

PREPARATION, DEVELOPMENT AND APPLICATIONS OF NANOMATERIALS-REVIEW

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ABSTRACT

The prefix 'nano' is derived from the Greek word for dwarf. One nanometre (nm) is equal to one-billionth of a metre, 10^{-9} m. The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist Richard Feynman. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. Metal

nanoparticles are used as various types of catalysts, adsorbents, sensors and ferrofluids. Nanoparticles have potential applications in many different fields. Engineered nanoparticles are specifically designed and formed with customized physical properties in order to fulfill the requirements of specific applications. Nanomaterials are used such as electronics, Energy, Automobile, Aerospace, Medical, Cosmetics, Food, Sports equipment, Textile industry, Technology and home appliances.

KEYWORDS: Nano, Nanomaterials, Nanoparticles and Nanoscale.

INTRODUCTION

The prefix 'nano' is derived from the Greek word for dwarf. One nanometre (nm) is equal to one-billionth of a metre, 10^{-9} m. A human hair is approximately 80,000nm wide, and a red blood cell approximately 7000nm wide. Figure 2.1 shows the nanometre in context. Atoms

are below a nanometre in size, whereas many molecules, including some proteins, range from a nanometre upwards.

The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist Richard Feynman. 'There's plenty of room at the bottom' (Feynman 1959). Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale.

Nanomaterials describe, in principle, materials of which a single unit is sized (in at least one dimension) between 1 to 1000 nanometers (10^{-9} meter) but usually is 1 to 100 nm (Buzea et al., 2007).

Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties (Jump up et al., 2010).

Nanomaterials are slowly becoming commercialized (Jump up, Eldridge, T., 2010) and beginning to emerge as commodities (Jump up, McGovern, C. 2010). Nanomaterials are not simply another step in the miniaturization of materials or particles. They often require very different production approaches. There are several processes to create various sizes of nanomaterials, classified as 'top-down' and 'bottom-up'. Although large numbers of nanomaterials are currently at the laboratory stage of manufacture, many of them already are being commercialized. Below we outline some examples of nanomaterials and the range of nanoscience that is aimed at understanding their properties. As will be seen, the behavior of some nanomaterials is well understood, whereas others present greater challenges.

Significance of the nanoscale

A nanometre (nm) is one thousand millionth of a metre. For comparison, a single human hair is about 80,000 nm wide, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. People are interested in the nanoscale (which we define to be from 100 nm down to the size of atoms (approximately 0.2 nm)) because it is at this scale that the properties of materials can be very different from those at a larger scale. We define nanoscience as the study of phenomena and manipulation of materials at atomic, molecular

and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale. In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades and nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies.

Properties of nano-materials

The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties. Second, quantum effects can begin to dominate the behaviour of matter at the nanoscale - particularly at the lower end - affecting the optical, electrical and magnetic behaviour of materials. Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles).

Preparation of nanoparticles

Metal nanoparticles are used as various types of catalysts, adsorbents, sensors and ferrofluids. They have applications in optical, electronic and magnetic devices. Most of these applications critically depend on the size and shape of the nanoparticles. Therefore, the synthesis of well-controlled size and shape of these nanoparticles is important for these applications.

The reduction of metal complexes to form metallic colloid dispersions is a very common technique. Various precursors, reducing agents and polymeric stabilizers are used in the preparation of metallic colloid dispersions. Some of these are presented in Table 4.0.

Table 4.0 Precursors, reducing agents and polymeric stabilizers used in the preparation of metallic nanoparticles.

Category	Name Precursor
Precursor	Metal anode Palladium chloride Potassium tetrachloroplatinate II Silver nitrate Chloroauric acid Rhodium chloride
Reducing agent	Hydrogen Sodium citrate Citric acid Carbon monoxide Methanol Formaldehyde Hydrogen peroxide Sodium tetrahydroborate
Polymeric stabilizer	Poly(vinylpyrrolidone) Polyvinyl alcohol Sodium polyphosphate Sodium polyacrylate

The size of metallic colloids varies significantly with the type of the reducing agent. A strong reducing agent promotes a fast reduction reaction, and if the reaction is fast, generally small nanoparticles are formed. On the other hand, a weak reducing agent induces a slow reaction and usually large particles are formed.

