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A Review on the Synthesis and Characterization of Nanostructurd Metal Oxides

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Abstract: Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1-100 nanometers (nm). Synthesis Methods play very important role to control the size and surface area of nanomaterials. Inert gas evaporation technique and sputtering technique are most widely used techniques to produce NSMs. In the Chemical Vapour Deposition (CVD) method, the solid is deposited on a heated surface via a chemical reaction from the vapor or gas phase. The chemical process offer over other methods is good chemical homogeneity, as chemical synthesis offers mixing at molecular level. Several synthesis methods are available for the same. Few of them have been described in this article. The understanding of the characterization techniques is equally important. Some of the characterization techniques such as Scaaning Electron Microscope (SEM), X-ray Diffractometer (XRD), Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) etc have been discussed in the present article.

Keywords: Nanomaterials, CVD, Mechanical attrition, Characterization techniques, SEM etc

I. INTRODUCTION

In the recent years, a new branch of research has raised up, broadly referred as “nanoscale and nanotechnology [1-2]. The ability of science to manipulate the matter virtually atom by atom has been supported by the development of new instruments and approaches that allow the investigation of material properties with a resolution close to the atomic level. Such new tools had allowed the extensive understanding of the unusual physical and chemical properties characterizing the matter at the nanometer scale revealing the way to the employ of nanomaterial in a wide variety of applications involving materials science, engineering, physics, chemistry and biology [3-7].An aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which makes possible new quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer scale has reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials are the subject of nanomechanics research. Catalytic activities also reveal new behaviour in the interaction with biomaterials [8-9].

Nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of these properties. Additionally, traditional disciplines can be re-interpreted as specific applications of nanotechnology. This dynamic reciprocation of ideas and concepts contributes to the modern understanding of the field. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make use of physical properties associated with small scales [10].As mentioned above, materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials attain catalytic properties (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a strong chemical catalyst at nanoscales [11].

II. NANOMATERIALS

Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small featuresize, have the potential for wide-ranging industrial, biomedical, and electronic applications [12-14]. As a result of recent improvement in technologies to see and manipulate these materials, the nanomaterials field has seen a huge increase in funding from private enterprises and government, and academic researchers within the field have formed many partnerships.A nanomaterial is a field which takes a materials science-based approach to nanotechnology.

It studies materials with morphological features on the nanoscale, and especially those which have special properties stemming from their nanoscale dimensions. Nanoscale is usually defined as smaller than a one tenth of a micrometer in at least one dimension, though this term is sometimes also used for materials smaller than one micrometer [15].

Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1-100 nanometers (nm). The unit of nanometer derives its prefix nano from a Greek word meaning dwarf or extremely small. One nanometer spans 3-5 atoms lined up in a row. By comparison, the diameter of a human hair is about 5 orders of magnitude larger than a nanoscale particle. Nanomaterials are not simply another step in miniaturization, but a different arena entirely; the nano-world lies midway between the scale of atomic and quantum phenomena, and the scale of bulk materials. At the nanomaterial level, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials do [16-17].

Although widespread interest in nanomaterials is recent, the concept was raised over 40 years ago. Physicist Richard Feynman delivered a talk in 1959 entitled "There's Plenty of Room at the Bottom", in which he commented that there were no fundamental physical reasons that materials could not be fabricated by maneuvering individual atoms. Nanomaterials have actually been produced and used by humans for hundreds of years - the beautiful ruby red color of some glass is due to gold nanoparticles trapped in the glass matrix. The decorative glaze known as luster, found on some medieval pottery, contains metallic spherical nanoparticles dispersed in a complex way in the glaze, which give rise to its special optical properties. The techniques used to produce these materials were considered trade secrets at the time, and are not wholly understood even now [18-19].

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous, from extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging films, super absorbents, components of armor, and parts of automobiles. General Motors claims to have the first vehicle to use the materials for exterior automotive applications, in running boards on its mid-size vans. It is clear that researchers are merely on the threshold of understanding and development, and that a great deal of fundamental work remains to be done.What makes these nanomaterials so different and so intriguing? Their extremely small feature size is of the same scale as the critical size for physical phenomena - for example, the radius of the tip of a crack in a material may be in the range 1-100 nm. The way a crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. Fundamental electronic, magnetic, optical, chemical, and biological processes are also different at this level. Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, and medical diagnostics.

III. SYNTHESIS OF NANOMATERIALS

Nanomaterials behave differently than other similarly-sized particles. It is therefore necessary to develop specialized approaches to synthesizing and monitoring their effects on human health and on the environment.Synthesis Methods play very important role to control the size and surface area of nanomaterials [20-21]. There are several synthesis methods, some of them are described below. There are basically two broad areas of synthetic techniques for NSMs.

