1. INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGY

Introduction – Nanoscience and Nanotechnology – Nanomaterials – Quantum confinement in semiconductors – Special characteristic features of Nanomaterials – Classification of Nanomaterials – Types of Nanomaterials – Different forms of Nanomaterials – Synthesis of Nanomaterials – Preparation of Nanomaterials

Introduction

In the current scientific research, Nanoscience and Nanotechnology have introduced new trends that involve the ability to prepare, characterize and manipulate artificial structures, whose features are controlled at the nano-sized level. Nanoscience and Nanotechnology plays a very important role in many areas of engineering, physics, chemistry, materials science and molecular biology. Nanoscience refers to the science and discipline and nanotechnology refers to the applied part of it, including the engineering to control, manipulate and structure matter on an unimaginably small scale: the nano scale. This scale is also referred to as 'atomic' or 'molecular', which is 100 nanometers or smaller. This 'nano' capability gives us the ability to build materials, devices or shapes, and products on that scale. Materials on the micrometer scale mostly exhibit the same physical properties as those of the bulk form; however, materials on the nanometer scale may exhibit physical properties distinctively different from those of the bulk. Nanotechnology is an area of modern science which deals with ability to control and manipulate matter at a scale ranging from less than a nanometer up to 100 nm. It deals with fabrication and structures of objects with dimensions in order of nanometers. The research in this area has been set off by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties, with resolution close to an atomic level. Nanoscience deals with sciences related to the systems structured by nanotechnology.

Generally in the nanometer region, most physical, chemical, biological, mechanical, electrical etc. become size-dependent.

Nanotechnology is distinguished by its interdisciplinary nature, and its investigations at the nano-level occur in a variety of academic fields which include: physics, chemistry, biology, computer science, electrical engineering, mechanical engineering etc. In order to explore novel physical and chemical properties, and realize the potential applications of nanostructures, the ability to fabricate and process nanomaterials and nanostructures is the first corner stone in nanoscience and nanotechnology. On the technological front, there is a strong demand to develop new techniques to fabricate and measure the properties of nanomaterials and related devices. It has been demonstrated that materials on the nanoscale have unique physical and chemical properties compared to their bulk counterparts, and these properties are highly promising for a variety of technological applications.

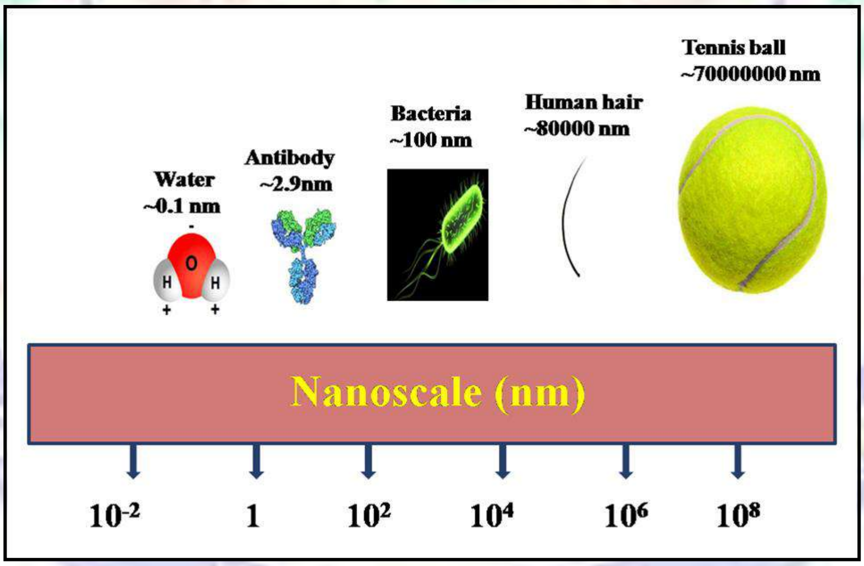

Fig. 1.1 Illustration of Nanoscale materials

Often, nanoscaled materials exhibit altogether different or superior properties than large particle-sized materials. Due to their small size they have a high surface-to-volume ratio that increases the surface energy leading to distinctively different chemical, electronic, optical, magnetic, and mechanical properties. As a result, unexpected properties can be obtained compared to those of both the individual atoms/molecules and the bulk counterparts of the same chemical composition. The size- and shape-dependent properties of nanocrystals can be tuned by changing the dimension and designing the shape. Due to their nanoscale, low coordination number, and surfaced edge and corner atoms are usually chemically reactive, catalytically active and polarisable surface, contributing to their high chemical potential (shown in Fig.1.1). For example, the high surface area is of particular importance regarding heterogeneous catalytic reactions, because of the increase in the interaction of reactive molecules and active sites on the catalyst surface. Furthermore, the particle size not only affects their surface area, but also produces new properties, due to quantum-size effects like electron confinement and surface effect. For example, nanoparticles-based semiconductors sensors exhibit higher sensitivity towards air pollutants for lower detection thresholds, at lower operating temperatures. Also, nanomaterials are playing a greater role in electrical, optical, bio-analytical and environmental remediation appliances.

In electronics, design and assembly of functional materials and devices based on Nano scale building blocks can be seen as the natural, inevitable evolution of the trend toward miniaturization. Therefore, the development of a morphologically controllable synthesis of nanomaterials by a simple and economical method is an important issue. Several methods have been used to develop the synthesis of nanocrystalline materials. In addition, the characterization of the nanomaterials has also become an important issue from the viewpoint of technological applications. The topic of nanometer structures is an exciting area, intellectually challenging and rapidly expanding. It has crossed the boundaries of the physical and chemical sciences, biology and engineering.

1.1 Nanomaterials

Materials are composed of grains, which in turn comprise of many atoms. These grains can be visible or invisible to the naked eye, depending on their size. Conventional materials have grains varying in size anywhere from hundreds if microns to centimeters. Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanomaterials are commonly defined as materials with an average grain size less than 100 nanometers or the materials that consist of or contain nanoparticles, and can offer improved properties such as lower weight, or higher strength. A nanometer is one millionth of a millimeter approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials constitute a bridge between atomic, molecular and bulk systems. New or enhanced size- and shape-dependent properties are unveiled compared with their counterpart bulk materials. Nanomaterials are of interest because at this scale unique and quite different, optical, magnetic, electrical, and other properties emerge. 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, which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery. Engineered nanomaterials are resources designed at the molecular (nanometer) 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 materials at the nano scale can have different properties are 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 and affect their strength. 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. Nanomaterials are already in commercial use, with some having been available for several years or decades. 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 nano-composites are finding uses in some nanomaterials occur naturally, but of particular interest are engineered nanomaterials), which are designed for, and already being used in many commercial products and processes.