A strong reducing agent generates an abrupt surge of the concentration of the growth species resulting in a very high supersaturation. Consequently, a very large number of nuclei are formed initially. For a given concentration of the metal precursor, the formation of a large number of nuclei results in small size of the nanoparticles.

The role of polymeric stabilizer is to form a monolayer on the surface of the nanoparticles and prevent their aggregation. The polymeric stabilizer is also known as a capping material. The monolayer of the polymer, however, can affect the growth process significantly. If the growth sites are occupied by the polymer, the rate of growth of nanoparticles may be reduced. If the polymeric stabilizer completely covers the surface of the growing particle, it may hinder the diffusion of the growth species from the surrounding solution to the surface of the particle.

The shape of the nanoparticles can be varied by the use of different amounts of the polymeric stabilizer. The shape and size of platinum nanoparticles have been controlled by changing the

ratio of the concentration of the polymer (sodium polyacrylate) to the concentration of the platinum cations (Ahmadi et al., 1996). They observed tetrahedral, cubic, irregular-p.

Gold nanoparticles are well known for their distinct colors. They have been used in glasses and enamels as coloring agents (see Fig. 4.1.2). A variety of methods exist for the preparation of gold nanoparticles. One of the most common methods is the reduction of chloroauric acid at 373 K by sodium citrate.

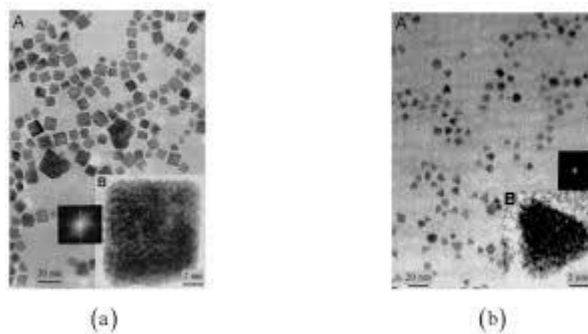


Fig. 4.1.2 TEM images of platinum nanoparticles: (a) cubic nanoparticles formed when the initial ratio of concentration of polymer (sodium polyacrylate) to that of the metal cation in the solution was 1:1, and (b) tetrahedral nanoparticles formed when the initial ratio was 5:1. The insets show high-resolution images of the particles (Ahmadi et al., 1996) (reproduced by permission from The American Association for the Advancement of Science, © 1996).



Fig. 4.2.2 Glass carafe in which gold nanoparticles are dispersed (this glass is known as ruby glass).

To prepare a colloidal dispersion of rhodium, the following reduction reaction, using methanol as the reducing agent, can be carried out in presence of a stabilizer such as polyvinyl alcohol.

2RhCl 3CH OH 2Rh 3HCHO 6HCl - 4.1.1

The size of nanoparticles depends on the reaction conditions. Ostwald ripening plays an important role in the size of the nanoparticles. Nanoparticles of platinum and palladium can be prepared by reduction using hydrogen: the salts K₂PtCl₄ and PdCl₂ are hydrolyzed to form hydroxides, which are then reduced.

PdCl Na CO 2H O Pd OH H CO 2NaCl - 4.2.2

Pd OH + H Pd + 2H O () - 4.2.3

Non-oxide semiconductor nanoparticles can be synthesized by the pyrolysis of organometallic precursor dissolved in anhydrate solvents at elevated temperatures in airless environment in presence of a polymeric stabilizer. The nanocrystals of CdS, CdSe and CdTe have been prepared in this method. The nanocrystals of GaN have been synthesized by a thermal reaction of Li₃N and GaCl₃ at 553 K under pressure using benzene as the solvent in argon atmosphere (Xie et al., 1996).

