Chapter 2
Experimental Techniques
Chapter: 2

Experimental Techniques

2.1 Introduction
The synthesis and analysis of nanomaterials have become a very important area due to wide applications of nanotechnology in various fields. Basically, there are two approaches used to synthesize nanoparticles, the 'top-down' and ‘bottom-up’ approaches. Top-down approach includes physical methods such as solid state route, ball milling, laser ablation, ion implantation, spray pyrolysis etc. While wet chemical routes like sol-gel, co-precipitation, hydrothermal etc., come under the category of bottom-up approach. In our work, we adopted chemical route i.e., sol-gel method for the synthesis of pure and doped SnO$_2$ nanoparticles. The modified Hummer’s method has been used for the synthesis of graphene oxide (GO). Further characterization of synthesized nanomaterials is very essential for investigating various properties. Many extensive analytical techniques have been used for the investigation of as-synthesized nanoparticles such as X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), Soft X-ray absorption spectroscopy (SXAS), Energy dispersive X-ray spectroscopy (EDX or EDS), Transmission electron microscopy (TEM), Fourier transforms infrared (FTIR) spectroscopy, Raman spectroscopy, UV-visible absorption, photoluminescence (PL) spectroscopies, LCR mete and Superconducting quantum interference device (SQUID) magnetometer etc. This chapter has been divided into two parts: (i) synthesis of nanomaterials (ii) characterization techniques.

2.2 Synthesis of Nanoparticles
As remarked above there are two approaches used to synthesize nanoparticles, the 'top-down' and ‘bottom-up’ approaches. The top-down approach includes physical methods, while chemical or biological methods come under the bottom-up approach. The “top-down” approach deals with the division of bulk solid into smaller and smaller portions, successively reaching to nanometer size as illustrated in Fig. 2.1. This approach may involve milling or attrition. The “bottom-up” method of
nanoparticle fabrication involves the condensation of atoms or molecular entities in a gas phase or in solution to form the material in the nanometer range. The latter approach is more popular for the synthesis of nanoparticles owing to several advantages associated with it. There are several bottom-up synthesis process for metal oxide nanomaterials that have adopted earlier such as combustion synthesis [1], hydrothermal method [2], gas-phase methods [3], microwave synthesis [4], sol-gel processing [5] etc. In this chapter, sol-gel method is discussed in details. The various synthesis process which comes under the category of top-down and bottom-up have been shown in Fig. 2.2.

**Fig. 2.1** Schematic representation of ‘Top-down’ and 'Bottom-up' approaches.
2.2.1 Solution Combustion Method

The solution combustion process involves the use of salts, such as nitrates, carbonates, metal sulfates as oxidants and reducing reagents, fuels such as citric acid, glycine, urea, sucrose, or other water soluble carbohydrates. Nitrate works as an oxidizer for the fuel during the combustion reaction. The powder may be a pyrolysed product of a single phase, but generally it is a mixture of metal oxides and in certain cases it requires subsequent heat to form single-phase products. The solution combustion synthesis is a method based on the principle that once a reaction is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval, resulting in a powder as a final product. The exothermic reaction begins at the ignition temperature and generates a certain amount of heat that is manifested in the maximum temperature or temperature of combustion. Solution combustion synthesis has the advantage of rapidly producing fine and homogeneous powders. Since it is an exothermic, auto-propagated process, and with a high heat release rate, it can be dangerous and should be undertaken with extra precautions.
2.2.2 Hydrothermal Method

Hydrothermal synthesis is extensively adopted for the synthesis of metal oxide nanoparticles which can be easily achieved through hydrothermal treatment of peptized precipitates of a metal precursor with water [6]. When the reaction is performed using water as a solvent, the method is called hydrothermal synthesis. In hydrothermal process a pressurized vessel known as an autoclave is used in which reaction occurs in aqueous solution. The temperature in the autoclave can be increased above the boiling point of water, getting the pressure of vapor saturation. This method can be convenient to control morphology, grain size, crystalline phase and surface chemistry through regulation of the reaction temperature, solution composition, solvent properties pressure, additives and aging time [7].

2.2.3 Microwave Synthesis

This method is of increasing interest as it needs relatively low energy and is less time consuming [8]. The reaction time reduces from some hours to several minutes irrespective of particles size or purity. High heating rates, which favor rapid nucleation and the formation of small, highly mono-dispersed particles are employed to achieve faster reaction rates. Microwave-assisted process involves rapid and constant heating of the reaction medium with no variation in temperature via two mechanisms: ionic conduction and dipolar polarization. Manipulation of particle size, crystallinity and morphology are reaction conditions, which are controlled by automation [9]. The selection of starting materials and solvents can run reaction success, crystal structure and particle size.

