Experimental and characterization techniques

2.1 Introduction:

Recently nanostructured semiconducting materials are synthesized by both physical and chemical methods such as sol-gel [1], pyrolysis [2], sputtering [3], hydrothermal method [4-5], microwave accelerated hydrothermal method [6-7], high temperature calcine method [8] and acid precipitation method [9-12]. The structural and electronic properties, and primary particle size distribution are majorly dependent on the preparation method. Lot of efforts have been devoted in synthesis of WO$_3$ nanostructures with various implementation techniques, the precipitation approach stands out as a promising route owing to energy conservation, low temperature technique having simple experimental setup. The advantages of precipitation method are greater homogeneity, greater reactivity, high purity and fine particle size.

For tuning the morphology and to obtain hierarchical structures hydrothermal synthesis is a superior technique for low-temperature production of nanomaterials. Hydrothermal process is well known as a morphology oriented route to obtain thousand morphologies in thousand autoclaves, only by varying hydrothermal conditions, and hence has become effective and popular method. To modulate the crystal growth wide choice of structure directing agents are available including inorganic salts, organic acids, polymers and surfactants for obtaining the hierarchical structures.

Secondly the developed material needs to be characterized in a systematic way, with the help of diverse array of characterization tools. The correct interpretation of experimental results will lead to better understanding of the developed material and thereby its applications. In the following, we shall discuss the most often used characterization techniques and the specific consequences that nanostructure induces in their corresponding physicochemical observables. The basic principles underlying in these techniques are described briefly. The characterization of any material would consist of phase analysis, compositional characterization, structural explanation, micro-structural examination and surface analysis, which have strong aspect on the properties of materials synthesized. This became a cause for an exposure of design of advanced techniques in the field of materials science. In the present work pristine and doped tungsten oxide nanocrystalline powders were synthesized facile hydrothermal and precipitation
route. Screen printing technique was used to prepare thick films from these nanopowders. Gas sensing measurements of the thick films towards various analyte gases at different temperatures was carried out by a locally fabricated unit.

This chapter gives an account of the synthesis of WO$_3$ nanopowder and thick films preparation employed to obtain the WO$_3$ nanopowder and the characterization techniques used for analyzing the various physical, chemical properties. These characterization techniques are XRD, TGA-DTA, FESEM/EDS elemental mapping, TEM, HRTEM and SAED.

2.2. Procedure details for acid precipitation method:

So far many efforts have been done in synthesizing WO$_3$ nanostructure by various techniques, and the precipitation method appears to have an excellent potential to energy conservation, low temperature synthesis and easy experimental setup. The method is quite versatile since almost all mixed metal oxides can be prepared just by selecting appropriate metal salts and precipitating agents. In this method, sodium tungstate ions are precipitated by adding nitric acid and acidified with sulphuric acid.

![Figure 2.1 Process sequence of precipitation method](image-url)

**Figure 2.1 Process sequence of precipitation method**
2.3 Procedure details for hydrothermal method:

A hydrothermal apparatus is also commonly known as an autoclave. The design of the autoclave varies according to the requirement of the user and it also depends on the nature of material and experimental conditions under investigation. Basically, an ideal autoclave in the hydrothermal unit should have the following characteristics such that no machining or treatment is needed after each experimental run.

a) Inertness to acid, bases and oxidizing agents.

b) Assembly and dis-mantle should be easy.

c) Leak-proof within the working temperature and pressure.

d) Stable and rigid enough to bear the elevated pressure and temperature.

e) Long working cycles durability.

In order to guard the autoclave from being attacked by the corrosive solvent used in the experiment, most autoclave is fitted with a appropriate lining for its inner wall or liners placed in the autoclave separately. There are various types of material that can be used as the reactor linings, such as titanium, silver, Teflon, Pyrex, quartz and so on. The choice of the liner precisely depends on the experiment temperature, pressure and the solvent used. For the high purity crystals growth in extensive corrosive media, containers of Teflon called Teflon liners are used. It is also the most commonly utilized lining material for materials handing out under moderate hydrothermal conditions for pressure below 250 bars and temperature below 300°C. The home-made autoclave and the separate liner employed in our experiment is made of 316 stainless steel and a Teflon liner (Figure 2.2). The closure of the Teflon beaker is specially machined to guarantee that tension will be given to seal the beaker when the metal lid is fastened. The detachable Teflon liner fits comfortably into the autoclave without leaving space. In-situ pressure or temperature monitoring system is not provided with the system in use. Temperature gradients are noticeably lesser in the liners comparing to the autoclaves without liner. This variation becomes further prominent when Teflon liners are utilized. The experimental temperature mentioned in the thesis is the nominal temperature of the oven.
2.4 Thick-film technology:

Thick film technology was launched for about three decades before as a technique of preparing hybrid circuits. Hybrid microelectronics based on thick and thin film technologies has shown rapid growth in the previous few years and is rising as an important technique for a small-scale representation of electronic systems. Its main features are lower cost of design and production, higher frequency, power capability and more give in design and fabrication. These attractive features of thick film technologies has become extremely popular and assured special applications where size reduction necessity is not as much as in monolithic IC’s but the performance requirements are stringent. The thick film process is more broadly used than thin film technique in hybrid microelectronics, because it requires very smaller initial investment, but produces circuits with superior performance for all common applications. over the years, several major changes are going through the thin film and thick film technologies. There have been numerous new developments in the methods of deposition of films.

Thick-film technology is very stable in case of, on-glass and ceramic compositions in critical situations such as elevated temperature or freezing environments. Thick-film technology is reliable for packages, excess-reliability modules and electronic devices such as sensors. Conventional thick-film technique commonly uses 96% alumina substrates that are pre-fired. Manufacturing procedure consists of sequentially printing, drying and sintering process of a chain of functional material layers such as dielectrics, conductors, sensor materials, resistors and in excess of shiny coating. By using screen-printing deposition of the layers is most often carried out in a bulk volume and economic production. It is an effective method for
prototypes supply. Each layer is printed with a paste comprising of a functional material and a temporary organic vehicle. The technology used for sensor fabrication plays a significant role in order to improve the sensor characteristics like gas response, selectivity, and response and recovery time. Mainly three methods are being used for sensor fabrication viz. pellets, thick film, and thin film. Amongst these, thick film technology is commercially employed as compared to other technologies due to its simplicity in fabrication, low cost and compactness. Thick film technology was introduced to produce hybrid circuits which have found application in electronics industry.

‘Thick film’ (more correctly ‘printed-and-fired’) technology, uses resistive, conductive and insulating pastes containing an inorganic binder, deposited on alumina substrate by screen printing. The films are typically in the range 5–20 µm thick. In screen-printing technology, ink of the sensor functional material is formulated in the paste form by using a temporary binder (organic vehicle), a permanent binder (inorganic) along with the functional material to obtain the adhesion of the film on to the substrate. The paste is printed on an insulating substrate (alumina) which can withstand at higher temperatures using screen-printing. The procedure for fabricating the Thick-film Sensor has been described by the following subsections as:

(i) Paste formulation
(ii) Substrates
(iii) Screen printing

(i) Paste formulation:

For paste formulation, nanocrystalline tungsten oxide powders synthesized by precipitation method and hydrothermal method is employed as a functional material, Ethyl Cellulose (EC) is used as an organic temporary binder and Butyl Carbetol Acetate (BCA) as an organic vehicle which facilitates easy printing. A blend of solvents and polymers or resins commonly designated as an organic vehicle that are required to provide a homogeneous suspension of the particles of the functional materials appropriate for the fabrication of thick film. The vehicle is temporary, sacrificial ingredient which should be evaporated later to dry the deposit, a surface-active agent to permit the solid particles are moisten by the vehicle and properly dispersed in it. The paste formulation is a two step process. In the first step, the functional material and the temporary binder were mixed together with the organic vehicle. The
second step of the process is a thorough mixing of these components to produce homogeneous ink or paste in order to print on an insulating alumina substrate. All the required materials are taken in the desired weight proportion EC is mixed and BCA is added drop wise until the required viscosity is achieved.

Thick film has two phases viz. solid and liquid phase. As indicated above, the functional material and permanent binder form the solid phase whereas organic vehicle forms the liquid phase. The liquid phase of the paste controls the thixotrophy of the paste depending upon the extent of added organic part in its formulation i.e. on solid to liquid ratio.

(ii) Substrates:

The substrates used in thick film technology serve following functions.

- To support the circuit and to provide means for mounting.
- To protect the circuit from mechanical damage.
- To dissipate heat
- To provide electrical separation and chemical inertia.