Nano-coatings and nano-composites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butylrubber/nano-clay composites. Nano-scale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nano-scale silica is being used as filler in a range of products, including cosmetics and dental fillings.

1.2 Quantum confinement in semiconductors

On the other hand, especially since the emergence of the nanotechnology, novel electrical, mechanical, chemical and optical properties are introduced with the reduction in size, which are largely believed to be the result of surface and quantum confinement effects. The optical properties of nanoparticles and nanowires are affected by their particle size as a consequence of the change in band structure of nanocrystals as compared to its bulk properties.

Semiconductors contain an almost-empty conduction band and an almost full valence band. The energy difference between the bottom of the conduction band and the top of the valence bands is called the band gap energy (E_g) which can be direct or indirect band gaps, depending on the band structure as shown in Fig.1.2. For direct band gap semiconductors, the minimum of the conduction band and the maximum of the valence band occur at momentum k =0 (k is the wave vector) as illustrated in Scheme (a). In contrast, for indirect band gap semiconductors, the minimum of the conduction band and the maximum of the valence band are not at the same value k (Scheme b).

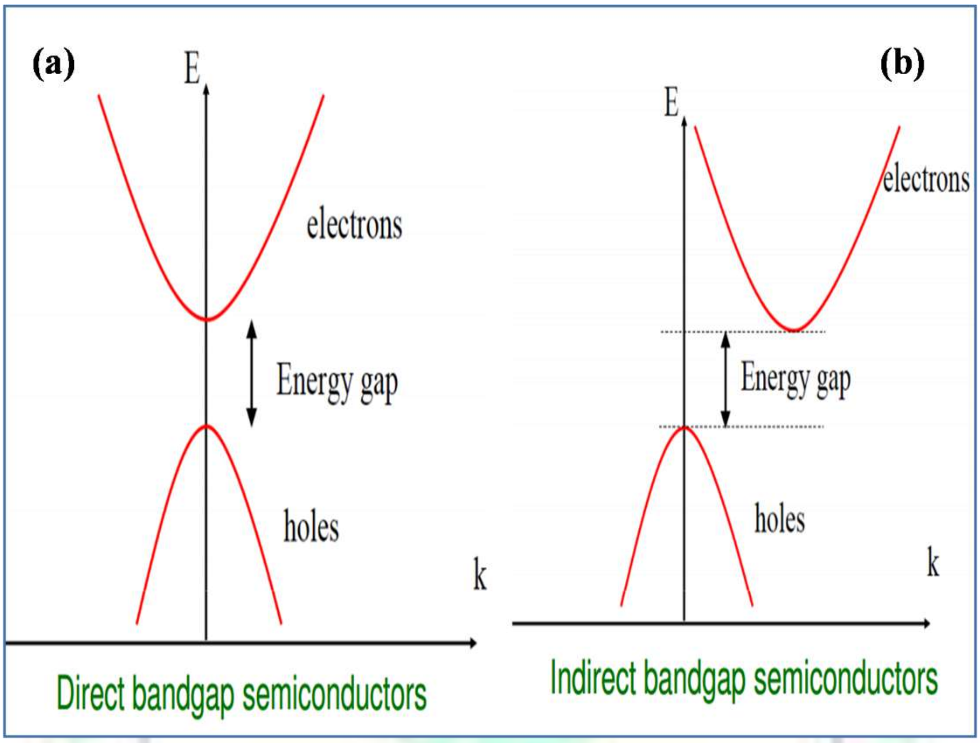

Fig. 1.2 Schematic representation of (a) Direct band gap (b) Indirect band gap semiconductors

When light with photon energy larger than the band gap energy enters a semiconductor, it excites an electron from the valence band into the conduction band, and generates one electron-hole pair which is called an exciton. The distance in the electron-hole pair in bulk semiconductor, expressed as an exciton Bohr radius, provides an approximate dimension for onset of quantum confinement effects. In fact, the absorption process in semiconductors is quite complicated. For a direct band gap process, the photon energy is sufficient to excite an electron simply straight up into a free state of almost the same k value. But, for an indirect band gap process the photons with sufficient energy to excite the electron must still fulfill the conservation of momentum which is achieved by the additional absorption or emission of a phonon.

Quantum confinement occurs when an electron-hole pair is squeezed into a semiconductor nanocrystal with one or more dimensions approaching the bulk exciton Bohr radius. The band gap of the semiconductor nanocrystals exhibits strong size dependence, which is a consequence of the quantum confinement effects. Nanocrystals contain limited number of molecular units and therefore the band gap energy is between that of the macrocrystals and of the molecule, i.e, larger than the crystal band gap but smaller than the molecular energy. Numerous research studies have demonstrated the blue shift in the absorption edge, reflectivity edge and emission from bulk semiconductor nanocrystal with the reduction in crystallite size.

1.3 Special characteristic features of nanomaterials

In our nature makes nano objects of varying kind. The recent growth of technology suggests that reductions are needed in the dimensions of devices and active materials. With all these developments, new nanotechnology products will indeed reach the marketplace in the immediate future. It is well-known that, in addition to smaller grain size, nanomaterials contain less number of atoms. In contrast, the crystallite sizes of conventional materials vary from a few microns to a few millimeters and contain several billions of atoms. These basic differences make nanomaterials unique and special from others. Further, nanomaterials contain a very large number of grain boundaries which may be 50% or more of the total volume of the material. This unique microstructure makes these materials to exhibit different properties such as tremendous strength, hardness, formability and toughness. Surface passivation and suitable functionalization make the system chemically inert and thermally stable. In fact, various attributes can be added to the nanocrystal by appropriate modification. This includes chemical and biological compatibility, hydrophobicity, hydrophylicity, etc. For example, nanostructured copper is five times stronger than ordinary copper. A nanotube-based single molecule field effect transistor has already been built. The performance of this device is comparable to that of semiconductor-based devices, but the integration of this into circuits will require a lot of effort.

1.4 Classification of nanomaterials

Classification of solids can be based on atomic arrangement, binding energy, physical and chemical properties or the geometrical aspects of the crystalline structure. The atoms are arranged in a regular order, these solids are referred to as crystalline solids. The atoms in a solid are set in an irregular manner; these solids are commonly known as non-crystalline or amorphous materials. The crystalline solids can be further divided into two categories; the single crystalline and the poly crystalline solids. However, the regular order exists only over a small region of the crystal with a grain size ranging from a few hundred angstroms to a few nanometers.

