

CHEMISTRY

Module -V

NEW MATERIALS

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5.1. Introduction to Nanomaterials

The word 'nano' means 'dwarf' and is derived from the Greek word *nanos* or Latin word *nanus*. Nanomaterials are generally classified as those materials, which has atleast one dimension in the nanometre range, i.e. within 1 to 100 nm. A nanometre is one billionth of a metre or 10^{-9} m. One nanometre is approximately the length equivalent to 10 hydrogen atoms or 5 silicon atoms aligned in a line. Nanomaterials are synonymous to nanostructured materials or nanostructures or nanoparticles. In a broader sense, material objects can be represented on two size-scales, namely, macroscopic and microscopic. The macroscopic objects refer to the large objects visible to the naked eye. The lower size limit of the objects, which are visible to the naked eye, is around $10\ \mu\text{m}$. Thus, all the objects larger than ten micron fall within macroscopic scale, such as a house fly and human hair (size $\approx 15\text{-}180\ \mu\text{m}$). The objects that are smaller in size than the eye's visibility limit and that require a microscope to be detected or observed clearly, fall within the microscopic scale. A comparison of the sizes of different objects at the scale of nanometre is shown in Fig. 1.

The branch of science dealing with systematic study of nature and behaviour of nanomaterials based on the experimental observations and formulation of general laws describing their properties is called nanoscience. In other words, the study of fundamental relationships between physical properties, phenomena and materials dimension in the nanometre scale is also referred to as nanoscience. On the other hand, nanotechnology deals with the creation and exploitation (application) of nanomaterials. Nanotechnology cuts across all disciplines, physics, chemistry, materials science, biology and almost all branches of engineering and hence is truly multidisciplinary in nature.

Nanotechnology is new, but research on nanometre scale is not new at all. The study of biological systems and engineering of many materials such as colloidal dispersions, metallic quantum dots and catalysis have been in the nanometre regime for centuries. For examples, Chinese are known to use gold nanoparticles as an inorganic dye to introduce red colour into their ceramic porcelains more than thousand years ago. Colloidal dispersion of gold prepared by Faraday

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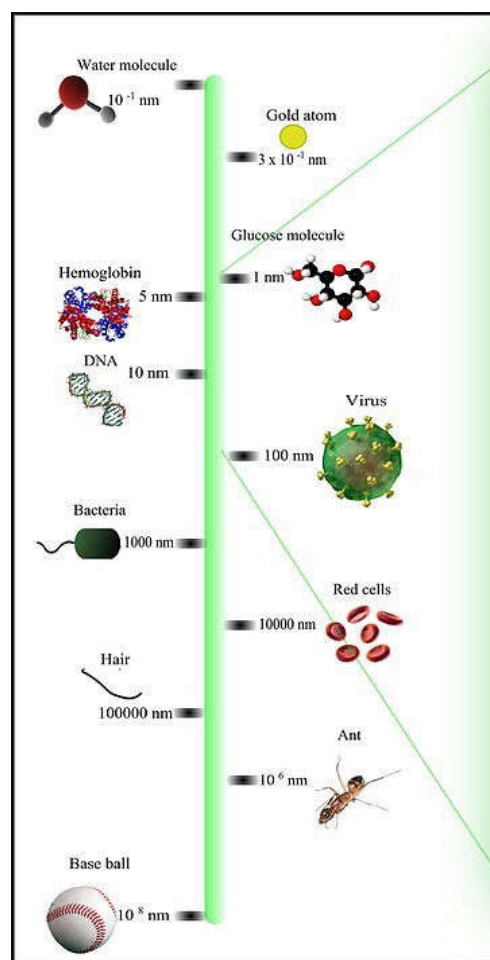


Figure 5.1: Comparison of the sizes of different objects in the scale of nanometre.

before being destroyed during world war-II. Colloidal gold was, and is still, used for the treatment of arthritis. A number of diseases were diagnosed by the interaction of colloidal gold with spinal fluid obtained from the patient. However, the really new thing about nanotechnology is the combination of our ability to see and manipulate materials on the nanoscale and our understanding of atomic scale interactions. The craze for nanotechnology is at least partly driven by the availability of characterization and manipulation techniques at the nanometre level. The nanomaterials exist in nature long before we realise it. For examples, the cell parts, such as, proteins are of sizes about 5 nm. The bone is basically a nanocomposite of inorganic hydroxyapatite crystallites dispersed in the organic matrix, collagen.

