1. CHARACTERIZATION STUDIES OF NANOMATERIALS

Introduction – Thermal Analysis – Powder XRD Analysis – FTIR Analysis – Raman Analysis – VSM Analysis – SEM and EDX Analysis – TEM Analysis – XPS Analysis – UV-visible absorption Analysis – Photoluminescence Analysis

Introduction

Characterization refers to the broad and general process by which a material's structure and properties are probed and measured. It is a fundamental process in the field of materials science, without which no scientific understanding of engineering materials could be ascertained. The techniques to be used would depend upon the type of materials and information about the size, crystalline type, composition and chemical state, optical, magnetic and other properties. Different characterization techniques provide different information. Depending upon what information is required particular characterization technique is used.

The characterization and manipulation of individual nanostructures require not only extreme sensitivity and accuracy, but also atomic-level resolution. Therefore, it leads to various microscopies' that play a central role in the characterization and measurements of nanostructured materials. The development of novel tools and instruments is one of the greater challenges in nanotechnology. 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, morphology, composition and then the chemical state, optical, magnetic and other properties etc. The different characterization techniques used for the as-synthesized nanomaterials are given below in detail.

4.1 Thermal Analysis

In general, thermal analysis can provide important information on the temperature dependent properties of materials and on thermally induced processes such as phase transition, decomposition, etc. Thermal analysis is advantageous it gives a general view of the thermal behaviour of a material under various conditions and requires a small amount of sample. The term thermal analysis can be applied to any technique which involves the measurement of a physical quantity while the temperature is changed or maintained in a controlled and measured fashion. Thermal analysis is used to establish thermodynamic properties which are essential for understanding the behavior of material under different heating and cooling rates, under inert, reduction or oxidation atmosphere or under different gas pressures. Thermal analysis comprises a group of techniques in which the physical property of a substance is measured to a controlled temperature program.

The thermogravimetric analysis (TGA) is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. The TGA records the change in mass, from dehydration, decomposition, and oxidation of a sample with time and temperature. Characteristic thermogravimetric curves are given for the specific materials and chemical compounds, due to the unique sequence from the physicochemical reactions occurring over the specific temperature ranges and heating rates. These unique characteristics are related to the molecular structure of the sample. The differential thermal analysis (DTA) is a calorimetric technique, recording the temperature and heat flow associated with the thermal transitions in a material. This enables phase transitions such as the melting point, glass transition temperature and crystallization to be determined. The sample and the reference material are heated in one furnace. The difference between the sample and the reference material temperatures is recorded during the programmed heating and cooling cycles. A plot of this differential provides information on the exothermic and endothermic reactions taking place in the sample. The thermogravimetry analyzer (TGA) system, which combines thermogravimetry (TG) and differential thermal analyzer (DTA), is widely used in the fields of gas–solid interactions, fuels, catalysis, polymers and chemical synthesis.

Table 4.1: Classification of Thermo-analytical Techniques

Physical Property	Derived Technique
Mass	Thermogravimetry (TG)
	Isobaric mass change determination
	Evolved Gas Detection (EGD)
	Evolved Gas Detection (EGD)
	Emanation Thermal Analysis (ETA)
Temperature	Heating or cooling curve determination
	Differential Thermal Analysis (DTA)
Enthalpy	Differential Scanning Calorimetry (DSC)
Dimensions	Thermodiliatometry
Mechanical characteristics	Thermochemical measurements
	Dynamic Thermochemical measurements
Acoustic characteristic	Thermosonimetry
	Thermosonimetry
Optical characteristic	Thermoptometry
Electrical characteristic	Thermoelectrometry
Magnetic characteristic	Thermomagnetometry

As solid is heated, the extent of lattice vibrations within the solid are increased and a temperature would be reached during heating where following changes can occur:

Melting: the forces of attraction between the constituents decrease which maintain an orderly arrangement of the solid and comes down to a more disordered system called liquid state.

Phase transition: a new arrangement of the lattice structure.

Sublimation: direct transformation from the solid state to the gas phase occurs.

Decomposition: sometimes the molecular rearrangements of bonds within the solid during heating also result in formation products chemically different from the solid. These products can be a solid or gasses. This occurs over a range of temperature.

Thus by obtaining gravimetric data of heating a solid sample with time or temperature in a specified atmosphere, one would easily predict about the volatility, thermal stability and physical state of the sample at a particular temperature.

4.2 Powder XRD Analysis

X-ray diffraction (XRD) is a powerful tool for materials characterization, as well as for detailed structure elucidation. X-ray diffraction is a rapid analytical technique primarily used for the phase identification of a crystalline material, and can provide information on unit cell dimensions. Further, the X-ray diffraction method can be used to distinguish the crystalline materials from the nanocrystalline materials. This method uses a monochromatic source of X-rays and measures the pattern of diffracted radiation, which is a result of the constructive interference due to the crystalline structure of the powder. The structure identification is made from the X-ray diffraction pattern analysis, comparing it with the internationally recognized database containing the reference pattern (Joint Committee on Powder Diffraction Standards (JCPDS)).

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When the electrons have sufficient energy to dislodge the inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). $K_{\alpha1}$and $K_{\alpha2}$ is sufficiently close in wavelength, such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. When the geometry of the incident X-rays impinging the sample satisfies the Bragg's equation ($n\lambda=2d\sin\theta$), constructive interference occurs and a peak with intensity occurs. Bragg's law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted (shown in Fig. 4.1). The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ, while the X-ray detector mounted on an arm to collect the diffracted X-rays, rotates at an angle of 2θ. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. The position of a diffraction peak is dependent only on the size and shape of the unit cell. Each peak represents a certain lattice plane and can therefore be characterized by a Miller index. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns.