Due to the reduction in the spatial dimension, or confinement of particles or quasi particles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence classification of the nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometer range. Nanoparticles are intermediate between atomic and bulk level. At nano level, the properties greatly changed, as the size of the particles changed owing to their large surface to volume ratio. Nanoparticles are like ultrafine particles sized between 1 and 100 nm, though the size limitations can be restricted to two dimensions.

In general, nanomaterials can be classified into four categories based on their confinement. They are zero-dimensional (0D) (nano-clusters), one-dimensional (1D) (lamellar), two-dimensional (2D) (filamentary) and three dimensional (3D) (equiaxed) as shown in Fig. 1.3.

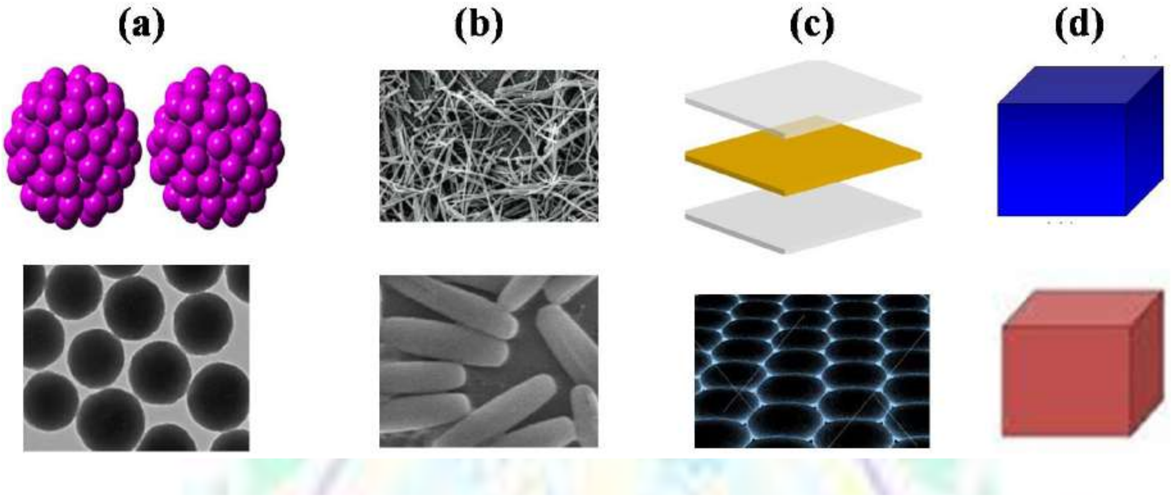

Fig. 1.3 Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nano-fibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nano-scale in one dimension (e.g. surface films), two dimensions (e.g. strands or fibers), or three dimensions (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). Nanomaterials may be classified as those materials which have at least one of their dimensions in the nano-metric range, below which there is significant variation in the property of interest compared to microcrystalline materials. Siegel classified nanostructured materials into four categories according to their dimensionality as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

Nanomaterials are materials which are characterized by an ultra-fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayer's), two (ultrafine-grained over-layers or buried layers), and three (nano-phase materials consisting of equiaxed nanometer sized grains) as shown in Fig. Study of one dimensional (1D) materials has become a leading edge in nanoscience and nanotechnology.

1.5 Types of nanomaterials

There are two types of nanomaterials: Natural nanomaterials and synthetic nanomaterials. Biological systems viruses, the wax materials covering a lotus leaf, spider, butterfly wing scales, nature colloids, paper, cotton, nacre, corals, bones etc., are all natural organic materials. Natural inorganic nanomaterials occur from crystal growth in the diverse chemical conditions of earth's crust. Clay, pigments, cement, fumed silica etc., are examples of natural inorganic nanomaterials.

The organic nanomaterials fullerene is a class of allotropes of carbon which are graphene sheets rolled into tubes or spheres. These include the carbon nanotubes which are of its mechanical strength and electrical properties. The inorganic materials such as quantum dots, nanowires and nanorods are made from metals, semiconductors or oxides are of great interest for their mechanical, optical, electrical, electrochemical, magnetic and other properties.

1.6 Different forms of nanomaterials

Nanoparticles: particle with one or more dimensions at the nanoscale. The particle size is in the order of 10^{-9}m.

Nanorods: Nanostructures which are shaped like long sticks or rods with diameter in nanoscale and a length very much longer. Nanorods are one dimensional structure which provides a directed path for electrical transport and are used to control the band gap by varying the radius of rods and using the quantum size effect

Nanowires: A nanowire is an extremely thin wire with a diameter on the order of a few nanometers or less and with lengths orders of magnitude larger than its diameter. Two processes in nanotechnology by which nanowire can be manufactured are suspension and deposition.

Nanotubes: The carbon nanotubes are the wires of pure carbon like rolled sheets of graphite or like soda straws.

Nanodots: Nanoparticles which consist of homogeneous material, especially they are almost spherical or cubical in shape.

Cluster: A collection of units (atoms or reactive molecules) upto about 50 units.

Colloids: A stable liquid phase containing particles of size 1-1000 nm range.

(i) Nanostructured materials

The classical laws of physics and chemistry do not readily apply at this very small scale for two reasons. Firstly, the electronic properties of very small particles can be very different from their larger cousins. Secondly, the ratio of surface area to volume becomes much higher, and since the surface atoms are generally most reactive, the properties of a material change in unexpected ways. For example, when silver is turned into very small particles, it takes on antimicrobial properties while gold particles become any color you choose. Properties of nanomaterials are different and often superior to their conventional counterparts available in polycrystalline form as they depends on the microstructure which is determined by the chemical composition, grain size, atomic structure, crystallographic orientation, coordination number and dimensionality. Because of the fine grain dimensions significant volume fraction of atoms in nanomaterials is located at the grain boundaries that confer special attribute to them.

The properties of materials at the nanoscale are very different from those at a larger scale. When the dimension of a material is reduced from a large size, the properties remain the same at first and then small changes occur, until finally when the size drops below 100 nm, dramatic changes in properties can occur. If only one length of a three-dimensional nanostructure is of nano dimension, the structure is referred to as a quantum well; if two sides are of nanometer length, the structure is referred to as a quantum wire. A quantum dot has all three dimensions in the nano range. The term quantum is associated with these three types of nanostructures because the changes in properties arise from the quantum-mechanical nature of physics in the domain of the ultra small.