2.2.4 Sol–Gel Method

Sol–gel method is one of the well-established synthetic approach to prepare novel metal oxide NPs as well as mixed oxide nanocomposites. This method has potential control over the textural and surface properties of the materials. Sol-gel process essentially go through a few steps to deliver the final metal oxide protocols, and which are hydrolysis, condensation and drying process. The formation of metal oxide contains different sequential steps, initially the precursor materials undergo quick hydrolysis to make the metal hydroxide solution and then immediately condensation takes place, forming the three-dimensional gels. After heating, gel is obtained which is subjected to drying process, and the obtained product is readily converted into
xerogel or aerogel based on the mode of drying. In the sol–gel approach, nature of metal precursor and solvent plays a remarkable role in the synthesis of metal oxides NPs. The reaction pathway for the production of metal oxide nanostructures in the sol–gel method is shown in Fig. 2.3.

![Fig. 2.3 Basic reaction pathway for the synthesis of metal oxide nanostructures in the Sol–Gel method](image)

Sol-gel technique has several advantages over other synthesis process:

- Sol-gel method involves wet chemical synthesis of materials, so the composition of the materials can be tailored at molecular level. As a result, homogeneous control of the dopant is easily achieved.
- Since liquid precursors are used so it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers, and monoliths, etc., without machining or melting process.
- The precursors, such as metal alkoxides, with very high purity are commercially available, which makes it easy to fabricate high quality materials.
- It has better homogeneity in the mixing at molecular levels.
It’s cost effective because the temperatures required in the process are low, close to room temperature, and no delicate vacuum system is needed.

2.3 Characterization Techniques

This section describes the basic principles of various characterization techniques which are used in the present work and they are tabulated in Fig. 2.4.

![Characterization Techniques Diagram]

**Fig. 2.4** Characterization techniques used in the present work.

2.3.1 X-ray Diffraction (XRD)

In 1912, the German Physicist, Von Laue was the first who studied the problem of X-ray diffraction with the reason that if the atoms were arranged in a regular fashion in a crystal which may be treated as scattering centers for X-rays, if it was assumed that X-rays were electromagnetic waves of wavelength about equal to the distance between atomic planes in crystals, then it is possible that X-rays should be diffracted by the crystals [10]. X-ray diffraction is most widely used technique for the structural study of the materials. Huge information can be obtained from the XRD data. This is a suitable technique for all types of samples like powder, sintered pellets, coatings on substrates, thin film etc. This technique tells about the nature of the material, whether material is crystalline or amorphous. One can also know the phase, lattice parameter and grain size [11]. The position and shape of the lines give the information about the microstructural parameters like microstrain, grain size, etc. In case of thin films, the
variation in lattice parameter as compared to the bulk gives the information about the nature of strain present in the system. The scattering of X-rays with crystalline sample is governed by Bragg’s law, which describes a relationship between the X-ray wavelength, diffraction angles and interplanar distance of the crystal planes. According to Bragg’s law, the X-ray diffraction can be understood as X-rays diffract from a series of crystallographic planes as shown in Fig. 2.5, for constructive interference pattern, the path difference must be equal to the integral multiple of wavelength (nλ, n being an integer). In a quantitative way Bragg’s law can be expressed by following equation.

\[ 2d_{hkl} \sin \theta = n \lambda \]  

(2.1)

where \( d_{hkl} \) is the interplanar spacing for a given set of \( hkl \) and \( \theta \) is the Bragg’s angle.

![Fig. 2.5 Geometrical illustrations of crystal planes and Bragg’s law.](image)
The broadening of diffraction peaks in the XRD pattern is related to the size of the particles (crystallites). The displacement of the atoms from the lattice site may occur due to the all types of defects. M.A. Krivoglanz in 1969 [12] gave an equation for the intensity of the Bragg’s peaks from a crystal defect, which allowed all the defects to be categorized conventionally into two groups. The defects in the first group only reduce the intensity of the diffraction peaks, but are not associated with the broadening. Usually, the broadening of the Bragg’s peak occurred due to the defects of second group. These defects are micro-deformations, inhomogeneity (non-uniform composition of the substance over their volume) and the small particle size.

The size of nanoparticle can be obtained from the peak broadening and then determined using the Scherrer formula as given by the Eq. 2.2, provided that the nanocrystalline size is less than 100 nm.

