

## CHAPTER - I

### INTRODUCTION

#### 1.1 GENERAL INTRODUCTION

The prefix nano in the word nanotechnology means a billionth ( $1 \times 10^{-9}$ ). Nanotechnology deals with various structures of matter having dimensions of the order of a billionth of a metre. While the word nanotechnology is relatively new, the existence of functional devices and structures of nanometer dimensions is not new, and in fact such structures have existed on earth as long as life itself. The abalone, a mollusk, constructs very strong shells having inner surfaces by organizing calcium carbonate into strong nanostructured bricks held together by a glu made of a carbohydrate-protein mix. Cracks cannot be easily formed on the outside of the shells because of the nanostructured bricks. The shells which represent a natural demonstration of a structure fabricated from nanoparticles, can be much stronger.

In the past decades, nanoscience and nanotechnology has been making significant progress, and the effect of nanoscience and nanotechnology on every field has been acknowledged in the world. Therefore, their strategic position in the 21<sup>st</sup> century has already been established. The study of nanomaterials and nanostructures is one field with the earliest starting that obtained rich achievements in nanoscience and nanotechnology. Nanomaterials and nanostructures play a vital role in applications of nanoscience and nanotechnology in the field of fabrication such as information and techniques, energy sources, environments, health and medical treatments, etc.

Nanomaterials and nanostructures are established as the knowledge frame of an important branch of learning. This will promote the study of nanomaterials and nanostructures to develop deeply and expansively. Although the preparative science of

nanomaterials make remarkable progress such as the synthesis of a series of materials with new structures and new properties which have never been seen in the traditional material field, and the discovery of some special physical properties and proposal of some new concepts, the field of nanomaterial as a new branch of learning did not develop perfectly. Descriptions of the new and unique physical and chemical phenomena, which are discovered, still stop at the explanation step when using the traditional theory. In a strict sense, the relatively independent new theory of nanomaterials and nanostructures has yet to be established.

The research of new laws is not systematical. The new effects appeared in the nanofield, such as the quantum confinement effect, coulomb blockade effect, etc., are also established according to the traditional quantum theory. The research of nanomaterials and nanostructures at the new step is expanded around the scientific problems like establishment of the thermodynamics of nanomaterials systems, establishment of controlled growth dynamics of nanomaterials, new laws of matter and energy transport of nanosystems, new principles and new methods of regulation and control of structures and properties, etc. It will inevitably provide the basis for designing nanomaterials with special structural control of the properties of nanomaterials and nanostructures. Therefore, an establishment of the self-scientific frame of nanomaterials is a significant and extremely difficult assignment. It must be established on the basis for a deeper study of nanomaterials and nanostructures. Now, the important assignment is to realize three transitions based on the nanomaterial research, and to push nanomaterials to develop towards a newer more profound level. One transition is that the preparation realizes scientifically from random growth to controlled growth. The growth dynamics of nanomaterials, nanostructures, and the thermodynamics of the

confinement systems are studied. The second one is the transition from the exploration of random new phenomena to the more profound exploration of new laws, the conditions for unique property appearance, the change in the laws of properties and the factors which affect the property stability are systematically studied, so that the properties become controllable. The third transition is that of the research focus of gravity from preparation and synthesis as the main focus is to the study of the relation between nanomaterials and nanostructures. The study of the law and process of nanostructure development and the effect on properties and the investigation of the relation of preparation processes of nanostructures and properties, etc. theoretically provide the theoretical basis for designing nanostructures with the required properties and structures through the preparation methods. When the sample size reaches the order of nanometers, this does not imply the appearance of new properties. The new properties occurring in single element nanomaterials and nanostructures certainly do not satisfy the applied requirements. Therefore, through heterogeneous doping composite and heterogeneous nanostructure designing, the largest limit excavation of nano effects and optimization, modulation and control of properties are realized. All of these problems are the most challenging in the research field of nanomaterials and nanostructures, and are also the important market of the deep research of nanomaterials and nanostructures.

In the usual and standard language, when we talk about material science and material technology, we normally mean ceramics or crystalline materials, glasses or non-crystalline materials, polymers or heavy chain molecular materials and metals or cohesively-bonded materials. All these materials have a wide variety of applications in the diverse fields towards the service for the betterment of human life. The world of

materials is rapidly progressing with new brand technologies, and obviously novel applications. Nanotechnology is creating waves in the modern times among the modern and sophisticated technologies. Actually, nanotechnology includes the concept of physics and chemistry of materials. So, nanotechnology is an interesting but emerging field of study which is under constant evolution offering a very wide scope of research activity.

Nanotechnology, which is an advanced technology, deals with the synthesis of nanoparticles, processing of the nanomaterials, and their applications. Normally, if the particle sizes are in the 1-100 nm ranges, they are generally called nanoparticles or nanomaterials. For oxide materials, the diameter of one oxygen ion is about 1.4 Å. So, seven oxygen ions will make about 10 Å or 1 nm, i.e. the lower side of the nano range. On the higher side, about 700 oxygen ions in a spatial dimension will make the so-called limit of the nano range of materials. The trend in the materials world is particularly in ceramics always to prepare finer powder for the ultimate processing and better sintering to achieve dense materials with dense fine-grained microstructure of the particulates with better and useful properties for various applications. The fineness can reach up to a molecular level by special processing techniques. More is the fineness; more is the surface area and it increases the reactivity of the material. So, the densification and consolidation of ceramic systems improve the properties of materials like abrasion resistance, corrosion resistance, mechanical properties, electrical properties, optical properties, magnetic properties, and a host of other properties for various useful applications in diverse fields. A noted natural nanotechnological phenomenon is in the beautiful colors of stained-glass windows. It is a result of the presence of small metal oxide clusters in the glass having a size comparable to the

wavelength of light. Particles of different sizes scatter different wavelengths of light, imparting different colors to the glass. Small colloidal particles of silver are a part of the process of image formation in photography. Water, at ambient temperature, consists of clusters of hydrogen-bonded water molecules.

## **1.2 DIMENSIONS OF NANOMATERIALS**

Nanomaterials give a bridge that links single elements with single crystalline bulk structures. Quantum mechanics has successfully described the electronic structure of single elements and single crystalline bulks. The well established bondings such as ionic, covalent, metallic and secondary are the basis of solid state structure. The theory of transition in energy levels from discrete for fundamental elements to continuous bands for bulk is an outstanding question in basic science. Thus, a thorough understanding on the structure of nanomaterials can provide deep insight in the structural evaluation from single atoms to crystalline solids.

A specific parameter, introduced by nanomaterials, is the surface/interface-to-volume ratio. A high percentage of surface atoms introduce many size-dependent phenomena. The finite size of the particle confines the spatial distribution of the electrons leading to the quantized energy levels due to size effect. This quantum confinement has applications in semiconductors, opto-electronics and nonlinear optics. A nanostructure provides an ideal system for understanding quantum effects which could lead to major discoveries in solid state physics.

In the past decades, significant progress has already been made in the field of zero-and two-dimensional nanomaterials and nanostructures, since the discovery of pure carbon nanotubes (George 2011), and one-dimensional (1D) nanomaterials have stimulated a great interest. Due to their potential interests to the understanding of

physical concepts and for applications in constructing nanoscale electronic and optoelectronic devices (Hu et al 1999, Dai et al 2003, Law et al 2004, Miao et al 2004, Li et al 2006, Whitesides 2005, Fang et al 2005), they are the ideal systems for investigating the dependence of electrical transport, optical, and mechanical properties on size and in dimension (Xia et al 2003). Up to now, 1D nanomaterials and nanostructures, such as nanotubes (Ajayan 1999, Ye et al 2002, Wu et al 2004), nanorods (Zhang et al 2005, Yu et al 2003, Zhu et al 2005), nanowires (Morales and Lieber 1998, Zhang et al 2001, Xu et al 2004), nanobelts or nanoribbons (Pan et al 2001, Wang et al 2001, Wang et al 2003), nanocables (Zhang et al 1998, Meng et al 1998, Lin et al 2004, Li et al 2005), and nanosheets (Yu et al 2002, Fang et al 2004, Cao et al 2005) have been successfully synthesized by a variety of methods.