GaCl Li N GaN 3LiCl - 4.1.4

The yield of GaN was 80% and the size of the particles was 30 nm. The product comprised of mostly hexagonal GaN with a small amount of rocksalt GaN.

A well known method for synthesizing oxide nanoparticles is sol–gel processing. The sol–gel process typically consists of hydrolysis and condensation of the precursors. The typical precursors are metal alkoxides, or inorganic and organic salts. The precursors are dissolved in aqueous or organic solvents. Sometimes catalysts are used to promote the hydrolysis and condensation reactions.

GaCl Li N GaN 3LiCl - 4.1.5

Hydrolysis: $M(OEt)_4 + x H_2O \rightleftharpoons M(OEt)_{4-x}(OH)_x + x EtOH$ -4.1.6

Condensation: $2M(OEt)_{4-x}(OH)_x \rightleftharpoons (OEt)_{4-x}MOM(OEt)_{4-x} + H_2O$ - 4.1.7

where M represents the metal. The nanoclusters formed by condensation often have organic groups attached to them, which may result due to incomplete hydrolysis.

The size of the nanoclusters and the structure of the final product can be tailored by suitably controlling the reactions. Colloidal dispersions of metal hydroxides consisting of particles of considerable uniformity in size and shape have been synthesized by keeping the salt solutions of the respective metals at elevated temperatures for various periods of time.

The particle shape and composition depend most strongly on the pH and on the nature of the anions contained in the aging systems. Ferric oxide nanoparticles were synthesized by aging ferric salt solutions with the corresponding acid at 373.

Electron micrographs of ferric oxide nanoparticles formed from $\text{Fe}(\text{NO}_3)_3$ & HNO_3 , and $\text{Fe}(\text{ClO}_4)_3$ & HClO_4 solutions are shown in 4.1.3.

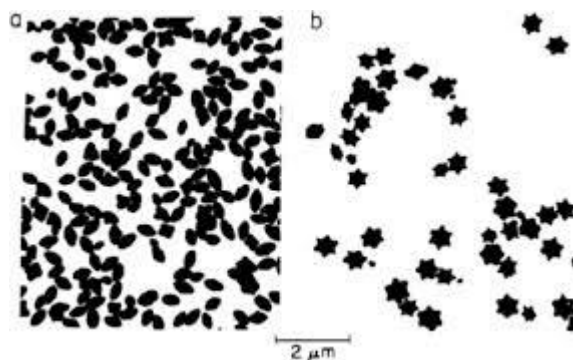


Fig. 4.1.3 Electron micrographs of iron oxide nanoparticles obtained by aging the solutions at 373 K for one day: (a) $\text{Fe}(\text{NO}_3)_3$ (18 mol/m³) + HNO_3 (104 mol/m³), and (b) $\text{Fe}(\text{ClO}_4)_3$ (18 mol/m³) + HClO_4 (104 mol/m³) (Matijević, 1977) (reproduced by permission from Elsevier Ltd., © 1977).

Development of Nanomaterials

Nanoparticles are in the size range of 1-200 nm and demonstrate exotic catalytic, optical and electronic properties. Their properties vary with the manufacturing technique used for controlling their size and shape, thus making them interesting building blocks for nanoscale structures, assemblies and devices. Miniaturization of structures by electron-beam lithography and mechanical techniques is approaching the theoretical limits of about 50 nm. Hence, it is necessary to develop alternative methods to enable further miniaturization of chemical objects.

Nanoparticles have potential applications in many different fields. Engineered nanoparticles are specifically designed and formed with customized physical properties in order to fulfill

the requirements of specific applications. They can serve as the end product, like sensor for special purposes, pharmaceutical drugs and quantum dots, or they can serve as components in end products, as in the case of carbon black in rubber products. For both purposes, the physical properties of the nanomaterials play a key role in their performance. The novel physical and chemical properties of nanomaterials pave way to interface electronic signal transduction with biological recognition events and to design advanced bioelectronic devices with innovative functions.