The lattice parameters are calculated by the formula,

$$\frac{1}{d^2} = \left[\frac{4}{3}\ \frac{(h^2 + k^2 + h * k)}{a^2} + \frac{l^2}{c^2}\right]$$

where d is the inter-planar spacing, a and c are the lattice constants of the hexagonal crystal and h, k and 1 are the miller indices of the Bragg's plane.

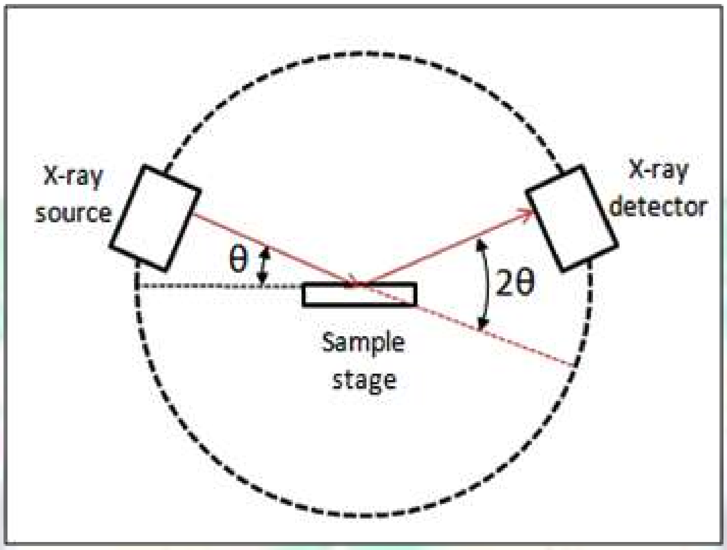

Fig. 4.1 X-ray diffraction from a powder sample

From the X-ray diffraction pattern the following information can be obtained:

1. Study the formation of a particular material system.
2. Estimating the unit cell structure, lattice parameters and miller indices.
3. Identification of phases present in the materials
4. Estimation of the crystalline/amorphous content in the sample.
5. Evaluation of the average crystallite size from the width of the peak in a particular phase pattern. Large grain size gives rise to sharp peaks, while the peak width increases with decreasing grain/particle size.

Powder X-ray diffraction is usually used to determine the crystal structure, grain size, phase and purity of the sample. The crystallite size can be obtained either by direct computer simulation of the X-ray diffraction pattern or from the Full Width at Half Maximum (FWHM) of the diffraction peaks using the Debye-Scherer's formula.

$$D=0.9\lambda/\beta\cos\theta$$

where,

λ - Wavelength of X-rays,

β - FWHM in radian,

θ - Peak angle.

4.3 FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy is a powerful tool for identifying the types of chemical bonds (functional groups) in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". The wavelength of the light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (mathematical algorithm) is required to convert the raw data into the actual spectrum. It is a measurement technique, whereby the spectra are collected based on the measurements of the coherence of a radiative source, using the time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation. Samples for the FTIR studies can be prepared in a number of ways. For liquid samples, the easiest way is to place one drop of the sample between two plates of sodium chloride (salt), which is transparent to infrared light, whereas the solid samples can be milled with potassium bromide (KBr- transparent in the IR region) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed.

The IR region is commonly divided into three smaller areas: near - IR (400 - 10 cm^{-1}), mid-IR (4000 - 400 cm^{-1}), and far-IR (14000 – 4000 cm^{-1}). Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. For a vibration to give rise to the absorption of infrared radiation, it must cause a change in the dipole moment of the molecule.