During the past decade, many methods have been developed to synthesize 1D nanomaterials and nanostructures. Overall, they can be categorized into two major approaches based on the reaction media that are used during the preparation: solution and gas-phase based process. Solution-based approaches include template-directed synthesis (Martin 1994, Masuda et al 1995, Li et al 2003, Li et al 2005, Wu et al 2004), solution-liquid-solid method (Holmes et al 2000), and solvothermal chemical synthesis (Li et al 1998, Sun et al 2002, Yao et al 2005, Wang et al 2005). Gas-phase based process for 1D nanomaterials and nanostructures mainly include four growth mechanisms. One is a well-accepted so-called vapor-liquid-solid (VLS) process of nanowire and nanowhisker growth proposed by Wagner and Ellis (Wagner and Ellis 1964). According to this mechanism, the anisotropic crystal growth is promoted by the presence of the liquid alloy/solid interface. The detailed description about the VLS growth mechanism can be found in the literature by Yang (Yang et al 2002). It is

conceivable that the size and diameter of the as-synthesized products can be controlled by selecting different size catalysis. For example, monodisperse silicon nanowires are synthesized by exploiting well-defined gold nanoclusters as catalysis for 1D growth via a VLS mechanism in the Lieber group (Cui et al 2001). Transmission electron microscopy (TEM) studies of the materials grown from 5, 10, 20, and 30 nm nanocluster catalysis show that the nanowires had mean diameters of 6, 12, 20, and 31 nm, respectively, and are thus well-defined by the nanocluster sizes. The positions of 1D nanostructure can be controlled by the initial position of Au or other catalyst clusters or thin films. In addition, by applying the conventional epitaxial crystal growth technique into the VLS process, it is possible to achieve precise orientation control during the nanowire growth. Second is the vapor - solid (VS) growth process. In this process, vapor is first generated by evaporation, chemical reduction or gaseous reaction. The vapor is subsequently transported by a carrying gas, and condensed onto a substrate. Some metal, oxide and other nanomaterials and nanostructures have been successfully synthesized by the VS process (Martin 1994, Yang and Liber 1997, Fang et al 2005, Wang et al 2002). It is generally believed that growth temperature and gas-phase supersaturation determines the growth rate of surface planes and the final morphology of the crystals with other experimental parameters playing minor roles in the VS process. Third is oxide-assisted growth. It is a new nanowire growth route and is proposed by Lee (Zhang et al 2003). This synthesis technique in which oxides instead of metals play an important role in the nucleation and growth of nanowires. It is capable of producing a series of nanowires. Fourth is the combination of the anodic alumina membrane (AAM) and chemical vapor deposition (CVD). For example, Zhang report that large-scale single crystalline GaN nanowires in anodic alumina membrane are

achieved through a gas reaction of Ga<sub>2</sub>O vapor with a constant flowing ammonia atmosphere at 1273 K (Cheng et al 1999). Ordered ZnO nanowire arrays have also been fabricated via this method by Lee (Liu et al 2003).

Exploration of nanomaterials and nanostructures that exhibit functionality is the key to nanotechnology. Among the 1D nanomaterials and nanostructures, functional oxides are the fundamental ingredients of smart systems, because the physical and chemical properties of the oxides can be tuned and controlled through adjusting cation valence state and anion deficiency. The structures of functional oxides are very diverse and colorful, and there are endless new phenomena and applications. Such unique characteristics have made oxides the most diverse class of materials, with properties covering almost all aspects of condensed matter physics and solid state chemistry in areas including semiconductivity, superconductivity, ferroelectricity, magnetism, and piezoelectricity (Wang 2004). Up to now, much attention has been paid to the preparation of binary oxide nanomaterials and nanostructures (Rao et al 2003).

An important issue in the self-organized growth and application of 1D nanomaterials and nanostructures is how to control the composition, size, morphology, position, orientation and crystallinity etc in an effective and controllable way. The significance of the controllability manifests in both the chemistry of small-size material synthesis and the realization of their applications. A significant challenge for the chemical synthesis is how to rationally control the nanostructure assembly so that their size, dimensionality, interfaces, and ultimately, their two-dimensional and three-dimensional superstructures can be tailor-made towards desired functionality (Yang et al 2002). Controllable synthesis of nanowires and nanobelts has started to emerge only recently.

### 1.3 PROPERTIES AND APPLICATIONS OF NANOCRYSTALLINE MATERIALS

Nanocrystalline materials have generated interest in recent years in terms of both the challenges they pose to fundamental scientific understanding and the opportunities they present for technological applications. This interest stems from the unusual and often beneficial properties nanocrystalline materials possess owing to the emergence of grain boundary-dominated physics as the grain size approaches nearly 100 nm and below (Gleiter 1989, Gleiter 2000, Aus et al 1992, Grossinger et al 2003, Herzer 2005, Jiles 2003, Kim et al 2004, Kumar et al 2003, Kumar et al 2003, Lu et al 2004, Lund and Schuh 2005, Mcherry et al 1999, Meyers et al 2006, Schiotz and Jacobsen 2003, Suzuki et al 2002, Wang 2006, Wolf et al 2005, Yamakov et al 2003, Youseef et al 2004). At these extremely fine lengths-scales, grain boundaries are no longer characterized as planar defects, as their volume becomes comparable to that of the grain interior. This concept is simply illustrated through the geometric construction of Palumbo (Palumbo et al 1990), who expressed the volume fraction of crystalline grain interior  $f_g$ , as a function of grain size 'd', and grain boundary thickness 't', as:  $f_g = 1 - f_{gb} = (d-t/d)^3$  where  $f_{gb}$  represents the volume fraction of grain boundaries. This relationship is plotted in Fig.1.1 assuming a reasonable value of  $t = 1$  nm. Below a grain size of nearly 5 nm, a crossover is observed where the volume fraction of grain boundaries exceeds that of the grain interior. Given the unique, relatively disordered structure of grain boundaries (Sutton and Balluffi 1995, Ahmadi et al 1996, Lnk et al 1999) it may be speculated that material properties should strongly depend on grain through this transition.

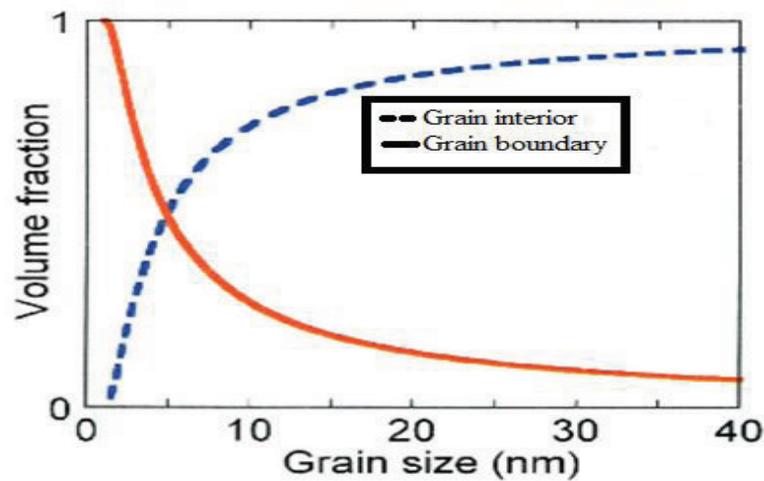


Fig. 1.1. Volume fraction of grain interior and boundary regions as a function of grain size.

### 1.3.1 Novel Mechanical Properties

It is known that mechanical properties of a solid depend strongly on the density of dislocations, interface-to-volume ratio, and grain size. An enhancement in damping capacity of a nanostructured solid may be associated with grain-boundary sliding (Berry and Pritchett 1979) or with energy dissipation mechanism localized at interfaces (Su et al 1993) a decrease in grain size significantly affects the yield strength and hardness (Weertmen and Averback 1996). The grain boundary structure, boundary angle, boundary sliding and movement of dislocations are important factors that determine the mechanical properties of the nanostructured materials. One of the most important applications of nanostructured materials is in superplasticity, the capability of a polycrystalline material to undergo extensive tensile deformation without necking or fracture. Grain boundary diffusion and sliding are the two key requirements for superplasticity.

### **1.3.2 Unique magnetic properties**

The magnetic properties of nano-size particles differ from those of bulk mainly in two points. The large surface-to-volume ratio results in a different local environment for the surface atoms in their magnetic coupling/interaction with neighboring atoms, leading to the mixed volume and surface magnetic characteristics. Unlike bulk ferromagnetic materials, which usually form multiple magnetic domains, several small ferromagnetic particles could consist of only a single magnetic domain. In the case of a single particle being a single domain, the super paramagnetism occurs, in which the magnetizations of the particles are randomly distributed and they are aligned only under applied magnetic field, and the alignment disappears once the external field is withdrawn. In ultra-compact information storage (Gunther 1990), for example, the size of the domain determines the limit of storage density. Magnetic nanocrystals have other important applications such as in color imaging, bio-processing (Marchessault et al 1992), magnetic refrigeration (Marchessault RD et al 1992), and ferrofluids (Anton et al 1990).