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(2.2)

where \( D \) is the average crystallite size, \( \theta \) is the diffraction angle, \( \lambda \) is the X-ray wavelength, \( k \) is the Scherrer constant. Its value equals to 0.9 for spherical particles and value of \( k \) depends on the shape of the particle (crystallite, domain) and on diffraction indices (hkl). \( \beta \) is the full width at half maximum of the peaks. The Scherrer formula is quite satisfactory for small grains (large broadening) in the absence of significant microstrain. A microstrain defines the relative mean square deviation of the lattice spacing from its mean value. Based on the grain size dependence of the strain, it is reasonable to assume that there is a radial strain gradient but from X-ray diffraction only a homogeneous volume-averaged value is obtained. In our work, the structures and the average crystallite size of all samples have been determined by using Miniflex-II Rigaku X-ray diffractometer with Cu-Kα radiations (\( \lambda = 1.5406 \text{ Å} \)) at scan rate of 2^0/min in 2\( \theta \) in the range of 20-80^0.

2.3.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM technique is extensively used to get topographical features, surface morphology, crystal orientation, crystal structure, presence and location of defects as well as dimension, shape and distribution of the particles [13]. In FESEM, electrons are generated from a source and accelerated in a high electrical field gradient in the presence of the high vacuum column (10^-4–10^-10 torr). The accelerated beam of electrons (monoenergetic) having energies in the range of few hundred of eV to tens
of keV, so-called primary electrons, is focused with the help of electromagnetic lens to produce a very narrow scan beam that falls on the object. Secondary electrons are produced from each spot on the object. These are detected to produce an electronic signal. The surface of the sample is scanned over an area. The obtained signal conveys information about the morphology of the sample. Some of these electrons get scattered elastically from the coulomb field of the nucleus whereas, some electrons are inelastically scattered from the electrons of the host atoms giving secondary or auger electrons. These auger electrons reflect bare characteristic of the element from which they are emitted [13]. The secondary electrons detected by a detector at every position of the incident electron beam are used to form an image. The collected signal is amplified and is made to form a synchronous image on a cathode ray tube. A camera is used to capture the image or it may be digitized and processed on a computer. A schematic diagram of typical scanning electron microscope is given in Fig. 2.6. In this technique, the sample should be conductive. The surface of nonconductive samples is made conductive, usually by coating a thin layer of gold. The determination of depth and resolution of the images is carried out by the beam current and the final spot size, respectively, which are adjusted with one or more condenser lenses and the probe forming objective lenses. The interaction between electrons and samples takes place from few nanometers to several microns of the surface of the sample which depends on the beam parameters and the sample type. Primarily, electrons are emitted from the sample as either backscattered or as secondary electrons, and are detected by scintillation photomultiplier detector. Secondary electrons have the energy of 3–5 eV and are generally used for the visualization of surface morphology and roughness, as they can spot the exact position of the beam on the sample surface and give morphological information with high resolution [13]. In the present study, the morphological and element compositional analysis has been carried out by FESEM (SU-8000, Hitachi, Japan).
Chapter 2

Fig. 2.6 Schematic details of FESEM.

FESEM has following advantages over conventional SEM:

- FESEM gives clearer and less distorted images with resolution down to 1.5 nm, which is about 3 to 6 times better than conventional scanning electron microscopy (SEM).

- Smaller-area contamination spots can be examined at electron accelerating voltages compatible with energy dispersive X-ray spectroscopy.

- Reduced penetration of low kinetic energy electrons probes closer to the material surface.

- FESEM provides ultra-high resolution imaging at low accelerating voltages and small working distances.

2.3.3 Transmission Electron Microscopy (TEM)

As we know, typical nanoparticles exhibit sizes of only a few nanometers, which is beyond the resolution of the naked eye, optical microscope and even usual scanning electron microscope. The most fashionable technique used for this purpose is transmission electron
microscopy (TEM). TEM gives most direct evidence of the size, shape and crystallinity of prepared nanocrystals.

The instrumental details of TEM is shown in Fig. 2.7. It is composed of several components, which includes a vacuum system, specimen stage, electron gun, electromagnetic lenses (condenser, objective) and apertures. The source of illumination, electron beams of very short wavelength is emitted from the electron gun at the top of an evacuated chamber and travel through the vacuum to avoid the collision of electrons with air molecules and hence scattering of electrons. Just like glass lenses placed in light microscopy, magnetic coils are placed in specific intervals, which worked as electromagnetic condenser lens system to focus the electron beam on the specimen.