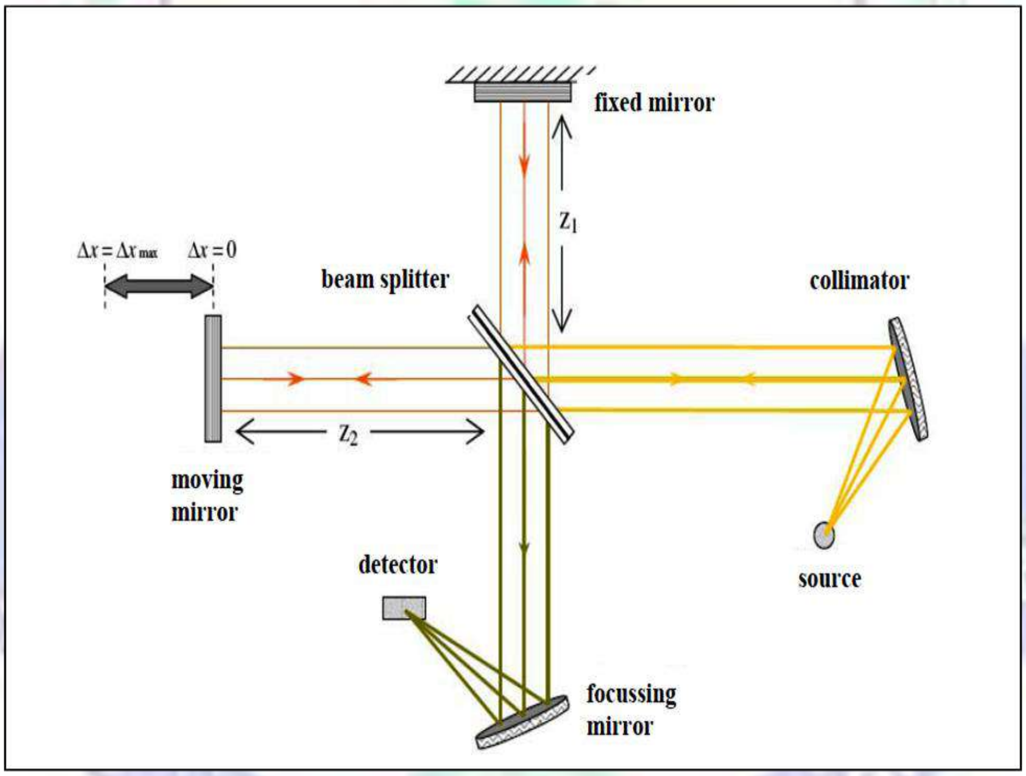

Fig. 4.2 Schematic diagram of a Michelson interferometer, configured for FTIR

The principle approach is the fact that structural features of a molecule produce characteristic and reproducible absorptions in the spectrum. The absorption of electromagnetic radiation at frequencies is correlated to the vibration of specific sets of chemical bonds within the molecule. The fundamental requirement for absorption of infrared radiations is that there must be a net change in dipole moment during the vibration of the molecule or the functional group in the molecule. The schematic diagram of a Michelson interferometer, configured for FTIR is shown in Fig.4.2.

Fourier Transform Infrared Spectroscopy is a strategy which is utilized to get an infrared range of absorption and emission. FTIR testing distinguishes compound mixes in buyer products, paints, polymers, coatings and different items. It offers quantitative and subjective investigation for natural and inorganic examples. It also distinguishes substance bonds in an atom by creating an infrared absorption range. The spectra produce profile of the specimen, a particular subatomic finger impression that can be utilized to screen and output tests for various parts. It is effective systematic instrument for identifying functional groups and describing covalent bonding information.

4.4 Raman Analysis

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. It is based on the inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in the monochromatic light changes upon interaction with a sample. The photons of the laser light are absorbed by the sample and then reemitted. The frequency of the reemitted photons is shifted up or down in comparison with the original monochromatic frequency, which is called the Raman effect. This shift provides information about the vibrational, rotational and other low frequency transitions in the molecules. Raman spectroscopy requires little to no sample preparation and is insensitive to aqueous absorption bands. This property of Raman facilitates the measurement of solids, liquids, and gases not only directly, but also through transparent containers such as glass, quartz, and plastic. Raman spectroscopy can be used to study solid, liquid and gaseous samples. Similar to FT-IR, Raman spectroscopy is highly selective, which allows it to identify and differentiate molecules and chemical species that are very similar. Using Raman spectral libraries, it is easy to see how easily Raman spectra can be used for material identification and verification. When a beam of photons strikes a molecule, the photons are scattered elastically (Rayleigh scattering) and inelastically (Raman scattering) generating Stoke's and anti-Stokes lines as shown in Fig. 4.3.

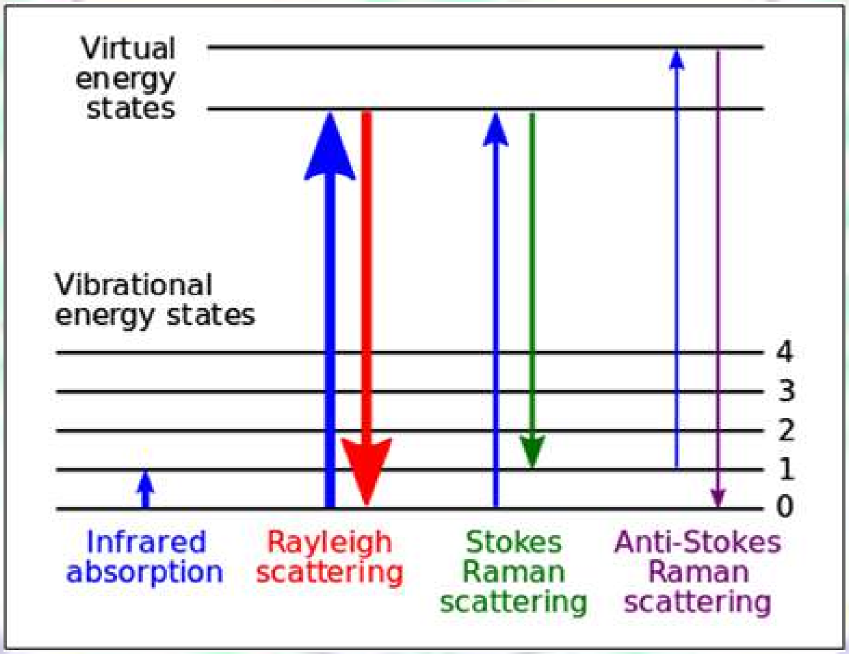

Fig. 4.3 Energy-level diagram showing the states involved in Raman spectra

Raman spectroscopy is another vibrational technique and differs from the infrared spectroscopy by an indirect coupling of high-frequency radiation, such as visible light, with vibrations of chemical bonds. It is very sensitive to the lengths, strengths and arrangements of the chemical bonds in a material, but less sensitive to the chemical composition. The Raman effect is extremely weak and, thus, intense monochromatic continuous gas lasers are used as the exciting light. In many nanomaterials, the Raman spectrum remains sufficiently similar to that of the corresponding single crystal to facilitate direct identification of the phases.