The size of the nanoparticles grains strongly effect the property changes in the bulk material. For instance, the overlapping of different grain sizes affects the physical strength of the material. Also, when the crystallites of a material are reduced to the nanometer scale, there is an increase in the role of interfacial defects: grain boundaries, triple junctions, and elastically distorted layers. The long established Hall-Petch model that shows the inverse relationship between grain size and material yield strength has been proven to hold with nanoparticles as well.

$$\sigma_y = \sigma_o + \frac{K}{\sqrt{d}}$$

Where σ_y is the yield stress, σ_o is a material constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), k is the strengthening coefficient (a constant specific to each material), and d is the average grain diameter.

(ii) Nanocomposites:

Nanocomposites are a combination of two materials in which one of the material is called reinforcing phase, is in the form of fibers, sheets or particles are embedded in the other material called the matrix phase. Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile or rough material. Nanocomposites are a multiphase solid material where one of the phases has 1, 2 or 3 dimensions of less than 100 nm. The area of the interface between the matrix and reinforcement phase is an order of magnitude greater than conventional composite materials. This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have observable effect on the macro scale properties of the composite. Nanocomposites have greater mechanical, magnetic, electrical, catalytic and corrosion resistant properties. Ceramic matrix composites, metal matrix composites and polymer matrix composites are three types of nanocomposites. Nanocomposites have enhanced optical properties, dielectric properties, heat or mechanical properties such as stiffness, strength and resistance to wear and damage.

Nanocomposite materials formed by metallic or oxide particles dispersed in polymer, ceramic or vitreous matrices have important application in areas such as catalysis and electronics. An interesting class of nanocomposite materials is formed by nanometer sized magnetic particles dispersed in insulating matrix. These nanocrystalline particles have a high surface/volume ratio, leading to magnetic properties different from those of bulk materials. Such properties are also highly dependent on the particle size distribution as well as on the aggregation of particles when compared to different production methods. Co-precipitation process has proved to be an efficient method to prepare ultra- fine particles dispersed in different matrices and, particularly, to produce thin film. Through this method, a good control of the sample morphology, texture, structure, and chemical composition can be attained by carefully monitoring the preparation parameters. The use of an inorganic matrix allows narrow dispersion of particle size, and homogeneous distribution.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

The inorganic components can be three-dimensional framework systems such as zeolites, two dimensional layered materials such as clays, metal oxides, metal phosphates, and also chalcogenides. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non- linear optics, battery cathodes and Ionics, nano-wires, sensors and other systems.

The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio ceramics and bio-mineralization in which in-situ growth and polymerization of biopolymer and inorganic matrix is occurring. Further, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. Since the remarkable properties of conventional composites are mainly due to interface interactions, the materials dealt with here could provide good model systems in which such interactions can be studied in detail using conventional bulk sample (as opposed to surface) techniques. Inorganic layered materials exist in great variety. They possess well defined, ordered intra lamellar space potentially accessible by foreign species. This ability enables them to act as matrices or hosts for polymers, yielding interesting hybrid nano-composite materials.

(iii) Polymeric nanoparticles

The polymeric nanoparticles are defined as particulate dispersion and solid particles with size in range of 10-1000 nm. The polymeric nanoparticles have been extensively studied as particulate carriers in various fields such as pharmaceutical and medical fields. They are also used for drug delivery system. The several polymeric nanoparticles are synthesized from biodegradable and biocompatible polymers. The several types of drugs are dissolved in polymeric nanoparticles. They increase stability of any volatile pharmaceuticals agents. They are also used in cancer therapy and delivery of vaccines.

(iv) Core-shell nanoparticles

Core/shell nanoparticles are nanostructures that have core made of a material coated with another material. They are in the size range of 20-200nm. Also, composite structures with these core/shell particles embedded in a matrix material are in use. The necessity to shift to core/shell nanoparticles is the improvement in the properties. Taking into consideration the size of the nanoparticles, the shell material can be chosen such that the agglomeration of particle can be prevented. This implies that the mono disparity of the particles can be improved. The core/shell structure enhances the thermal and chemical stability of the nanoparticles, improves solubility, makes them less cytotoxic and allows conjugation of other molecules to these particles. The shell can also prevent the oxidation of the core material. "When a core nanoparticles is coated with a polymeric layer or an inorganic layer, because the polymeric or an inorganic layer would endow the hybrid structure with an additional function/property on top of the function/property of the core hence synergistically emerged functions can be envisioned". Recently, core/shell nanoparticles are finding widespread application. There is a class of Core/shell nanoparticles that has its entire constituent in the nanometer range.

(v) Carbon-based Nanostructures

The carbon based nanostructures are important types of nanoparticles and having different types such as graphene, diamond, nanotube and nanofibers. They have high surface area for the deposition of conducting polymer and metal oxide nanoparticles and which fascinate the efficient ion diffusion phenomenon and contribute towards higher specific capacitance of carbon based composite material with excellent cyclic stability. They have small dimensions, high chemical stability, high thermal conductivity and low resistivity.

The main requirements of suitable supports for fuel cell catalysts are high surface area, good electrical conductivity, suitable porosity to allow good reactant flux, and acceptable stability (e.g., corrosion resistant) in acidic fuel cell environment. The high availability and low cost make carbon-based nanostructures (CBs) the most used support for low-temperature fuel cell catalysts. Recent studies have revealed that the physical properties of the carbon support can greatly affect the electrochemical properties of the fuel cell catalyst. It has been reported that carbon materials with both high surface area and good crystallinity cannot only provide a high dispersion of Pt nanoparticles but also facilitate electron transfer, resulting in better performance.

Among the new carbon materials, carbon nanotubes (CNTs) are the most investigated as catalyst support for low-temperature fuel cells. They normally possess an outer diameter of 10–50 nm, an inside diameter of 3–15 nm (pore size), and a tube length of 10–50 μm. The high crystallinity of CNTs makes these materials highly conductive; the high specific surface area and high amount of mesopores result in a high metal dispersion and a good reactant flux in tubular structures. Moreover, CNTs have a positive effect on platinum (Pt) structure, resulting in a higher catalytic activity and a higher stability than CBs. A problem for the commercialization of CNTs is their higher cost compared with that of CBs. The number of the Pt particles inside the tube will be more when the tube length of CNT increases. So, a decrease in the Pt active area and the electrochemical activity of the catalyst has to be expected.