5.2. Classification of Nanomaterials

Dimensionality plays an important role in determining the properties of nanomaterials. So, depending on how many physical dimensions are in nanometre scale, and consequently, degree of charge carrier confinement, nanomaterials are classified mainly into four categories, as discussed below:

- (i) Zero-dimensional nanomaterials (0D): These structures have all the three dimensions in the nanometre scale. For example, nanoparticles, nanospheres, quantum dots etc.
- (ii) One-dimensional nanomaterials (1D): 1D structures are those that exhibit at least two dimensions in the nanometre range. Some examples of 1D nanomaterials include, nanorods, nanotubes, nanowires, nanobelts, nanoribbons, nanofibers, nanotips etc.
- (iii) Two-dimensional nanomaterials (2D): 2D structures have at least one dimension in the nanometre order. Some examples of 2D nanomaterials are thin films, nanoplates, nanosheets, nanoflowers, quantum wells etc.
- (iv) Three-dimensional nanomaterials (3D): The 3D structures are actually microscale porous materials with pore diameters in the nanometer range. For example, zeolite, mesoporous materials etc.

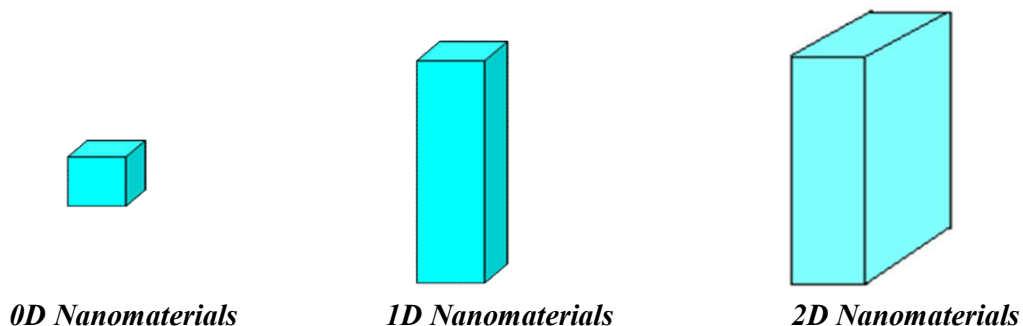


Figure 5.2: Schematic representation of 0D, 1D and 3D nanomaterials.

5.3. Size-dependent Properties of Nanomaterials

Nanomaterials have structural features intermediate between that of atomic or molecules and the bulk materials. So the nanomaterials may exhibit remarkably specific properties, which are in between that of atoms or molecules and the bulk forms. Thus, they have distinctively different properties from that of their bulk or microscopic counterparts. Again, the properties of these nanostructured materials are strongly influenced by their dimensionality, size and morphology. The difference in the properties of the nanomaterials due to size factor can mainly be attributed to their large surface to volume ratio, high surface energy, spatial confinement and reduced imperfections. As the size of the objects decreases, the number of atoms on the surface of the particles significantly increases compared to the number of atoms lying inside the particles. When the particle size approaches the nanoscale limit of about 100 nm, a transition occurs in the materials properties. There is shifting of the size-independent classical behaviour to size-dependent quantum mechanical behaviour. The surface-to-volume ratio of these particles increases with decrease in size and their surface properties start dominating the bulk properties. As per quantum mechanical laws, they possess discrete energy states like those of atoms or smaller molecules. Thus the properties of nanomaterials are much different from those of atoms and bulk materials and can be tuned to get desired property by adjusting the size, shape and extent of agglomeration. Some of the size-dependent properties are discussed below.