Raman spectroscopy usually consists of three parts: Laser, spectrometer and charge-coupled device array (CCD) detector. The spectrometer itself is a commercial "triple-grating" system. Physically, it can be separated into two stages, i.e. monochromator and spectrograph. Monochromater consists of two diffraction gratings (G1 and G2), bandpass slit between G1 and G2, and input/output focusing mirrors, which is mainly used as a filter. The incoming signal focused on G1 is separated into spread-out lights with different wavelengths travelling in different directions. These spread-our lights then pass through the band pass slit. We can adjust the slit width to only make the lights within user defined range pass through and refocused on G2. The dispersion pattern in G2 is the mirror image of that from G1 so that the purpose of G2 is only to compensate for any wavelength dependence in the dispersion of G1. After that, the light is finally refocused and sent out to the second stage of spectrograph which consists of another diffraction grating (G3) and two sets of lens. The filtered light from monochromater will be focused on the G3 and dispersed again. The dispersed light as a function of wavelength is recorded by a multichannel charge-coupled device array in which different wavelengths can be read simultaneously. The obtained wavelength/intensity information is then input into a computer and converted by software into frequency/intensity. This is the raw data of Raman spectrum, which can be analyzed to obtain some information about structural properties.

When a light come into a specimen, it will be scattered out. The light scattering process can be divided into two types, i.e. Rayleigh scattering and Raman scattering. For Rayleigh scattering, the incident photon is scattered elastically with unchanged frequency. For Raman scattering, the incident photon is inelastically scattered with a shift in frequency. It is well known that the frequency shift of Raman scattered light is related to the excitation frequency. However, it is worth to note that the magnitude of the shift is not dependent on the excitation frequency but the crystal structure. Therefore, this "Raman shift" can be attributed to an intrinsic property of the specimen. No doubt, Raman scattering is a powerful light scattering technique used to diagnose the internal structure of molecules and crystals.

4.5 VSM Analysis

A vibrating sample magnetometer (VSM) is a scientific instrument that measures magnetic properties of materials as a function of magnetic field, temperature and time. Using this technique, the magnetization of a sample on the application of some magnetic field can be measured. The instrument is based on the principle that an oscillatory magnetic field can be created by vibrating a magnetic sample. The magnetization in the sample is induced by applying a uniform magnetic field to the sample. The induced changes in the magnetic field are detected by a search coil. The applied magnetic field is usually quite large, but being constant is not detected by the search coil. Generally, the constant magnetic field is not really constant but slowly varied, so that the induced magnetization in the sample at different fields can be investigated. One can assume this slowly varying magnetic field as constant, compared to the vibrating field (Hz). In most of the standard set ups a large electromagnet with 0 to 2.5 tesla field is used. The pole pieces of the electromagnet are such that a large uniform magnetic field that prevails for a sample may be a thin film or powder sample held in a glass capillary attached to a special drive.

Paramagnetic, diamagnetic, ferromagnetic and other samples can be distinguished by plotting the magnetization versus applied magnetic field. Provision can be made to heat or cool the samples during the magnetic measurements. This enables one to study the magnetic phase transitions.

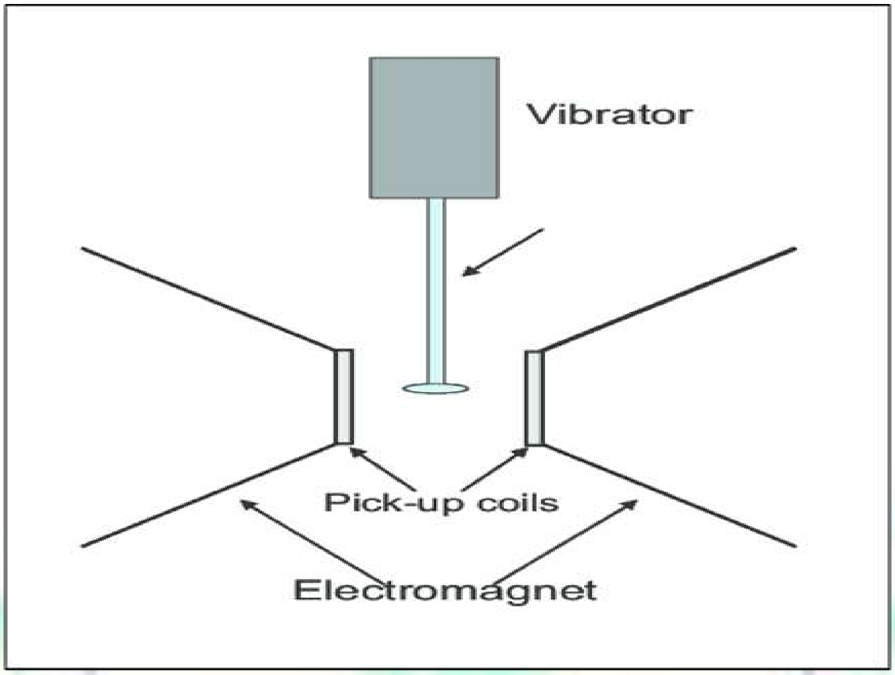

Fig. 4.4 Schematic diagram of VSM

For this scheme the first crucial step is construction of a vibrating mechanism which can vibrate the sample with measurable and controllable amplitude (Fig. 4.4). Then we need an electromagnet to provide the magnetic field required to magnetize the sample. Finally detection coils are required to detect the magnetic field perturbations produced by vibrating the magnetized sample in the applied magnetic field.

