Chapter 2

Experimental Methods and Characterization Techniques

2.1. Introduction

This chapter gives a brief description regarding the synthesis of nanotitania and principles underlying the various characterization techniques employed in this work.

2.2. Methods of Preparation

2.2.1. Synthesis of TiO₂ Nanostructures by Microwave Method

The general synthetic strategy adopted for the synthesis of titania nanostructures was using Titanium trichloride (TiCl₃) as Ti precursor by varying the precipitating agents under different pH conditions. The experimental details are as follows:

(1) Sample 1 (S1) - TiCl₃ (5 mL) was added drop by drop to 200 mL of 1.5 M NH₃ (pH =11) solution [1] and the irradiation was done for 20 min for complete precipitation.

(2) Sample 2 (S2) - TiCl₃ (5 mL) was added drop wise with continuous stirring to 200 mL of 5 M NaCl solution (pH = 7) [2] and the reaction mixture was irradiated for 60 min for complete precipitation.
(3) Sample 3 (S3) - TiCl₃ (5 mL) was added drop wise to 200 mL of 5 M NH₄Cl solution (pH = 5.9) and irradiated in a similar manner as in the previous case for 60 min.

The precipitated sol was irradiated in a microwave oven in on and off mode for different durations depending upon the precipitation rate in each case. The completion of the reaction is checked by noting the colour change (blue to colourless) of the reaction mixture. The white precipitate formed in each case was aged for 24 hours and washed thoroughly with distilled water. The precipitated titania was then dried in an air oven at 100°C and further calcined in a muffle furnace at 400°C for 4 hours.

2.2.2. Synthesis of Noble Metal Loaded TiO₂ Nanostructures

The microwave synthesized TiO₂ nanostructures having cubical (S1), spherical (S2) and rod like (S3) morphology were loaded with noble metal (1 wt% Au, 1 wt% Ag, 0.5 wt% Pd and 0.75 wt% Pt) using metal sol method [3]. For this a suitable amount of PVA solution (1 wt%) was added to an aqueous solution (0.1 mg noble metal/ml) of the respective noble metal salts, HAuCl₄, AgNO₃, PdCl₂ and H₂PtCl₆ under vigorous stirring. Then, a freshly prepared solution of NaBH₄ (molar ratio NaBH₄/Au = 4) was slowly added drop wise into the mixture. The TiO₂ samples were added after the pH was adjusted to 6.0 by NH₄OH or HCl solution. The mixture was stirred at 60°C for 3 hrs, then filtered and washed until no Cl⁻ was detected by AgNO₃ solution. After being dried at 100°C overnight, the samples were calcined at 550°C in air for 4 hrs [4]. The noble metal loaded on samples S1, S2 and S3 are represented as AuS1, AuS2 and AuS3 for gold, AgS1, AgS2 and AgS3 for
silver, PdS1, PdS2 and PdS3 for palladium and PtS1, PtS2 and PtS3 for platinum respectively.

### 2.2.3. Synthesis of Bare and Noble Metal Loaded TiO\textsubscript{2} Nanostructures by Hydrothermal Method

In this investigation hydrothermal route was also employed for the synthesis of three types of bare titania nanostructures (S1*, S2* and S3*) using the same reaction medium (1.5 M NH\textsubscript{4}OH, 5 M NaCl and 5 M NH\textsubscript{4}Cl). The reaction mixture was transferred into a stainless steel teflons lined autoclave kept at 200°C for 2.0 hrs. After the completion of the autoclaving treatment, the powders were filtered, washed with water and acetone, dried at 100°C overnight, calcined at 550°C in air for 4 hours and loaded with noble metal using metal sol method. The noble metal loaded on hydrothermally synthesized samples S1*, S2* and S3* are represented as AuS1*, AuS2* and AuS3* for gold, AgS1*, AgS2* and AgS3* for silver, PdS1*, PdS2* and PdS3* for palladium and PtS1*, PtS2* and PtS3* for platinum respectively.