Graphene, a single-layer graphite with closely packed conjugated hexagonal lattices, is recognized as the basic building block of all dimensional graphitic materials. Also, graphene nano-ribbons can be prepared by longitudinal unzipping of CNTs. So, graphene not only possesses all advantages of CNTs as catalyst supports, for example, high electrical conductivity and huge specific surface area, but also avoids the drawback of catalyst particles existing inside the nanotube. Furthermore, the large size of graphene (layer diameter >1 μm) can also eliminate the possible health problems caused by CNT pollution. Thus, graphene has been exploited as the support of Pt catalyst. These improved properties are attributed to the smaller aggregation of Pt particles immobilized on graphene. In addition, Pt nanoparticles are supported on graphene nano-platelets, and this catalyst also showed a good electrochemical durability (two to three times that of the Pt/CNT). Beside Pt nanoparticles, the graphene-supported Pt-on-Pd bimetallic nanodendrites and Pt-Ru nanoparticles are also prepared for methanol and ethanol oxidations. Compared with CB, graphene strongly enhanced the oxidation efficiencies of both methanol and ethanol.

In addition, nanostructured electro-ceramic materials are increasingly used in intermediate-temperature solid oxide fuel cells (IT-SOFCs). For example, SOFC microstructure components fabricated by starting with nanosized particles possess different electrocatalytic and ion-conduction properties from the typical polycrystalline materials. Furthermore, by decreasing the particle size in the electro-ceramics, the quantum confinement effect causes an increase in the band gap and, thus, favors the occurrence of a purely ionic domain.

(vi) Metal sulphide nanomaterials

In recent years, wide band gap II–VI semiconductors are expected to be novel materials for optoelectronic devices. Zinc sulphide (ZnS), which is an important member of this family with a wide direct band gap of 3.6 eV, has been extensively investigated, as it has numerous applications. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability, compared to other Chalcogenides. Recently, considerable efforts have been devoted to the synthesis of ZnS phosphors with controllable size and morphology. Various methods have been proposed to prepare ZnS materials, such as solid-phase reactions, gas phase reaction with H_2S, sol-gel process, hydrothermal and solvo-thermal route, precipitation, and gamma-irradiation technique.

Furthermore, research on the synthesis of narrow band gap IV-VI semiconductor nanoparticles, such as PbS, SnS, and SnTe has also attracted increasing interest as they are optically active in the near infrared region (NIR) and infrared region (IR), thus they have potential applications in photovoltaic, near-infrared detectors and biomedical applications such as targeted cancer cell hyperthermia.

In the past decade, much attention has been given to the synthesis of monodisperse chalcogenides nanoparticles with cubic crystal structures such as CdS, CdSeS, CdSe and PbS due to their ease of synthesis. In contrast, SnS adopts an orthorhombic (anisotropic unit cell) layered crystal structure where the Sn and S atoms are tightly bonded in the layer and the layers are bonded by weak van der Waals forces. The synthesis of uniform size IV-VI semiconductor nanoparticles with layered structures that are small enough to be in the quantum confinement regime is still a significant challenge.

Conventional SnS synthetic techniques such as spray pyrolysis, chemical vapour deposition and electron beam evaporation have been applied most often for the fabrication of bulk SnS films. Investigations into SnS nanoparticles synthesis are comparatively few. From the literature survey, it is observed that the preparation of SnS nanoparticles through a precipitation reaction between tin chloride dihydrate and thioacetamide in an acidic aqueous solution. Trioctylphosphine (TOP) and Oleic acid were used as surfactant in the reaction which renders the synthesized SnS nanoparticles hydrophobic. To achieve one-pot synthesis of water-soluble nanoparticles it is required to perform reactions either in an aqueous solution or in a hydrophilic organic solution. SnS has been synthesized in H_2O using bi-functional surfactant, together with tin chloride dehydrate and sodium sulphide or thioacetamide or thiourea as the tin and sulfur precursor, respectively, but it produced nanorods or nanosheets rather than nanoparticles. Another important feature in the development of Sn (II) oxide and chalcogenides materials is the ability to control oxidation state, so as to suppress the production of higher oxidation state materials (i.e. Sn_2O_3, SnO_2, Sn_2S_3 SnS_2, Sn_2Se_3 and $SnSe_2$), the presence of which can be detrimental to the performance of binary Sn(II) oxide or chalcogenides materials.

1.7 Synthesis of nanomaterials

The methods for the synthesis of nanomaterials are broadly classified into two ways:

(i) Top-down process

(ii) Bottom-up process

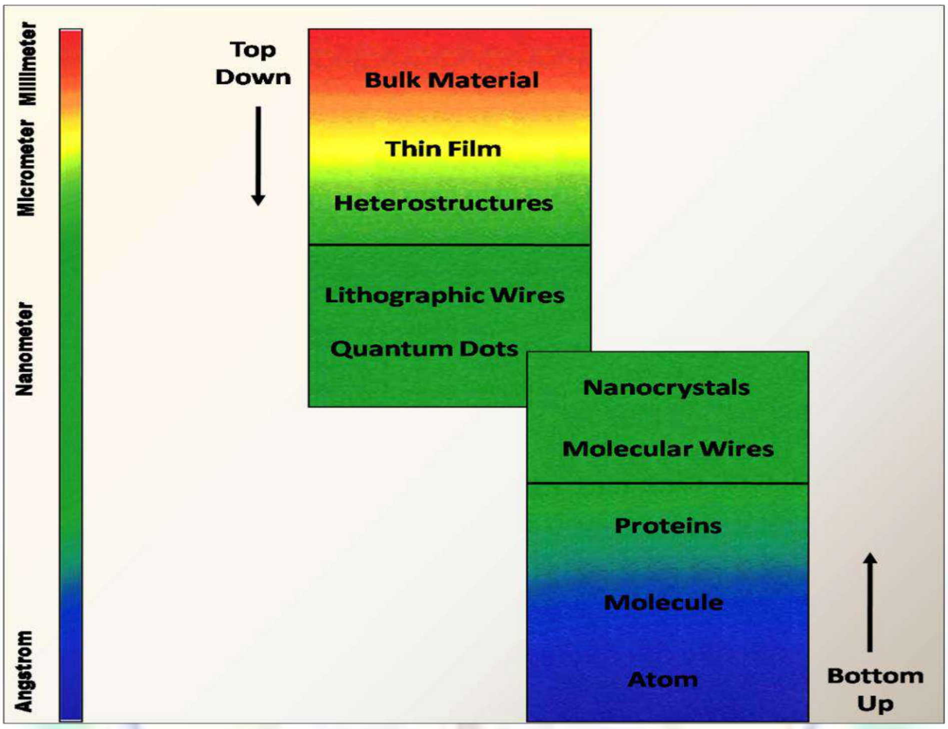

Fig. 1.4 Schematic representation of the Top down and Bottom up approaches

(a)Top down process

In this process, the bulk materials are broken into nano sized particle. It is an example of solid-state processing of materials. Example: Mechanical alloying (or) Ball milling

(a) Bottom-up process

In this process, nanomaterials are produced by building of atom by an atom. The schematics of the Top down and Bottom up approaches are shown in Fig. 1.4.

