

## CHAPTER - 2

### Synthesis methods and characterization techniques

#### 2.1. Introduction

In this chapter, an overview of several synthesis methods used for the preparation of nanostructured materials of different shapes and sizes have been described. Further, a brief description of various characterization techniques such as powder X-ray diffractometry (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDXA), surface area measurements (Brunauer–Emmett–Teller method) were illustrated. X-ray photoemission spectroscopy (XPS), superconducting quantum interference device (SQUID), field cooled-zero field cooled (FC-ZFC), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy and UV-visible diffuse reflectance spectroscopy (DRS) used for characterizing the synthesized products have also been present in this chapter.

#### 2.2. Methods of synthesis

Various synthetic methods have been developed to prepare nanostructured materials over the past several decades.

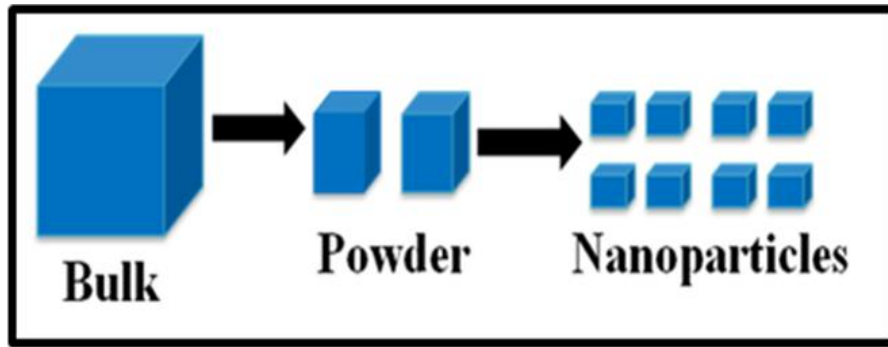
Regardless of the technique, the aim of particle synthesis usually focuses on:

- (i) Minimizing and controlling particle size.
- (ii) Maintaining a narrow size distribution.
- (iii) Control of particle morphology.
- (iv) Control of crystallinity.

The particle size enables the variation of material properties, while the narrow size distribution allows greater precision and is required for studies of size-dependent effects. Particle shape and crystal structure can also influence material properties (physical, chemical, biological).

Basically, nanoparticle synthesis techniques can be classified in two general groups:

- **Top-down method:** The top-down approaches (Figure 2.1) required materials to reduce to nanosized dimensions using milling or attrition, cutting and etching techniques, i.e., nanomaterials are prepared from larger entities without atomic-level control. The major problem with top-down approach is the imperfection of the surface structure. It is well known that the conventional top-down techniques such as lithography can cause significant crystallographic damage to the processed and additional defects may be introduced even during the etching steps. For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on surface. Such imperfections would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials, since the surface over volume ratio in nanostructures and nanomaterials is very large. The surface imperfection would result in a reduced conductivity due to inelastic surface scattering, which in turn would lead to the generation of excessive heat and thus impose extra challenges to the device design and fabrication. The nanoparticles produced by the attrition have a relatively broad size distribution and various particle shape or geometry. Additionally they may contain significant amount of impurities.

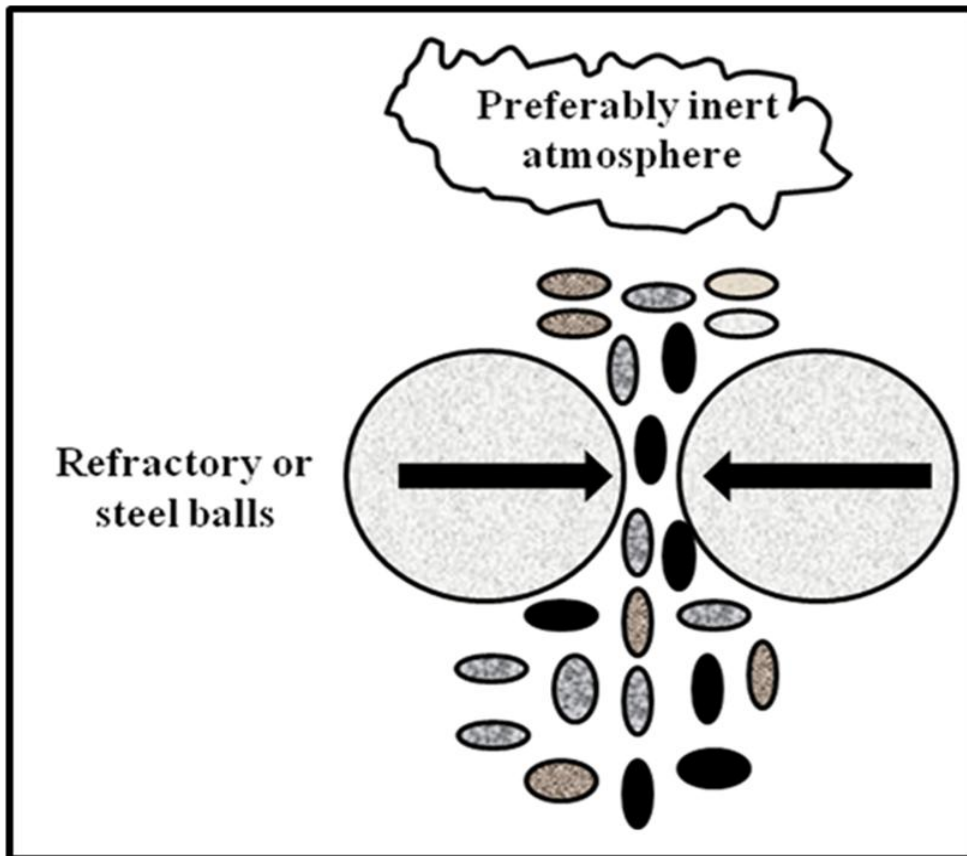


**Figure 2.1.** Schematic representations of top–down approach.

Mechanical milling: Mechanical grinding is a common example of ‘top down’ method of synthesis of nanomaterials, where the material is synthesized not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment is needed and applicable to all classes of materials. Mechanical milling (Figure 2.2) is achieved using high energy shaker, tumbler mills or planetary ball. The energy transferred to the powder from refractory or steel balls depends on the rotational or vibrational speed, number of the balls, size and ratio of the ball to powder mass, the milling atmosphere and the time of milling. The main advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for different applications.

