UNIT -2

Unit 2.CHARACTERIZATION OF NANOMATERIALS

1. Introduction

The current revolution in nanoscience was brought about by concomitant development of several advances in technology. One of factor responsible for the nanotechnology revolution has been the improvement of old and the introduction of the new instrumentation systems for evaluating and characterizing nanostructures. Although the techniques to be used would depend upon the type of material and information one needs to know, usually one is interested in first knowing the size, crystalline type, composition and then chemical state, optical, magnetic and other properties. Some of the commonly used techniques are:

- **Microscopy:** Microscopy is useful to investigate morphology, size, structure and even composition of solids depending upon the type of microscope. Some of the microscopes are able to resolve structures up to atomic resolution. Combined with some other techniques, microscopes can give information about optical, magnetic and other properties of nanomaterials.
  Optical microscope, Confocal Microscope, Scanning Electron Microscope(SEM), Transmission Electron Microscope (TEM) , Scanning Tunnelling Microscope (STM), Atomic Force Microscope (AFM), Scanning Near-Field Optical Microscope (SNOM).
- **Spectroscopy:** Spectroscopies are useful for chemical state analysis (bonding or charge transfer amongst the atoms), electronic structure (energy gaps, impurity levels, band formation, transition probabilities etc.,) and other properties of materials.
  UV-VIS-IR spectroscopy, Fourier Transform Infra Red (FTIR), Atomic absorption Spectroscopy, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR), Raman Spectroscopy, Auger Electron Spectroscopy.
- **Diffraction:** Diffraction techniques are often used in average particle size analysis as well as structural determination.
  X-ray Diffraction, Electron Diffraction, Neutron Diffraction, Small Angle X-ray scattering (SAXS), Small Angle Neutron Scattering (SANS).

2. Atomic structure

To understand a nanomaterial we must, first, learn about its structure, meaning that we must determine the type of atoms that constitute its building blocks and how these atoms are arranged relative to each other. Most nanostructures are crystalline, meaning that their thousands of atoms have a regular arrangement in space on what is called a crystal lattice. This lattice can be described by assigning the positions of atoms in a unit cell, so the overall lattice arises from the continual replication of this unit cell throughout space. There are 17 possible types of crystal structures called space groups, meaning 17 possible arrangements of atoms in unit cells in two dimensions. The characteristics of the parameters are a, b, and . In three dimensions the situation is much more complicated. There are now three lattice constants a, b, c, for the three dimensions x, y, z with the respective angles between them. There are seven crystal systems in three dimensions with a total of 230 space groups The objective of a crystal structure analysis is to distinguish the symmetry and space group, to determine the values of lattice constants and angles, and to identify the positions of the atoms in the unit cell.

Certain special cases of crystal structures are important for nanocrystals, such as those involving simple cubic (SC), body-centered cubic(BCC), and face-centered cubic(FC) unit cells. Another important structural arrangement is formed by stacking planar hexagonal layers, which for a monoatomic crystal provides the highest density of closest-packed arrangement of identical spheres. If the third layer is placed directly above the first layer, the fourth directly above the second, and so on, in an A-B-A-B… type sequence, the hexagonal

close-packed (HCP) structure results. If, on the other hand, this stacking is carried out by placing the third layer in a third position and the fourth layer above the first, and so forth, the result is an A-B-C-A-B-C-A….. sequence, and the structure is FCC. The later arrangement is more commonly found in nanocrystals.
Some properties of nanostructures depend on their crystal structure, while other properties such as catalytic reactivity and adsorption energies depend on the type of exposed surface.

Spectroscopy

The spectroscopic techniques described below do not provide a three-dimensional picture of a molecule, but instead yield information about certain characteristic features. A brief summary of this information follows:

- **Mass Spectrometry**: Sample molecules are ionized by high energy electrons. The mass to charge ratio of these ions is measured very accurately by electrostatic acceleration and magnetic field perturbation, providing a precise molecular weight. Ion fragmentation patterns may be related to the structure of the molecular ion.
- **Ultraviolet-Visible Spectroscopy**: Absorption of this relatively high-energy light causes electronic excitation. The easily accessible part of this region (wavelengths of 200 to 800 nm) shows absorption only if conjugated pi-electron systems are present.
- **Infrared Spectroscopy**: Absorption of this lower energy radiation causes vibrational and rotational excitation of groups of atoms. within the molecule. Because of their characteristic absorptions identification of functional groups is easily accomplished.
- **Nuclear Magnetic Resonance Spectroscopy**: Absorption in the low-energy radio-frequency part of the spectrum causes excitation of nuclear spin states. NMR spectrometers are tuned to certain nuclei (e.g. ^{1}H, ^{13}C, ^{19}F & ^{31}P). For a given type of nucleus, high-resolution spectroscopy distinguishes and counts atoms in different locations in the molecule.