Metallic hetero-structured multilayers comprised of alternating ferromagnetic and nonmagnetic layers such as Fe-Cr and Co-Cu have been found to exhibit giant magneto resistance (GMR), a significant change in the electrical resistance experienced by current flowing parallel to the layers when an external magnetic field is applied (Baibich et al 1998). GMR has important applications in data storage and sensors.

### **1.3.3 Crystal-Shape-Dependent Thermodynamic Properties**

The large surface-to-volume ratio of nanocrystals greatly changes the role played by surface atoms in determining their thermodynamic properties. The reduced coordination number of the surface atoms greatly increases the surface energy so that

atom diffusion occurs at relatively lower temperatures. The melting temperature of Au particles drop to as low as  $\sim 300$  °C for particles with diameters of smaller than 5 nm, much lower than the bulk melting temperature 1063 °C for Au (Buffat and Borel 1976). Nanocrystals usually faceted shape and mainly enclosed by low index crystallographic planes. It is possible to control the particle shape, for example, cubic Pt nanocrystals enclosed by  $\{111\}$  facets. The rod-like Au nanocrystals have also been synthesized and they are enclosed by  $\{100\}$  and  $\{100\}$  facets. The density of surface atoms changes significantly for different crystallographic planes, possibly leading to different thermodynamic properties.

#### **1.3.4 Semiconductor Quantum Dots for Opto-Electronics**

Semiconductor nanocrystals are zero-dimensional quantum dots in which the spatial distribution of the excited electron-hole pairs is confined within a small volume resulting in the enhanced non-linear optical properties (Prokes 1993, Brus 1991, Alivisatos 1996, Murray et al 1993). The density of states concentrates carriers in a certain energy range and it is likely to increase the gain for electro-optical signals. The quantum confinement of carriers converts the density of states to a set of discrete quantum levels. This is fundamental for semiconductor lasers. With consideration, the small size of a semiconductor nanocrystal and its electronic properties are significantly affected by the transport of a single electron, giving the possibility of producing single electron devices (Klein et al 1997). This is likely to be important in quantum devices and nanoelectronics in which the sizes of the devices are required to be in the nanometer range.

Nanostructured porous silicon has been found to give visible photoluminescence (Lomov et al 2012, Pickering et al 1984). The luminescence

properties of silicon can be easily integrated with its electronic properties, possibly leading to a new approach for opto-electronic devices. The mechanism has been proposed to be associated with either quantum confinement or surface properties linked with silica. This is vitally important to integrate optical circuits with silicon based electronics. The current research has been concentrated on understanding the mechanism for luminescence and improving its efficiency.

### **1.3.5 Quantum Devices for Nanoelectronics**

As the density of logic circuits per chip is approaching  $10^8$ , the average distance between circuits is  $1.7 \mu\text{m}$  between which all of the circuit units and interconnects must be accommodated. The size of devices is required to be less than 100 nm and the width of the inter connects is less than 10 nm. The miniaturization of devices breaks the fundamental set by classical physics based on the motion of particles. Quantum mechanical phenomena are dominant such as the quantization of electron energy levels (e.g. the 'particle in a box' quantum confinement problem), electron wave function interference, quantum tunneling between the energy levels belonging to two adjacent nanostructures, and discreteness of charge carriers (e.g. single electron conductance). The quantum devices rely on tunneling through the classically forbidden energy barriers. With an appropriate voltage bias across two nanostructures, the electron energy levels belonging to the two nanostructures line up and resonance tunneling occurs, resulting in an abrupt increase in tunneling current. The single-electron electronics uses the energy required to transport a single electron to operate a switch, transistor or memory element.

These new effects not only raise fundamental question in physics, but also call on challenges in new materials. There are two outstanding material's issues. One is the

semiconductor nanocrystals suitable for nanoelectronics. Secondly, for the operation of high density electronics system, new initiatives must be made to synthesize interconnect. With minimum heat dissipation, high strength and high resistance to electro migration, the most challenging problem is how to manipulate the nanostructures in assembling devices. This is not only an engineering question but rather a science question because of the small size of the nanostructures.

Semiconductor heterostructures are usually referred to as one-dimensional artificially structured materials composed of layers of different phases/compositions. This multilayered material is particularly interesting if the layer's thickness is less than the meanfree-path length of the electron, providing an ideal system for quantum well structure. The heterostructured semiconductor material is the optimum candidate for fabricating electronic and photonic nanodevices (Pickering et al 1984).

### **1.3.6 Carbon Fullerenes and Nanotubes**

Research in nanomaterials opens many new challenges both in fundamental science and in technology. The discovery of  $C_{60}$ , fullerene (Canham 1990), for example, has sparked a great research effort in carbon related nanomaterials. Besides diamond and graphite structures, fullerene is a new state of carbon. The current most stimulating research focuses on carbon nanotubes, a long-rod-like structure comprised of cylindrical concentric graphite sheets (Cammarata 1996). The finite dimension of the carbon nanotube and the chirality angle following which the graphite sheet is rolled results in unique electronic properties such as ballistic quantum conductance, electron field emission, strong mechanical strength, extremely high elastic limit, reversible high mechanical flexibility etc (Kroto et al 1985, Iijima 1991, Frank et al 1998).

Fullerene and carbon nanotubes can be chemically functionalized and they can serve as sites/cells for nano-chemical reaction (Tans et al 1998). The long, smooth and uniform cylindrical structure of the nanotube is ideal for probe tips in scanning tunneling microscopy and atomic force microscopy (De Heer et al 1995). The covalent bonding of the carbon atoms and the functionalized nanotube tip gives birth to the chemical microscopy (Han et al 1997) which can be used to probe the local bonding, bond interactions and chemical forces.

### **1.3.7 Ordered Self-Assembly of Nanocrystals**

Size and even shape selected nanocrystals behave like a molecular matter and are ideal building blocks for two- and three-dimensional cluster self-assembled superlattice structures (Dai et al 1996, Wong et al 1998, Whetten et al 1996, Yin and Wang 1997). The electrical, optical, transport and magnetic properties of the structures depend not only on the characteristics of individual nanocrystals, but also on the coupling and interaction among the nanocrystals arranged with long-range translational and even orientational order (Murray et al 1995, Sun and Murray 1999). Self-assembled arrays involve self-organization into monolayers, thin films, and superlattices of size-selected nanocrystals encapsulated in a protective compact organic coating. Nanocrystals are the hard cores that preserve ordering at the atomic scale; the organic molecules adsorbed on their surfaces serve as the interparticle molecular bonds and as protection for the particles in order to avoid direct core contact with a consequence of coalescing. The interparticle interaction can be changed via control over the length of the molecular chains. Quantum transitions and insulator to conductor transition could be introduced, possibly resulting in tunable electrical, optical and transport properties (Wang 1998).

### **1.3.8 Photonic Crystals for Optically-Active Devices and Circuits**

Photonic crystals are synthetic materials that have a patterned periodic dielectric constant that creates an optical bandgap in the material (Harfenist et al 1996). To understand the mechanism of photonic crystals, one starts from the energy band structure of electrons in a crystalline solid. Using the fermi velocity of the electrons in a solid, it can be found that the electron wavelength is compatible to the spacing between the atoms. Electron motion in a periodic potential results in the quantized energy levels. Bands are formed in the energy regions filled with energy levels. An energy gap between the conduction band and the valence band would be formed, which is a key factor in determining the conductivity of the solid. If the bandgap is zero, the material is conductive; for a small bandgap the material is semiconductor; and the material insulator, if the band gap is large.

The wavelength of photons is in the order of a few hundred nanometers. It is necessary to create artificially a dielectric system which has periodically modulated dielectric function at a periodicity compatible with the wavelength of the photon. This can be done by processing materials that are comprised of patterned structures. As a result, photons, with energies lying within the bandgap cannot be propagated unless a defect causes an allowed propagation state within the bandgap, leading to the possibility of fabricating photon conductors, semiconductors and insulators. Point, line, or planar defects can be shown to act as optical cavities, waveguides, or mirrors and offer a completely different mechanism for the control of light and advancement of all-optical integrated circuits (Collier et al 1997, Joannopoulos et al 1997, Gadot et al 1997). By using particle sizes in the nanometer regime with different refractive indices than the

host material, these effects should be observable in the near infrared and visible spectral regions.