4.6 SEM and EDX Analysis

The scanning electron microscope (SEM) is a type of electron microscope that helps in forming an image of the sample surface by scanning. It is one of the most widely used techniques used in the characterization of nanomaterials and nanostructures. The electrons in the beam interact with the atoms in the surface to generate signals that reveal valuable light properties like composition, topography and electrical conductivity. Various types of signals produced by the SEM include back-scattered electrons (BSE), secondary electrons, characteristic X-rays, specimen current, light (cathodoluminescence) and transmitted electrons. The signals show the information about the sample, including chemical composition, crystalline structure, external morphology (texture), and orientation of the materials which make up the sample. Secondary electrons and backscattered electrons (BSE) are most commonly used for the purpose of imaging the samples: secondary electrons depict the morphology and topography of the samples, while the BSEs depict the contrasts in the composition of multiphase samples. BSEs are the beam of electrons that are reflected from the sample by elastic scattering. BSEs are often used in analytical SEM along with the spectra made from the characteristic X-rays (Fig. 4.5). Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample very accurately. Characteristic X-rays are released when the electron beam removes an electron from the inner shell of the sample, thus causing a higher energy electron to occupy the shell, and hence, release energy in the form of X-rays. These characteristic X-rays are, in turn, used to find out the composition of the material and also measure the presence of elements in the sample as well as the level of impurities. The percentage of elements present in the material can be obtained from Energy Dispersive X-ray spectroscopy (EDX), which is most commonly attached with the SEM in a typical measurement.

The EDX technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as 1µm or less can be analyzed. When the sample is bombarded by the SEM's electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state, and an x-ray is emitted to balance the energy difference between the two electrons' states.

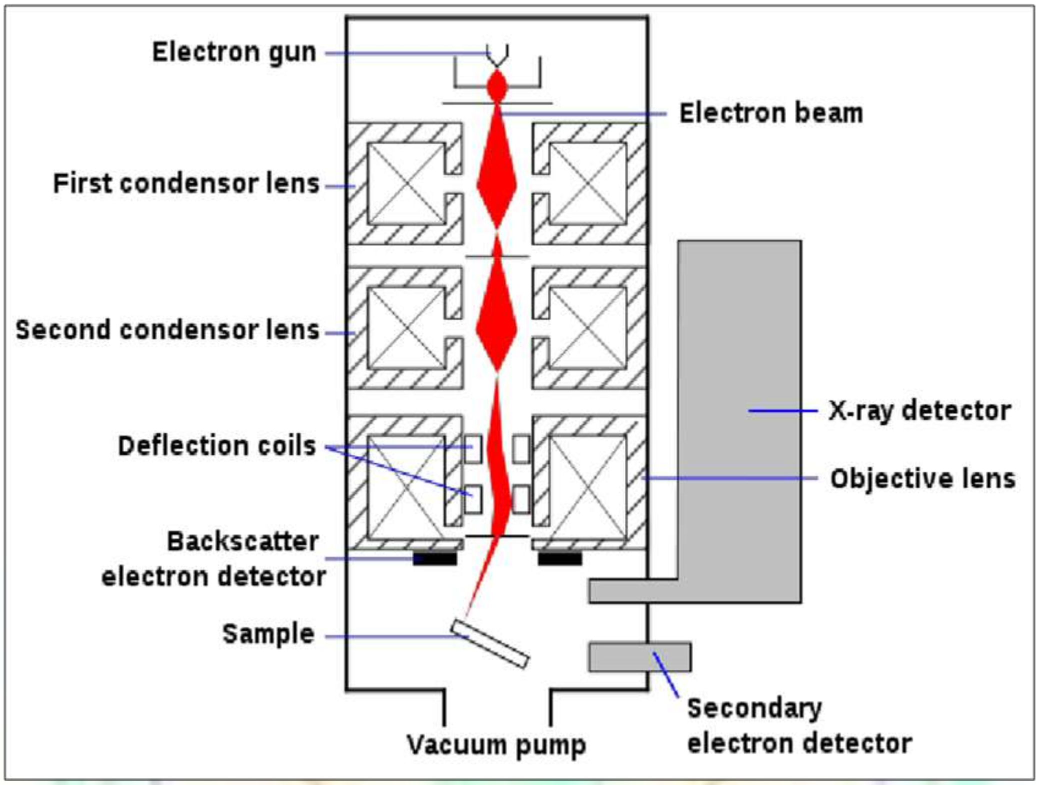

Fig. 4.5 Schematic diagram of SEM

The EDX detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium-drifted silicon, solid-state device. When an incident X- ray strikes the detector, it creates a charge pulse that is proportional to the energy of the X-ray. The charge pulse is converted to a voltage pulse (which remains proportional to the x-ray energy) by a charge-sensitive preamplifier. The signal is then sent to a multichannel analyzer where the pulses are sorted by voltage. The energy as determined from the voltage measurement, for each incident X-ray is sent to a computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.

4.7 TEM Analysis

Transmission Electron Microscopy (TEM) is a microscopy technique first developed in the 1930’s. It is a powerful instrument for the characterization of nanomaterials. It affords an improved understanding of the relationship between the atomic structure of materials and their chemical and physical properties.

The transmission electron microscope (TEM) provides highly coherent electrons of sufficient energy and allows investigating a sample in terms of its morphology, structure and orientation at a very high spatial resolution. Imaging over a big range of magnifications offers the possibility to determine the size distribution of particles by measuring a few hundreds of them at a low resolution, and to determine the shape and structure of the individual particles at a higher resolution. In the TEM, electrons are accelerated to 100 KeV or higher (up to 1MeV), projected onto a thin specimen (less than 200nm) by means of the condenser lens system, and made to penetrate the sample thickness either undeflected or deflected. In the TEM, one can switch between imaging the sample and viewing its diffraction pattern, by changing the strength of the intermediate lens (Fig. 4.6). TEM has the advantage of not only providing the images of the specimen but its diffraction patterns also, which enables one to make a detailed crystal structure analysis of the sample. To characterize the sample for its crystal lattice, the lattice parameters, orientation relation between two or possibly a large number of single crystals, and the crystallographic orientation of defects of all kinds, dislocations, stacking faults, voids, boundaries etc., the Selected Area Electron Diffraction (SAED) is performed. For a crystalline specimen, the peak of the intensity occurs in the diffraction pattern in the form of concentric rings, if the specimen is polycrystalline, or as regularly spaced diffraction spots if the specimen is a single crystal.