Melting point:

Crystals in nanometer scale have a low melting point (the difference can be as large as 1000 °C) or phase transition temperature and reduced lattice constants. This is because; the number of atoms or ions on the surface and the surface energy are significantly high and play important roles in thermal stability.

Electrical behaviour:

Bulk semiconductors become insulators when the characteristic dimension is sufficiently small (in a couple of nanometers). The widening of bandgap of semiconductors occurs, when the size of the materials reaches de-Broglie's wavelength. Bandgap engineered quantum devices, such as lasers and heterojunction polar transistors, have been developed with unusual electronic transport and optical effects.

When the critical dimension of this films and nanowires is smaller than the electron mean free path, the motions of the electrons will be interrupted through collision with the surface, thereby increasing the electrical resistivity. In a polycrystalline material, since the crystalline size becomes smaller than the electron mean free path, a contribution to electrical resistivity from grain boundary scattering arises. Proton conductivity of the polycrystalline antimony oxide films was found to decrease with small grain sizes, which was attributed to grain boundary scattering. Thus, electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, electrical conductivity of nanomaterials could also be enhanced appreciably due to better ordering in microstructures, e.g. polymeric fibrils.

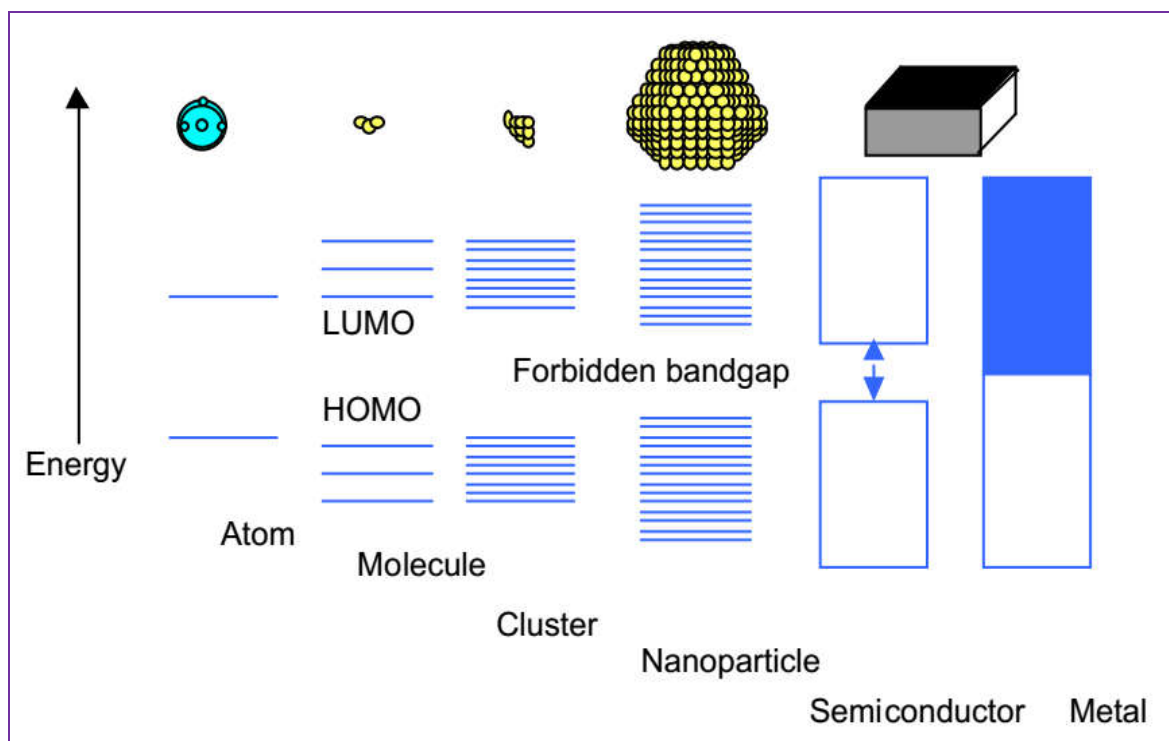


Figure 5.3: The variation of bandgap (energy level) spacing at different stage of a material, i.e., atomic, molecule, cluster, nanoparticle and bulk.