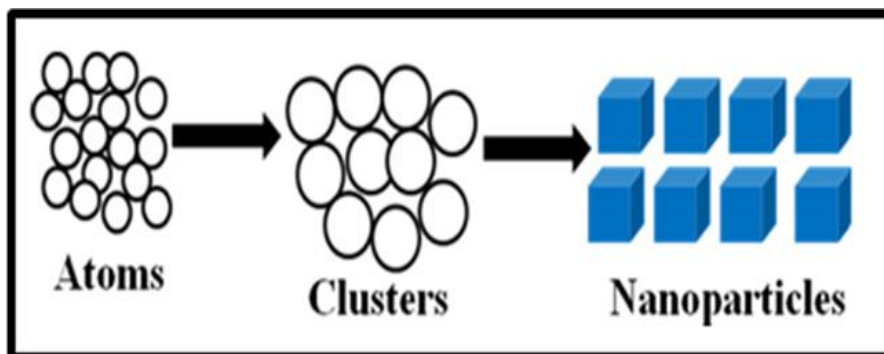
Disadvantages of top–down approach:

- Introduces internal stress.
- Surface defects.
- Contaminations.



**Figure 2.2.** Schematic representation of the principle of mechanical grinding.

- Bottom-up method:** Implies assembling single atoms/or molecules so as to build larger nanostructures from them or build-up of a material from the bottom: atom-by-atom/or molecule-by-molecule (Figure 2.3). Bottom-up approaches are more favorable and popular in the synthesis of nanoparticles and many preparation techniques of bottom-up approach have been developed.



**Figure 2.3.** Schematic representations of bottom-up approach.

Advantages of bottom-up approach are as follows:

- Obtain nanostructures with less defects.
- More homogeneous chemical composition.
- Fabrication is much less expensive.
- Better short and long range ordering due to driven mainly by the reduction of Gibbs free energy, therefore closer to a thermodynamic equilibrium state.

The preparation methods may be grouped in two main streams based upon the liquid-solid and gas-solid [Buzby *et al.* (2007)] nature of the transformations. Liquid-solid transformations are possibly the most broadly used in order to control morphological characteristics and generally follow a “bottom-up” approach or chemical processes.

### **2.2.1. Liquid-solid transformations (chemical methods):**

#### **(i) Co-precipitation method**

The normally used solution method for the synthesis of multi component oxide ceramics is co-precipitation method [Suslick *et al.* (1991)], which produces a “mixed” precipitate comprising of two or more insoluble species that are simultaneously removed from solution. The precursors used in this method are mostly inorganic salts (nitrate, chloride, sulfate, etc.) that are dissolved in water (or other solvent) to form a homogeneous solution with clusters of ions. The solution is then subjected to pH adjustment or evaporation to force those salts to precipitate as hydroxides, hydrous oxides, or oxalates. The crystal growth and their aggregation are influenced by the concentration of salt, temperature, the actual pH and the rate of pH change. After precipitation, the solid mass is collected, washed and dried in hot air oven. The washing and drying procedures applied for co-precipitated hydroxides affect the degree of agglomeration in the final powder and must be considered when nanosized powders are the intended product. Generally, a calcination step is necessary to transform the hydroxide into crystalline oxides. In most of the binary,

ternary and quaternary systems, a crystallization step is necessary, which is generally achieved by calcinations.

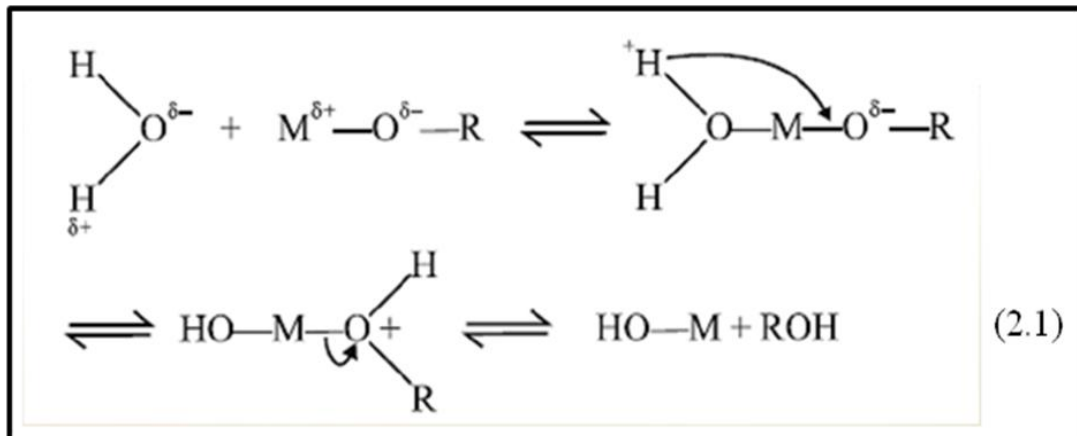
The major advantages of co-precipitation reactions are as follows:

- The homogeneous distribution of components.
- The relatively low reaction temperature.
- The fine and uniform particle size with weakly agglomerated particles.
- Low cost.

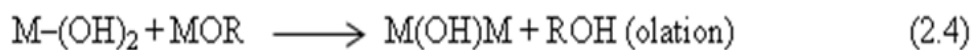
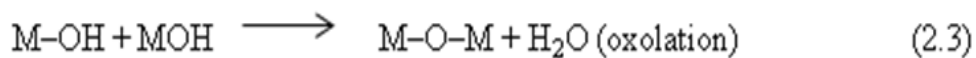
### **(ii) Sol-gel processing**

The synthesis of metal oxides or mixed metal oxides nanoparticles by sol-gel technique is one of different liquid phase methods that are the most widely employed and has been widely reviewed [Interrante and Smith (1998), Liliane (1994)]. Basically, three steps are used to prepare sol-gel ceramic materials as shown in the flow chart Figure 2.4, which are distinguished by the nature of the starting material. They are (i) an aqueous solution of inorganic salt, (ii) an aggregate of colloidal particles in a solvent (sol) and (iii) a network-forming species in organic or aqueous solution (gel). The last step is the most acceptable because network formers can be tailor-made or modified to control the chemistry and processing of the gel and ultimately its morphology. Usually, alkoxides, bimetallic- $\mu$ -oxoalkoxides and heterometallic (double, ter, tert-) alkoxides are used as precursors in alcoholic solutions. Other precursors include metal  $\beta$ -diketonates and metal carboxylates.