In a transmission electron microscope (TEM), the electrons are generated from a source and this electron beam interacts with the sample, the electrons passing through the sample, are focused by an objective lens, and amplified by a magnifying (projector) lens, then finally the desired images are produced. Since electrons interact very strongly with matter as compared to X-rays or neutrons. Thin films or particles show too little scattering to get useful images and in case of thick films or materials multiple scattering events dominate, making the image blurred and difficult to interpret. Thick specimens can be studied by detecting backscattered electrons. Selected area electron diffraction (SAED) pattern was also recorded to know the crystallinity of the samples. A transmission electron microscope can form images by the use of the SAED aperture located between the objective and projector lenses. The main part of the electron beam transmitted by the sample consists of electrons that have not undergone any scattering. The beam also contains electrons that have lost energy through inelastic scattering with no deviation of their paths, and electrons that have been reflected by various (hkl) crystallographic planes. In order to produce bright-field image, the aperture is inserted which allows only the main undeviated transmitted electron beam to pass. The bright-field image is observed at the detector or viewing screen. In the present study, TEM micrographs and SAED pattern were captured with a JEOL, JEM-2100.
2.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectrometers generally fall under two categories namely: dispersive and interferometer instruments. Conventional spectrometers are dispersive instruments using a prism or grating as dispersive elements. In order to overcome shortcomings of these devices, spectrometers based on interferometer technique were developed. This type of instrument records the interferogram of the signal and later with the help of fourier transform methods, it is converted into a conventional spectrum and these instruments are called FTIR spectrometers. Fourier transform spectrometers have substituted dispersive instruments for various applications because of their higher speed and better sensitivity. They have significantly extended the performance of infrared spectroscopy and have been applied to many areas which are very problematic or nearly impossible to examine by dispersive instruments. There are three basic spectrometer components in an FT system: radiation source, interferometer and detector. A simplified optical layout of a typical FTIR spectrometer is illustrated in Fig. 2.8.

IR spectra involve the study of interactions between matter and electromagnetic fields in the IR region. In this spectral region, the EM waves couple with the
molecular vibrations. Molecules are excited to a higher vibrational state by absorbing IR radiation. The IR frequency when absorbed would actually interact with the molecule at a certain frequency. Hence IR spectroscopy is a very powerful technique which provides fingerprint information on the chemical composition of the sample. Using IR Spectroscopy both qualitative as well as quantitative analysis of fiber samples can be carried out. FTIR spectrometry is found to be the most analytical type of techniques available in laboratories. FTIR works on the principle of fourier transformation. Interferogram is determined experimentally in FTIR spectroscopy. The spectrum is plotted against the corresponding wave number against transmittance values. This transformation is carried out automatically and the spectrum is displayed/infrared spectroscopy results in a positive identification (qualitative analysis) and the size of the peaks in the spectrum is a direct indication of the amount of material present.

Fig. 2.8 Schematic diagram of FTIR spectrometer.

The FTIR spectrometer has several prominent advantages:

- The signal-to-noise ratio of spectrum is significantly higher than the previous generation infrared spectrometers.
- The accuracy of wavenumber is high. The error is within the range of $\pm 0.01 \, \text{cm}^{-1}$.
- The scan time of all frequencies is short (approximately 1sec).
- The resolution is extremely high ($0.1 \sim 0.005 \, \text{cm}^{-1}$).
- The scan range is wide ($1000 \sim 10 \, \text{cm}^{-1}$).
The interference from stray light is reduced. Due to these advantages, FTIR spectrometers have replaced dispersive IR spectrometers.

In the present study, the presence of functional vibrational bonds in the prepared samples was examined by a Perkin-Elmer fourier transform infrared (FTIR) spectrometer in the wavenumber in the range 400–4000 cm\(^{-1}\) using KBr as a background.

### 2.3.5 Raman Spectroscopy

The Raman Effect, named for the Nobel Prize work by Sir Chandrasekhara Venkata Raman in 1928 [14] is an optical analysis technique that measures the intensity of inelastically scattered light over a range of frequencies. Fig. 2.9 shows schematic illustrating Raman set-up. When monochromatic light is incident on a material, most of the light is elastically scattered (Rayleigh scattering) and a small part of the scattered light is inelastically scattered (Raman scattering).

![Fig. 2.9 Schematic diagram of micro Raman spectrometer.](image)