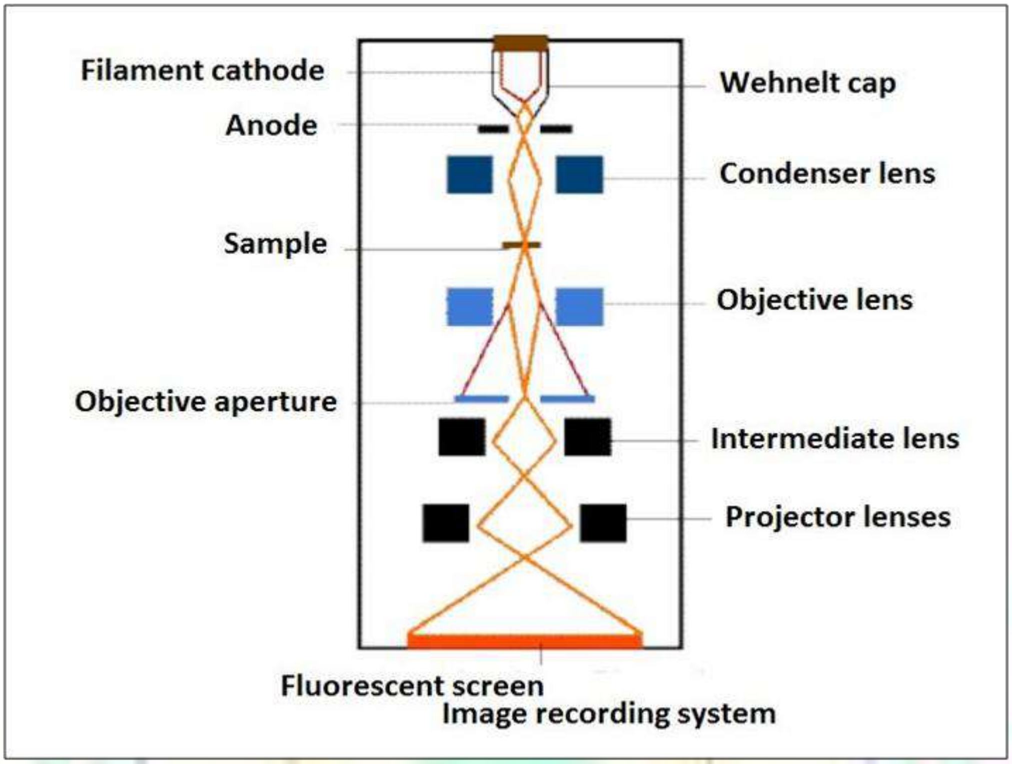

Fig. 4.6 Schematic diagram of TEM

The high-resolution transmission electron microscope (HRTEM) is one of the most powerful tools used for the characterization of nanomaterials. The most important contrast mechanism for high resolution electron microscopy is the phase-contrast. Even though HRTEM is the most used technique to determine the structure of a single isolated nanoparticles, the structure determination of small particles is often difficult and not always possible, especially when the nanoparticles are very small, i.e., less than 2 nm in diameter. Small single crystals down to the size of 5 nm can be selected in the image mode, and their diffraction characteristics can be studied, simply by changing to the diffraction mode.

4.8 XPS Analysis

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS is a surface analytical technique based on photo-ionization effect. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed. In principle, when an X-ray beam illuminates the surface of a specimen, the core electron of an atom on the surface will absorb the entire X-ray photon energy. If the X-ray photon energy is higher enough, the core electron will then escape from the atom and emit out of the surface with certain kinetic energy, which is also called photoelectron. The kinetic energy E_k of these photoelectrons can be determined by the X-ray photon energy hν and the respective binding energies E_b:

$$E_k=h\nu-E_b$$

The experimentally measured energies of the photoelectrons can be given by:

$$E_k = h_\nu - E_b - E_w$$

Where E_w is the work function of the spectrometer. Since we already known the X-ray photon energy and E_w, the kinetic energy is only determined by the binding energy. Every element owns more than one atomic orbital. The electron located at each atomic orbital has its unique binding energy like a “fingerprint”. With the X-ray excitation, each element will exhibit a set of peaks depended on the kinetic energies in the XPS spectrum. Usually, we plot the XPS spectrum as a function of binding energy instead of kinetic energy. According to the work principle of XPS, we can identify almost all elements except for hydrogen and helium by measuring the binding energy of its core electron. Obviously, the presence of peaks at particular energies indicates the presence of a specific element in the sample. Furthermore, It is also worth to note that the chemical environment strongly influence the binding energy of core electron. With bonding to different chemical species, the binding energy of a same atom varies, which leads to the shift of the corresponding XPS peak in the range of 0.1 eV ~ 10 eV. This effect is termed as "chemical shift", which can be applied to studying the chemical status of element in the surface. In addition, the peak intensity in XPS spectrum is determined by the concentration of the corresponding element within the surface, thus XPS is also used to quantify the chemical composition.