### **1.3.9 Mesoporous Materials for Low-loss Dielectrics and Catalysis**

Mesoporous materials can be synthesized by a wide range of techniques such as chemical etching, sol gel processing, and template-assisted techniques. Ordered self-assembly of hollow structures of silica (Krauss et al 1996), carbon (Sievenpiper et al 1996), and titania (Velev et al 1997, Zakhiov et al 1998) has drawn much attention recently because of their applications in low-loss dielectrics, catalysis, filtering and photonics, the ordered hollow structure is made through a template-assisted technique. The monodisperse polystyrene (PS) particles are used as the template to form an ordered and self-assembled periodic structure. Infiltrating the template by metal-organic liquid and a subsequent heat treatment form the ordered pores. The structure is ordered on the length-scale of the template spheres and the pore sizes are in submicron to micron range. Alternatively, ordered porous silica, with much smaller pore sizes in nanosize range ( $< 30$  nm), produced deliberately by introducing surfactants. A combination of the template-assisted pore structure and the surfactant introduced in the infiltration liquid, results in a new structure that have porosity at double-length scales (Wijnhoven and Vos 1998). The low density ( $\sim 10$  of the bulk density) of the material results in very low dielectric constant, a candidate for low-loss electronic devices. The large surface area of the porous materials is ideal for catalysis. The synthesis of mesoporous materials can be useful for environmental cleaning (Holland et al 1998) and energy storage (Yin and Wang 1999).

#### 1.4 SYNTHESIS OF NANOCRYSTALLINE MATERIALS

In general, there are two approaches to nanoparticle production that are commonly referred to as top-down and bottom-up. Top-down nanoparticles are generated from the size reduction of bulk materials. They generally rely on physical, the combination of physical and chemical, electrical or thermal processes for their production. Such methods include high-energy milling, mechano-chemical processing, electro-explosion, laser ablation, sputtering and vapour condensation. Bottom-up approaches generate nanoparticles from the atomic or molecular level and thus are predominantly chemical processes. Commonly used techniques are crystallisation/precipitation, sol-gel methods, chemical vapour deposition and self-assembly routes. Some processes may use a combination of both. Either, approach may be performed in all three states of matter, i.e., vapour, solid or liquid (or combination of these) and the limits to the physical size of nanoparticles produced by either approach are converging and may overlap. Consequently, the choice of particle size, from a product design perspective, is directly influenced by process economics, capability to supply and the adequacy and type of performance required in the target application. To meet performance criteria, not only does the nanoparticle material have to have (or be able to impart) desired functionality but also that functionality must be predictable and reliable. The latter is often determined by extrinsic factors such as the degree of dispersion, the level of contamination and the working environment. Apart from characteristic size range significant commonality is not apparent between the technologies used to produce nanoparticles although some techniques appear to be more flexible than others. Nanoparticles have a size dimension ranging from the atomic and

molecular (~0.1 to 3 nm) up to 100 nm and thus represent a bridge between the quantum and real world (micro and macro).

## **1.5 TOP-DOWN PROCESSES**

There is a range of top-down processes that can be used to produce nanoparticles. The most significant of these are physical methods (highenergy milling), the combination of physical and chemical methods (chemical-mechanical milling) and vapour phase condensation (using laser ablation, electro-explosion, sputtering and vapour condensation using thermal methods).

### **1.5.1 High-energy milling**

There are in general two methods by which nanoparticles can be produced using high-energy milling: (i) milling alone and (ii) combining chemistry and milling (referred to as chemical-mechanical milling or mechanochemical processing). It is suggested that these methods offer the advantage of being easily scaled. References (Zhang 2004) and (Koch 1997) are good starting points for further reading.

High-energy milling processes involve the comminution of bulk materials. The principle of comminution is centred on applying physical forces to bulk material so as to affect breakage into smaller sizes. The forces required to effect breakage are usually a combination of either impact or shear. Material is introduced into a milling chamber in which grinding (milling) media are contained. Milling occurs when the media is made to move either by stirring (using a rotor) or by shaking/vibrating the chamber and contacts the bulk material thus imparting, depending on the milling parameters, either impact or shear forces on it. Breakage can occur through a variety of mechanisms and are generally described as attrition, abrasion, fragmentation or chipping and occur both

at the macro and microscopic level (Verkoeijen et al 2002). This is illustrated in Figs 1.2 and 1.3.

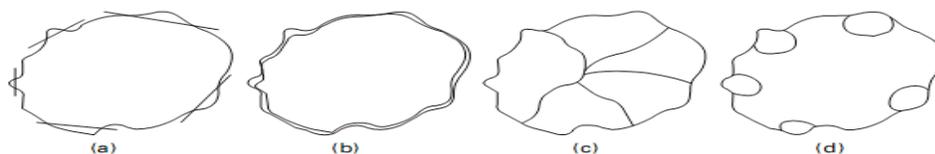
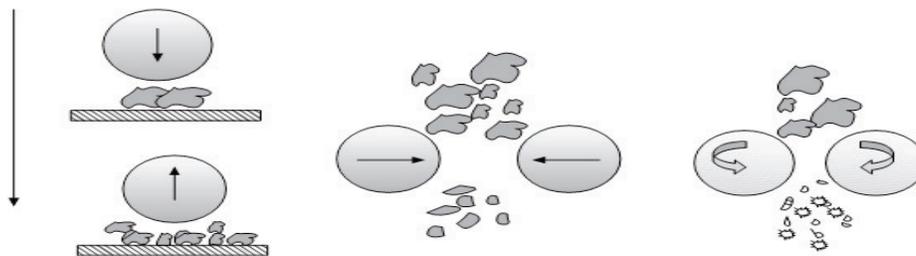


Fig. 1.2. Breakage mechanisms; (a) attrition, (b) abrasion, (c) fragmentation, (d) chipping.

Macroscopic level

Before event

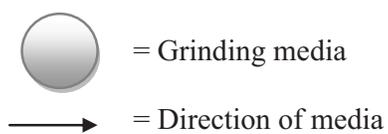


After event

Force type: Impact

Impact

Shear



Microscopic level

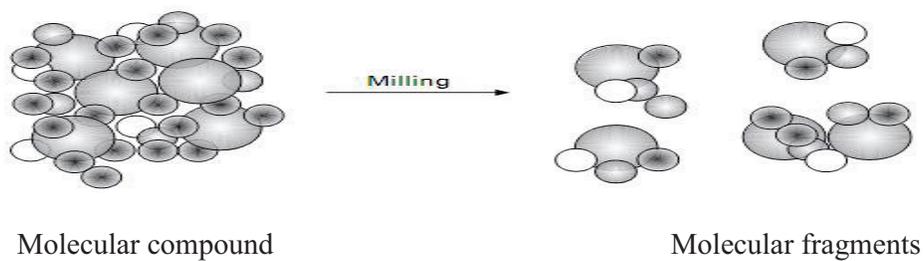


Fig. 1.3. Breakage at the micro and macro level.

For non-metallic compounds (carbides, oxides, etc.) the reduction in grain size is consequent on fracturing and cold welding and the limit to minimum grain size is determined by the minimum size that does not support nucleation and propagation of cracks within the grain. For metallics, on the other hand, it is thought that the reduction in grain size is a process where localised plastic deformation is induced, subgrains are formed (by eradication of dislocations) which combine (through intimate mechanical contact) to form discrete grains. The latter process is analogous to recrystallisation observed during hot forming of metals and alloys but in these circumstances at low temperatures. In intermetallics, the process is thought to be different again in that grain formation is due to nucleation (on a nanoscale) followed by a limited growth of the generated phase (Koch 1997, Jankovic 2003). There are numerous examples in the literature of alloy and mixed metal oxide production using this technique (Koch 1997, Yang et al 2004). Few examples can be found where single-phase powders or particles are produced at the nanoscale level (Hellstern et al 1989, Gaffet et al 1997, Boily et al 1996).

### **1.5.2 Chemical-mechanical milling**

Mechanochemical routes to the production of nanoparticles utilise the (usually simultaneous) combination of chemical and physical forces. Variants include (i) milling under controlled atmosphere and (ii) milling precursor materials that react to form a product phase during milling. There are a few examples in the literature where milling has been performed using a reactive atmosphere in an attempt to produce nanophase alloys, referred to as Chemical Mechanical Alloying (CMA) or Controlled Reactive Mechanical Alloying (CRMA) and the work is developmental and has focused primarily on the synthesis of nitrides of Ti, Al, Si, Cr, Zr and hydrides of Mg-Fe

(Campbell et al 2000, Varin et al 2004). In these processes, a metal is milled under ammonia or nitrogen (for nitride formation) or hydrogen (for hydride formation). The metal itself may have been pre-milled under an inert atmosphere such as argon or helium before the reactive alloying step. Experimental studies have produced evidence that nanophase product was formed, however, the mechanisms by which this occurred are complex and not well understood.