In materials science progress has been made by developing and applying new methods of investigation and by preparing materials with novel structural features and properties. There are two basic approaches commonly used to prepare nanoparticles; top-down approach and Bottom-up approach. Attrition or milling is a typical top-down method in making nanomaterials, whereas colloidal dispersion is a good example for the Bottom-up approach in the synthesis of nanomaterials. The ‘Top-down’ approach utilizes lithography and precision engineered tools like cutting, etching, grinding etc., to fabricate nanoscale objects out of bulk materials. In the ‘Bottom-up’ approach, materials and devices are built from molecular components which assemble themselves chemically, using the principle of molecular recognition. The ‘Bottom up’ approach refers to the buildup of a material from the bottom, i.e., atom by atom, molecule by molecule or cluster by cluster. In addition, the different synthesis processes of nanomaterials are shown in Fig.1.5.

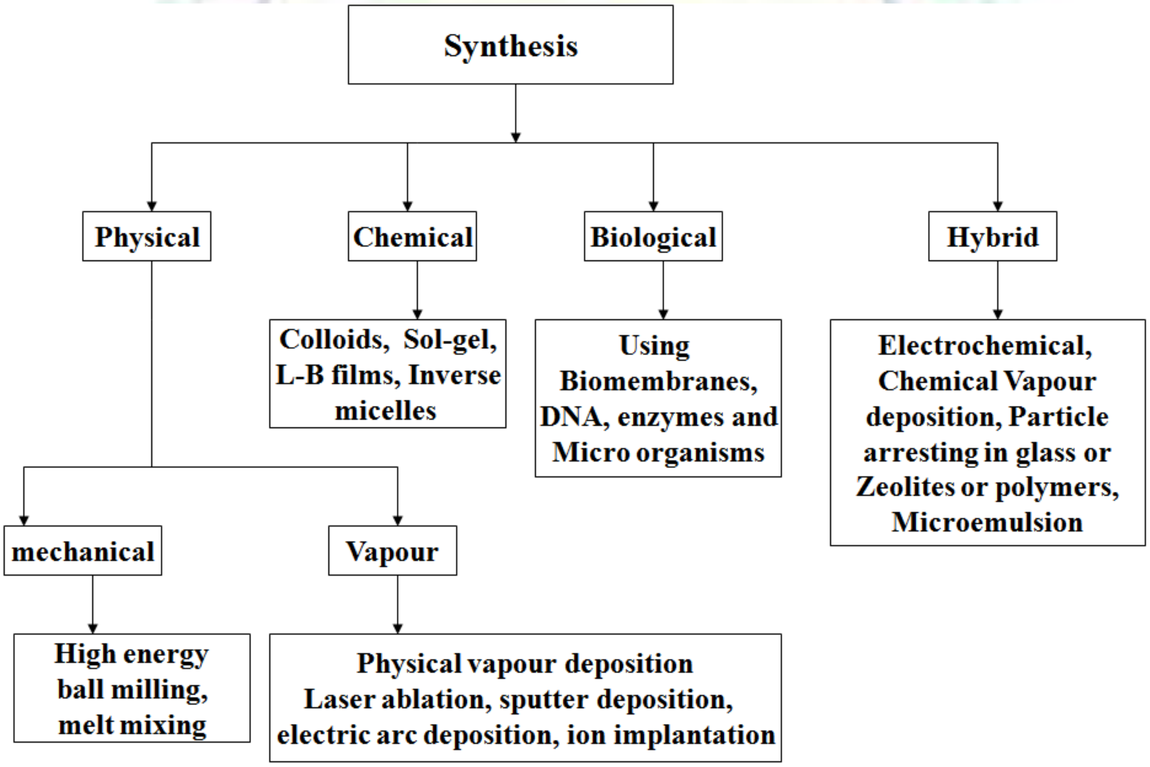

Fig.1.5 Synthesis process of nanomaterials

Chemical methods are promising, in terms of cost reduction and the ability to produce large amounts of small band gap material, which shows interesting size quantization effects (below the Bohr radius, i.e., 30 Å), and the nanomaterials can be obtained in macroscopic amounts for various characterizations. An important aspect of research on nanomaterials has been to prepare size selected particles in order to study various size-dependent features.

Semiconductor nanomaterials generated by chemical methods have proved to be more effective, as they provide better control as well as enable different sizes, shapes and functionalization, compared with the physical methods such as laser ablation, arc-discharge and evaporation chemical synthesis of nanomaterials. In recent years most of the metal oxide, metal sulphide and composite nanomaterials can be produced by soft chemical methods, such as sol-gel, hydrothermal, co-precipitation and solvothermal synthesis etc.

1.8 Preparation of Nanomaterials

Nanomaterials prepared by chemical methods have proved to be more effective, as they provide better control as well as enable different sizes and shapes compared to physical methods, such as laser ablation, arc-discharge, mechanical milling etc. In recent years most of the nanomaterials can be produced by wet chemical methods. Besides other methods, wet chemical methods have several advantages as follows:

- Simple techniques
- Inexpensive, less instrumentation compared to many physical methods
- Low temperature synthesis
- Doping of foreign atoms possible during synthesis
- Large quantities of the materials can be obtained
- Variety of sizes and shapes are possible
- Materials are obtained in the form of liquids but can be converted into dry powder or thin films quite easily
- Self assembly or patterning is possible
- Although the chemical synthesis of nanomaterials may appear as a complex process, by understanding how nucleation and growth of particles takes place, it is possible to control the various steps and try to achieve monodisperse nanomaterials.

There are few widely known methods to produce nanomaterials. They are

(i) Sol-Gel method

(ii) Hydrothermal method

(iii) Solvothermal method

(iv) Precipitation method

(v) Chemical vapour deposition

(vi) Microemulsion method

(vii) Sonochemical method

(viii) Thermal decomposition method

(ix) Ball milling

(x) Plasma arcing

(xi) Electro-deposition

(xii) Inert gas synthesis

(xiii) Laser synthesis

Using the above techniques it is possible to produce nanomaterials in the form of nanopowders, nanocrystals, nano-films, nanowires, nanotubes, nano-dots, nanofibers etc. From these methods, let us discuss the few methods briefly.