The source of inelastic scattering can be due to the transitions between the various states in the materials induced by the incident radiation. Mainly three types of transitions are possible namely: (i) rotational, (ii) vibrational, (iii) electronic or a combination. Most of the transitions observed in solids by Raman spectroscopy are vibrational. Raman spectroscopy can be used for the study of solids, liquid and gases, both crystalline and amorphous. In this technique, the spectra are obtained as plots between the intensity of the inelastically scattered light and the shift in the
wavenumber of the incident radiation. Each peak corresponds to one or more
symmetry-allowed Raman active vibrational modes of the solid. Raman activity
depends on the point group symmetry of a molecule and the space group symmetry of
a crystalline solid. However, the symmetry of the crystal is embodied in its
crystallographic point group [15]. Raman measurements provide information like the
strength of interatomic and intermolecular bonds, the mechanical strain in a solid, the
composition of multicomponent matter, the degree of crystallinity and the effects of
pressure and temperature on phase transformations. When a photon is incident on a
solid, the inelastically scattered photon can have the frequency lesser or greater than
the frequency of the incident photon, the associated scatterings are identified as
Stokes or anti-Stokes Raman scattering, respectively. When an electron excited by the
incident photon returns back to the same state, then the electron is elastically scattered
and this is called Rayleigh scattering, but if it returns to some excited state, then it
loses some energy to the system and the scattered photon has a frequency lower than
that of the incident photon, this gives rise to Stokes lines as shown in Fig. 2.10. If the
system is initially in an excited state and then the incident photon excites it to some
higher excited state, the electron can return back to the ground state with the scattered
photon having energy larger than the incident photon, this is the origin of anti-Stokes
lines. Statistically, most of the electrons will be in the ground state at room
temperature, Stokes lines have higher intensities as compared to the anti-Stokes lines.
The sample is illuminated using monochromatic light from a laser and the scattered
light is collected using suitable collection optics. The light is then passed through the
spectrometer and the Raman spectra are obtained. In the collected light, the dominant
contribution is from Rayleigh scattering. Because of imperfections in the gratings and
mirrors within the spectrometer, a portion of the Rayleigh scattered light is present in
the Raman spectra in the range of 0 to 200 cm$^{-1}$. Although the fraction of the Rayleigh
scattering in this region is very small, it can overshadow the Raman spectra as the
intensity of Rayleigh component is very high. Thus, the Raman peaks in this region
can be observed only when the Rayleigh scattered light is strongly reduced. For this
purpose, a notch filter is used; it removes the Rayleigh scattered radiation (as well as
Brillouin scattered light and Mie scattering from dust particles).
In this study, the Raman spectra for the samples were collected at room temperature using micro Raman system from Jobin Yvon Horiba LABRAM-HR (50 cm$^{-1}$ to 4000 cm$^{-1}$) coupled with excitation laser source (Argon 488 nm).

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a widely used surface sensitive technique which functions under ultra-high-vacuum. When soft X-rays fall on a sample surface, electrons are ejected from valence and core levels of both surface and near surface atoms [16]. The kinetic energies of ejected photoelectrons are not only characteristic of the atoms from which they are emitted, but can also provide information on the chemical states of those atoms. Fig. 2.11 shows the basic process involved in XPS. It was found that during irradiation, electrons are only emitted from surface atoms when the energy of the X-rays is greater than a critical energy known as the surface work function, which is the energy required to excite an electron from its valence orbital to the continuum. For electrons emitted from lower lying orbitals, the binding energy of the electron also has to be overcome, reducing the kinetic energy of the emitted electron further [17].
Fig. 2.11 The mechanism of photoelectron emission in X-ray photoelectron spectroscopy.

In XPS, the kinetic energy of ejected photoelectrons is measured by an analyzer. The recorded kinetic energy is translated into a binding energy for the specific atomic orbital of an electron. Since each element has a unique set of energy levels, each element also has a unique set of binding energies of electrons present in these levels. The binding energy is described by the Eq. 2.3.

\[
E_B = h\nu - \phi - E_K
\]  

(2.3)

where \(E_B\) signifies the electron binding energy/eV, \(h\) is the Planck’s constant /eV.s, \(\nu\) is the frequency of incident X-rays /s\(^{-1}\), \(E_K\) stands for kinetic energy of electron /eV and \(\phi\) is the surface work function /eV.

For a given element, slight variations in the location of corresponding photoelectron peaks result from small shifts in core energy levels, related to the oxidation state and bonding of the atoms. These peaks shifting are typically on the order of 1-5 eV, and can be detected by most XPS spectrometers if having energy resolutions of 0.1-0.2 eV. XPS photoelectron peaks are named after the core level from which the electron has been emitted. For example, an electron from the iron 2p orbital gives a Fe 2p peak. Ionization of \(s\) orbital leaves only a single energy ionic state, while \(p\), \(d\) and \(f\) orbitals create two states of different energies, which appear in the spectra as two photoelectron peaks of different intensities. In the present work, XPS measurements were carried out with a Thermo Fisher ESCALAB with optimum energy resolution of approximately 0.5 eV.
2.3.7 Ultraviolet / Visible (UV-Vis) Absorption Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) uses light in the visible and adjacent UV ranges. At these wavelengths, the molecules undergo electronic transitions. In this technique, the light passes through the sample to be analyzed, and some of the light is absorbed by the sample. Thus, the sample has to be thin enough such that some of the light is transmitted. Another factor is that the sample must be placed onto a supporting substrate, for example, quartz, that is transparent at the wavelengths of light used. When visible or ultraviolet light is absorbed by the valence electrons of the material, these electrons are promoted from their ground states to higher energy excited states. The energies of the orbitals involved in electronic transitions have fixed values. The difference between the initial and final intensities is recorded. When plotted into a spectrum as wavelength against absorbance, the absorbance is defined by using the Beer-Lambert law given by Eq. 2.4.