### **1.5.3 Mechanochemical processing**

The production of nanoparticles by milling a combination of compounds to form a new product by a solid-state displacement reaction has received increasing attention over recent years. The process is referred to as Mechanochemical Processing (MCP). In this process two or more materials are simultaneously milled to produce, through an exchange reaction, a nanoscale composite that can be further processed into dispersed nanopowders by removing the matrix phase. A range of materials has been produced by this method commercially and in the laboratory. These include oxides, sulfides, carbonates doped metal oxides and metals.

Precursors can be selected from oxides, carbonates, sulphates, chlorides, fluorides, hydroxides and reported products are not limited to those cited above but vary across a range of metals including, for example, Cu, Ni, Al, Cd, Pb and Se. Process control is dependent on a number of variables, which include milling time, the level of diluent and the choice of starting material and thermal treatment parameters (Taufuku and McCormick 2001, Yang et al 2004, Yang and Zhang 2004, Dodd and McCormick 2002, Yang and Qiu 2004, Taufuku and McCormick 1999, Balaz et al 2003, Hos and McCormick 2003, Ding et al 1995).

#### **1.5.4 Vapour phase processes**

In many ways the vapour phase process, and in particular condensation from the vapour phase of nanoparticulate materials, is currently the most versatile synthesis process. It has the ability to generate non-agglomerated nanopowders, which are sinterable at relatively low temperatures. In this approach, a vaporisable material source is used to generate the powder particles, which are convectively transported and collected on a cold substrate. Particles are formed in a thermal zone above the material source, due to interactions between the hot vapour species and the much colder inert gas atoms. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or preferably a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired ceramic powder particles.

#### **1.5.5 Laser ablation**

When an adequately powerful laser beam is focused on material surface nanoparticles can be generated by evaporation of the targeted material into a surrounding gas where the vaporised material condenses to form nanoparticles. Here incident photon energy is high enough to break the chemical bonds of the target material directly, the material is dissociated into its chemical components and in some cases no liquid phase transition occurs. Nanoparticles of various compositions can be produced by this technique simply by changing the composition of the target material. Particle purity depends on the purity of the target material and the purity of the environment into which the material vaporises. Normally, a strategically located substrate would be used to collect these particles and it is therefore regarded as a potentially useful tool for manufacturing and depositing nanoparticles on surfaces. Typical particle sizes are in the 5-30 nm range and include a variety of metals (Ag, Au, Ni, Fe, Al, Ti, Si) alloys, oxides

and nitrides (Wegner et al 2002, UYlmann et al 2002, Mafune kondow 2003). More recent studies have examined target materials (usually a metal) immersed in liquids (water, alcohols, and salt solutions). A variant on this technique is surfactant controlled laser ablation in solution (SC-LAS) (Simakin et al 2004, Dolgaev et al 2002, Bae et al 2002, Becker et al 1998). The effect of different target material geometry such as microspheres (referred to as laser ablation of microspheres (LAM)) has also been examined (Cai et al 1997). Reactive ablation occurs when the surrounding atmosphere or environment is reactive to the vaporised material. For example, metal oxide particles made by this method are a consequence of metal particles vaporising from a metal foil and subsequently reacting with an imposed oxygen environment.

#### **1.5.6 Electro-explosion**

In this process nanoparticles are prepared by the electro-explosion of metal wires (referred to as Electro-Explosion of Wires (EEW)), usually in nonoxidising environments. When a short (microsecond) high-current, high voltage electric power impulse (1.5-2.0 times higher than the sublimation energy) is applied to a metal wire, it causes it to explode. Extremely high temperatures ( $>20,000$  °C) and cooling rates in the supersonic shock wave ( $10^6$ – $10^8$  °C/s) can be achieved. Nanoparticles formed through this method have unusual intrinsic thermal properties that give rise to ‘self sintering’. This enhanced reactivity allows subsequent alloying to occur at substantially reduced temperatures. Initial metal clusters are  $\sim 8$ – $10$  nm with subsequent coalescence into crystallites of  $\sim 100$  nm. The process can be applied to any ductile metal in wire form and products include transition and precious metals. The process can be modified to produce metal oxide and nitride powders (Sen et al 2003, Tepper et al 2001).

### **1.5.7 Sputtering**

Sputtering is a form of physical vapour deposition (PVD) often used for production of metal films, sputtering involves knocking metal atoms off a disc of pure metal with charged, energetic, chemically inactive atoms called ions produced in plasma. The metal ions will re-deposit onto a substrate the wafer to build up the desired metal film (Terauchi 1995).

### **1.5.8 Spark discharge generation**

In this process a metal is vaporised by charging electrodes until breakdown voltage is reached. The arc (spark) formed across the electrode vaporises a small amount of metal. Condensation and capture of generated particles is similar to that previously stated.

## **1.6 BOTTOM-UP PROCESSES**

Bottom-up processes produce nanoparticles by combination to generate material from the atomic or the molecular level. Consequently, synthesis using this approach relies heavily on chemical processes that are performed in the liquid and/or gas phase. The most common are chemical vapour deposition (CVD), sol-gel, solvo-thermal method and atomic or molecular condensation. The following section reviews some of these techniques.

### **1.6.1 Liquid phase - Precipitation/crystallisation**

Wet chemical methods traditionally are used to produce particles and powders of precipitation and crystallisation. For example, large-scale production of alumina and titania, utilises these processes, as does the production of catalytic materials such as zeolites. The majority of products in the chemical industry undergo crystallisation/precipitation at some stage of their manufacture and information related

to these processes is largely proprietary. Crystallisation occurs when a solution is cooled to such an extent that it becomes supersaturated leading to nucleation and crystal formation. Precipitation, on the other hand, occurs when an insoluble product is formed as a consequence of a chemical reaction. In both cases the product usually requires filtration, washing, drying and sometimes calcination steps.

The most effort in using these two techniques for nanoparticle production has come from the pharmaceutical and catalyst production sectors by reason that increasing surface area will enhance chemical reactivity and dissolution; production infrastructure and know-how already exist for the particle formation route. Specialised products for application in both areas usually demand high purity with well-defined specifications and to meet these requirements well-controlled processes have been developed. The greatest challenge in using these nanoparticle production approaches for pharmaceutical and catalytic application is to control the size, shape and stability of the product. Consequently, other competing methods and technologies are being explored (Zhong et al 2004). The use of micro-reactor technology for its potential to control product specifications such as particle size is of increasing interest (Michael Freemantle 2003).

### **1.6.2 Sol-gel method**

In simple terms sol-gel processing involves the transition from a sol (very finely divided solid particles dispersed in a liquid which will not settle out) to a gel (a dispersion of a liquid throughout a solid matrix). It is a long-established process with the key controlling processing steps being sol formation and gelling, drying, curing and sintering. Starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Typically, the precursor is subjected to a series of hydrolysis and polymerisation reactions to form a

colloidal suspension. This suspension can be further processed to make materials in different forms from thin films and aerogels to nanocomposites and nanoparticles. The advantages of the process are perceived to be (i) low processing (ii) high homogeneity and purity of products and (iii) versatility with respect to the materials that can be formed. Typical sizes of nanoparticles produced by this method are 5-30 nm (Walt 2002, Zarzycki 1997). In particular sol-gel processing offers unique opportunities to generate gels of organic-inorganic materials (Sakka 1997).

The new generation of sol-gel produced hybrid materials was pioneered by the preparation of non-crystalline organic-inorganic materials that were named Ormocers. The physical and mechanical properties of these materials can be tailored by manipulating the ratio of inorganic-organic which when applied on a substrate in gel and dried forms give rise to different surface morphologies. Resultant 'super-repellent' surfaces are based on a physical structure rather than chemical character (Schmidt et al 2000). Another new group of materials that have been spawned by this preparation method are the biological composites. The demonstration that an organic dye could be entrapped in a porous silica cage led to the greater aspiration of incorporating biologically active materials in inorganic matrices to control reactions arising from the transport of materials in or out of the matrix (Uhlmann and Teowee 1998).