Hydrolysis and condensation of metal alkoxides: the sol-gel method is actually a two-step inorganic polymerization. In the first step, polymerization starts by hydrolysis at the metal-alkoxy linkage yielding alcohol and new reactants formed are hydroxylated metal centers (M-OH). The mechanism of this reaction can be summarized as below:



In the second step, condensation or three-dimensional propagation occurs when hydroxylated species condense to form oxypolymers. Polycondensation involves alkoxylation, oxolation, or olation, a reaction that creates oxygen bridges and releases ROH species.

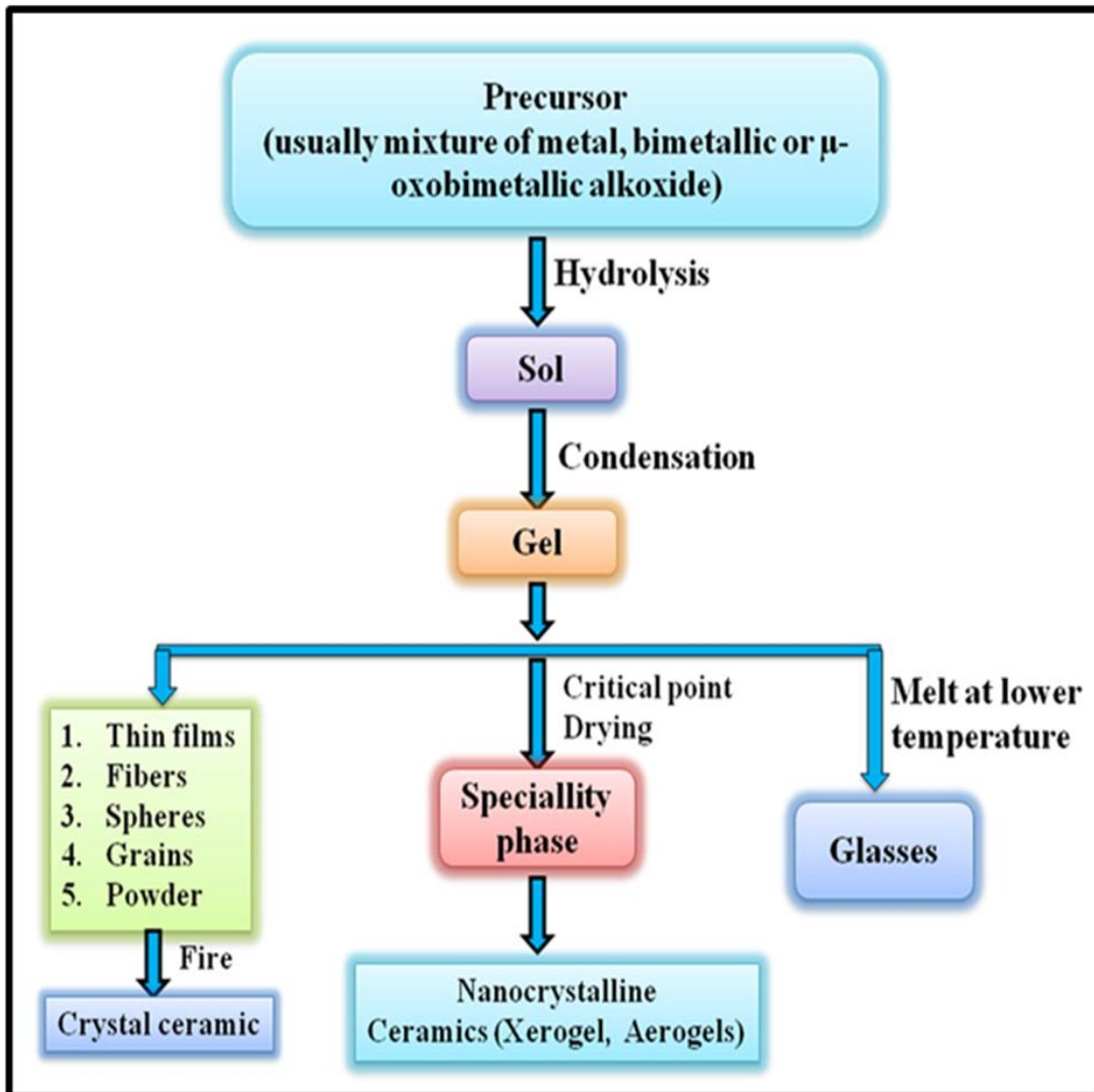


The rates of hydrolysis and condensation depend upon the nature of metal in terms of its electrophilicity and ability to expand its coordination number. The hydrolysis rates of transition metal alkoxides are very high, as metal centers are highly electrophilic and exhibit several coordination numbers.

The main advantages of sol-gel method are:

- Produce homogenous materials.
- The chemical elements become uniformly distributed during the gel formation step.
- Good stoichiometric control.

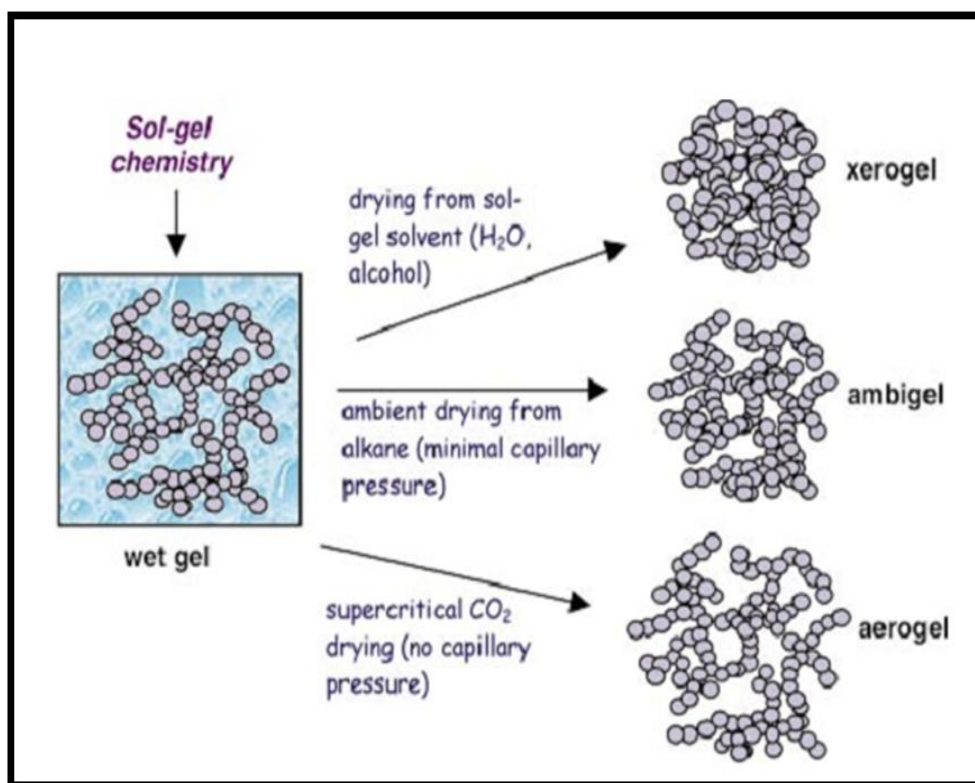
- Production of ultrafine particles with narrow size distribution at comparatively low temperatures.