Optical behaviour:

Optical properties of the nanomaterials can be significantly different from bulk crystals. The size dependence of the nanomaterials on optical properties can be because of two reasons – (i) due to increased energy level spacing as the system becomes more confined. (ii) the other one is due to surface plasmon resonance. For example, the optical absorption peak of a semiconductor nanoparticle shifts to a shorter wavelength due to an increased bandgap. The surface inelastic scattering of electrons and phonons would result in a reduced thermal conductivity of nanomaterials and nanostructures, similar to surface inelastic scattering on electrical conductivity. Theoretical studies suggest that thermal conductivity of silicon nanowires with a diameters less than 20 nm would be significantly smaller than that of the bulk counterpart.

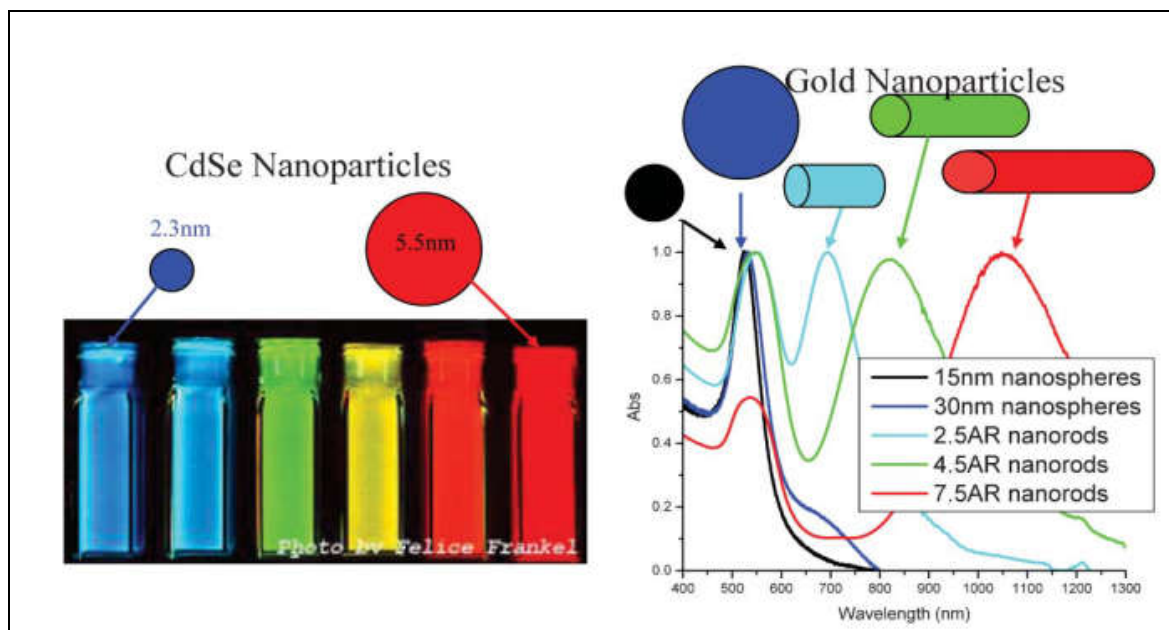


Figure 5.4: The change in optical behaviour of CdSe nanoparticles with variation in size

Magnetic properties:

Crystal structures stable at elevated temperatures are stable at much lower temperatures in nanometer sizes. So ferroelectrics and ferromagnetic materials may lose their ferroelectricity and ferromagnetism, when the materials were shrunk to the nanometer scale. Ferromagnetism of bulk materials disappears and transfers to superparamagnetism in nanometer scale due to the huge surface energy. Ferromagnetic particles become unstable, when the particle size decreases below a certain size. Since the surface energy provides a sufficient energy for domains to spontaneously switch polarization directions, ferromagnetic become paramagnetics. However, nanometer-sized ferromagnetic turned to paramagnetic behaves differently from the conventional paramagnetic and is referred to as superparamagnetics.