### 2.3. Electron Microscopy

Electron microscopy is a rather straightforward technique to determine the size and shape of nanomaterials. Depending on the sample thickness a fraction of the electrons passes through the sample without suffering energy loss. As the attenuation of the beam depends on the density and thickness, the transmitted electrons form a two dimensional projection of the sample. Electrons are diffracted by the particles if these are favourably oriented towards the beam enabling one to obtain dark field images as well as crystallographic information. Electrons can collide with atoms in the sample and be scattered back; back scattering is more effective when the mass of the atom increases. If a region of the sample contains heavier atoms than the surroundings, it can be distinguished due
to the higher yield of the backscattered electrons. Auger electrons and X-rays are formed in the relaxation of core ionized atoms. Electrons excite characteristic vibrations in the sample, which can be studied by analyzing the energy loss suffered by the primary electrons. Many electrons lose energy in a cascade of consecutive inelastic collisions. Most of the secondary electrons emitted by the sample had their last loss process in the surface area.

The emission of a range of photons from UV to IR, called cathodoluminescence is mainly caused by the recombination of electron hole pairs in the sample. Thus the interaction of the primary beam with the sample provides a wealth of information on morphology, crystallography and chemical composition. Three types of electron microscopes are commonly used for the characterization of nonmaterial [5-8].

2.3.1. Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscope is one of the widely used techniques used for the characterization of nanomaterials. FESEM is a microscope that uses electrons rather than light to form an image. In FESEM, the surface of the solid sample is scanned in a raster pattern with a beam of energetic electrons. When these electrons strike the surface of the solid sample, back scattered, secondary and Auger electrons are emitted. Commonly used signals are back scattered and secondary electrons. The secondary electrons have mostly low energies (∼ 5-50 eV) and originate from the surface of the sample. Back scattered electrons come from deeper part and carry information on the composition of the sample, because heavy elements are more efficient scatterers and appear brighter in the image. As the electron strikes and penetrates the surface, a number of interactions occur that result in the emission of electrons and photons from the sample. The FESEM images
are produced by collecting the emitted electrons on a cathode ray tube (CRT). FESEM provides image of the morphology and microstructure of nanomaterials. It also provides detailed information of chemical composition and distribution.

There are many advantages to using the FESEM instead of a light microscope. The FESEM has large depth of field, which allows a larger amount of the sample to be in focus at one time. The FESEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the sample is relatively easy since most scanning electron microscopes only require the sample to be conductive.

The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation makes the FESEM one of the most heavily used instruments in research and development.

Under vacuum, electrons generated by a field emission source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. As a result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor.

The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

Nowadays, three-dimensional features can be observed due to the large depth of field available in the FESEM. The addition of energy dispersive X-ray
detector combined with digital image processing is a powerful tool in the study of materials, allowing good chemical analysis of the material. The FESEM is a major tool in materials science research and development [5-8].

2.3.2. Transmission Electron Microscope (TEM)
Transmission electron microscope is one of the widely used techniques used for the characterization of nanomaterials. TEM is an imaging technique whereby a beam of electrons is focused on to a specimen causing an enlarged version to appear on a fluorescent screen or on a photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938.

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. Transmission electron microscope uses electrons as ‘light source’ and their much lower wavelength make it possible to get a resolution a thousand times better than with a light microscope. We can see objects of the order of a few Angstroms. The possibility for high magnification has made the TEM a valuable tool in both medical, biological and materials research. Magnetic lenses guide the electrons, ‘light source’ at the top of the microscope emits the electrons that travels through vacuum in the column of the microscope. Instead of glass lens focusing the light in the light microscope, the TEM uses electromagnetic lens to focus the electrons into a very thin beam. The electron beam then travels through the specimen under characterization. Depending on the density, the electrons are scattered and disappear from the beam. At the bottom of the microscope, the unscattered electrons hit a fluorescent screen, which gives rise to a ‘shadow image’ of the specimen with its different parts
displayed in varied darkness according to their density. The image can be studied directly by the operator or photographed with a camera.