\[ A = -\log_{10} \left( \frac{I}{I_0} \right) \]  

(2.4)

where \( A \) is the measured absorbance, \( I_0 \) is the intensity of the incident light at a given wavelength, and \( I \) is the transmitted intensity, respectively. The wavelength of maximum absorbance is a characteristic value, referred as \( \lambda_{\text{max}} \). In order to determine the optical band gap, the Tauc’s relation is used which is given by the Eq. 2.5.

\[ \alpha h\nu = A(h\nu - E_g)^n \]  

(2.5)

where \( \alpha \) is the absorption coefficient (2.303A/h), \( A \) is the absorbance and \( t \) is the width of the sample container, \( \nu \) is the frequency of photon, \( h \) is Planck’s constant and \( E_g \) stands for band gap. The value of the exponent \( (n) \) can have different values depending on the type of transition. For direct transition the value of \( n \) is taken \( \frac{1}{2} \) and for indirect band transition its value is taken 2.

The band gap is determined by extrapolating the linear part of a plot between \((\alpha h\nu)^2\) and photon energy \((h\nu)\). The intercept of this line with the energy axis gives the value of the optical band gap [18]. In the present work, a UV-visible spectrophotometer (Perkin Elmer Lamda 11) was used to monitor the changes in absorbance of the ablated solution, allowing the optical band gap to be calculated and its schematic diagram is shown in Fig. 2.12. After using the deionised water or ammonia solution as background, a small amount of the collected liquid suspension...
(containing ablated products) was pipetted into a quartz cuvette with a 10 mm pass length without dilution. The cuvette was shaken slightly by hand to ensure the NPs were dispersed uniformly.

Fig. 2.12 A schematic representation of UV-visible spectrophotometer.

2.3.8 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) is a phenomenon of light emission from any form of matter after the absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photoexcitation (i.e. photons that excite electrons to a higher energy level in an atom). Photoluminescence spectroscopy is a nondestructive, multipurpose, powerful optical technique to probe the electronic structure of materials. Light is focused onto a sample, where it is absorbed and imparts extra energy into the material in a process called photoexcitation. In this process excess energy can be dissipated by the sample through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is known as photoluminescence. Therefore, under optical excitation photoluminescence is the spontaneous emission of light from a material. This light can be collected and examined spectrally, temporally and also spatially. The intensity and spectral content of this photoluminescence is a direct measure of many important material properties.
Photo excitation allows electrons to move within the material into allowed excited states. When these electrons come back to their equilibrium states, the excess energy is released and may comprise the emission of light (a radiative process) or may not (a non radiative process) as shown in Fig. 2.13. The emitted light energy tells about the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. PL spectroscopy gives information only on the low lying energy levels of the investigated system. In semiconductor systems, the most common radiative transition is between states in the conduction and valence bands, with the energy difference being known as the band gap. During a PL spectroscopy experiment, excitation is provided by light with an energy greater than the optical band gap. The photo excited carriers are electrons and holes, which relax towards their respective band edges and recombine by emitting light at the energy of the band gap. Radiative transitions in semiconductors may also involve localized defects or impurity levels, therefore the analysis of the PL spectrum leads to the identification of specific defects or impurities, and the magnitude of the PL signal decides their concentration. The respective rates of radiative and nonradiative recombination can be estimated from a careful analysis of the temperature variation of the PL intensity and PL decay time. At higher temperature nonradiative recombination channels are activated and the PL intensity decreases exponentially. Thus photoluminescence is a process of photon excitation followed by photon emission and important for determining band gap, purity, crystalline quality
and impurity defect levels of semiconducting material. It also helps to understand the underlying physics of the recombination mechanism. In the present study, PL spectra have been recorded by a fluorescence spectrometer (Perkin Elmer LS-55).