Mechanical properties:

Mechanical properties of nanomaterials increase with decreasing size. The mechanical strength may reach the theoretical strength, which is one or two orders of magnitude higher than that of single crystals in the bulk form. This enhancement in the mechanical strength is simply due to the reduced probability of defects.

5.4. Top-Down and Bottom-up approaches to Fabrication of Nanomaterials

Many technologies have been explored for the fabrication of nanostructures and nanomaterials. These technical approaches can be grouped in several ways. One of the ways is to group them according to their fabrication techniques -- Top-down and bottom-up approaches.

As the nanomaterials have structural features between that of bulk materials and atoms or molecules, nanomaterials can be prepared either by breaking the bulk materials into smaller pieces of nanometer sizes or by building the nanomaterials from the building blocks, i.e., atom by atom. The first one is called top-down approach and the latter one is called bottom-up approach.

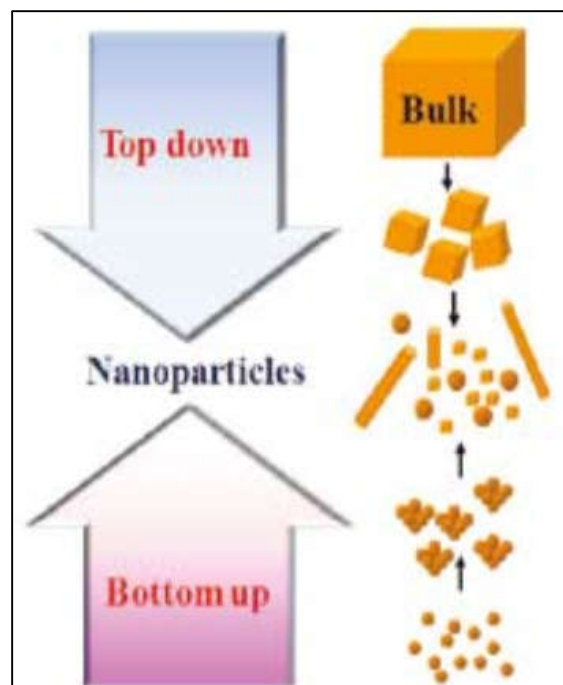


Figure 5.5: Schematic representation of top-down and bottom-up approaches for fabrication of nanomaterials.

5.4.1. Top-down Approaches:

According to this approach, a bulk or macro-sized material is gradually reduced, in one or more dimensions, to the nanoscale by the use of mechanical processes like crushing, milling or grinding. Ball milling is a typical top-down approach to produce nanomaterials by mechanical attrition, in which kinetic energy from a grinding medium is transferred to a material undergoing reduction. Etching is another method, in which a single crystal is etched into nano-sized particles in aqueous solution. Porous silicon is synthesized by using electrochemical etching.

On the other hand, lithography (literally meaning *stone writing*) may be considered as a hybrid approach, since the growth of thin layer (films) is bottom-up approach whereas etching is top-down approach. Lithographic technique basically transfers the mask pattern of any structure onto a substrate in semiconductor fabrication using a radiation-sensitive polymer resistive material. These methods are means of making printed circuits and computer boards for several decades now. Depending on the exposure radiations used; there are three

types of lithography- Photolithography, electron beam lithography and X-rays lithography. The resist is specific to the type of radiation used for each type of lithography.