**Figure 2.4.** Steps involved in sol-gel technique.

The technique used for conversion of dry solid with variable porosity from the wet gel is shown in Figure 2.5.





**Figure 2.5.** The technique used to extract the pore fluid from a wet gel creates a dry solid with variable porosity: strong capillary forces create a xerogel, weak capillary forces create an ambigel and zero capillary force creates an aerogel [Rolison and Dunn (2001)].

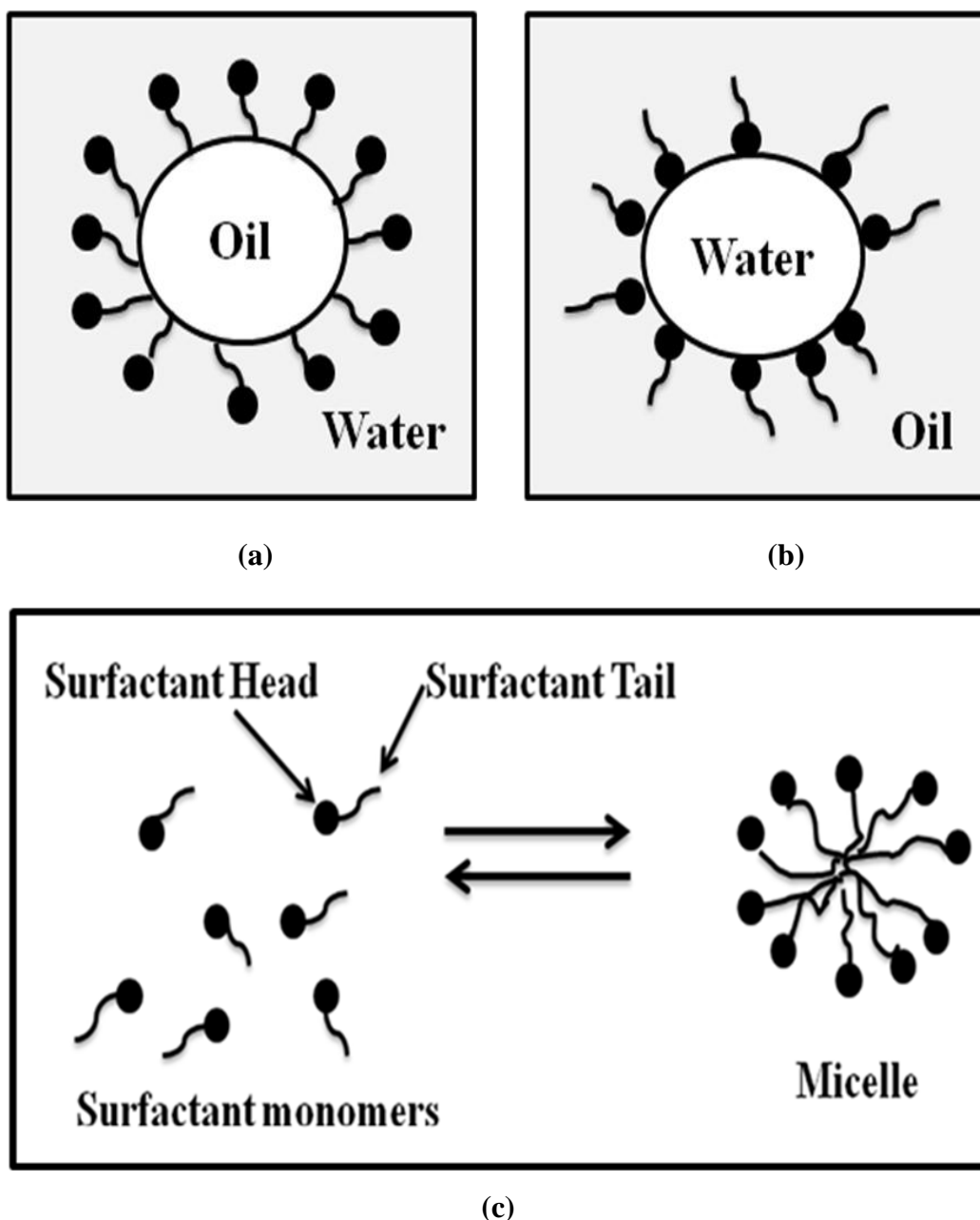
### (iii) Microemulsion method

Microemulsion (reverse micelles or colloidal) is a procedure for the synthesis of nanoparticles in which two immiscible fluids such as water in oil (W/O) or oil in water (O/W) become a thermodynamically stable dispersion with the aid of a surfactant (Figure 2.6). A characteristic emulsion is a single phase of three components, water, oil and a surfactant [Herrig and Hempelmann (1996)]. Usually oil and water are immiscible but with the addition of a surfactant, the oil and water become miscible because the surfactant is able to bridge the interfacial tension between the two fluids. Surfactants have water loving (hydrophilic) and oil-loving (lipophilic) moieties [Holmberg *et al.* (2002)]. Microemulsion consists of surfactant aggregates that are in the ranges of 1 nm to 100 nm. The location of water, oil and surfactant phases affects the geometry of aggregate. The product of oil in water and surfactant (O/W) is called micelles, which is an aggregate

formed to reduce free energy. Hydrophobic surfactants in nanoscale oil and micelles point toward the center of aggregate, whereas the hydrophobic head groups toward water, the bulk solvent. The water in oil microemulsion carries oil or organic solvent as bulk. The system is thermodynamically stable and called reverse micelles. When the microemulsions material including reactants are mixed together, reactants exchange takes place during the colliding of water droplets in microemulsion. The reactant exchange is too fast and precipitation reaction occurs in the nano droplets, which is followed by nucleation, growth, and coagulation of primary particles, resulting in the formation of the final nanoparticles surrounded by water and/or stabilized by surfactants. Advantages of these reactions are reduced crystal lattice defects and cation distributions that are equalized throughout the particles due to the reaction speed being slow.

