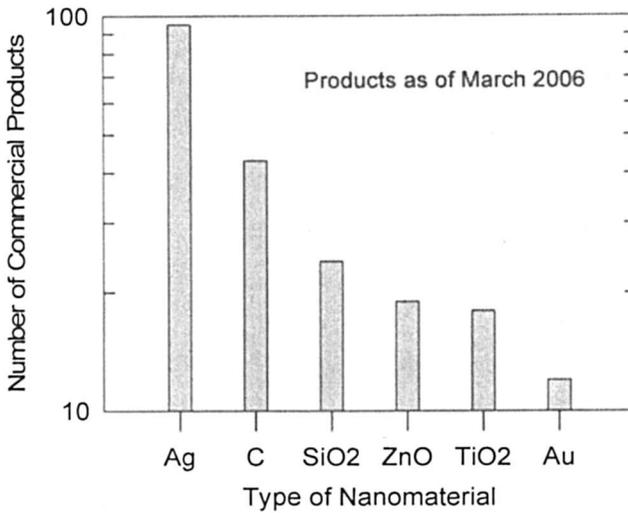


Figure 7. The use of nanoparticles of the specified kind in commercial products. C refers to fullerenes and carbon nanotubes (2).

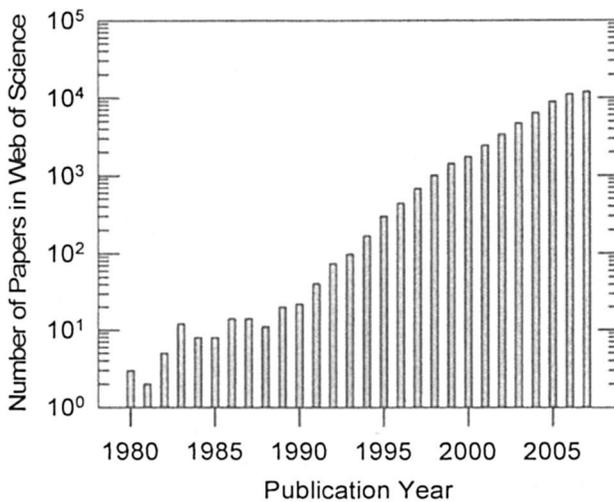


Figure 8. Number of publication entries in the Web of Science for the keyword 'nanoparticles'. The number for 2007 covers only eleven months.

particles then have to be assembled into devices or integrated into other solid matrices to create the final nanoproducts. The tremendous diversity of nanoparticles possible because of their wide chemical nature, shape and morphology, medium in which they are present, their state of dispersion and the nature of surface modifications make this a rich field for scientific investigations.

### **Acknowledgements**

Work supported by In-House Laboratory Independent Research (ILIR) Program, Natick Soldier Research, Development & Engineering Center.

### **References**

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