The contrast in the TEM image is not like the contrast in a light microscope image. A crystalline material interacts with the electron beam mostly by electron diffraction rather than absorption, although the intensity of the transmitted beam is still affected by the volume and density of the material through which it passes. The intensity of diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam. At certain angles the electron beam is diffracted strongly, sending electrons away from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern transmission electron microscopes are often equipped with specimen holders that allow the users to tilt the specimen to a range of angles in order to obtain specific diffraction conditions and apertures placed below the specimen allow the users to select electrons diffracted in a particular dimension.

A high contrast image can therefore be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons to pass through. This produces a variation in the electron intensity that reveals information on the crystal structure and can be viewed on a fluorescent screen, or recorded on photographic film or captured electronically. (5-8)

2.3.2.1. Applications of TEM

The TEM is used heavily in material science/metallurgy and in biological sciences. In both cases the specimens must be very thin and be able to withstand the high vacuum present inside the instrument.
For biological specimens, the maximum specimen thickness is roughly one micrometer. To withstand the vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding.

In material science/metallurgy, the specimens tend to be naturally resistant to vacuum, but must be prepared as a thin foil or etched, so some portion of the specimen is thin enough for the beam to penetrate. Preparation techniques to obtain an electron transparent region include ion beam milling and wedge polishing. The focused ion beams (FIB) is a relatively new technique to prepare thin samples for TEM examination for larger specimens. Because the FIB can be used to micro-machine samples very precisely, it is possible to mill very thin membranes from a specific area of a sample, such as a semiconductor or metal [5-8].

2.3.3. Scanning Probe Microscope (SPM)

The most recent developments in determining the surface structure are the atomic force microscope (AFM) and scanning tunneling microscope (STM). These techniques are capable of imaging the local surface topography with atomic resolution [5-8].

2.3.3.1. Atomic Force Microscope (AFM)

Atomic force microscope (AFM) or scanning force microscope (SFM) is the most generally applicable member of the SPM family, which is the key tool in nanotechnology research and development. It is based on minute but detectable forces between a sharp tip and atoms in the surface. In 1986, Gerd Binning invented the atomic force microscope (AFM). The tip is mounted on a flexible arm called cantilever, and is positioned at subnanometer distance from
the surface. When the tip is brought close to a sample surface the interatomic forces between them causes the cantilever to bend and this motion is detected optically by a laser beam which is reflected off the back of the cantilever. If the tip is scanned over the sample surface then the deflection of the cantilever can be recorded as an image, which in its simplest form, represents the three dimensional shape of the sample surface. If the sample is scanned under the tip in the X-Y plane, it feels the attractive or repulsive force from the surface atoms and hence it is deflected in the Z direction.

Atomic force microscope is used to identify a sample’s atomic level surface characteristics, including its magnetic and electrical properties and the topography. An AFM creates a highly magnified three-dimensional image of a surface. With the AFM it is possible to directly view features on a surface having a few nanometer-sized dimensions including single atoms and molecules on a surface. This gives scientists and engineers an ability to directly visualize nanometer sized objects and to measure the dimensions of the surface features.

2.3.3.2. Scanning Tunneling Microscope (STM)

Scanning tunneling microscope is one of the key tools in nanotechnology, which belongs to the SPM family. Scanning tunneling microscope was invented by Gerd Binning and Heinrich Rohrer in 1982. Scanning tunneling microscopy is used to study the properties of surfaces at the atomic level. The basic principle of STM is based on the tunneling current between the metallic tip, which is sharpened to a single atom point and a conducting material. A small bias voltage is applied between an atomically sharp tip and the sample. If the distance between the tip and the sample is large, no current flow. However, when the tip is brought very close without physical contact, a current flows across the gap between the tip and the sample. Such current is
called tunneling current which is the result of the overlapping wave functions between the tip atom and the surface atom. In the presence of small bias voltage, the electrons can travel across the vacuum barrier separating the tip and sample in the presence of small bias voltage. The magnitude of the tunneling current is extremely sensitive to the gap distance between the tip and the sample, the local density of electronic states of the sample and the local barrier height. With the help of STM, atomic information of the surface can be mapped out.