Microemulsion process has also some drawbacks:

- Low product yield.
- High waste product.
- High cost.
- Product also requires a heat treatment if the desired crystallinity is not achieved in the micelles.

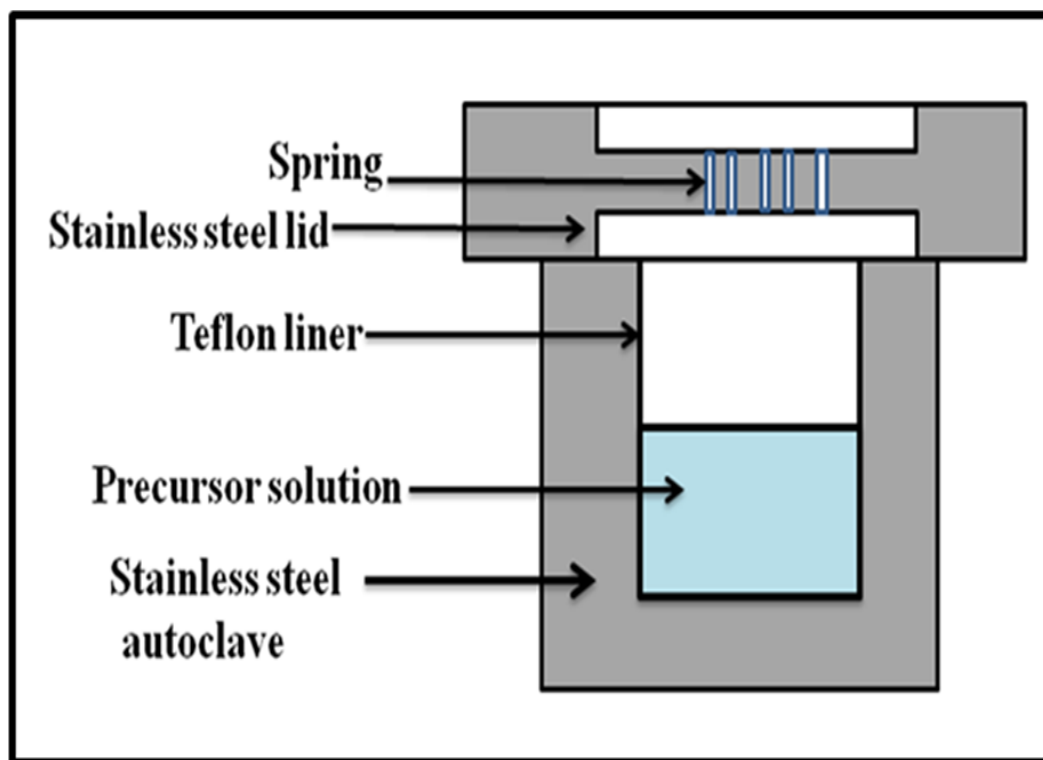


**Figure 2.6.** (a) Oil/water microemulsion (normal micelle), (b) water/oil microemulsion (reverse micelle) and (c) spontaneous self-assembly of surfactants into micelles in aqueous solution.

**(iv) Solvothermal method**

In the solvothermal processes, metal complexes are decomposed thermally either by boiling in an inert atmosphere or using an autoclave with the help of pressure as shown in Figure 2.7 [Cansell *et al.* (1999)]. A suitable surfactant agent is usually added to the reaction media to control particle size growth and limit agglomeration. When water is used as solvent, it is called a hydrothermal process. Hence solvothermal synthesis allows

for the precise control over the size, shape distribution, and crystallinity of metaloxide nanoparticles or nanostructures. These characteristics can be altered by changing certain experimental parameters, including reaction temperature, reaction time, solvent type, surfactant type and precursor type.



**Figure 2.7.** Schematic diagram of solvothermal synthesis setup.

#### (v) Sonochemical method

In the sonochemical process, powerful ultrasound radiations (20 kHz to 10 MHz) were applied to molecules to enhance the chemical reaction [Gedanken (2004)]. The major advantages of the sonochemical method are its simplicity, operating conditions (ambient conditions) and easy control of the size of nanoparticles by using precursors with different concentrations in the solution. Ultrasound power affects the occurring chemical changes due to the cavitation phenomena involving the formation, growth and collapse of bubbles in liquid. The sonolysis procedure involves passing sound waves of fixed frequency through a slurry or solution of selected metal complex precursors. One of these theories explains the mechanism of breaking a chemical bond during a bubble collapse.

According to one of these theories, bubble collapse at very high temperatures (5000–25,000 K) during the sonochemical process [Gedanken (2004)]. Sonoelectrochemical synthesis employs both electrolytes and ultrasonic pulses for the production of nanoparticles. Bath temperature, current density, current pulse time, ultrasound intensity, ultrasound pulse time and stabilizer are required to control the formation of nanoparticles.

#### **(vi) Microwave synthesis**

In the microwave method [Lagashetty *et al.* (2007)], microwave radiations are introduced in the reaction solution. Microwaves are a form of electromagnetic energy, with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.456 GHz. The microwave ovens used in microwave chemistry range from simple household multimode ovens to large-scale batch as well as continuous multimode ovens. The main reasons for using microwave are the fast and homogeneous reaction conditions during the microwave synthesis. Compared with conventional heating methods, microwave assisted heating presents a more rapid and simultaneous environment for the formation of nanoparticles due to the fast and homogeneous heating effects of microwave irradiation. Thus, microwave assisted heating method has the advantages of short reaction time, high energy efficiency and the ability to induce the formation of particles with small size, narrow size distribution and high purity.

#### **(vii) Thermal decomposition**

Thermal decomposition or thermolysis is based on decomposing and oxidizing metal precursors in an organic medium by using high temperatures [Song *et al.* (2004), Ghosh *et al.* (2006)]. The decomposition temperature of a substance is the temperature at which the substance chemically decomposes. The reaction is generally endothermic as heat is required to break chemical bonds in the compound undergoing decomposition. The major disadvantage of this approach is that most of the reactions are air-sensitive therefore,

glove box or schlenck line techniques must be used for getting nanoparticles in nonpolar solvents.