A. Physical Methods

Several different physical methods are currently in use for the synthesis & commercial production of NSMs. Inert gas evaporation technique and sputtering technique are most widely used techniques to produce NSMs [22].

1) Gas Condensation

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as a Joule heated refractory crucibles, electron beam evaporation devices, in an atmosphere of 1-50 m bar. In gas evaporation, a high residual gas pressure causes the formation of ultra fine particles (100 nm) by gas phase collision. The ultrafine particles are formed by collision of evaporated atoms with residual gas molecules. Gas pressures greater than 3 MPa (10 torr) are required. Vaporization sources may be resistive heating, high energy electron beams, low energy electron beam and inducting heating. Clusters form in the vicinity of the source by homogenous nucleation in the gas phase grew by incorporation by atoms in the gas phase. It comprises of a ultra high vacuum (UHV) system fitted evaporation source, a cluster collection device of liquid nitrogen filled cold finger scrapper assembly and compaction device. During heating, atoms condense in the super saturation zone close to Joule heating device [23]. The nanoparticles are removed by scrapper in the form of a metallic plate. Evaporation is to be done from W, Ta or Mo refractory metal crucibles. If the metals react with crucibles, electron beam evaporation technique is to be used.

The method is extremely slow. The method suffers from limitations such as a source-precursor incompatibility, temperature ranges and dissimilar evaporation rates in an alloy. Alternative sources have been developed over the years. For instance, Fe is evaporated into an inert gas atmosphere (He). Through collision with the atoms the evaporated Fe atoms loose kinetic energy and condense in the form of small crystals, which accumulate as a loose powder. Sputtering or laser evaporation may be used instead of thermal evaporation. Sputtering is a non-thermal process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding species of atomic/molecular size [24]. Typical sputtering uses a glow discharge or ion beam. Interaction events which occur at and near the target surface during the sputtering process in magnetron sputtering has advantage over diode and triode sputtering. In magnetron sputtering, most of the plasma is confined to the near target region. Other alternate energy sources which have been successfully used to produce clusters or ultra fine particles are sputtering electron beam heating and plasma methods [25]. Sputtering has been used in low pressure environment to produce a variety of clusters including Ag, Fe and Si.

2) *Vacuum Deposition and Vaporization*

Before proceeding to the other methods, it is important to understand the terms vacuum deposition and vaporization or vacuum evaporation. In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum. The vaporization source is the one that vaporizes materials by thermal processes [26]. The process is carried out at pressure of less than 0.1 Pa (1 m Torr) and in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is fairly high. A useful deposition rate is obtained at a vapor pressure of 1.3 Pa (0.01 Torr).

Vapor phase nucleation can occur in dense vapor cloud by multibody collisions, the atoms are passed through a gas to provide necessary collision and cooling for nucleation. These particles are in the range of 1 to 100 nm and are called ultra fine particles or clusters. The advantages associated with vacuum deposition process are high deposition rates and economy [27]. However, the deposition of many compounds is difficult. Nanoparticles produced from a supersaturated vapor are usually larger than the cluster.

3) *Chemical Vapour Deposition (CVD) and Chemical Vapour Condensation (CVC)*

CVD is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapor or gas phase. CVC reaction requires activation energy to proceed. This energy can be provided by several methods. In thermal CVD the reaction is activated by a high temperature above 900^{o}C. A typical apparatus comprises of gas supply system, deposition chamber and an exhaust system [28]. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700°C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy, to break the chemical bond in the reactant molecules [29]. In this process, the reaction is photon activated and deposition occurs at room temperature.

4) *Mechanical Attrition*

Mechanical attrition produces its nanostructures not by cluster assembly but by the structural decomposition of coarser grained structures as a result of plastic deformation. The ball milling and rod milling techniques belong to the mechanical alloying process which has received much attention as a powerful tool for the fabrication of several advanced materials. Mechanical alloying is a unique process, which can be carried out at room temperature [30-32]. The process can be performed on high energy mills, centrifugal type mill and vibratory type mill, and low energy tumbling mill. High energy mills include: Attrition Ball Mill, Planetary Ball Mill, Vibrating Ball Mill, Low Energy Tumbling Mill, and High Energy Ball Mill.

a) *Attrition Ball Mill: The milling procedure takes place by a stirring action of a agitator which has a vertical rotator central shaft with horizontal arms (impellers). The rotation speed was later increased to 500 rpm. Also, the milling temperature was in greater control [33].*
b) *Planetary Ball Mill: Centrifugal forces are caused by rotation of the supporting disc and autonomous turning of the vial [34]. The milling media and charge powder alternatively roll on the inner wall of the vial and are thrown off across the bowl at high speed (360 rpm).*
c) *Vibrating Ball Mill: It is used mainly for production of amorphous alloys The changes of powder and milling tools are agitated in the perpendicular direction at very high speed (1200 rpm) [35].*
d) *Low Energy Tumbling Mill: They have been used for successful preparation of mechanically alloyed powder. They are simple to operate with low operation costs. A laboratory scale rod mill was used to prepare homogenous amorphous* $Al_{30}Ta_{70}$ *powder.*