(a) Sol-gel Method

As the name suggests sol-gel involves two types of materials or components, ‘sol’ and ‘gel’. Sol-gels have been known since the time when M. Ebelman synthesized them in 1845. Sols are solid particles in a liquid. They are thus a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid). A sol-gel process involves the formation of ‘sols’ in a liquid, and then connecting the sol particles (or some subunits capable of forming a porous network) to form a network (shown in Fig. 1.6). Sol-gel processing is a wet chemical route for the synthesis of colloidal dispersions of inorganic and organic-inorganic hybrid materials, particularly oxides and oxide-based hybrids. From such colloidal dispersions, powders, fibers, thin films and monoliths can be readily prepared. The sol-gel method has several advantages over the others, such as phase-purity, chemical homogeneity, stoichiometric control, ease of preparation and ease of introducing dopants, composition and the ability to produce thin film coatings or porous powders.

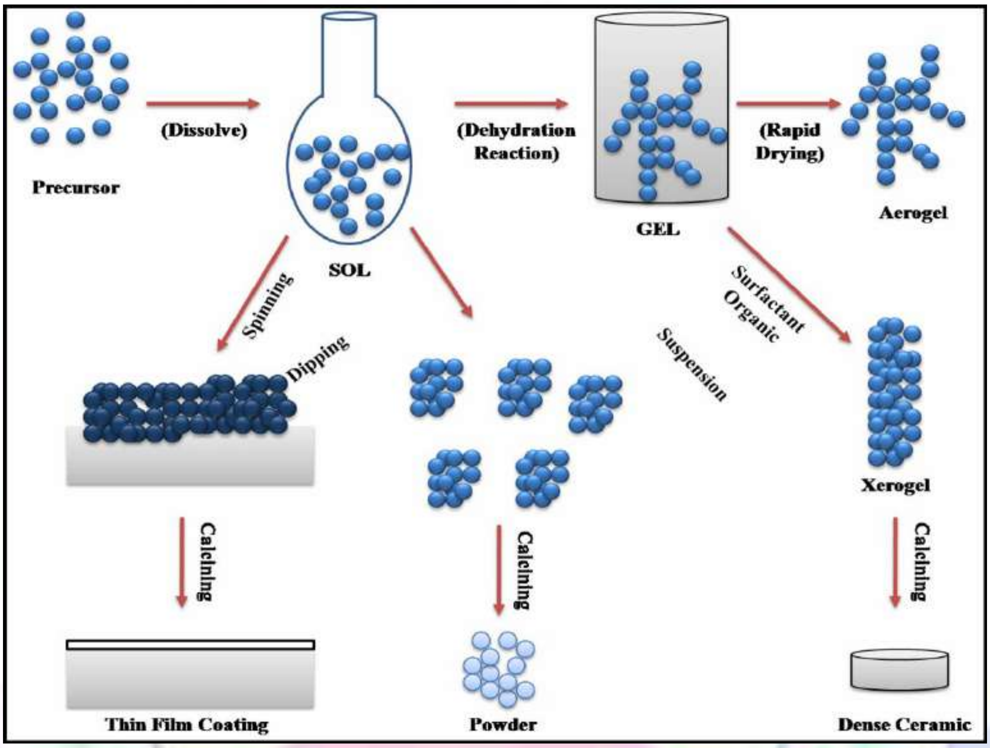

Fig. 1.6 Sol-gel process of synthesis of nanomaterials

In some cases sol-gel can be an economical route, provided the precursors are not very expensive. Some of the benefits like getting unique materials such as aerogels, zeolites, and ordered porous solids by organic-inorganic hybridization are unique to the sol-gel process. The synthesis of sol-gel, in general, involves the hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation, and drying by various routes, as shown in Figure. The sol-gel method is particularly useful to synthesize ceramics or metal oxides; metal sulphides and nitrides are also possible. Precursors (starting chemicals) are to be chosen in such a way that they should have a tendency to form gels.

(b) Hydrothermal Method

Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions, to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. It can be also defined as a method of synthesis of small crystals, which depends on the solubility of minerals in hot water under high pressure.

Hydrothermal synthesis is typically carried out in a Teflon-lined stainless steel pressurized vessel called an autoclave, with the reaction in an aqueous solution (shown in Fig. 1.7). The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. A gradient of temperature is maintained at the opposite ends of the growth chamber, so that the hotter end dissolves the nutrient and the cooler end causes the seeds to take additional growth. Hydrothermal synthesis is widely used for the preparation of metal oxide nanoparticles which can easily be obtained through the hydrothermal treatment of peptized precipitates of a metal precursor with water, and it can be useful to control the grain size, particle morphology, crystalline phase and surface chemistry through the regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time.

A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: an element, simple and complex oxides, tungstates, molybdates, carbonates, silicates, germinates etc. The method has been proved to be extremely efficient both in the search for new compounds with specific physical properties, and in the systematic physicochemical investigation of intricate multi-component systems at elevated temperatures and pressures. The possible advantages of the hydrothermal method over the other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can be grown by the hydrothermal method

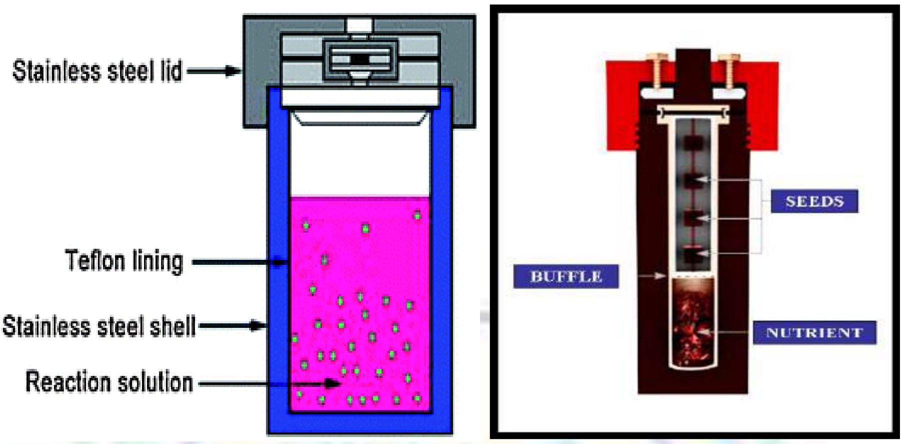

Fig. 1.7 Autoclave

It offers several advantages over the other methods, such as high purity, crystal symmetry, high crystallinity, lower sintering temperature, single-step processes, sub micron to nanoparticles with a narrow size distribution using simple equipment, lower energy requirements, fast reaction times, high reactivity with ease of sintering, and so on.