Thermal decomposition or thermolysis has many advantages:

- It produces highly monodispersed nanoparticles with a narrow size distribution.
- Reaction does not need any additional reducing agents.

### **2.2.2. Gas-solid transformations:**

#### **(i) Chemical vapor deposition (CVD)**

Chemical vapour deposition is a technique where one or more volatile precursors are transported via the vapour phase to the reaction chamber, where they decompose on a heated substrate [An *et al.* (2010)]. In thermal chemical vapour deposition the reaction is activated at high temperature above 900 °C. In photo-laser chemical vapour deposition, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy to break the chemical bond in the reactant molecules. In this method, the reaction is photon activated and deposition occurs at room temperature.

The major advantages of chemical vapor deposition technique are as follows:

- An excellent control of size, shape, morphology, crystallinity and chemical composition.
- Highly pure materials can be obtained.
- Multicomponent systems formed easily.
- Easy control of the reaction mechanisms.

#### **(ii) Pulsed laser deposition (PLD)**

Pulsed laser ablation method is a generally used method for the preparation of nanoparticles in colloidal form in a variety of solvents [Zeng *et al.* (2005)]. The pulse laser ablation technique takes place in a vacuum chamber and in the presence of some inert gas. In this technique, a high-power pulsed laser beam is focused inside a vacuum

chamber to strike a target in the material to create plasma, which converted into a colloidal solution of nanoparticles. There are many factors that affect the final product such as the type of laser, number of pulses, pulsing time and type of solvent.

### **[iii] Electrospray**

A simple technique to produce nanoparticles is to evaporate micron-sized droplets of a dilute solution. By choosing the appropriate solute concentration, nanosized particles consisting of the solid residue can be obtained [Rulison *et al.* (1994)].

### **[iv] Spray pyrolysis**

In spray pyrolysis method, a droplet containing a solute is evaporated or dissociated by a chemical reaction. During the shrinkage of the droplet, a supersaturated solution is created, as the amount of solute remains constant and small particles may form inside the droplet [Krunks and Mellikov (1995)].

### **[v] Sputtering**

Sputtering is a way of vaporizing materials from a solid surface by bombardment with high-velocity ions of an inert gas, causing an ejection of atoms and clusters [Phanichphant (2014)]. Sputter sources such as an ion gun or a hollow-cathode plasma sputter source are generally used in vacuum systems, below  $10^{-3}$  mbar, as a higher pressure hinders the transportation of the sputtered material.

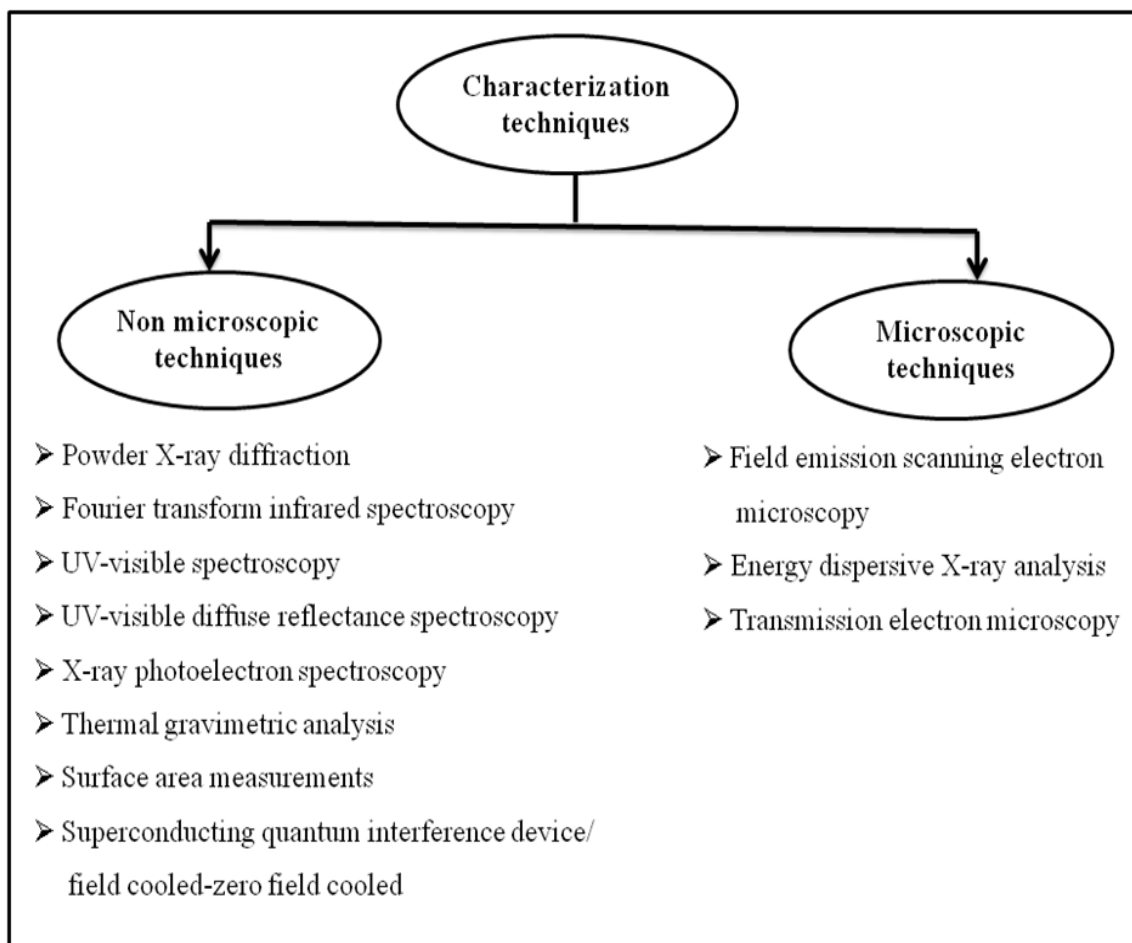
Gas-phase synthetic methods feature the rapid cooling of evaporated material to induce nucleation and growth of nanoparticles, normally within a confined region. Depletion of the supersaturated vapor prevents excessive growth of the particles, which have a tendency to show a log-normal size distribution [Kiss *et al.* (1999)]. Particle size depends on material properties as well as the evaporation conditions. Size, morphology and crystallinity control in gas-phase synthetic methods can be intricate, lots of materials can be synthesized without contaminants such as solvents or stabilizers.