By using S.S. cylinder rods. Single-phase amorphous powder of AlxTm100-x with low iron concentration can be formed by this technique [36].

e) High Energy Ball Mill: High-energy ball milling is an already established technology, however, it has been considered dirty because of contamination problems with iron. However, the use of tungsten carbide component and inert atmosphere and /or high vacuum processes has reduced impurity levels to within acceptable limits [37]. Common drawbacks include low surface, highly poly disperse size distribution, and partially amorphous state of the powder. These powders are highly reactive with oxygen, hydrogen and nitrogen. Mechanical alloying leads to the fabrication of alloys, which cannot be produced by conventional techniques [38]. It would not be possible to produce an alloy of Al-Ta, because of the difference in melting points of Al (933 K) and Ta (3293 K) by any conventional process. However, it can be fabricated by mechanical alloying using ball milling process.

B. Chemical Methods

The advantage of chemical synthesis methods is its versatility in designing and synthesizing new materials that can be refined in to final product. The chemical process offer over other methods is good chemical homogeneity, as chemical synthesis offers mixing at molecular level [39].The major advantage of this method is to control size and surface area of the nanomaterials [40]. There are several methods such as-

1) Precipitation Method

a) Modified Emulsion Precipitation Method

This method provides the particular advantage of avoiding agglomeration of the particles formed in the individual bubbles. This in turn makes possible subsequent processing routes at unusually low temperatures [41-42]. To take full advantage of the method for multicomponent oxides precipitation routes need to be designed so that an intimate mixture of atoms is formed during precipitation and chemical homogeneity is maintained during subsequent processing. This offers special challenges since emulsion co-precipitations tend to be carried out with sample precursors that do not affect emulsion stability but generally show a tendency to precipitate at different rates leading to at least partial phase segregation.

This method involves the preparation of thermally stable emulsion systems prepared by adding appropriate amounts of surfactants to a water oil system. Within the emulsion system, there are a small number of atoms per droplet. It is necessary that exchange of reactive species take place between droplets in order to form a stable precipitate. From the Einstein-Smoluchowski equation, the normal rate of the particle growth is faster than the equivalent rate of exchange between droplets. Therefore, the nucleation and growth in emulsions are retarded in comparison to those in homogeneous solution, avoiding the formation of large particles. Multisurfactants are effective in forming thermally stable emulsion and controlling droplet size. Other additives play a role as steric particle stabilizer after removal of water. Before the particle dispersion by filtration of decantation of the organic phase, the emulsions were prepared by mixing the oil phase (Cyclohexane or n-heptane) with tergitol surfactants and octan-1-ol as cosurfactant. To the system stoichiometric amounts of water were added followed by vigorous mixing until a translucent emulsion was formed. The emulsion was added drop wise to alcohol solutions of alkoxides and stirred for several hours. After removal of solvents in dispersion the residue was taken up in acetone to destroy the micelles. The solid product obtained after decantation of the organic phase was dried and transformed to nanocrystalline spinals after calcinations.

b) Hydrothermal Synthesis / Solvothermal Synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. George W. Morey at the Carnegie Institution and later, Percy W. Bridgman at Harvard University did much of the work to lay the foundations necessary to containment of reactive media in the temperature and pressure range where most of the hydrothermal work is conducted.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth [43].

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method.

The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows [44].

c) Sol-gel Method

The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metalalkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions [45].

In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification [46]. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product [47]. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, sensors, medicine, reactive material and in chromatographytechnology.

d) Aerosol Methods

Aerosol processes are used routinely for the commercial production of ultrafine particles ($d_p < 100$ nm) and materials fabricated from them, and for pilot and laboratory scale production as well. Aerosol reaction engineering refers to the design of such processes, with the goal of relating product properties to the material properties of the aerosol precursors and the process conditions [48]. The most important process conditions are usually the aerosol volume concentration (volume of particles per unit volume of gas) and the time/temperature history of the system.

Fine particle formation by aerosol processes almost always takes place by gas-to-particle conversion. Condensable molecules produced by physical or chemical processes self-nucleate to form particles. The nuclei may be as small as a single molecule for refractory materials, but subsequent collision and coalescence leads to the formation of larger particles. Lotsof investigations have done made to demonstrate novel methods for particle synthesis or to elucidate the mechanisms of particle formation [49].