### 2.3.9 Dielectric Measurements

In the present study, the dielectric constant (\(\varepsilon\)), dielectric loss (\(\tan\delta\)) and ac conductivity (\(\sigma_{ac}\)) measurements have been carried out as a function of composition and frequency (42Hz - 5MHz) using Hioki-36532-50 HI-Tester LCR meter. LCR meter set up is shown in Fig. 2.14. The sample material was pelletized using a circular shape dye of 10 mm diameter. The thickness of pellets was ~1 to 2 mm. For dielectric and ac impedance measurements, silver paste was coated on the opposite faces of the pellet to make parallel plate capacitor geometry. Every material exhibits a unique set of electrical features, which are dielectric properties such as permittivity, permeability, resistivity, conductivity, etc. A material is known as “dielectric” if it could store energy under the influence of an external electric field. In other words, materials, which are electric insulators or in which an electric field can be sustained with a minimum dissipation of power, are classified as dielectric materials. Basically, dielectrics are insulating materials. In dielectrics all the electrons are bound to their parent molecules and there are no free charges. Even with normal voltage or thermal energy the electrons are not released. Nonmetallic is also known as dielectrics which have high specific resistance and have a negative temperature coefficient of resistance.

![Fig. 2.14 Schematic diagram of the LCR meter setup.](image)
The dielectric properties of the material are essential to investigate the lattice dynamics in the crystal. It is important to note that permittivity and permeability are not constant. They can change with frequency, orientation, temperature, pressure, mixture, and molecular structure of the material.

(i) Dielectric constant ($K$) or Relative Permittivity ($\varepsilon_r$)

Dielectric constant is defined as the ratio of the capacitance ($C$) of a capacitor filled with the given material to the capacitance ($C_0$) of an identical capacitor in a vacuum without the dielectric material. The dielectric constant can also be defined as the ratio of the permittivity of the dielectric material ($\varepsilon$) to the permittivity of vacuum ($\varepsilon_0$). The dielectric constant, is therefore, also known as the relative permittivity ($\varepsilon_r$) of the material. Sometimes it is also referred as the absolute permittivity as given by Eq. 2.6

\[
\text{Dielectric constant } (K) = \varepsilon_r = \frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0}
\]  

(2.6)

Since the dielectric constant is just a ratio of two similar quantities, it is dimensionless and is always greater than 1. It is a measure of polarization in the dielectric material. It denotes a large-scale property of dielectrics without specifying the electrical behavior on the atomic scale. Dielectric constant was calculated using following formula [19] given by Eq. 2.7.

\[
\varepsilon' = \frac{C_p d}{\varepsilon_0 A}
\]

(2.7)

where $C$ is the capacitance, $d$ is the thickness of the pellet, $\varepsilon_0$ is the vacuum dielectric constant (permittivity of free space, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m) and $A$ is the area of the pellet.

(ii) Complex Relative Permittivity ($\varepsilon^*$)

Permittivity is determined by the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. Thus, permittivity relates to the ability of a material to transmit (or permit) an electric field. The response of normal materials to external fields generally depends on the frequency of the field. This frequency dependence reflects the fact that the polarization of the material does not respond instantaneously to an applied field. The response must always be causal which can be represented by a phase difference. For this reason
permittivity is often treated as a complex function. The response of materials to alternating fields is characterized by a complex permittivity as given by Eq. 2.8.

\[
\varepsilon^* = \varepsilon' - j\varepsilon''
\]  
(2.8)

where \(\varepsilon'\) is the real part of the relative permittivity (i.e. the dielectric constant), which is related to the stored energy within the medium; and \(\varepsilon''\) is the imaginary part of the relative permittivity, which is related to the dissipation (or loss) of energy within the medium.

(iii) Dielectric Loss (tan\(\delta\))

The dielectric loss is a loss of energy which eventually produces a rise in temperature of a dielectric placed in an alternating electrical field. In other words, it is a measure of the energy absorbed by dielectric. It is the electrical energy lost as heat in the polarization process in applied AC electric field. The ratio of imaginary part to the real part of the relative permittivity is known as dielectric loss or the dissipation factor \(D\) which is determined by Eq. 2.9.

\[
D = \tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]

(2.9)

The dissipation factor is measured along with the capacitance at room temperature using the LCR meter.

(iv) AC conductivity (\(\sigma_{ac}\))

In order to explain frequency dependence of electrical behavior of materials, ac conductivity measurement is often useful. The ac conductivity of the prepared samples is determined using the following relation.

\[
\sigma_{ac} = \varepsilon'\varepsilon_0 \omega \tan \delta
\]

(2.10)

In general, the total conductivity is given in terms of band conduction and the hopping parts [19] as given by Eq. 2.11.

\[
\sigma_{ac} = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_o}\right)^n\right]
\]

(2.11)

The Jonscher’s universal power law [20] is given as

\[
\sigma(\omega) = C \omega^n
\]

(2.12)
where $\sigma_{dc}$ is the DC conductivity, $\omega_c$ is the crossover frequency which separates the DC regime (plateau region) from decreased conduction, and $n$ is the dimensionless exponent and its value lies in the range (0 < $n$ < 1). Zero value of exponent ($n = 0$) corresponds to frequency independent electrical conduction or dc conduction and $C$ is a constant which has the dimension of electrical conductivity.