Additionally, several vapor-phase particle growth techniques are used in continuous, industrial reactors that are easy with mass production.

### **2.3. Classification of the characterization techniques**

The analysis of phase purity, particle size, surface morphology, elemental composition, specific surface area, chemical-states of the elements, magnetization nature, thermal properties, catalytic properties and optical properties were carried out by powder X-ray diffractometry, transmission electron microscopy, field emission scanning electron microscopy, energy dispersive X-ray analysis, surface area measurements (Brunauer–Emmett–Teller method), X-ray photoemission spectroscopy, superconducting quantum interference device, field cooled-zero field cooled, thermogravimetric analysis, fourier transform infrared spectroscopy, ultraviolet-visible absorption spectroscopy and UV-visible diffuse reflectance spectroscopy, respectively. Primarily, all the used characterization techniques have been classified in two most important groups are shown in Figure 2.8.





**Figure 2.8.** Classification of the characterization techniques used in the present work.

## 2.4. Non microscopic techniques

### 2.4.1. Powder X-ray diffraction (XRD)

Powder X-ray diffraction is a valuable analytical technique employed to identify the crystalline phases present in materials and to measure the phase composition, phase purity, preferred orientation, crystallite size, strain state and defect structure of these phases [Smart and Moore (2005), Giacobazzo (2002)]. This technique uses a monochromatic source of X-rays and measures the pattern of diffracted radiation, which is a result of the constructive interference due to the crystalline structure of the powder. A crystal is a homogenous solid with a repeating 3-D pattern of atoms with a fixed distance between them. Since this repeating pattern of crystal XRD, give characteristic peak intensities and positions which correspond to particular crystal phases. Intensity and peak

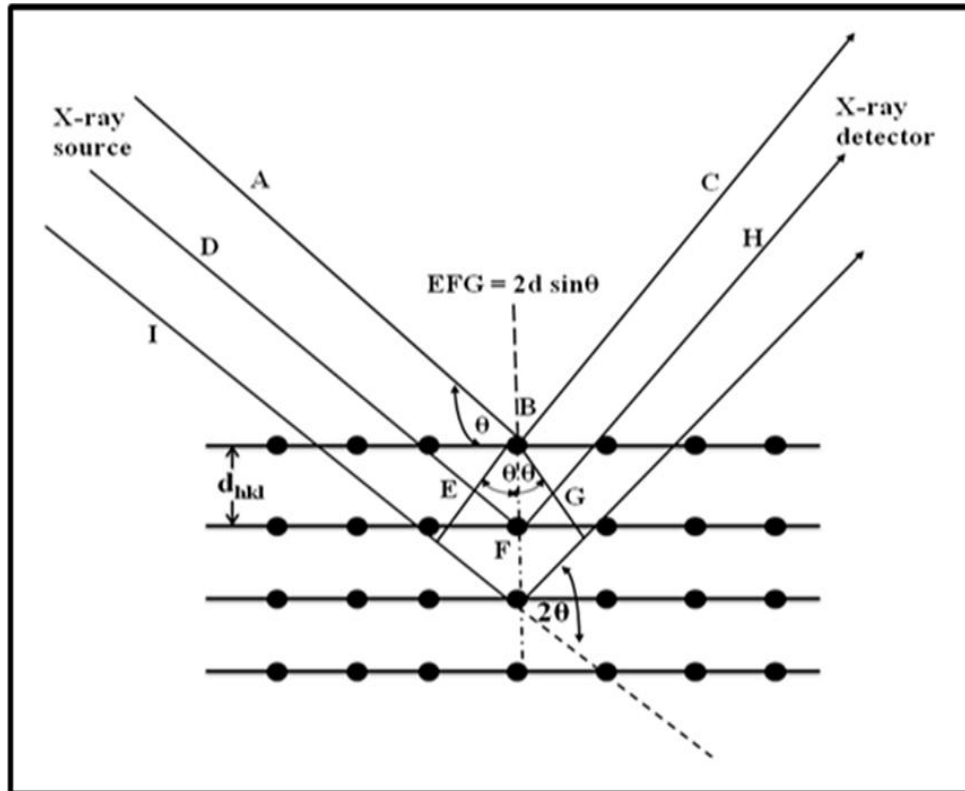
width depend on type of unit cell, position of atoms within the unit cell, thermal motion and population parameters. Lattice planes within a unit cell are characterized by Miller Indices. These Miller Indices are useful in identifying an unknown sample.

A beam of X-rays of a fixed wavelength  $\lambda$  (1.54 Å for a Cu- $K_{\alpha}$  source) is directed to the crystal at an angle  $\theta$  to the atomic planes. The interaction between X-rays and the electrons of the atoms is visualized as a process of X-ray reflections by the atomic planes. If the interplanar crystalline spacing ( $d$ ) is an integer multiple of the X-ray's wavelength, the diffracted X-ray will constructively interfere. This results in the diffracted X-ray beam possessing the same angle as the incident beam (Bragg's Law). The Bragg's law is given as:

$$n\lambda = 2d\sin\theta \quad (2.5)$$

where  $n$  is an order of diffraction,  $\lambda$  is the wavelength of the X-ray radiation,  $d$  is the interplanar spacing of the crystal and  $\theta$  is the angle of reflection or incidence (Bragg's angle). This is shown in Figure 2.9. The diffracted beam intensity is plotted against the corresponding  $2\theta$  diffraction angle to obtain the diffraction pattern, which then compared to known patterns for identification purposes or used to calculate various parameters. It is well known that the width of a diffraction peak increases when the crystallite size is decreased below a certain limit ( $< 100$  nm).

In diffraction patterns, there are three important factors that cause peak broadening: strains, faulting, and crystalline domain size. However, if the sample is faulty and strain free, the broadening of the XRD pattern will correspond to the average nanoparticle size.