Photolithography: To illustrate the working of the photolithographic process, let's take the nanolayer of GaAs to be structured into a quantum dot, which is supported on an insulating substrate. The steps are as follows:

- Resist coating and pre-bake: A thin positive resist film is spun on the surface of the GaAs layer. The photoresist is then soft baked at 80-100 °C to drive out the solvent from photoresist.
- UV exposure and post-bake: The sample is then exposed to an appropriate dose of UV radiation through a photo mask making the exposed part of the resist soft, while leaving the rest of the unexposed resist hard. The wafer is then post-baked at 100-120 °C to improve photoresist adhesion to the underlying GaAs layer and further densify and reduce its dissolution in the unexposed region.
- Development: The image of photo-mask pattern is then developed into the resist by dissolving the soft part of the photo resist in developer solution.
- Etching: The pattern is etched into the GaAs layer by wet chemical or dry etching process through window openings in the resist.
- Stripping: The remaining resist is dissolved, leaving behind the GaAs layer in the form of a quantum dot.

Electron beam lithography: As per de Broglie theory, an electron beam behaves as a particle and a wave simultaneously. Since the wavelength of electron beam is very small, the use of e-beam in lithography produces high resolution small features and is highly appropriate for nanostructure fabrication. E-beam lithography uses a focussed beam of electrons to expose the resist (generally PMMA) and the pattern is directly written into the resist by scanning the electron beam without the need for a mask.

X-ray Lithography: In this case, X-ray radiation is used for resist exposure and pattern development. The X-ray mask consists of a thin membrane of Si or SiC with the pattern absorber of a high atomic number material such as gold, tungsten or titanium and the membrane is supported on a glass frame. Considering the refractive index of X-ray is close to unity, the reflection of X-rays at most of the interfaces is negligible and the exposure at the unwanted places can be prevented.

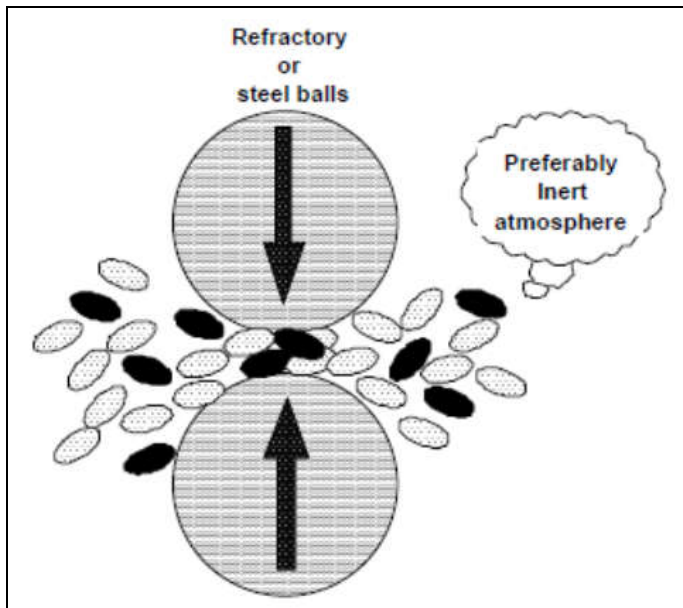


Figure 5.6: Schematic representation of mechanical milling- one of the top-down approaches for fabrication of nanomaterials.

Disadvantages of top-down approaches:

- Usually top-down routes are not suitable for preparing uniformly shaped materials, and it is very difficult to realize very small particles even with high energy consumption.
- Imperfection of the surface structure is the biggest problem in top-down approaches, like lithography. The lithography process can cause significant crystallographic damage to the processed patterns and additionally introduce internal stress, surface defects and contamination (may be introduced during etching steps). Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials, since the surface-to-volume ratio in nanostructures is very large.
- The surface imperfections may result in a reduced conductivity due to inelastic surface scattering, leading to generation of excess heat.

Regardless of all these disadvantages, top-down approaches will continue to play an important role in the synthesis of nanomaterials.