### **1.6.3 Self-assembly**

Self-assembly of functional nanomaterials has received a substantial amount of attention over the last decade. It is a predominantly chemical process rather than a specific technique. A wide range of materials have been processed using self-assembly techniques. The inspiration for self-assembly comes from nature itself and it is no coincidence that a major focus of nanoparticle self-assembly (as distinct from

nanostructures or nanostructured materials) is on particles associated with biological systems including lipids, organic molecules, peptides, proteins and DNA. However, peptides and proteins are used as the main building blocks because their folding behaviour and stability is relatively well understood together with the influences on protein-protein interactions (Mackenzie 2003, Depero and Curri 2004, Petit and Pileni 2000, seip and oconnor 1999, Pileni 2003).

#### **1.6.4 Chemical vapour deposition**

This method involves depositing nanoparticulate material from the gas phase. Material is heated to form a gas and then allowed to deposit as a solid on a surface, usually under vacuum. There may be direct deposition or deposition by chemical reaction to form a new product which differs from the material volatilised. This process readily forms nanopowders of oxides and carbides of metals if vapours of carbon or oxygen are present with the metal. Chemical vapour deposition can also be used to grow surfaces. An object to be coated is allowed to stand in the presence of the chemical vapour. The first layer of molecules or atoms deposited may or may not react with the surface. However, these first formed depositional species can act as a template on which material can grow.

#### **1.6.5 Electrodeposition**

Electrodeposition has been used for a long time to make electroplated materials. By carefully controlling the number for electrons transferred the weight of material transferred can be determined in accordance with Faraday's law of electrolysis. This states that the number of moles of product formed by an electric current directly proportional to the number of moles of electrons supplied i.e. the quantity of electricity. If the surface was perfectly flat, then knowing the diameter of a copper atom it should

be possible to calculate the height and number of atoms in the copper layer. In practice the surface is rocky so a coverage factor needs to be included which is related to root mean squared roughness or average roughness.

In nanotechnology, the aim is to place only a single layer or more of coverage on a surface by electrodepositing in a very controlled way. Thus, hypothetically if an atom of 10 nm diameter, which packs cubically (that is, at the corners of a square), is to be deposited as a monolayer at 50% coverage of a 1 cm<sup>2</sup> surface then  $0.5 \times 10^{12}$  atoms are needed. The current and time must be carefully measured and any other factors involved in consuming current, such as impurities, must be known in great details. Nevertheless, nanostructured films of platinum can be produced by electro deposition from liquid crystalline mixtures. The films obtained are mechanically robust, remarkably flat, uniform, and shiny in appearance. They also have surface areas comparable with those of the platinum deposited from conventional electroplating baths, and exhibit quite different and favourable electrical properties than conventional platinum deposits. The concept of electroplating from liquid crystalline mixtures can be used for other metals including Pd, Ni, Au, organic polymers (for example, polyaniline), oxides and semiconductors. The unique nature of nanostructured films from liquid crystals makes them of considerable interest for a very wide range of applications. These include batteries, fuel cells, and solar cells, windows that can disperse heat and change properties depending on the environment (electrochromic windows), sensors, field emitters, and photonic devices.

Electrodeposition can be used to fill holes to make dispersed nanomaterials. Nanoholes have been strategically placed in membranes. These materials start with the bombardment of a polymer sheet by energetic heavy ions accelerated by a cyclotron.

The heavy ions pass through the sheet and leave minuscule damage tracks. Chemical etching is used to turn these tracks into holes (nanoholes) with diameters in the range of 10 to 100 nm. Filling nanosize holes in polymer membranes with various combinations of metals produces nanocomposites, which have different uses. For example, if some holes are filled with a conducting metal like gold, then they can be charged and this can influence the nature of ions that will go through the unfilled holes. If there is a device at the other end that responds to charge then the device becomes a specific ion detector. Other nanocomposite materials can be produced with designer optical, electrical magnetic or chemical properties. Such materials can be used as screening materials for heat, light or radiation for example as thermo liners in ovens and utensils, and in mobile phones (Cassell et al 1999).

#### **1.6.6 Microwave-assisted solution method**

The principle involved in this method is, when materials are irradiated with microwaves they absorb energy from the microwave field. In this, a microwave oven is used to heat up the material substance (reactants). It is well known that the interaction of dielectric materials, liquids, or solids with microwave leads to what is generally known as dielectric heating. Unlike, conventional method, microwave synthesis has the advantages of very short time, small practical size, narrow particle size distribution and high purity.

#### **Basis of the microwave strategy**

Since 1986, microwave irradiation as a heating method finds number of applications in chemistry. The microwave synthesis which is generally quite fast, simple, energy efficient has been developed and widely used for ceramic materials etc. It is suggested that these advantages could be attributed to fast homogeneous nucleation.

Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of material is somewhat unclear and speculative. However, it is well known that the interaction of dielectric materials, liquids or solids with microwave leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to friction between molecules which subsequently generate heat. The microwave assisted route is yet a novel method to synthesis varieties of nanomaterials and is a very rapidly developing area of research. Also it is well known that microwave has electromagnetic field components. The electric field applies a force on charged particles as a result of which the charged particles start to migrate or rotate. Due to the movement of charged particles further polarization of polar particles take place.

When materials are irradiated with microwaves they absorb energy from the microwave field. The power absorbed  $P$  is given by  $P = 2\pi f \epsilon_0 \epsilon_r \tan \delta E_i^2$  where  $f$  is the frequency,  $\epsilon_0$  is the permittivity in free space,  $\epsilon_r$  is the dielectric constant,  $\tan \delta$  is the dielectric loss and  $E_i$  is the amplitude of the electric field. Therefore in a given instrumental set up,  $E_i$  and  $f$  held constants.  $P$  is determined by  $\epsilon_r$  and  $\tan \delta$ .  $\epsilon_r$  is generally high for materials containing molecules or complex ions of high dipole moment and therefore, high molar polarization. Therefore when a mixture of two materials A and B of different dielectric constant  $\epsilon_r^1$  and  $\epsilon_r^2$  is exposed to microwave field, the materials with higher values of  $\epsilon_r$  absorbs energy preferentially and gets heated rapidly compared to the other. For the microwave decomposition of a material in a mixture, the absorption of microwave energy can be used to get advantage. The precursor material can be chosen such that it has a high value of  $\epsilon_r$  and decomposes by preferential microwave absorption to yield the desired nanoparticles. Thus if a material

organic or an inorganic complex salt of reasonably high value of dielectric constant ( $\epsilon_r$ ) must be dissolved in a suitable liquid medium of low dielectric constant and irradiated with micro waves. We can expect the formation of the nanoparticles generally forms as a suspension in the chosen liquid. It would of course be better to choose a precursor which has high value of both  $\epsilon_r$  and dielectric loss ( $\tan \delta$ ), but  $\tan \delta$  values are often not readily available and are also highly temperature dependent. This may result in a disadvantage occasionally if  $\tan \delta$  decreases with temperature.

## **1.7 EXPERIMENTAL TECHNIQUES AND INSTRUMENTATION**

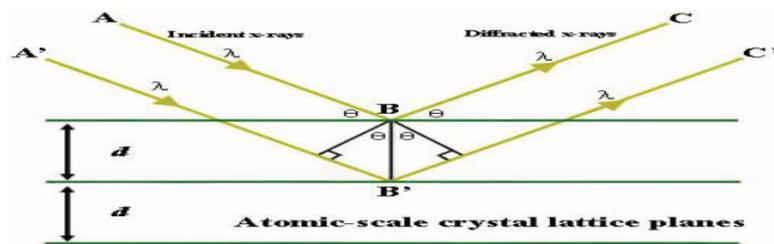
The  $\text{MnO}_2$  and  $\text{TiO}_2$  nanoparticles, PANI/ $\text{MnO}_2$  and PANI/ $\text{TiO}_2$  nanocomposites are obtained through the present microwave assisted solution method; sol-gel method and In situ polymerization are crystalline. The structure and phase purity of the materials were studied by X-ray diffraction technique and presence of the chemical groups in the samples were identified by FT-IR spectroscopy. The surface morphology and the particle morphology of the nanopowders were studied by Scanning Electron Microscopy (SEM) and HR Transmission Electron Microscopy (HRTEM), respectively. The absorption was determined from UV-Vis spectra. Dielectric studies are studied by Impedance Spectroscopy. Using Thermogravimetry, the TG/DTA was performed. The different experimental techniques used in the present work are discussed in detail in this chapter.