**Figure 2.9.** Bragg's law of diffraction.

Thus, XRD patterns can be used to estimate the average size of very small crystallites, from the measured width of the diffraction patterns by the Scherrer equation. The Scherrer equation is:

$$\delta = k\lambda/(\beta\cos\theta) \quad (2.6)$$

where  $\delta$  is the crystallite size in nanometers,  $k$  represents a dimensionless constant ( $\approx 0.9$ )  $k$ ,  $\lambda$  is the wavelength of Cu-K $\alpha$  (0.15406 nm),  $\beta$  is the full width at half maximum (FWHM in radian) of prominent intensity peak (using the 100% relative intensity peak will be used) and  $\theta$  is the diffraction angle (degree). Usually, there will be a contribution to line broadening from the instrument due to several factors and this natural width is corrected as:

$$\beta^2 = \beta_M^2 - \beta_i^2 \quad (2.7)$$

where  $\beta_M$  is the measured peak width at half peak height and  $\beta_i$  is the contribution from the instrumental line broadening, in radians.  $\beta_i$  is obtained from the width of the XRD

pattern of a standard bulk material. In the present study, the phase analysis of the samples was carried out using a Bruker AXS D8 diffractometer operating with Cu-K $\alpha$  radiation.

#### **2.4.2. Fourier transform infrared (FT-IR) spectroscopy**

Fourier transform infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule and it gives information about the chemical bonding in a material. In infrared spectroscopy, infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. An infrared spectrum represents a fingerprint of a sample with absorption peaks which match to the frequencies of vibrations between the bonds of the atoms making up the material. The absorption of infrared radiation increase due to vibration which cause a change in the dipole moment of the molecule. The larger change in the dipole moment give more intense the absorption band. In the present study, a Thermo Nicolet Nexus Fourier FT-IR spectrometer was used for recording IR spectra of the samples using KBr pellet in the range of 4000 to 400 cm<sup>-1</sup>.

#### **2.4.3. UV-visible diffuse reflectance spectroscopy**

UV-Visible diffuse reflectance spectroscopy is one of the important techniques to reveal the energy structures and optical properties of the nanomaterials. This method is very useful in studying optical properties of nanomaterials due to change in electronic properties of the materials at nanoscale range. The optical properties including energy band gap ( $E_g$ ) of the synthesized samples were determined with the help of a Shimadzu UV-2450 UV-Visible spectrophotometer attached with a diffuse reflectance accessory in the wavelength range 200 to 800 nm using BaSO<sub>4</sub> as the reference.

#### **2.4.4. X-ray photoelectron spectroscopy (XPS)**

X-Ray photoelectron spectroscopy is a surface analysis technique used for finding chemical information about the surfaces of solid materials. X-Ray photoelectron spectra are obtained by irradiating a material with a beam of X-ray and measuring the kinetic

energy (KE) and number of electrons that escape from the surface of the material being analyzed. In our work, X-ray photoemission spectra of the samples were executed on a KRATOS (Amicus model) high-performance analytical instrument using Mg  $K_{\alpha}$  X-ray source ( $h\nu = 1253.6$  eV) under  $1.0 \times 10^{-6}$  Pa pressure. All X-ray photoemission spectra were calibrated with C 1s peak which has a standard position at 284.65 eV.

#### **2.4.5. Thermal gravimetric analysis (TGA)**

Thermal gravimetric analysis is an analytical technique which observes the weight change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Thermo gravimetric analysis (TGA) was carried out on a Perkin Elmer Thermal Analyzer (Pyris Diamond) in nitrogen atmosphere at a heating rate of 5 °C/min. Weight losses of the synthesized sample in the heating process is recorded using a thermobalance. During the whole process, the change in weight measured at different temperatures is considered as an estimate of the substance of volatile or decomposable molecules. In addition, thermal gravimetric is used to characterize the decomposition, purity and thermal stability of materials under a variety conditions [Hatakeyama and Quinn (1995)].

#### **2.4.6. Surface area measurement (BET)**

The most common process used to determine surface area of solid materials is the Brunauer-Emmett Teller (BET) method [Brunauer *et al.* (1938)] where the sample is cooled to liquid nitrogen temperatures and exposed to a nitrogen gas adsorbant. In BET method, physical adsorption of a gas on the surface of the powder sample and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The specific surface area of the samples was measured using Brunauer–Emmett–Teller (BET) method by Micromeritics Chemisorb 2720 instrument using nitrogen physisorption.

#### **2.4.7. Superconducting quantum interference device (SQUID)**

The superconducting quantum interference device is one of the most sensitive magnetometers used for magnetic characterization of nanoparticles over a wide range of temperatures and applied magnetic fields [McElfresh (1994)]. The presence of a superconducting coil in SQUID magnetometers requires the employ of liquid helium in order to operate and to determine samples at low temperatures. Magnetic measurements were performed on a superconducting quantum interference device (SQUID) (Quantum Design, MPMS 3). Field-dependent magnetization curves were obtained in the temperature range 10-300 K up to a maximum field of 7 T. Two kinds of measurements were performed, temperature-dependent magnetization curves were recorded under zero field cooled (ZFC) and field cooled (FC) conditions from 2 to 300 K under an applied field of 500 Oe.

### **2.5. Microscopic techniques**

#### **2.5.1. Field emission scanning electron microscopy (FE-SEM)**

The field emission scanning electron microscope is a versatile, non-destructive technique that produces images of the sample surface by scanning it with a high-energy beam of electrons. FE-SEM is a type of electron microscope able of producing high resolution images of a sample surface for the various demanding applications in the field of nano technology. It reveals detailed information about the morphology and the composition of materials.

Morphology of the samples along with elemental analysis data were also obtained from EDX attached with a field emission scanning electron microscope (FE-SEM) using FEI Quanta 200 F operating at an accelerating voltage of 20 kV. The EDX analysis system works as an integrated feature of a scanning electron microscopy (SEM). The EDX

analysis was used to identify materials and their relative concentrations on the surface of the sample.

### **2.5.2. Transmission electron microscopy (TEM)**

Transmission electron microscopy is a microscopy technique to study the particle size, shape, morphology and crystal structure. In TEM a beam of electrons is focused onto a specimen causing a magnified version to appear on a layer of photographic film or fluorescent screen. It operates on the same basic principles as the light microscope but uses electrons instead of light. In addition, it is very valuable for determination of the lattice planes and the detection of atomic-scale defects in areas of few nanometers in diameter with the help of selected area electron diffraction (SAED) method [Williams and Carter (1996)].

TEM images of the nanocrystalline powder were recorded using a FEI TECNAI G2 electron microscope operating at an accelerating voltage of 200 kV. For preparation of TEM sample, the powder was dispersed in ethanol using low power sonicator and a few drops of the solution were allowed to dry on the carbon coated copper grids in air.