### 2.3.10 Superconducting Quantum Interference Device (SQUID)

Josephson junctions are commonly used in SQUID. It consists of a closed superconducting loop including one or two Josephson junctions in the loop's current. SQUID is capable of resolving changes of external magnetic field of $10^{-15}$ tesla. It does not detect directly the magnetic field from the sample. It functions as a highly linear current to voltage converter. SQUID magnetometer can be used to measure very small magnetic moment of the order of $10^{-6}$ emu [21]. In this magnetometer, a magnetic sample passes through a set of sensing coils which are superconducting coils separated by thin (> 30 Å) insulating layers called Josephson junctions. Cooper pairs in superconductors could tunnel through an insulating layer between the superconductors [22]. The pair tunneling creates a super current below the critical current and no voltage is produced across the junction. However, a voltage appears for currents greater than the critical value. The presence of the thin insulating layer typically restricts the value of the super current flowing in the coil to value less than $10^{-5}$ A. Most of the low $T_C$ SQUIDs are made from Niobium thin films that have a transition temperature around 9.25 K and are also mechanically very stable. Tunnel junctions are patterned from Nb/AlOx/Nb trilayers in which an AlOx barrier is formed by oxidization of a few nanometers of aluminum [23]. Fig. 2.15 represents a schematic of a Josephson junction.

There are two types of SQUIDs. The RF SQUID based on the AC Josephson effect contains a single Josephson junction which is placed into a superconducting loop. In case of the DC SQUID, two parallel Josephson junctions are connected with a superconducting loop which operate under the voltage state with a current bias. The sample is kept in superconducting pick-up coil that is attached to the actual SQUID. Since the magnetic flux through a superconducting ring is quantized, the sample will induce a super current in the pickup coils that will keep the flux at a constant value. Brian David Josephson in 1962 stated that the electrical current density through a
weak electric contact between two superconductors depends on the phase difference ($\Delta \phi$) of the two superconducting wave functions.

![Schematic diagram of the SQUID setup.](image)

Fig. 2.15 Schematic diagram of the SQUID setup.

Moreover, the time derivative of $\Delta \phi$ is correlated with the voltage across this weak contact. In a superconducting ring with one (so-called rf SQUID) or two (dc SQUID) weak contacts, $\Delta \phi$ is additionally influenced by the magnetic flux $\Phi$ through this ring. Therefore, such a structure can be used to convert magnetic flux into an electrical voltage. This is the basic working principle of a SQUID magnetometer. In the present study, all DC magnetic measurements as a function of field and temperature were carried out by superconducting quantum interference device (SQUID: Model MPMS®3; Quantum Design).

### 2.3.11 Photodegradation Experiment

The photocatalytic activity of the prepared samples was evaluated by photodegrading aqueous suspensions of organic dye under UV-light irradiation in a photochemical reactor as shown in Fig. 2.16. The photochemical reactor is made of Pyrex glass, which is equipped with a magnetic stirring bar, a water circulating jacket and an opening for supply oxygen.
The temperature of the reactor was maintained at 25°C throughout the experiment to avoid any thermal reaction. For each experiment, 180 mg of the catalyst was suspended in 180 mL of aqueous solution of dye and sonicated for 2 min to disperse the catalyst. After sonication, the solution was allowed to stir for 30 min in dark to maintain the adsorption-desorption equilibrium between catalyst and organic pollutants before irradiation. Irradiation was carried out in the presence of 125 W medium pressure mercury lamp, which is vertically placed inside the photochemical reactor and water is continuously circulated to eliminate IR-radiation as well as short wavelength UV-radiation. At certain time intervals, 5 ml aliquots were taken and centrifuged to remove the catalysts from the solution. Subsequently, the filtrate solution of dye was analyzed by a Perkin Elmer Lambda UV-Vis spectrophotometer (lambda 35). The degradation efficiency of the catalysts has been evaluated by the Eq. 2.13.

\[
\text{Degradation efficiency (\(\eta\))\%} = (1 - \frac{C}{C_0}) \times 100
\]

(2.13)

where \(C\) is the concentration of dye at different time intervals \((t)\) during degradation and \(C_0\) is the initial concentration of dye when adsorption-desorption equilibrium was attained.
References

Chapter 2