4.9 UV-visible absorption Analysis

Ultraviolet-visible spectroscopy (UV-vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. It is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, and highly conjugated, and biological macromolecules. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with the transitions from the excited state to the ground state, while absorption measures the transitions from the ground state to the excited state. Samples for UV-vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. A complete spectrum of the absorption at all wavelengths of interest can often be produced directly by a more sophisticated spectrophotometer. When the sample molecules are exposed to light, having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam; hence, it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The absorption of incident radiation by bonding/non-bonding electrons represents a high energy (100 kCal/ mole) transition. This corresponds to a high frequency, i.e. low wavelength, absorption band which is observed at 200–800 nm in the UV and visible range of detection.

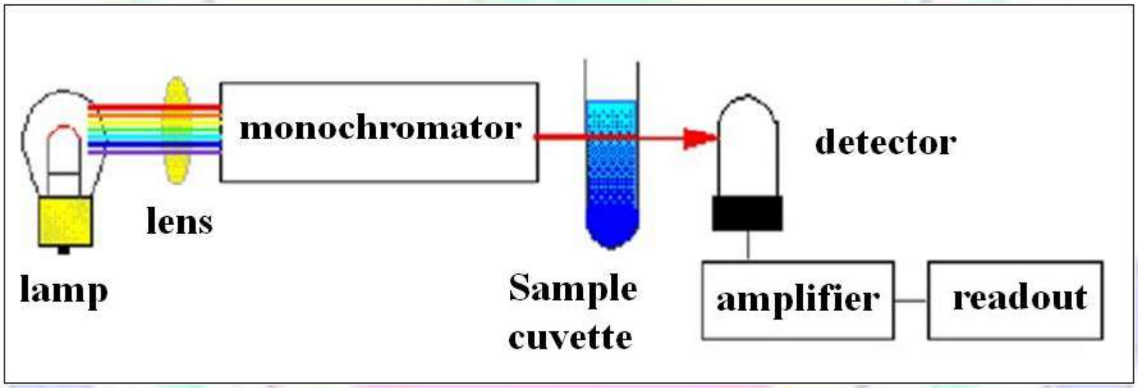

Fig. 4.7 Schematic diagram of UV-visible spectrophotometer

The principle of UV-vis absorption spectroscopy is that molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbital's. The more easily excited the electrons, the longer the wavelength of light it can absorb. Different compounds may have very different absorption maxima and absorbance. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms are generally avoided. Due to the absorbance of a sample will be proportional to its molar concentration in the sample cuvette (Fig. 4.7), a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds and is given by:

$$\text{Molar Absorptivity, } \varepsilon = A / C\,L$$

where A- absorbance, C- sample concentration in moles/liter and L-length of light path through the cuvette in cm

Beer Lambert law is often used in a quantitative way to determine concentrations of an absorbing species in solution. Lambert's law stated that absorbance of a material sample is directly proportional to its thickness (path length). After sometime, August Beer discovered another relation. Beer's law stated that absorbance is proportional to the concentrations of the attenuating species in the material sample. The modem derivation of the Beer-Lambert law combines the two laws and correlates the absorbance to both, the concentrations of the attenuating species as well as the thickness of the material sample. Law is given by:

$$A = -\log (I/I_o) = \varepsilon\, C\, L$$

where A is the measured absorbance, I is the intensity of the incident light or of sample beam, I_o is the reference beam intensity, L the path length through the sample, and C the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptivity.

With reduction in the particle size a shift in the absorption edge can occur. The shift is usually to a shorter wavelength, and therefore, known as a blue shift. Also the peak widths for metals or semiconductor nanoparticles depend upon the size, as well as the size distribution of particles. UV-vis absorption is an important characterization method for nanomaterials, because the absorption features give information about the nanoparticles formation, the band gap and the size distribution of the nanomaterials. However, it is an indirect method for determining the particle size. The band gap of the particles can be calculated from excitonic peak position, which is used to determine the particle size with the help of the curves of the energy gap versus size, obtained from the theoretical models.

A Tauc plot is used to determine the optical gap, or Tauc gap, in semiconductors. The Tauc gap is often used to characterize practical optical properties of amorphous materials. A Tauc plot is a convenient way of displaying the optical absorption spectrum of a material, pioneered by Jan Tauc, who proved that momentum is not conserved even in a direct optical transition. Typically, a Tauc plot shows the quantity hv (the energy of the light) on the abscissa and the quantity $(\alpha hv)^{1/r}$ on the ordinate, where α is the absorption coefficient of the material. The value of the exponent r denotes the nature of the transition:

r = 1/2 for direct allowed transitions

r = 3/2 for direct forbidden transitions

r = 2 for indirect allowed transitions

r = 3 for indirect forbidden transitions

4.10 Photoluminescence Analysis

Photoluminescence spectroscopy (PL) is used to study the optical properties of the materials. PL spectroscopy is a contactless, nondestructive method to probe the electronic structure of materials. The PL spectrum provides the transition energies, which can be used to determine the electronic energy levels. It is light emission from any form of matter after absorption of photons. When light of sufficient energy illuminates a material, photons are absorbed and electrons absorb the energy and move to higher energy states. These excitations relax in higher energy state and when they come to a lower energy state they emit a photon. The PL can be collected and analyzed to provide information about the photo-excited states. PL investigations can be used to characterize a variety of material parameters. PL spectroscopy provides electrical characterization, and is a selective and extremely sensitive probe for determining discrete electronic states. Features of the emission spectrum can be used to identify the surface, interface, and impurity levels, and to gauge alloy disorder and interface roughness. In addition, time-resolved PL can be very fast, making it useful for characterizing the most rapid processes in a material. Observation of photoluminescence at a certain energy can be viewed as indication that excitation populated an excited state associated with this transition energy. The excitations then undergo energy and momentum relaxation towards the band gap minimum. Finally, the electrons recombine with holes under emission of photons. Time periods between absorption and emission may vary: ranging from short femto second-regime for emission involving free-carrier plasma in inorganic semiconductors up to milliseconds for phosphorescent processes in molecular systems; and under special circumstances delay of emission may even span to minutes or hours.