Scanning tunneling microscopy (STM) measures the topography of surface electronic states using a tunneling current that is dependent on the separation between the probe tip and a sample surface. It is typically performed on conductive and semiconductive surfaces. A common application consists of atomic resolution imaging, electrochemical STM, scanning tunneling spectroscopy (STS) and low current imaging of poorly conductive samples.

2.4. Spectroscopic Methods

The common spectroscopic methods that are used mainly for this work are fourier transform infrared spectroscopy, UV-visible spectroscopy and fluorescence spectroscopy [9-16].

2.4.1. Fourier Transforms Infrared Spectroscopy (FTIR)

Infrared spectroscopy is the subset of spectroscopy that deals with the Infrared part of the electromagnetic spectrum. As with all spectroscopic techniques, it can be used to identify a compound and to investigate the composition of the sample.

Infrared spectroscopy plays a major role in the study of inorganic compounds. The term infrared spectrum covers the range of the electromagnetic spectrum between 12800-10 cm\(^{-1}\). It is useful to divide infrared regions into three
sections: viz., near (12800-4000 cm\(^{-1}\)), mid (4000-2000 cm\(^{-1}\)) and far (200-100 cm\(^{-1}\)). The most useful IR region lies between 4000-670 cm\(^{-1}\) and the region between 1430-910 cm\(^{-1}\) is known as the fingerprint region.

The far infrared lying adjacent to the microwave region has low energy and may be used for rotational spectroscopy. The mid infrared may be used to study the fundamental vibrations and associated rotational-vibrations structure, whilst the higher energy near infrared region can excite overtone or harmonic vibrations.

In a molecule, the atoms are not held rigidly apart. Instead they can move, as if they are attached by a spring of equilibrium separation. This bond can either bend or stretch. If the bond is subjected to infrared radiation of a specific frequency, it will absorb the energy, and the bond will move from the lowest vibrational state, to the next highest. In a simple diatomic molecule, there is only one direction of vibration, stretching etc. This means there is only one band of infrared absorption. Weaker bonds require less energy, as if the bonds are springs of different strengths. If there are more atoms, there will be more bonds, and therefore more modes of vibrations. This will produce a more complicated spectrum. For a linear molecule with ‘n’ atoms there are 3n-5 vibrational modes, if it is nonlinear, it will have 3n-6 modes. For a molecule to absorb IR radiation, the vibrations within the molecule must cause a net change in the dipole moment of the molecule. The alternating electric field of the radiation interacts with the fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule, then radiation will be absorbed, causing a change in the amplitude of the molecular vibration. Examination of IR spectra gives information about the metal-oxygen bond absorption in the present work [10].
2.4.2. UV-visible Spectroscopy

Ultraviolet and visible spectroscopy is a reliable and accurate analytical laboratory assessment procedure that allows for the analysis of a substance. Specifically, ultraviolet and visible spectroscopy measures the absorption, transmission and emission of ultraviolet and visible light wavelengths by matter.

Ultraviolet and visible spectroscopy is used to study molecules and inorganic ions in solution as well as in the solid state. Although they are distinct regions of the electromagnetic spectrum, the ultraviolet and visible region of the electromagnetic spectrum are linked in UV-visible spectroscopy because the similarities between the two regions allow many of the research techniques and tools to be used for both region. Many molecules absorb ultraviolet or visible light. The wavelength that is absorbed depends on the chemical composition and the intensity of the band is directly proportional to the concentration of an absorbing group or molecule. UV-visible spectroscopy enables the characterization of functional groups in a molecule as well as the determination of their concentration.

Ultraviolet and visible light comprises only a small portion of the wide ranging electromagnetic spectrum. Although lower in frequency and therefore lower in energy than cosmic, gamma or X-rays, ultraviolet and visible light are of a higher frequency and therefore of higher energy, than infrared, microwave and radio waves.