Products

The following are the products offered by EMFUTUR Technologies:

- Calcium, zirconium, cerium, strontium, zinc, tin, indium, aluminum, copper, magnesium, and iron oxide
- Lead, nickel, platinum, silver, gold, cobalt and copper nanoparticles
- Titanium boride
- Silicon dioxide
- TiO₂ nanoparticles
- Titanium silicium, aluminum carbide and nitride
- MnCO₃ nanoparticles
- CaCO₃ nanoparticles

Application of Nanomaterials

Electronics

Application of nanomaterials in electronics is significantly increased in recent years. The most common nanomaterial which is enormously investigated for the application of electronic science is carbon based nanotube and semiconductor nanocrystal (quantum dots).

Due to their superior electrical properties carbon nanomaterials such as one-dimensional (1D) carbon nanotubes and two-dimensional (2D) graphene are evolving as significant tools which provide a faster and more power-efficient electronics. In addition, high surface to volume ratio, robust and durable mechanical properties has established them a highly sensitive and lower energy consuming building block for nano sensors. All the carbon nanotubes have an ability to emit electrons in the presence of an electric field. This property has been utilized in the field emission devices like television, computer screens and other instruments which are based on cathode-ray emission. The chemical and physical state of the environment may alter the electrical conductivity of carbon nanotubes and thus carbon nanotubes have been

developed as chemical and physical sensors. The efficiency of carbon nanotubes to detect any changes in chemical composition of the environment is three times higher in magnitude than conventional solid state sensors. The other advantage of these electronic chips is smaller in size and can be used at room temperature.

Energy

The future generations will be striving to explore the alternative energy sources like solar energy, hydrogen based fuel to fulfill their requirements. A new device that combines graphene with special metallic nanostructures could lead to emerge as more efficient solar cells. The nano structures are fabricated on top of graphene samples to concentrate the electromagnetic field in the region of the material where light is converted to electrical current, so as to dramatically increase the generated photo voltage. Compared to silicon, which is a material currently being used in solar cells, graphene is more conductive and can absorb longer range spectrum of sunlight, and that may boost the efficiency of solar cells. There is a considerable research program is going on to develop alternative source of energy in form of hydrogen fuel by splitting water (H_2O) using sunlight in presence of titanium dioxide (TiO_2) nanomaterials. The evolving hydrogen generated by this process can itself become a very good source of fuel for automobiles and other purposes.

Automobile

In automobile industry, polymers have been mixed with nanomaterials (mainly carbon nanotubes and metal nanoparticles) to develop robust and durable parts of vehicles. Cars are spray painted with tiny size nanoparticles that provide smooth, fine and thin attractive coating. In addition, nano coat based paints can also alter the heat-reflecting properties depending on the intensity of the incident sunlight. This helps to regulate the temperature of the vehicle, making the air conditioning system more efficient, easier and less fuel consuming. Self-cleaning glass can be developed by dissolving small amount of titanium (TiO_2) with glass manufacturing ingredients like silica (SiO_2), CaO etc during the melting time. Titanium is able to dissociate organic dust in presence of UV light which is found in normal sunlight. The dissociated organic compound may fall down or simply evaporate and gives a clear sight. In automobile industry, tires of cars consume considerable amount of rubber causing not only increase in price but also add to its weight. The excess weight is related to reduction of speed and increase in fuel consumption. By using nanoparticles such as clay in polymers, light weight, less rubber consuming stronger tires can be manufactured within the reasonable cost.

Aerospace

The applications of nanotechnology in aero space industry are mainly based on the concept of using high strength, low weight nano composites. Space vehicles need high performance, multifunctional materials which can withstand harsh and extreme environments. Materials should also sustain high or low temperature and high or low pressure. Polymer nanocomposites using silica fibers and nanoparticles have high stiffness, low temperature coefficient of expansion and high impact strength. In addition, the radiation protections of nanoparticle-based composites are better as compared to microparticles- based composites.

This makes polymer nanocomposites as a good material for aerospace application.