2) Immobilization Methods

a) Citrate-gel Methods

In citrate gel methods, metal ions are stabilized by an organic network in precursor solutions, thus fine oxide powders are obtained after a heating process [50]. They have the ability of preparing multi-component compositions with good homogeneity and control of stochiometry. These methods utilize poly-chelates between the C-O legends of citric acid and metal ions. The chelates undergopolyesterification on heating with a polyfunctional alcohol. In the citrate method the chelating process takes place during the evaporation of the precursor solution containing metallic salts and citric acid.

Further heating produces a viscous resin, and a rigid transparent, glassy gel. Mixtures of different metal ions become immobilized in an early stage of the formation of this rigid system [51]. This greatly reduces the risk of segregation into different oxide compositions during subsequent calcinations.

b) Penchini Method

The process of the Penchinimethod [52] is almost the same as that of the Citrate-gel method, except that metal nitrates are dissolved in alcohol, instead of water.

c) Low Temperature Combustion Synthesis Method

The low temperature combustion synthesis (LCS) technique has proved to be a novel, extremely facile, timesaving and energy-efficient route for the synthesis of ultra fine powders [53]. This is based on gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuels, giving a voluminous and fluffy product with large surface area. Oxidizing metal salts such as metal nitrates, and a combination agent (fuel) such as citrate acid, polyacrylic acid or urea are used as starting materials. Citrate acid is more widely used, since it not only functions as a reductant /fuel agent, but also a chelating agent. The molar ratio of fuel to nitrates in the initial mixture imposes a great influence on calcination condition and the subsequent characteristics of the synthesized crystallites. By controlling the CA/NO_3 ratio and calcination temperature, homogeneous crystalline spinel powders are prepared with a nanoscale primary particle size [54].

In several methods, the sol-gel method has received major advantages however the cost of precursor materials and metal alkoxides is higher, than those of other methods and the right precursors are not always available [55]. Sol-gel processing has been of major importance for organic-inorganic hybrids and the preparation of innovative are very useful and possibly yield fine ceramic nanoparticles. Hydrothermal synthesis involves the same principle of hydrolysis of solution species as in the sol-gel method, but without the calcinations step required in the latter one. This method has not yet attracted the attention as the sol-gel method. Emulsion precipitation methods are convenient for single component nanoscale ceramic particles, while they are less suitable for producing multi-component ceramics. This is caused by different hydrolysis rates of various precursors and the difficulty to remove (co-) surfactants, which are added to keep emulsions stable.

IV. CHARACTERIZATION TECHNIQUES

A. Scanning Electron Microscopy

When a beam of electrons impinges on a solid surface, it undergoes numerous interactions at the solid surface depending on the incident beam. The incident electrons are transmitted, absorbed, scattered or reflected. The outgoing beams from the sample consist of electrons, X-rays, visible-IR photons. Each of these signals contains information about the surface conditions, compositions, structural defects and impurity contents of the sample [56].

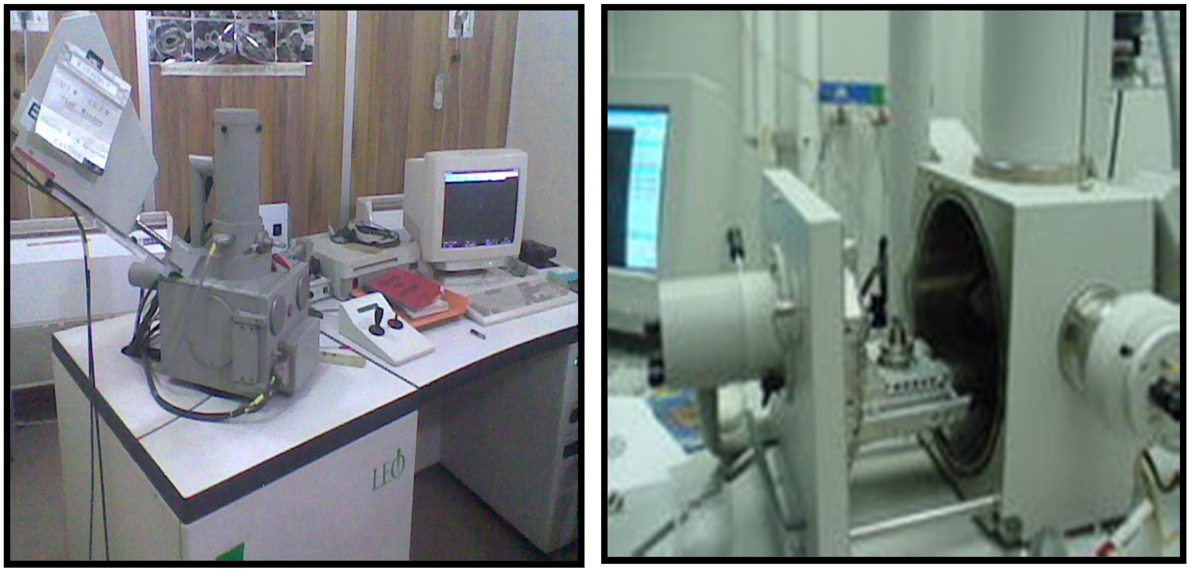

Figure 1. Scanning Electron Microscopy Unit

The SEM system, as shown in the figure 1, with the various detectors can provide the following facilities:

1) High-resolution imaging
2) Quantitative elemental analysis of the "bulk" material
3) Fast elemental mapping
4) Topographical, compositional and other information
5) Detection of small variations of trace element content
6) Analysis and imaging of samples in their natural and hydrated state
7) Digital output
8) Oil-free vacuum
9) Large specimen (150 mm square by 10 mm) capacity
10) Rapid (10 minute turn around) sample introduction

B. X-Ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials [57]. Monochromatic x-rays are used to determine the interplanarspacings of the unknown materials. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are "sampled" by the beam. When the Bragg conditions for constructive interference are obtained, a "reflection" is produced, and the relative peak height is generally proportional to the number of grains in a preferred orientation [Figure 2]

After the sample is loaded, the beam of X-rays moves around the sample from 10 to 90° then using Bragg’s law the bond length can be calculated. Bragg’s law states that when a multiple of the wavelength is divided by twice the bond length it is equal to the sine of the angle i.e.

$\lambda=2d\sin\theta$

λ: wavelength of the X-rays
d: the spacing of the layers
θ: the incident angle of the photons.

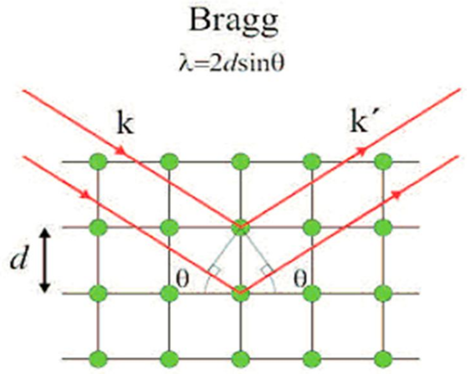

Figure 2. X-ray diffraction by the crystal lattice

THE DEBYE-SCHERRER FORMULA

Figure 3 shows that the rays A, D and M make precisely the Bragg angle θ_B with the reflecting planes. Ray D′, scattered by the first plane below the surface, is one wavelength out of phase with A′, ray M′ is n wavelengths out of phase with it. At the diffraction angle $2\theta_B$ all these rays are in phase and unite to form a beam of maximum amplitude. Ray B makes a slightly larger angle θ_1 with the reflecting plane, such that ray L′ from the n^{th} plane is (n + 1) wavelengths out of phase with B′. So the rays scattered by the upper half of the crystal cancel exactly with those scattered by the lower half of the crystal and θ_1 is the smallest angle where complete destructive interference occurs. This is also the case for an angle θ_2 which is a bit smaller than θ_B so that the path difference between the ray scattered by the first and the last plane is (n−1) wavelengths. These are the two limiting angles where the intensity of the diffracted beam drops to zero. This implies that the intensity is greater than zero all the way from θ_2 to θ_1 as depicted in figure 4.

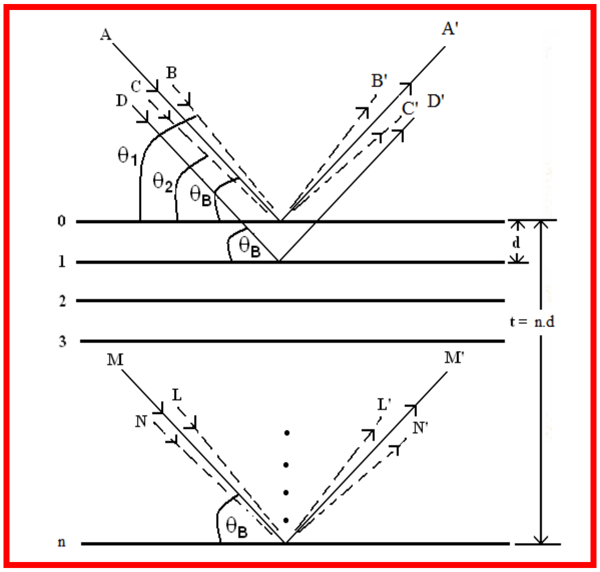

Figure 3. Scattering from a finite number of equidistant planes

The width of diffraction curves increases as the thickness of the crystal decreases, because the angular range ($2\theta_1 - 2\theta_2$) increases as n decreases. As a measure of the peak width, the full width at half maximum FWHM, denoted by β, is used. As an approximation $\beta = \frac{1}{2}(2\theta_1 - 2\theta_2) = \theta_1 - \theta_2$ is chosen, since this yields the exact FWHM for a Gaussian.