The ultraviolet band of the electromagnetic spectrum is further separated into three region termed UV-A, UV-B and UV-C. UV-A is generally considered to be light with wavelength between 320-400 nm; UV-B wavelengths are
generally considered to be those between 290-320 nm; UV-C wavelength usually fall between 200-290 nm.

When ultraviolet or visible light strike atoms or molecules they can either bounce off or cause electron to jump between energy levels. Absorption of ultraviolet or visible light electromagnetic radiation causes electron to move from lower energy levels to higher energy levels.

Absorption of ultraviolet or visible light electromagnetic radiation causes electron to move from lower energy levels to a higher energy levels. Ultraviolet-visible absorption spectroscopy measures the absorption of ultraviolet or visible light because the spectrum of an atom or molecule depends on its electron energy levels. The three types of electronic transitions observed in UV-visible spectroscopy are as follows

1. Transitions involving $\sigma$, $\pi$ and $n$ electrons
2. Transitions involving charge transfer electrons
3. Transitions involving $d$ and $f$ electrons

When atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered to have discrete energy levels.

The basic principle of UV-visible spectroscopy is the Beer-Lamberts law which states that “when a beam of monochromatic light radiation is passed through a solution of the absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution” [12, 17].
2.4.3. **Photoluminescence Spectroscopy**

Photoluminescence spectroscopy (PL) is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to 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 [12-17].

2.4.3.1. **Uses of Photoluminescence Study**

2.4.3.1.1. **Band Gap Determination**

The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the band gap. Band gap determination is particularly useful when working with new compound semiconductors.

2.4.3.1.2. **Impurity Levels and Defect Detection**

Radiative transitions in semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.
2.4.4. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, 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 vibrational 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. Historically, Raman spectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs either axial transmissive (AT), Czerny-Turner (CT) monochromator or Fourier transform (FT) spectroscopy and CCD detectors.

There are a number of advanced types of Raman spectroscopy, including surface-enhanced Raman, resonance Raman, tip-enhanced Raman, polarised
Raman, stimulated Raman (analogous to stimulated emission), transmission Raman, spatially-offset Raman and hyper Raman.

The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman effect, which is a form of light scattering, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman effect, which is a light scattering phenomenon, should not be confused with absorption (as with fluorescence) where the molecule is excited to a discrete (not virtual) energy level.

If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an Anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction [10, 12].

2.5. X-Ray Diffractometry

The physical methods and techniques that are used to analyze and study crystalline substances are quite different from those that are used in other branches of chemistry. Conventional thermal analysis techniques like TG and DSC alone can’t identify the reaction products that result from each thermal
event and thus cannot fully characterize the reaction. The identification of these products requires analytical techniques like X-ray diffraction.

X-rays are high energy electromagnetic radiations. They have energies ranging from about 200 eV to 1 MeV, which puts them between γ rays and ultraviolet radiation in the electromagnetic spectrum. There are no shape boundaries between different regions of the electromagnetic spectrum and that the assigned boundaries between regions are arbitrary. Gamma rays and X-rays are essentially identical, γ rays being somewhat more energetic and shorter in wavelength than X-rays. Gamma rays and X-rays differ mainly in how they are produced in the atom [17-19].

2.5.1. Production of X-rays
X-rays are produced in an X-ray tube consisting of two metal electrodes enclosed in a vacuum chamber. Electrons are produced by heating a tungsten filament cathode. The cathode is at a high negative potential, and the electrons are accelerated towards the anode, which is normally at ground potential. The electrons, which have a very high velocity, collide with water cooled anode. The loss of energy of the electrons due to the impact with the metal anode is manifested as X-rays. Actually only a small percentage of the electron beam is converted to X-rays; the majority is dissipated as heat in the water cooled metal anode.