Medical

Nanotechnology can be effectively used for diagnosis and drug delivery. Special sensor of nanorobots can be inserted into the blood under the skin to check different biological and chemical contents present in blood and trace out any possible diseases. They can also be used to check the sugar level present in the blood. Advantage at using such nanorobots is that they are very cheap to produce and easily portable. Nanotech is already used for the treatment and diagnosis of cancer, autoimmune diseases and parasitic infections. Due to larger surface area some drugs when manufactured as nanoparticles, which are thought to be more easily absorbed into the body because of their size. Nanoparticles with antibacterial properties are used in some hospital equipment, and magnetic nanoparticles are used to diagnose conditions, avoiding the risks of surgery. Further research investigation may explore the role of nanotechnology in tissue engineering and can be used as replacement of body parts. Ligand based target drug therapy for cancer patients become also effective after the invention of nanotechnology.

Cosmetics

Nano particles based cosmetics recently draw a lot of attention from the scientific community of cosmetics industry. Zinc oxide and titanium oxide containing nanoparticles of fairly uniform size are able to absorb ultraviolet light and protect the skin. The small particles in some of the creams scatter light in such a way that appearance of the wrinkles present in the face is diminished. The cosmetics that have a coloring function normally employ a variety of pigments that reflect light in certain ways, to generate many colors and color gradations. Due to their small size nanoparticles-based cream are preferred as they can be used in small

amount and they do not leave any gaps between them. This gives as smooth appearance. Nano based dyes and colors are quite harmless to skin and can be used in hair creams or gels.

Food

Nanotechnology based dietary supplements is one of the most common uses in food industry. Companies claim that because of their sizes, nanoparticles can be absorbed more quickly and easily as compare to their bulk components. USA based companies have developed a chocolate drink with more intense chocolate flavor using the nanotechnology. Nano-silver is also used effectively in some food packaging containers, particularly because of its antibacterial properties.

Sports equipment

Many sports equipment like cricket bat, the shaft and head of some tennis racquets are made of carbon nanotubes which stiffen the sports equipment, thus creating a high strength-to-weight ratio. In addition, Golf balls have been developed using nanotechnology which increases the flight of the balls.

Textile industry

Recent nanotechnology based clothing are highly effective to repel any form of dirt particles. Some textile industries are marketing dirt and stain resistant trousers and shirts.

Some sportswear companies also claim to make the use of the nanosilver based technology having the antibacterial properties to prevent apparels from getting smelly when they're worn, and reduce the need for repeated washing of these clothes.

Technology and home appliances

In recent years, plenty of mobile phones and computers are based on the science of modern nanotechnology. One of the most common applications is laptop keyboard which has been coated in nano-silver to prevent the spread of bacteria. The brightness of TV and computer displays can be enhanced by using carbon nanotubes. Nanotechnology is facilitating the production of brighter, clearer and more efficient displays for computers and television. Traditional TV's and monitors were based on cathode ray tubes (CRT's). Unfortunately; there can be problems in achieving comparable picture quality, brightness and view angle. Using nanomaterials, it may be possible to improve further on LCD technology through the use of field emission displays which is less power consuming and may ultimately be cheaper to

make. Some companies have deployed nanotechnology to prolong battery life. In the home, nanoceramics can help to reduce the friction on surfaces, and have been used in things such as frying pans and non-stick irons.

Nanomaterials Safety and regulations

The development of Nanomaterials has made the whole international deal with the benefits of the fast developing discipline of Nanomaterials and nanotechnology. It is envisioned that over 1500 manufactured- identified nanotech products are publicly to be had, with the brand new ones hitting the marketplace every week. The considerable range of ability products and programs offers nanotechnology its enormous boom prospects. The global nanotechnology industry will increase to reach Americas seventy five. Eight billion with the useful resource of 2020 making each sector of era and generation listen in making the nanotechnology and Nanomaterials play an vital characteristic in their future development.

- Measurement of health risk
- NanoToxicology
- Regulation and ethical impacts
- Risk assessment and management
- Exposure scenarios

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