The material properties of interest, for substrate applications are resistivity, relative dielectric constant, surface characteristics, strength, chemical reactivity, thermal conductivity, thermal expansions coefficient and dimensional stability.

The group of polycrystalline ceramics satisfies all above properties. The barium titanate, beryllium oxide and aluminum oxide are popularly used substrates materials. Because of high thermal conductivity beryllium oxide ceramics have high relative dielectric constant and it is achievable to make high capacity devices using substrate as dielectric. The aluminum oxide ceramics combine to give the best overall performance and are the most favorable ones. The unglazed alumina substrates having 96% purity are mostly used in the thick film industry.

In the present work alumina substrates (96% pure, Kyocera, Japan) were used for the deposition of thick films. Substrates were cut into (10 x 20 mm$^2$) size. The procedure for cleaning substrates is given below:

a) Substrates were immersed in chromic acid for half an hour and washed thoroughly by distilled water to remove the acid.

b) Again substrates were rinsed with distilled water.
c) Finally substrates were cleaned using ultrasonic cleaning for twenty minutes and dried under IR lamp.

(iii) Screen printing:

The screen printing is a method of thick film deposition on the substrate by forcing a paste through the screen. The screen serves an important part in the thick-film hybrid technology. It is accountable for the edge definition of the printed pattern and for the uniform thickness of the deposited films on the substrate surface. A few variables like thread diameter and mesh count in the screen has a vital role. Screen’s mesh is made of a monofilament nylon, monofilament polyester or stainless steel [13]. Screen is prepared by pasting an appropriate nylon cloth tighten on wooden frame with appropriate glue. The tension on the nylon cloth is a variable parameter which affects the pattern in terms of line definition and thickness of the print. There are various types of screens available depending on the number of mesh openings, viz. 140, 240, 360, 400 etc., per linear inch. Use of nylon cloth of 140 mesh count is preferred in the present experimentation.

In order to produce the film on the substrate, the paste is forced through the mesh openings by using a soft material with hard edge blade called a “squeegee”. Material of the squeegee must be compatible with water and solvents used in the paste. It should neither dissolve in water, nor react with the paste materials. Polyurethane, neoprene, viton are the most popular materials used for making the squeegee. Printing board forms a basic support for housing the screen and the substrate. The stencil frame was fixed to the rectangular wooden bar with a C-clamp.

A gap of 3 mm was kept between the substrate and the stencil. Appropriate amount of the paste was kept on the stencil, just outside the pattern. Squeegee was brought to get in touch with the stencil at an angle of 45°. As the squeegee moves over the resistive pattern, due to the thixotropic property of the paste and due to the applied pressure by the squeegee, the viscosity of the paste decreases and the paste is forced so that it can pass through that stencil to get deposited on the substrate. The squeegee is removed, thixotrophy is regained and the pattern is printed with required dimensions of 10 × 20 mm². These prints were allowed to settle, dry and were fired further. Figure 2.3 depicts the schematic drawing of the screen printing cycle.
2.4.1 Advantages of thick film technology:

The benefits of thick film technology are:

1) Its simplicity in fabrication and cost effective.
2) Porosity in the films can easily achieved which is very important parameter for the sensor performance.
3) Its ability to prepare thick-film integrated circuits in miniaturized packages.
4) This technology has ability to support other structures upon which other sensor materials can be deposited. For example, on one side of substrate gas sensor film can be deposited and on other side heater can be deposited.
5) Thick films are more robust, less susceptible to contamination and more sensitive.
6) Thick film technology offers important advantages such as high productivity and automation, also the time required to pass from prototypes to products being very short.
7) The thick film approach has contributed to the sensor development itself as a prime sensing element. Apart from gas sensors, these resistors are used as a strain gauge, temperature sensors, and magnetic sensors.

After deposition, the solvent in the vehicle is removed by drying, which allows the easy handling of sensor. The final operation is firing at an appropriate temperature. During firing, as temperature increases, particle to particle sintering and alloying occurs and this gives rise to decrease in resistivity of the composite.

Figure 2.3: Schematic diagram of the screen printing.
The electric contacts are prepared on the films by using conducting ink/paste. The conductor inks/paste generally contains noble metals or their alloys, like gold, platinum, silver or palladium.