The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction is widely used in two main areas viz., for the fingerprint characterization of crystalline materials and for the determination of structure. When an X-ray beam strikes a crystal surface, a portion of the beam is scattered by the atoms at the surface. The unscattered beam penetrates into the second layer of atoms where again a fraction is scattered and the remainder passes
on to the third layer. Interference between the scattered rays from two planes can occur. The cumulative effect of this scattering from the regularly spaced centers of the crystal is diffraction of the beam. Bragg considered the diffraction of X-rays from the crystals as a problem of reflection from atomic planes. He obtained an expression for the condition for maximum reinforcement of the diffracted X-rays. The Bragg’s equation is \( n\lambda = 2d \sin \theta \), where \( d \) is the interplanar spacing, \( \theta \) is the glancing angle, the angle at which the rays impinge on the surface of the crystal, \( \lambda \) is the wavelength of X-rays used and \( n \) is an integer and can have values 1, 2, 3 etc.

2.5.2. X-ray Powder Diffraction

For investigating powder sample, the X-ray powder method is most suitable.

A monochromatic beam of X-rays is allowed to fall on the sample. The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the \( K_{\alpha} \) radiation is 1.5418 Å. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation, \( 2\theta \). The diffracted rays enter the detection chamber and the intensity is plotted against the diffraction angle. The results are usually obtained in the form of a chart of intensity versus glancing angle.

An X-ray powder diffraction pattern thus consists of a set of lines or peaks, each of different intensity and position. For a given substance the line positions are essentially fixed and are characteristic of that substance. From the peak positions and the peak intensities, the composition of the sample can be estimated. Each crystalline substance has its own characteristic powder diffraction pattern, which can be used for its identification. The powder diffraction patterns of most known inorganic solids are included in an updated version of the powder diffraction file (PDF) known as the JCPDS file. The pattern obtained from the sample is
compared with the standard pattern from the JCPDS file and the unknown can be identified rapidly.

2.5.3. Particle Size Determination

The X-ray diffraction pattern consists of a series of peaks. The peak intensity is plotted on the ordinate (Y-axis) and the measured diffraction angle $2\theta$, along the abscissa (X-axis). Each peak in the diffraction pattern corresponds to X-rays diffracted from a specific set of intensities. The intensity is proportional to the number of X-ray photons of a particular energy that have been counted by the detector for each angle $2\theta$. The position of the peaks in an X-ray diffraction pattern depends upon the shape and size of the unit cell of the material. This enables us to determine the structure and lattice parameter of the material. As the symmetry of the crystal structure decreases, there is an increase in the number of peaks. For low values of $2\theta$ each reflection appears as a single sharp and for large values each reflection consists of a pair of peaks.

The particle size of the material can be calculated by the Scherrer equation

$$d = \frac{0.89\lambda}{\beta\cos\theta}$$

Where $d$ is the particle size, $\lambda$ is the wavelength of X-rays used, $\beta$ is the full width of the peak at half maximum [14-19].

2.6. BET Surface Area Analysis

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material [20].
Brunauer, Emmett Teller method is used to measure total surface area of the nanosized materials. In this technique, the amount of nitrogen adsorbed at constant temperature ($200^0\text{C}$) by a given weight of sample is measured using a surface area analyzer. The volume of the nitrogen adsorbed in a monolayer $V_m$ is calculated from the BET equation

$$\frac{P}{V_0(P_0 - P)} = \frac{1}{V_mC} + \frac{P(C - 1)}{V_mC P_0}$$

where $P = $ Nitrogen pressure

$P_0 = $ Vapour pressure of nitrogen at the temperature of the liquid $N_2$ calculated at STP

$V_0 = $ Volume of nitrogen adsorbed at pressure $P$ and temperature of the liquid $N_2$ calculated at STP

$C = $ Constant related to the difference between the heat of liquefaction of the adsorbate

A plot of $\frac{P}{V_0(P_0 - P)}$ against $\frac{P}{P_0}$ will give $\frac{C - 1}{V_mC}$ as slope and $\frac{1}{V_mC}$ as intercept, from which $V_m$ can be calculated.

Knowing the value of $V_m$, surface area ($S$) can be calculated by using the equation

$$S = \frac{N_A V_m A}{22414}$$

where $N_A = $ Avogadro number

$A = $ Area occupied by one $N_2$ molecule ($1.6 \times 10^{-20} \text{m}^2$)

$V_m = $ Monolayer volume at STP
References