### **1.7.1 Powder X-ray Diffraction Technique**

The structure of the nanopowdered  $\text{MnO}_2$ ,  $\text{TiO}_2$ , PANI/ $\text{MnO}_2$ , and PANI/ $\text{TiO}_2$  materials in this investigation were analyzed by powder X-Ray Diffraction (XRD) techniques. The powder X-Ray diffraction method is one of the most important tools for the qualitative analysis of materials. An X-Ray diffractometer utilizes a powdered

sample, a goniometer, and a fixed-position detector to measure the diffraction patterns of unknown powdered materials.

The powdered sample provides nearly all possible orientations of the crystal lattice, the goniometer provides a variety of angles of incidence, and the detector measures the intensity of the diffracted beam. When a crystal is bombarded with X-rays of a fixed wavelength and at certain incident angles, intense reflected X-rays are produced when the wavelengths of the scattered X-rays interfere constructively. In order for the waves to interfere constructively, the differences in the travel path must be equal to integral multiples of the wavelength (Kaeble 1967, Bason 1996, Klug and Alexander 1954). When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam.



**Fig. 1.4. Bragg's law reflection**

The diffracted X-rays exhibit constructive interference when the distance between paths ABC and A'B'C' differs by an integer number of wavelengths. To illustrate this feature, consider a crystal with crystal lattice planar distances  $d$  as shown in Fig. 2.3. When the travel path length difference between the ray paths ABC and A'B'C' is an integer multiple of the wavelength, constructive interference will occur for a combination of that specific wavelength, crystal lattice planar spacing and angle of incidence ( $\theta$ ). Each rotational plane of atoms in a crystal will undergo reflection at a single, unique angle (for X-rays of a fixed wavelength). The general relationship

between the wavelengths of the incident X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's law. i.e.  $n \lambda = 2 d \sin \theta$  where  $n$  (an integer) is the order of reflection,  $\lambda$  is the wavelength of the incident X-rays,  $d$  is the interplanar spacing of the crystal and  $\theta$  is the angle of incidence (Stout and Jensen 1968, Woolfson 1970).

The resulting analysis is described graphically as a set of peaks with percentage intensity on the Y-axis and goniometer angle on the X-axis. The exact angle and intensity of a set of peaks is unique to the crystal structure being examined (Buerger 1958, Chan 1961). A monochromator is used to ensure a specific wavelength reaches the detector, eliminating fluorescent radiation. The resulting trace consists of a recording of the intensity against contour angle ( $2\theta$ ). The trace can then be used to identify the phases present in the sample (Cullity and Stocks 2001). Diffraction data from many materials have been recorded in a computer searchable Powder Diffraction File (PDF/JCPDS File). Comparing the observed data with that in the PDF, the phases in the sample can be identified. In the present investigation, XRD spectra are recorded using a computerized X-ray Diffractometer (Model Bruker D-8) with Nickel filtered  $\text{Cu-K}_\alpha$  radiation and the model is shown in Fig. 2.4. Identification of the phases is done by comparing the  $d$  spacings and line strengths of the observed X-ray diffraction pattern of the sample with the standard reference data.

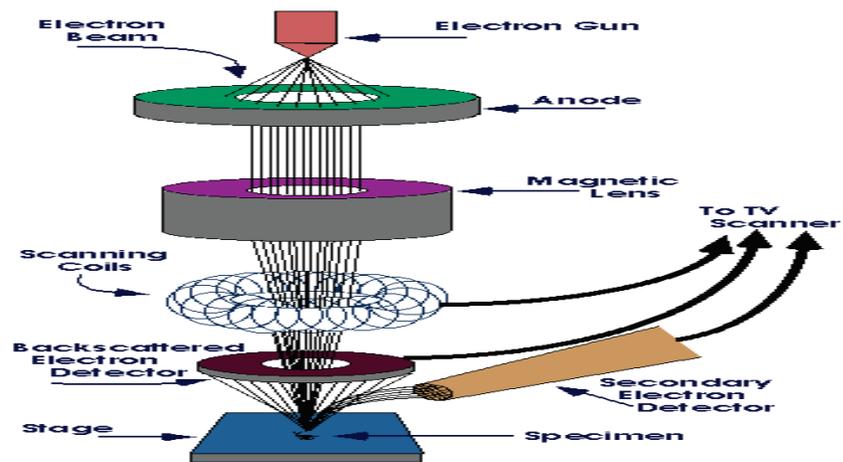


**Fig. 1.5. Powder X-ray Diffractometer**

### **1.7.2 Scanning Electron Microscope (SEM)**

Scanning Electron Microscope (SEM) is a type of electron microscope that records the image of a sample surface by scanning it with a high-energy beam of electrons in a raster\_scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. A beam of electrons is generated in the electron gun, located at the top of the column, which is pictured to the left as shown in Fig. 2.5. This beam is attracted through the anode, condensed by a condenser lens and focused as a very fine point on the sample by the objective lens. The image consists of thousands of spots of varying intensity on the face of a cathode ray tube (CRT) that correspond to the topography of the sample. There are many advantages of using the SEM instead of a light microscope. The SEM has a large depth of field which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation

makes the SEM one of the most heavily used instruments in research areas today (Newbury et al 1986, Goldstein et al 1992, Joy et al 1986). The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the magnetic electro-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam.



**Fig. 1.6. Schematic diagram of SEM.**

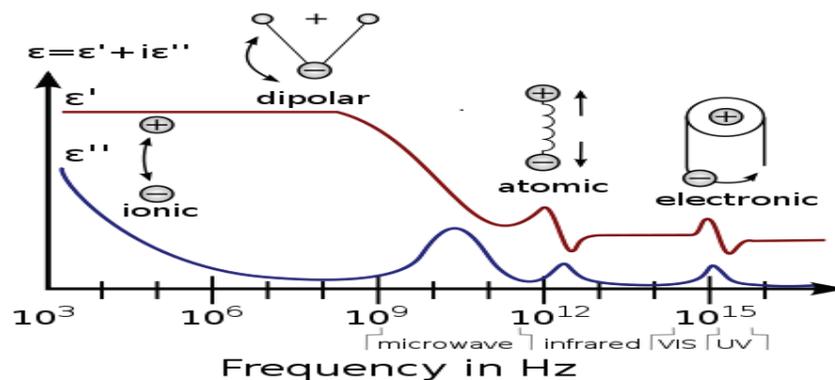
### 1.7.3 Impedance Spectroscopy

Dielectric spectroscopy (which falls in a subcategory of impedance spectroscopy) measures the dielectric properties of a medium as a function of frequency (Kremer and Schonhals 2003, Hippel 1954, Volkov and Prokhorov 2003). It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity.

It is also an experimental method of characterizing electrochemical systems. This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties, is revealed. Often, data obtained by electrochemical impedance

spectroscopy (EIS) is expressed graphically in a Bode plot or a Nyquist plot. Impedance is the opposition to the flow of alternating current (AC) in a complex system. A passive complex electrical system comprises both energy dissipater (resistor) and energy storage (capacitor) elements. If the system is purely resistive, then the opposition to AC or direct current (DC) is simply resistance. Almost any physico-chemical system, such as electrochemical cells, mass-beam oscillators, and even biological tissue possesses energy storage and dissipation properties. EIS examines them.

This technique has grown tremendously in stature over the past few years and is now being widely employed in a wide variety of scientific fields such as fuel cell testing, biomolecular interaction, and microstructural characterization. Often, EIS reveals information about the reaction mechanism of an electrochemical process: different reaction steps will dominate at certain frequencies, and the frequency response shown by EIS can help identify the rate limiting step.

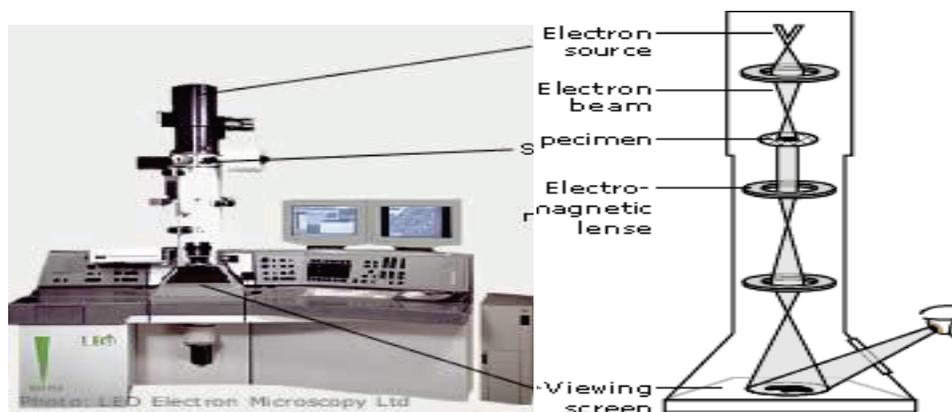


## 1.7. Dielectric Spectrum

### 1.7.4 Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) uses electrons as "light source" and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope. The possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

The working principle of the transmission electron microscope is explained from Fig. 2.7. An "electron source" at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen to be studied. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied intensity according to their density. The image can be studied directly by the operator or photographed with a camera.