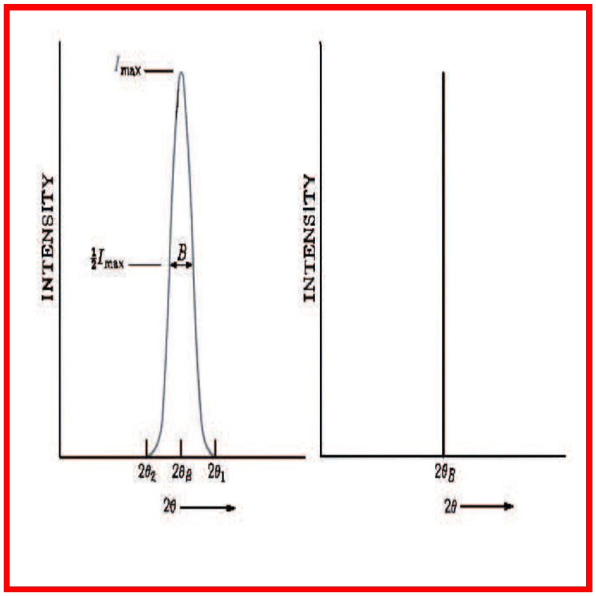

Figure 4. FWHM for a crystal of finite (left) and infinite (right) size

The path difference equations for these two angles related to the entire thickness of the crystal are given by:

$$2t \sin \theta_1 = (n + 1)\lambda$$

$$2t \sin \theta_2 = (n - 1)\lambda$$

Subtracting the above equations yields:

$$t(\sin \theta_1 - \sin \theta_2) = \lambda$$

$$\Rightarrow 2t \cos\left(\frac{\theta_1 + \theta_2}{2}\right) \sin\left(\frac{\theta_1 - \theta_2}{2}\right) = \lambda$$

Since θ_1 and θ_2 are very close to θ_B it is reasonable to make the following approximations:

$$\sin\theta_1 + \sin\theta_2 = 2\theta_B$$

$$\sin\left(\frac{\theta_1-\theta_2}{2}\right) = \left(\frac{\theta_1-\theta_2}{2}\right)$$

With these approximations we obtain

$$2t\left(\frac{\theta_1-\theta_2}{2}\right)\cos\theta_B = \lambda$$

and using the definition of the FWHM introduced above gives a crystal depth t = n.d of

$$t = \frac{\lambda}{\beta\cos\theta_B}$$

A more rigorous mathematical treatment of the problem results in the Debye-Scherrer Formula [58] is

$$\mathrm{D} = \frac{\mathrm{K}\lambda}{\beta\,\mathrm{Cos}\theta}$$

Here K is a dimensionless constant that may range from 0.89 to 1.39 depending on thespecific geometry of the scattering objects. For a perfect two-dimensional lattice, where every point on the lattice emits a spherical wave, numerical calculations yield the lower bound of 0.89 for K [59]. A cubic three-dimensional crystal is best described by K = 0.94, while analytical calculations for a perfectly spherical object yield K = 1.33.

C. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a common technique to reveal vibrational stretch frequency of metal-oxygen bonds [60]. In general, the goal of FTIR spectroscopy is to measure how well a sample absorbs or transmits light at each different wavelength. To use the Fourier Transform Infrared Spectroscopy, a continuum source of light is used to produce light over broad range of infrared wavelengths.The principal experimental method in this work is Fourier transform infrared [61]spectroscopy, which allows us to detect infrared (IR) absorption and reflection properties over a broad spectral region.

Figure 5. Schematic diagram of an FTIR

An FTIR is based on a Michelson interferometer, which consists of a beam splitter, a fixed mirror and a moving mirror (scanning mirror). As shown in Figure 5, light from the source is separated into two parts and then recombines at the beam splitter after reflection by the two mirrors. Due to the path difference between the two beams, an interference pattern is generated. The output beam from interferometer is recorded as a function of path difference, and is called the interferogram. The IR spectrum can be obtained by calculating the Fourier transform of the interferogram.

D. Energy Dispersive X-Ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles [62]. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused intothe sample being studied [63]. At rest, an atom within the sample contains ground state (or unexcited)electrons in discrete energy levels or electron shells bound to the nucleus. The incident beammay excite an electron in an inner shell, ejecting it from the shell while creating an electron holewhere the electron was. An electron from an outer, higher-energy shell then fills the hole, and thedifference in energy between the higher-energy shell and the lower energy shell may be releasedin the form of an X-ray. The number and energy of the X-rays emitted from a specimen can bemeasured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic ofthe difference in energy between the two shells, and of the atomic structure of the element fromwhich they were emitted, this allows the elemental composition of the specimen to be measured. The excess energy of the electron that migrates to an inner shell to fill the newly-created hole cando more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred toa third electron from a further outer shell, prompting its ejection. This ejected species is called anAuger electron, and the method for its analysis is known as Auger Electron Spectroscopy (AES).