(c) Microemulsion

. Microemulsion is thermodynamically steady, isotropic liquid combinations of oil, water and different surfactant as shown in Fig. 1.8. Microemulsion process is based on creating a thermodynamically stable and homogeneous dispersion of two immiscible levels (usually water and oil solvent) by using surfactant and to formed resulting interfaces. The microemulsion controls the size to form resulting nanostructures.

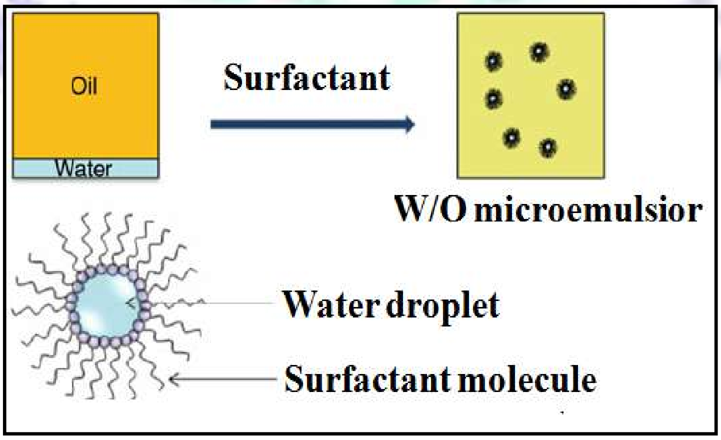

Fig. 1.8 Scheme diagram of microemulsion method

(d) Thermal decomposition

This method also called as thermolysis and it is a chemical deposition method. The thermal decomposition method is based on to decompose and oxidize the several types of precursors in an organic medium by using high temperature. In this method, reaction is usually endothermic and heat is essential to break chemical bonds in the compound enduring decomposition.

(e) Sonochemical synthesis

In chemistry, the study of sonochemistry is fruitful which considerate the effect of ultrasound in forming acoustic cavitations in liquids, resulting in the initiation or enrichment of the chemical activity in the solution. This method is based on the chemical effects produced by ultrasound waves rising from acoustic cavitations and which are growth and implosive collapse of bubbles in liquid medium. Therefore, the sound wave cannot affect that vibrational energy and therefore they are not directly increase the internal energy of a molecule.

(f) Precipitation method

The precipitation of solids from a metal ion containing solution is one of the most frequently employed production processes for nanomaterials. Metal oxides as well as non-oxides or metallic nanomaterials can be produced by this approach. The process is based on the reaction of salts in solvents. A precipitating agent is added to yield the desired particle precipitation, and the precipitate is filtered out and thermally post-treated. In precipitation processes, particle size and size distribution, crystallinity and morphology (shape) are determined by reaction kinetics (reaction speed). The influencing factors include, beyond the concentration of the source material, the temperature, pH value of the solution, the sequence in which the source materials are added, and the mixing processes. The advantages of this method are as follows

- Provides the only practical method of separation or concentration in some cases.
- High degree of concentration is possible.
- Provides a large range of scale (mg to industrial).
- Convenient, simple process.
- Not energy- or resource-intensive compared to other techniques (e.g., solvent extraction).

In addition, the metal titanate ($SrTiO_3$) and rare-earth metal oxide (La_2O_3) nanomaterials preparation processes are illustrated in flow chart for the sample work as shown in Fig. 1.9.

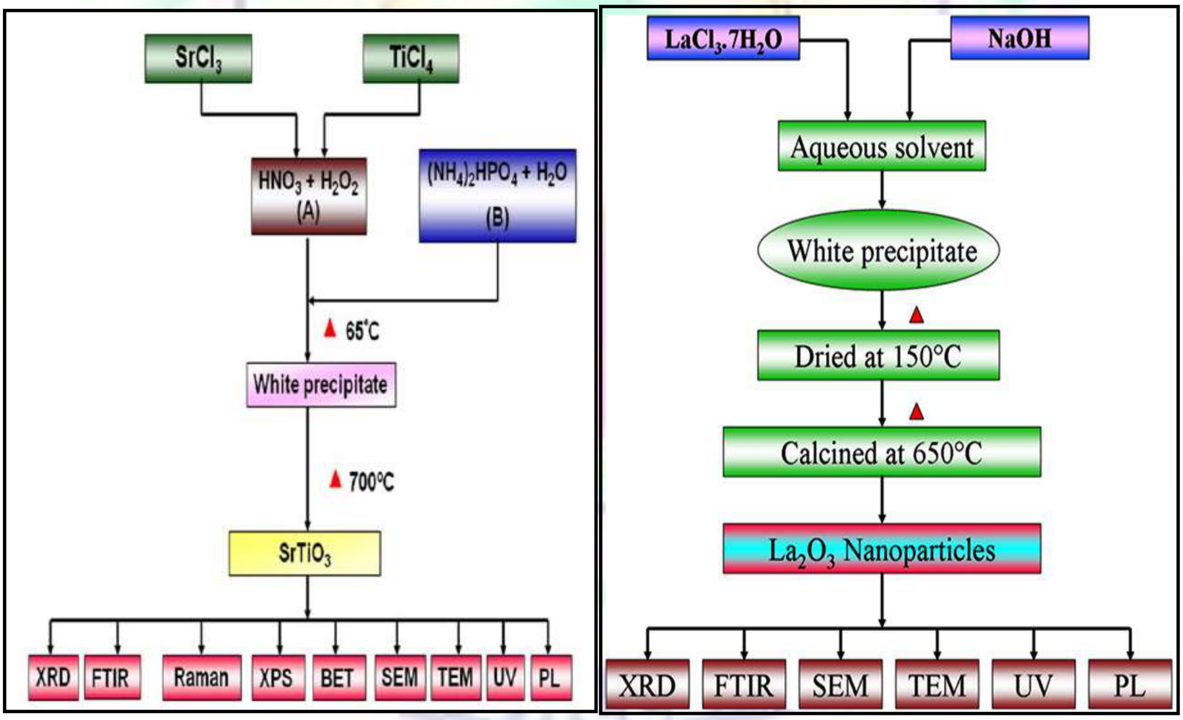

Fig. 1.9 Preparation of $SrTiO_3$ and La_2O_3 nanomaterials

Based on the above discussion and considering the merits of wet chemical synthesis, the most of the researchers are focused on the synthesis of metal, metal oxide, metal sulphide and metal composite nanomaterials by wet chemical synthesis.

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