5.4.2. Bottom-Up Approaches:

Bottom-up methods refers to build-up of a material from the bottom, i.e., atom-by-atom, molecule-by-molecule or cluster-by-cluster. Similar to the synthesis of polymers, where individual monomers are connected together, in bottom-up approaches, growth species (such as atoms, ions, or molecules) assembly into crystal structure one after the other. This route is

more often used for preparing most of the nano-scale materials with less defects, more homogeneous chemical composition and better short and long range ordering. This has also the ability to generate nanomaterials with uniform size, shape and distribution. Bottom-up approaches effectively cover chemical synthesis and precisely controlled reaction by inhibiting further particle growth. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

Chemical vapor deposition (CVD) is a gas-phase process by which reactive constituents react over a catalyst or pre-templated surface to form nanostructure materials. The economical synthesis of carbon nanotubes is by CVD. Atomic layer deposition is an industrial process that is capable of coating any material, regardless of size, with a monolayer or more of a thin film. Molecular beam epitaxy and MOCVD are other industrialized processes that are considered to be bottom-up. Electrodeposition and electroless deposition are very simple ways to make nanomaterials (dots, clusters, colloids, rods, wires, thin films). Anodizing aluminium to make a porous oxide structure is a simple way to make nanomaterials. The porous structure is a nanomaterial as well as any material synthesized within. Porous membranes are in many ways the ultimate template. Liquid phase methods are also numerous. It is within the liquid phase that all of self-assembly and synthesis occurs. Liquid phase methods are up-scalable and low cost. The liquid (solution) phase methods include hydrothermal method, microwave synthesis method, sol-gel method, sonochemical synthesis route.

5.5. Synthesis of Nanomaterials by Green Synthesis Routes:

The application of green chemistry in nanomaterials synthesis aims to reduce or avoid the use of toxic and hazardous substances and to minimize or prevent wastes generated from reactions without compromising the efficacy. These synthesis processes are rationally divided into nucleation and growth. It is found that the capping agent, reducing agent and the reaction solvent are of great importance for the synthesis of uniform sized, monodispersed nanoparticles with desired morphology. In this regard, these three factors should be considered from a green chemistry perspective, involving the use of nontoxic capping agents, less hazardous reducing agents, and selection of environmentally friendly solvents. In addition, development of green synthesis strategies that can overcome the heating efficiency problems associated with conventional methods, which largely depend on the convection currents and thermal conductivity of the reaction materials. Some of the environmentally benign synthetic routes (green synthetic methods) for fabrication of nanomaterials are microwave-assisted method and sonochemical method.

5.5.1. Microwave-assisted synthesis Route:

Synthesis of nanomaterials with the application of microwave radiation to the reaction mixture is known as microwave-assisted synthesis. Microwave radiations are high frequency

electromagnetic radiations capable of heating materials containing mobile electric charges, which is due to the conduction ions or polar molecules. Microwave heat up ionic materials when the ions or electrons within them generate a current and energy is lost due to the resistance. Polar solvents are heated up when the molecules align their dipoles within the external field and lose energy in collisions. Therefore, high dielectric solvents, i.e. dimethylsulfoxide (DMSO) and dimethylformamide (DMF), are preferably used to induce localized superheating and pressure effects. These often give rise to a higher heating rate in comparison with conventional heating and thus lead to the reduction of reaction time as well as the increase of reaction rate. This is due to the rapid and almost simultaneous precipitation of nanoparticles under the microwave irradiation of the reaction mixture. It should be noted that many nonpolar solvents used in conventional synthesis are often reluctant to absorb the microwave irradiation and therefore cannot be used in the microwave synthesis directly. In order to improve the feasibility of microwave technique towards more extensive reactions, a small amount of strong adsorbing agents, i.e. ionic liquids, could be introduced to promote the reactions without apparently affecting the nanoparticle formation. Frequencies between 1 to 2.5 GHz are generally used for the microwave synthesis in laboratories.

