Unit II

Nanochemistry

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter, approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because of their optical, magnetic, electrical, and other properties. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN). They can be found in sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items. They are also being used in medicine for purposes of diagnosis, imaging and drug delivery. Engineered nanomaterials are designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why nanomaterials have different properties- increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses in diversing the products such as sports equipment, bicycles and automobiles etc. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl rubber/ nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows.

Classification of nanomaterials

Nanomaterials have extremely small size having at least one dimension 100 nm or less. Nanomaterials can be one dimensional (e.g. surface films), two dimensional (e.g. strands or fibres), or three dimensional (e.g. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e. silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica). According to Siegel, nanostructured materials are classified as zero dimension, one dimension, two dimension, three dimension nanostructures.

Importance of nanomaterials

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

(i) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(ii) Nanostructured semiconductor shows various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties viz. luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

(iii) Nanosized metallic powders have been used for the production of gas tight materials and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(iv) Very small particles having special atomic structures with discrete electronic states give rise to special properties in addition to the super paramagnetism. Magnetic nanocomposites have been used for mechanical force transfer for high density information storage and magnetic refrigeration.

(v) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

Nanomaterial - synthesis and processing

Synthesis of nanosize materials is of great importance, as particles built up from a few hundred atoms posses properties different from bulk. There are two possible routes for the synthesis of nanomaterials – "bottom up" and "top down". In the bottom up approach nanostructures are built up from individual atoms or molecules (small to big). This approach also uses the principle of molecular recognization and self assembly.

In the top down approach the nanostructures are built up from breaking up bulk materials (big to small). In this method a bulk material is broken up into nanoparticles using grinder, lasers etc.

Methods for creating nanostructures

There are different methods of creating nanostructures: of course, macromolecules or nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly. Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application.

Mechanical grinding

Mechanical grinding is a typical example of 'top down' method for the synthesis of nanomaterials. This has become a popular method to make nanocrystalline materials because of its simplicity, needed relatively inexpensive equipment. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications.

In fact, the contamination problem is often given as a reason to dismiss this method, at least for some materials. The mechanisms responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallisation of amorphous materials. Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. For the production of fine particles an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials. Hence, it requires milling to take place in an inert atmosphere and that the powder particles are handled in an appropriate vacuum system. However, this method is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed.

Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (*sol*) and gelation of the sol to form a network in a continuous liquid phase (*gel*). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$. The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides can be described as follows:

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

$$MOH + ROM \rightarrow M\text{-}O\text{-}M + ROH \text{ (condensation)}$$

Sol-gel method of synthesizing nanomaterials is very popular and is widely employed to prepare oxide materials.

Gas phase synthesis of nanomaterials

The gas-phase synthesis methods are of increasing interest because they allow elegant way to produce size, shape and chemical composition controlled nanostructures. In conventional chemical vapour deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nano particles (condensation). Condensation occurs only when the vapour is supersaturated and in these processes homogeneous nucleation in the gas phase is utilized to form particles. This can be achieved both by physical and chemical methods.

Wet chemical synthesis of nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

Gas condensation processing (GCP)

In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar helium. Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase. The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo).

Sputtered plasma processing

In this method is yet again a variation of the gas-condensation method excepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and the constituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again reactive sputtering or multitarget sputtering has been used to make alloys or oxides, carbides, nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

Microwave plasma processing

The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. Generally, the microwave cavity is designed as a single mode cavity using the TE10 mode in a WR975 waveguide with a frequency of 0.915 GHz. The major advantage of the plasma assisted pyrolysis in contrast to the thermal activation is the low temperature reaction which reduces the tendency for agglomeration of the primary particles.

Laser ablation

Laser ablation has been extensively used for the preparation of nanoparticles and particulate films. In this process a laser beam is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications. The small dimensions of the particles and the possibility to form thick films make this method quite an efficient tool. The laser spark atomizer can be used to produce highly mesoporous thick films and the porosity can be modified by the carrier gas flow rate. ZrO_2 and SnO_2 nanoparticulate thick films were also synthesized successfully using this process with quite identical microstructure.

Properties of nanomaterials

Nanomaterials have the structural features in between of those of atoms and the bulk materials. The properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) larger surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, resulting in more “surface” dependent material properties. The metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity.

Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine. The optical properties of nanomaterials depend on some parameters such as size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. In CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles.

Electrical properties

Electrical properties of nanoparticles discuss about fundamentals of electrical conductivity in nanotubes and nanorods, etc. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.

Magnetic properties

Bulk gold and platinum are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different from bulk atoms, but they can also be modified by interaction with other chemical species. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, the non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range.

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

Selected application of nanomaterials

Nanomaterials have wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc. It is evident that nanomaterials split their conventional counterparts because of their superior chemical, physical, and mechanical properties and of their exceptional formability.

Catalysis

Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity, and can very well be utilized in manipulating the rate-controlling step.

Phosphors for high-definition TV

The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are used for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high definition televisions (HDTVs) and personal computers affordable to be purchased.

Elimination of pollutants

Nanomaterials possess extremely large grain boundaries relative to their grain size. Hence, they are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity of nanomaterials (Pd, Pt and Rh) can be used as catalysts to convert toxic gases such as carbon monoxide and nitrogen oxides to harmless gases.

Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF). The added advantage of nano skin blocks ZnO and TiO_2 protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

Sensors

Sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Using carbon nanotubes, chemical nanosensors have been fabricated to detect glucose levels, while ZnO nanotubes have been used to measure the concentration of hydrogens or ethanol.

Drug delivery

Drug delivery means, the drug will be taken through blood to the target. Conventional drug delivery method leads to the damage of normal cells and normal organs by the drug since they are toxic. In targeted drug delivery, drug is delivered to the target without affecting any other cells or organs. The drug can be dissolved, entrapped, adsorbed, attached or encapsulated into the nanoparticle matrix. Nanomaterial of varying morphology such as nanoparticles, nanospheres, nanoencapsules can be used as drug delivery systems. For example, ceramic nanoparticles such as organically modified silica nanoparticles entrapped with anticancer drug, 2-devinyl-2-(1-hexyloxyethyl) pyropheophorbide have been used to damage cancer cells.

Disadvantages of nanomaterials

(i) Instability of the particles - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles, they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

(ii) Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

(iii) Impurity - Because nanoparticles are highly reactive, they inherently interact with impurities as well. In addition, encapsulation of nanoparticles becomes necessary when they are synthesized in a solution (chemical route). The stabilization of nanoparticles occurs because of a non-reactive species engulfing the reactive nano-entities. Thereby, these secondary impurities become a part of the synthesized nanoparticles, and synthesis of pure nanoparticles becomes highly difficult. Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles. Hence retaining high purity in nanoparticles can become a challenge hard to overcome.

(iv) Biologically harmful - Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominantly owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver and blood could also prove to be harmful.

(v) Difficulty in synthesis, isolation and application - It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecules or materials. Free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure.

(vi) Recycling and disposal - There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with affects of nanomaterials is yet to be assessed in order to develop their disposal policies.

Important Questions

Q. What is ‘nanotechnology’? Write the application of carbon ‘nano tubes’ and ‘quantum dots’.

Q. Why are the properties of ‘nano materials’ different from the ‘bulk’? How can ‘nano materials’ be used as optical sensors

Q. Write the magnetic properties of ‘nanomaterials’.

Q. Write the working principle of LCD display

Q. Define ‘carbon nanotubes’ Write few methods of preparation and mention some of its applications

Q. Describe briefly about top down and bottom up approach for the manufacture of nano materials.

Q. Define ‘nano materials’? Discuss the electrical and mechanical properties of ‘carbon nanotubes’.