(a) Laser Scanning Confocal Microscopy (LSCM): Confocal laser scanning microscopy (**CLSM** or **LSCM**) is a technique for obtaining high-resolution optical images. The key feature of confocal microscopy is its ability to produce in-focus images of thick specimens, a process known as *optical sectioning*. Images are acquired point-by-point and reconstructed with a computer, allowing three-dimensional reconstructions of topologically-complex objects. Confocal laser scanning microscopy is a technique that allows a much better resolution from optical microscopes and three dimensional imaging.

Using a high NA objective also gives a very shallow depth of focus and hence the image will be blurred by structures above or below the focus point in a classical microscope. A way to circumvent this problem is the confocal microscope, or even better the Laser Scanning Confocal Microscope (LSCM). Using a laser as the light source gives better control of the illumintaion, especially when using fluorescent markers in the sample. The theoretical resolution using a 1.4 NA objective can reach 140nm laterally and 230nm vertically [1] while the resolution quoted in ref [2] is 0.5×0.5×1µm. The image in the LSCM is made by scanning the sample in 2D or 3D and recordning the signal for each point in space on a PC which then generates the image.

(b) Photoemission and X-ray spectroscopy: Photoemission spectroscopy (PES) measures the energy distribution of electrons emitted by atoms and molecules in various charge and energy states. A material irradiated with ultraviolet light (UPS) or X-rays (XPS) can emit electrons called photoelectrons from atomic energy levels with a kinetic energy.

X-ray microscopy uses X-rays to image with much shorter wavelength than optical light, and hence can provide much higher spatial resolution and use different contrast mechanisms. X-ray microscopy allows the characterization of materials with submicron resolution approaching the 10's of nanometers. X-ray microscopes can use both laboratory x-ray sources and synchrotron radiation from electron accelerators. X-ray microscopes using synchrotron radiation provide the greatest sensitivity and power, but are unfortunately rather large and expensive. X-ray microscopy is usually divided into two overlapping ranges, referred to as soft x-ray microscopy (100eV - 2keV) and hard x-ray microscopy (1keV-40keV). All x-rays penetrate materials, more for higher energy x-rays. Hence, soft x-ray microscopy provides the best contrast for small samples. Hard x-rays do have the ability to pass nearly unhindered through objects like your body, and hence also give rather poor contrast in many of the biological samples you would like to observe with the x-ray microscope. Nevertheless, hard x-ray microscopy allows imaging by phase contrast, or using scanning probe x-ray microscopy, by using detection of fluorescent or scattered x-rays. Despite its limitations, X-ray microscopy is a powerful technique and in some cases can provide characterization of materials or samples that cannot be done by any other means.

An **X-ray microscope** uses electromagnetic radiation in the soft X-ray band to produce images of very small objects.

Unlike visible light microscopes, X-rays do not reflect or refract easily, and they are invisible to the human eye. Therefore the basic process of an X-ray microscope is to expose film or use a charge-coupled device (CCD) detector to detect X-rays that pass through the specimen, rather than light which bounces off the specimen. It is a contrast imaging technology using the difference in absorption of soft x-ray in the water window region (wavelength region: 2.3 - 4.4 nm, photon energy region: 0.28 - 0.53 keV) by the carbon atom (main element composing the living cell) and the oxygen atom (main element for water).

Sources of soft X-rays suitable for microscopy, such as synchrotron radiation sources, have fairly low brightness of the required wavelengths, so an alternative method of image formation is scanning transmission soft X-ray microscopy. Here the X-rays are focused to a point and the sample is mechanically scanned through the produced focal spot. At each point the transmitted X-rays are recorded with a detector such as a proportional counter or an avalanche photodiode.

The resolution of X-ray microscopy lies between that of the optical microscope and the electron microscope. It has an advantage over conventional electron microscopy in that it can view biological samples in their natural state. Electron microscopy is widely used to obtain images with nanometer level resolution but the relatively thick living cell cannot be observed as the sample has to be sliced thinly and then dried to get the image.

Additionally, X-rays cause fluorescence in most materials, and these emissions can be analyzed to determine the chemical elements of an imaged object. Another use is to generate diffraction patterns, a process used in X-ray crystallography. By analyzing the internal reflections of a diffraction pattern (usually with a computer program), the three-dimensional

structure of a crystal can be determined down to the placement of individual atoms within its molecules. X-ray microscopes are sometimes used for these analyses because the samples are too small to be analyzed in any other way.

(c) Infra red and Raman Spectroscopy: Vibrational spectroscopy involves photons that induce transitions between vibrational states in molecules and solids, typically in infrared (IR) frequency range from 2 to 12x1013 Hz. The energy gaps of many semiconductors are in this same frequency region, and can be studied by infrared techniques.

Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify compounds or investigate sample composition. Infrared spectroscopy correlation tables are tabulated in the literature.

The infrared spectra of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures

A beam of infrared light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in. The beams are both reflected back towards a detector, however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.

A reference is used for two reasons:

- This prevents fluctuations in the output of the source affecting the data
- This allows the effects of the solvent to be cancelled out (the reference is usually a pure form of the solvent the sample is in

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering(**Raman scattering** or the **Raman effect** is the inelastic scattering of a photon. When light is scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering). The scattered photons have the same energy (frequency) and wavelength as the incident photons. However, a small fraction of the scattered light (approximately 1 in 1 million photons) is scattered by an excitation, with the scattered photons having a frequency different from, and usually lower than, the frequency of

the incident photons. In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect) of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary information.

Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Raman spectrometers typically use holographic diffraction gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, PMTs were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, the recent uses of CCD detectors have made dispersive Raman spectral acquisition much more rapid.

Raman spectroscopy has a stimulated version, analogous to stimulated emission, called stimulated Raman scattering.

Resonance Raman (RR) spectroscopy is a specialized implementation of the more general Raman spectroscopy. As in Raman spectroscopy, RR spectroscopy provides information about the vibrations of molecules, and can also be used for identifying unknown substances. RR spectroscopy has found wide application to the analysis of *bioinorganic* molecules. Although the technique uses a different part of the electromagnetic spectrum than infrared (IR) spectroscopy, the two methods are actually complementary. Both are used to measure the energy required to change the vibrational state of a chemical compound.

IR spectroscopy involves measuring the direct absorption of photons with the appropriate energy to excite molecular bond vibrations. The wavelengths of these photons lie in the infrared region of the spectrum, hence the name of the technique. Raman spectroscopy measures the excitation of bond vibrations in an indirect manner. The two methods are complementary because some vibrational transitions that are observed in IR spectroscopy are not observed in Raman spectroscopy, and vice versa. RR spectroscopy is an improvement of traditional Raman spectroscopy that has increased sensitivity and is better suited for the study of complicated systems.

X-Ray Raman Scattering

In the x-ray region, enough energy is available for making electronic transitions possible. At core level resonances, X-Ray Raman Scattering can become the dominating part of the x-ray fluorescence spectrum. This is due to the resonant behavior of the Kramers-Heisenberg formula in which the denominator is minimized for incident energies that equal a core level. This type of scattering is also known as resonant inelastic x-ray scattering (RIXS). In the soft x-ray range, RIXS has been shown to reflect crystal field excitations, which are often hard to observe with any other technique. Application of RIXS to strongly correlated materials is of

particular value for gaining knowledge about their electronic structure. For certain wide band materials such as graphite, RIXS has been shown to (nearly) conserve crystal momentum and thus has found use as a complementary bandmapping technique.

Conventional Raman spectroscopy is limited to a spatial resolution on the micron scale. By using novel techniques and materials, information can be gained from structures on a sub-micron or nanometre scale e.g. Raman may be used to classify the diameter of carbon nanotubes, given that the frequency of the radial breathing mode (RBM) is related to the tube diameter. Pioneering products such as the award winning Nanonics NSOM/AFM 100 Confocal™/Renishaw Raman microscope system have demonstrated superior spatial resolution than is possible with the normal far-field diffraction limit.

Surface Enhanced Raman Spectroscopy, often abbreviated **SERS**, is a surface sensitive technique that results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces. The enhancement factor can be as much as 10^{14}-10^{15}, which allows the technique to be sensitive enough to detect single molecules.

Raman scattering or the **Raman effect** is the inelastic scattering of a photon.

When light is scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering). The scattered photons have the same energy (frequency) and wavelength as the incident photons. However, a small fraction of the scattered light (approximately 1 in 1 million photons) is scattered by an excitation, with the scattered photons having a frequency different from, and usually lower than, the frequency of the incident photons. In a gas, Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect.

(d) Magnetic Resonance: Another branch of spectroscopy that has provided information on nanostructures is magnetic resonance. It involves the study of microwave (radar frequency) and radiofrequency transitions. Most magnetic resonance measurements are made in fairly strong magnetic fields, typically B~0.33 T for electron spin resonance (ESR), and B~10T for nuclear magnetic resonance (NMR).

Diffraction

Diffraction techniques using electrons, X-rays or neutrons produce information about crystal structure and are used to understand structure (Bravais lattice) of bulk materials and can be extended to investigate nanomaterials. The diffraction analysis relies on the long range periodic arrangement of atoms/molecules.

X-ray diffraction: There are different types of X-ray diffractometers available for crystal structure analysis. The most commonly used diffractometer is known as Powder Diffractometer or Debye- Scherrer diffractometer. This diffractometer allows determination of crystal structure of polycrystalline samples, thin films and nanoparticles. The diffractometer consists of a monochromatic source of X-rays (usually from a copper target), sample holder and an X-ray detector. Both sample and detector move around an axis passing through sample centre and normal to the plane of the paper. Samples in the form of powder, thin films etc. can be used. The diffracted rays make angle 2 at the detector with respect to incident beam direction. A plot of intensity (counts), as a function of angle 2 (20 to 60), is a

diffraction pattern. Detector is a suitable photon counter like Geiger Muller tube, scintillation counter etc. Due to finite size of X-ray beam ~1-2 mm2, smaller angles (<20) are not accessible using these diffractometers.

X-ray scattered by atoms enable us to understand about arrangement of atoms in solids.

alth of other exotic phenomena