Microwave irradiation is considered as a promising alternative for the synthesis of nanoparticles with environmental benefits. With the help of microwaves, various types of nanoparticles could be fabricated, including metals, oxides, chalcogenides and phosphates. Their applications in industries and technologies strongly motivate advances in microwave synthesis. In addition to the environmental benefits, microwave irradiation provides an adjustable heating manner to manipulate the formation of nanoparticles. Specifically, the wavelength of microwaves has a strong impact on the penetration depths in the reaction mixtures and thus largely determines the heating rate. Therefore the nucleation and the subsequent growth in the formation of nanoparticles are controllable.

5.5.2. Sonochemical Route

Application of ultrasound waves for the synthesis of nanomaterials involves acoustic cavitation process in a solution leading to rapid chemical reaction. In acoustic cavitation process, primary bubbles are generated and oscillated under the influence of acoustic waves, which grow to a certain size with continuously accumulating ultrasonic energy. Ultimately the bubbles with size exceeding the threshold for stabilization could collapse significantly and release considerable energy stored inside. The generated hot spots with high temperature of 5000 K and high pressure of 1000 bar serve as the motivation for nanoparticle synthesis. With these extremely remarkable reaction conditions that could not be satisfied by conventional synthetic methods, ultrasound is capable of producing nanoparticles with narrow size distribution as well as high phase purity. Compare to conventional methods, ultrasound synthesis is faster and is always carried under ambient conditions without extra demand of reducing agents. All of these advantages make sonochemical route, a promising technique for green synthetic strategy. A nontoxic solvent, water is frequently used in

sonochemical synthesis. The acoustic cavitation arouses the sonolysis of water leading to the harvesting of a large number of Hydrogen free radicals, the combination of these produce H_2 with reductive capabilities utilized in specific reactions.

5.6. Applications of Nanomaterials in Electronic Devices, Environmental and other Fields

Nanoparticles are being widely used to control environmental pollution. Nanoparticles on powder supports form a catalytic system used in the removal of pollutants such as oxidation of volatile organic compounds in chimneys. Oxidation of flue gases in the catalytic converters of petrol-burning IC engines in the presence Pt catalyst. NO_x is removed by reducing it to N_2 (catalyst Rh) and hydrocarbons are oxidized to CO_2 and H_2O using Pd catalyst. Nanocrystalline metal oxide films are used as gas (CO , CO_2 , CH_4 , NO_x) sensors. Nanophosphors find application as detectors for the leakage of gas.

Nanomaterials are widely used in electronic circuits such as television, radio, telephone, automobiles, aeronautics etc. Use of nanomaterials helps in reducing the size of these gadgets. Nanoscale magnetic materials are used for data storage devices such as computer hard discs. Silicon nanocrystals are used in manufacturing of solar cells. ZnO nanorods are extensively used to fabricate nanoscale electronic devices.

- Crystalline nanoparticles of zeolite are used as filters to convert crude oil to diesel fuel by a method cheaper than the conventional way.
- Nanocrystalline and nanoporous Si exhibits electroluminescence, photoluminescence and refractive index changes that can be controlled.
- Due to high mechanical strength, Nanomaterials of tungsten carbide, titanium carbide used for microdrills for microelectronic circuits.
- Nanocrystalline zirconia, alumina are used for coating combustion engine cylinders.
- Nanostructured metal oxide (MnO_2) used in rechargeable batteries.
- SiO_2 Nanoparticles are used in ketch up and table salt as free flowing agent. Also used in paint and varnishes for scratch-resistant surfaces. Nano silica used for dental fillings and cosmetics
- TiO_2 Nanoparticles are used in toothpaste, chewing gum and in sweets as color and anti-melting agent. It is also used in packaging materials as UV filter for storing beverages.
- Nanomaterials are also used in electronics, tyres, in medicine for purposes of diagnosis, imaging, drug delivery, sporting goods.

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