**Fig. 1.8. Picture showing the working of TEM.**

For the present study, powders obtained through the solvothermal method were examined using Transmission Electron Microscopy (TEM, Model: JOEL-J2000) at operating 200 kV. The samples for transmission electron microscope were prepared by ultrasonically dispersing the powder in ethanol and allowing a drop of this to dry on a carbon-coated copper grid. Transmission electron microscopy is widely used to characterize a lot of materials both from a morphological point of view and from the crystallographic but also for the elemental composition. Using TEM, a large variety of

materials such as ceramics, minerals, metals, alloy, semiconductors, glass and polymers can be observed. The main requirements for the samples are: due to the high vacuum ambient of work, they must not outgas and they have to be appropriately thinned to be observed (Robards and Wilson 1999). In this work, the transmission electron micrographs (TEM) and high resolution transmission electron micrograph (HRTEM) for the samples were taken using TEM, Model JEM 100 CX II and HRTEM Model JOEL-J2000 operating at 200 kV at SAIF-NEHU, Shillong.

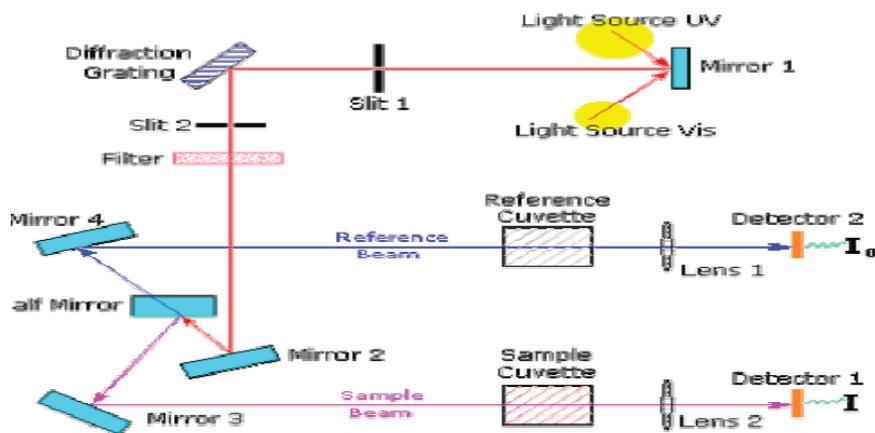
### **1.7.5 UV-Visible Absorption Spectroscopy**

UV-visible absorption spectroscopy involves the spectroscopy of photons in the UV-visible region. This means, it uses light in the visible, near ultraviolet (UV) and near infrared (NIR) ranges. The absorption in the visible ranges directly affects the colour of the chemicals involved. In this region of electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state (Jaffe and Orchin 1962).

Absorption of light by solution is one of the oldest and still one of the more useful instrumental methods. The wavelength of light that a compound will absorb is characteristic of its chemical structure. Specific regions of the electromagnetic spectrum are absorbed by exciting specific types of molecular and atomic motion to higher energy levels. Absorption of microwave radiation is generally due to excitation of molecular rotational motion. Infrared absorption is associated with vibrational motions of molecules. Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states. All

molecules will undergo electronic excitation following absorption of light, but for most molecules very high energy radiation is required. For molecules containing conjugated electron systems however, light in the UV-visible region is adequate. As the degree of conjugation increases, the spectrum shifts to lower energy ( Rao 1986, Colthup et al 1964).

A diagram of the components of a typical spectrometer is shown in Fig. 2.8. A beam of light from a visible and/or UV light source (coloured red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam, in turn, is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (coloured magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (coloured blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared.



**Fig. 1.9. Working of UV-Visible spectrometer.**

The intensity of the reference beam, which should have suffered little or no light absorption, is defined as  $I_0$ . The intensity of the sample beam is defined as  $I$ . Over a short period of time, the spectrometer automatically scans all the component

wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm. In this work, the ultraviolet-visible spectra of pure  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{PANI/MnO}_2$  and  $\text{PANI/TiO}_2$  samples were recorded using UV – 2600 series spectrophotometer in the absorption mode at PSNCET, Tirunelveli.

### **1.7.6 FT-IR spectroscopy**

Infrared spectroscopy deals with the study of vibrational spectra of molecules. An infrared absorption spectrum originates from molecular vibrations (vibrations of bonds) which cause a change in the dipole moment of the molecule. The vibrational frequencies, their relative intensities and shapes of the infrared bands recorded in a double beam spectrometer are used for the qualitative characterization of a sample. The term Fourier Transform Infrared Spectroscopy (FT-IR) refers to fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FT-IR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. Fourier transform infrared (FT-IR) technique is based on the blending of a Michaelson Interferometer with a sensitive infrared detector and a digital minicomputer. FT-IR spectrometers provide higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. The instruments also possess greater ease and speed of operation. By interpreting the infrared absorption spectrum, the functional groups of a compound and chemical bonds in a molecule can be determined (Albert et al 1973). FT-IR spectra of pure compounds are generally so unique that they are like a molecular fingerprint. While organic compounds have very detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an

unknown can be identified by comparison to a library of known compounds. Samples for FT-IR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt), which is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with Potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film and is frequently used for polymer identification (Nakamoto 1997, Ogata et al 2003). The FT-IR spectra of the samples were recorded in the range  $400 - 4000 \text{ cm}^{-1}$  on a JASCO FTIR-4100 spectrometer. The materials are finely dispersed in KBr using an agate mortar and ground well. The finely dispersed material is then pressed in the form of circular discs of  $\sim 10$  mm diameter and 0.5 mm thickness at a pressure 250 MPa. These pellets are then dried with IR light before the FT-IR spectra have been recorded.

### **1.7.7 Thermal analysis-TGA/DTA**

Thermal analysis is useful in both quantitative and qualitative analyses. Thermal methods are based upon the measurement of the dynamic relationship between temperature and some property of a system such as mass, heat of reaction or volume. Of the various thermal methods, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Basu and Maiti 1986) are most important.

In thermogravimetric analysis, the mass of the sample is recorded continuously as a function of temperature as it is heated or cooled at a controlled rate (Macdonal 1987, Parkash et al 1990). The usual temperature range for TG study is from ambient to

1200 °C in either inert or reactive atmospheres. In TG, the mass of the sample is continuously recorded as the temperature is increased. Samples are placed in a crucible or shallow dish that is positioned in a furnace on a quartz beam attached to an automatic recording balance. Linear heating rates from 5 to 20 °C/min are typical. The amount of sample required is from 10 to 300 mg. Computer software allows the computation of mass change which is important in kinetic interpretations of reactions and processes. A plot of mass as a function of temperature (thermogram) provides both qualitative and quantitative information. The apparatus required for thermogravimetric analysis includes a sensitive recording analytical balance, a furnace, a temperature controller and a recorder that provides a plot of sample mass as a function of temperature. Often an auxiliary equipment to provide an inert atmosphere for sample is also needed. Change in the mass of the sample occurs as a result of the rupture or formation of various physical and chemical bonds at elevated temperature that led to the evolution of volatile products or formation of reaction products. Thus the TGA curve gives information regarding the thermodynamics and kinetics of various chemical reactions, reaction mechanisms, intermediate and final products. In differential thermal analysis (DTA), the heat absorbed or emitted by a chemical system is observed by measuring the temperature difference between the system and an inert reference compound-such as alumina, silicon carbide or glass beads. As the temperature of both is increased at a constant rate (Hooper 1977), the corresponding deviation of the sample temperature from that of the reference ( $\Delta T$ ) versus the programmed temperature (T) is recorded and it explains whether the transition is endothermic or exothermic. The DTA studies along with TGA provide detailed information regarding the dehydration, decomposition and the phase transitions of a material during heating (Prabaker et al 2002, Hooper 1977). The thermal

characteristics of the grown crystals were studied using Perkin Elmer TG/DTA analyser. The temperature range selected for the present study was from ambient temperature to 1000 °C.