PL measurement is a kind of powerful and nondestructive technique, which has been carried out on most of semiconductors. To date, there are many different type lasers have been widely used in the PL setup, for example, He-Cd laser with 325 nm, Ar+ laser with 316nm/514 nm/488 nm, Nd:YAG pulsed laser with 266 nm , tunable solid state lasers and so on. When we use pump laser to provide pulsed excitation, the lifetime information of excited state can be obtained. Then the setup will be called Time-resolved PL. The typical PL experimental set-up is illustrated in Fig. 4.8.

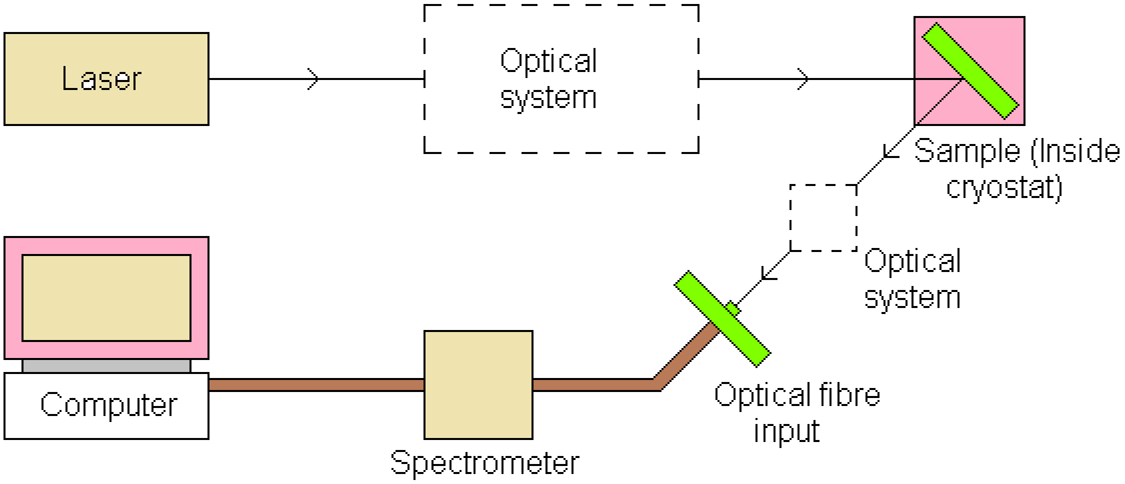

Fig. 4.8 Typical experimental set-up for PL measurements

Luminescence refers to the emission of light by a material through any process other than blackbody radiation. The emission of light can result from a variety of stimulations. In photoluminescence one measures the physical and chemical properties of materials, by using photons to induce excited electronic states in the material system, and analyzing the optical emissions as these states relax. Typically, light is directed onto the samples for excitation, and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photon detector. In PL, a material gains energy by absorbing photons at some wavelength, by promoting an electron from a lower to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal or polymer (electron-hole creation). The PL intensity gives a measure of the relative rates of radiative and non-radiative recombination. Yet, compared with other optical methods of characterization like reflection and absorption, PL is less stringent about beam alignment, surface flatness, and sample thickness.

The wavelength of luminescence, its efficiency and radiative lifetime depend upon the material. In the case of nanomaterials, additionally the size of the material plays an important role. In a particle with dimensions comparable to the Bohr diameter of the electron, the electron and hole wave functions can overlap. Therefore, the probability of efficient recombination increases. Due to the altered electronic structure in nanomaterials, the transition rules also relax in certain cases, and some transitions, which are forbidden in the bulk material, become possible. The fluorescent efficiencies, in general, are found to be enhanced in nanoparticles by doping. Dopants can introduce some energy levels in the band gap of the host material; such levels can be responsible for altering the luminescence properties of the host material, with more probability or higher luminescence efficiency, due to the increased overlap, because of the small size in the nanoparticles, of the wave functions. The process of luminescence may be due to the band edge luminescence and/or defect emission. Through PL measurement, we can obtain a variety of material parameters, which will be introduced respectively as follows:

(a) Impurity levels and defect detection: Usually, there are always some native defects and impurities in even pure semiconductors, which will form some localized defect levels between the band gap. These defect levels certainly participates the radiative transitions. The PL energy associated with these levels can be used to identify specific defects, and the PL intensity can be used to provide relative information concerning their concentration.

(b) Recombination mechanisms: It is well known that the "recombination" include both radiative and non-radiative processes due to the existence of the surface and defect levels in the band gap. The PL intensity depends on the power of photo-excitation and temperature, which is determined by the dominant recombination process. Thus, analyzing power/temperature/time dependent PL spectra will definitely help us understand the underlying physics of the recombination mechanism.

(c) Material quality: The non-radiative recombination process in a material shows an obvious evidence for the existence of the defects. It is obvious that these defects are harmful for device performance. Through PL measurement, we can quantify the component proportion of non-radiative recombination in the emission process, which will help us judge the optical quality of the material is good or not.

(d) Band gap determination: It is well known that the radiative transition between the band gap in semiconductors is the most important one. So the PL measurement not only helps us determine the band gap of a semiconductor especially for a new compound semiconductor, but also guides us to accomplish the band gap engineering, which is particularly significant for prompting the practical applications of a semiconductor in the industry.