X-ray Photoelectron Spectroscopy (XPS) is another close relative of EDS, utilizing ejectedelectrons in a manner similar to that of AES. Information on the quantity and kinetic energy ofejected electrons is used to determine the binding energy of these now-liberated electrons, whichis element-specific and allows chemical characterization of a sample. EDS is often contrastedwith its spectroscopic counterpart, WDS (Wavelength-Dispersive X-ray Spectroscopy). WDSdiffers from EDS in that it uses the diffraction patterns created by light-matter interaction as itsraw data. WDS has a much finer spectral resolution than EDS. WDS also avoids the problemsassociated with artifacts in EDS (false peaks, noise from the amplifiers and microphonics [64]. InWDS only one element can be analyzed at a time, while EDS gathers a spectrum of all elements,within limits, of a sample.

E. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry or DSC is a thermo-analytical technique in which thedifference in the amount of heat required to increase the temperature of a sample and referenceare measured as a function of temperature. Both the sample and reference are maintained atnearly the same temperature throughout the experiment. Generally, the temperature program fora DSC analysis is designed such that the sample holder temperature increases linearly as afunction of time. The reference sample should have a well-defined heat capacity over the rangeof temperatures to be scanned [65].The main application of DSC is in studying phase transitions, such as melting, glass transitions,or exothermic decompositions. These transitions involve energy changes or heat capacitychanges that can be detected by DSC with great sensitivity [66].

The technique was developed by E.S. Watson and M.J. O'Neill in 1960, and introducedcommercially at the 1963 Pittsburgh Conference on Analytical Chemistry and AppliedSpectroscopy [67]. The basic principle underlying this technique is that, when the sample undergoes aphysical transformation such as phase transitions, more or less heat will need to flow to it thanthe reference to maintain both at the same temperature. Whether more or less heat must flow tothe sample depends on whether the process is exothermic or endothermic. For example, as asolid sample melts to a liquid it will require more heat flowing to the sample to increase itstemperature at the same rate as the reference. This is due to the absorption of heat by the sampleas it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sampleundergoes exothermic processes (such as crystallization) less heat is required to raise the sampletemperature. By observing the difference in heat flow between the sample and reference,differential scanning calorimeters are able to measure the amount of heat absorbed or releasedduring such transitions. DSC may also be used to observe more subtle phase changes, such asglass transitions. DSC is widely used in industrial settings as a quality control instrument due toits applicability in evaluating sample purity and for studying polymer curing. Since DSC is moresensitive to phase transition temperature (with a precision of 0.01^{o}C) and is capable ofmonitoring the exact rate of energy exchange or reaction rate. Positions of all these peaks dependon heating rate. Increasing the heating rate caused every peak shift toward higher temperatures,with the first two endothermic peaks merged into one broad one. This is due to activation energyinvolved in such transition [68].

F. UV-Visible Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the UV-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions [69]. 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.

The instrument used in ultraviolet-visible spectroscopy is called a UV/visspectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log(\%T / 100)$$

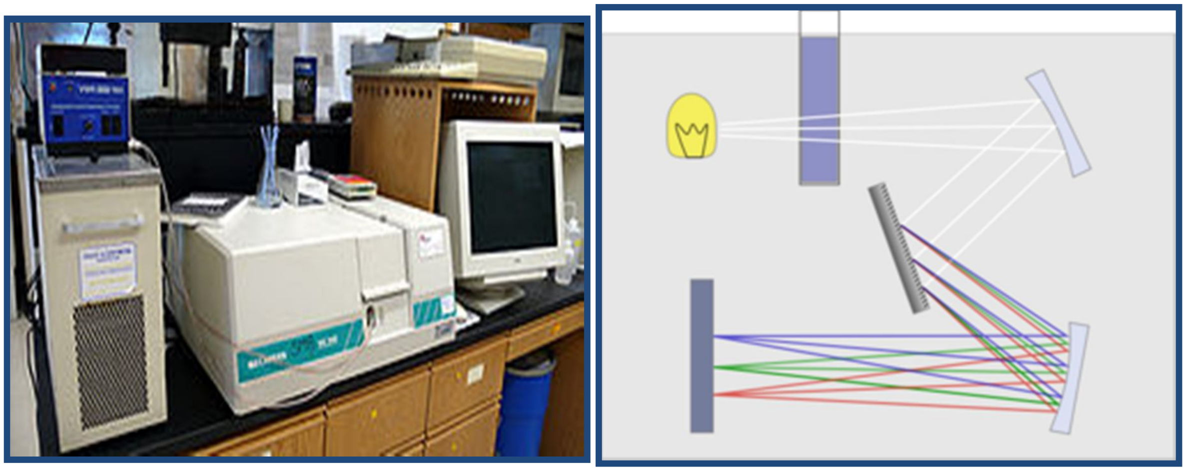

Figure 6. Diagram of a single-beam UV/vis spectrophotometer

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector as shown in the figure 6. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm) or more recently, light emitting diodes (LED) and Xenon Arc Lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam.

Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L, in the Beer-Lambert law.) Test tubes can also be used as cuvettes in some instruments. The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths [70].A complete spectrum of the absorption at all wavelengths of interest can often be produced directly by a more sophisticated spectrophotometer. In simpler instruments the absorption is determined one wavelength at a time and then compiled into a spectrum by the operator. A standardized spectrum is formed by removing the concentration dependence and determining the extinction coefficient (ε) as a function of wavelength.

V. CONCLUSION

Although several techniques for the synthesis and characterization of nanomaterials are available but the techniques discussed in this article are very common and easily available. This article may be very useful for the research scholars as well as the academicians working in other branches of science and technology.

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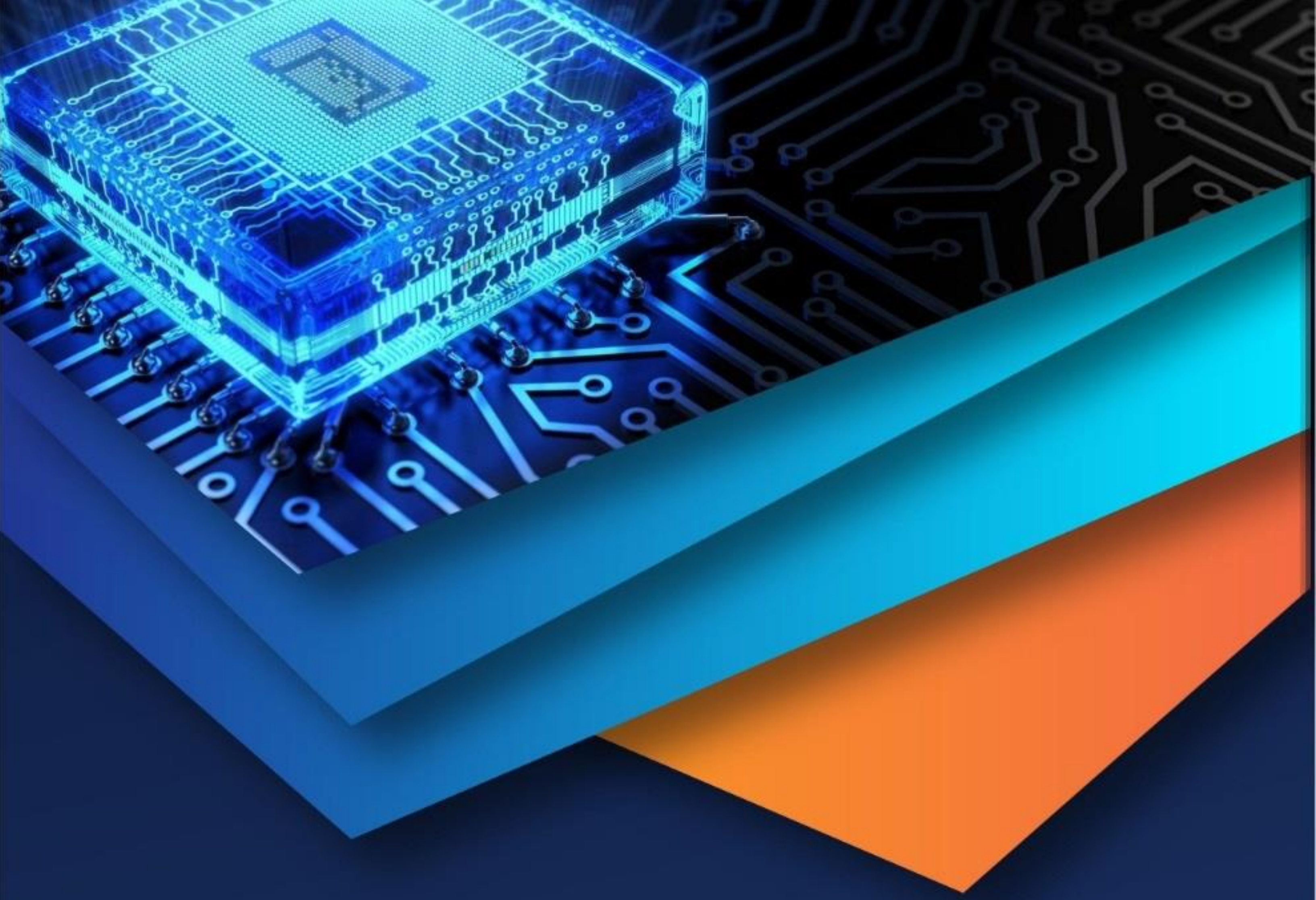

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