2.5 Experimental set-up for gas sensing measurements:

The dynamic set-up for the examination of gas sensing properties used in our laboratory is shown in Fig. 2.4. It consists of a test gas chamber owing volume of two liter in which a sensor in the type of thick-film is rested on the sample holder. The temperature of the sensor can be regulated through a temperature controller using a heating coil and a thermocouple. Change in resistance of thick film sensor for the specific test gas was measured by digital multimeter (Tektronix DMM 4050 6-1/2 digit precision multimeter) at its pre-requisite concentration. The sensitivity for the pristine WO₃ and Ru decorated and GO-doped WO₃ sensors was measured using an indigenous system and it is presented in Fig. 2.4. The sintered thick films of pure and doped samples were examined for studying the gas sensing properties. The temperature of the system was controlled from room temperature to 350°C within the precision of ±1°C, and the electrical resistance was calculated. Conducting silver paste was applied to make electrical contacts on both ends of thick film.

![Figure 2.4 Experimental set-up for the measurement of gas sensing properties.](image-url)
Two probe ceramic sample holder was used to mount the thick film in an insulated glass tube chamber which was installed coaxially in a tubular furnace. The film area was kept constant for all samples prepared for the measurements. In order to inject the test gas, Teflon plunger plastic syringe of 2 ml and 1 ml (with least count of 0.1 ml) capacity was utilized. The known amount of test gas was interjected in the gas-mixing chamber so that their required part per million (ppm) levels is attained. The resistance of the sensor was calculated as a function of time at different operating temperatures and concentrations of test gas. The sensor response of all samples were investigated for different reducing gases, viz. acetone, ethanol, ammonia, xylene, triethanolamine, diethanolamine, propanol and hydrogen sulphide, and for oxidizing gas NO\textsubscript{X} in temperature range 100-350\textdegree C under identical experimental conditions. All the gas responses were measured at 100 ppm of test gas to achieve maximum efficiency at an operating temperature (i.e. optimum temperature) whereas the selectivity is determined at the 1 ppm of test gas.

The most important experimentations are the optimization of (i) sensitivity (ii) the operating temperature, (iii) active region (ppm). The highest gas sensing performance uniqueness of the material prepared under the optimized processing parameters are further confirmed by using different measurements viz. repeatability, gas concentration range and response and recovery time.

The gas response (S %) of the sensor to a reducing test gas was calculated using equation (2.1) as:

\[ S(\%) = \frac{(R_a - R_e)}{R_a} \times 100 \]  

(2.1)

And the percent gas response (S %) to an oxidizing test gas was calculated using equation (2.2) as:

\[ S(\%) = \frac{(R_a - R_g)}{R_g} \times 100 \]  

(2.2)

Where \( R_a \) is sensor resistance in air and \( R_g \) is sensor resistance in test gas.
A reducing molecule (e.g., CO, H₂) or atom adsorbed on the surface of sensor, injects electrons and acts as a surface donor. The adsorption can be connected with dissociation or decomposition of test gas or vapor. The reverse phenomenon is seen during introduction to oxidizing gases like that of NOₓ. The resistance of the thick-film decreases in n-type semiconductors, when the sensor is in touch with reducing gas or vapor whereas the resistance increases when the sensor is in touch with the oxidizing gas or vapor is described in Fig. 2.5.

2.6 Experimental set-up for photocatalytic experiment:

![Figure 2.6: Set up for photocatalytic experiment](image-url)
A glass beaker with WO$_3$ catalyst containing 100 ml of stock was placed in direct sunlight. Constant stirring of the solution was achieved by using a magnetic stirring bar, and the beaker was capped to minimize evaporation of the solvent. The set-up is as presented in Figure 2.6. Prior to irradiation, the solution was kept in dark for 60 minutes with magnetically stirring to improve adsorption of the dye onto the catalyst surface.

2.6.1 Photocatalytic degradation:

The photocatalytic activity of pure and doped WO$_3$ samples were assessed by the degradation of Rhodamine B. The reaction suspension was formulated by adding 0.3 g catalyst powder into 100 ml of Rhodamine B aqueous solution (5 mg L$^{-1}$) at room temperature. Before placing the solution in sunlight, the suspension was constantly stirred in dark for 60 min to attain an adsorption–desorption equilibrium and subsequently, the solution was transferred in a beaker with magnetic stirring and irradiated in sunlight. The period of the experiment was between 11:00 and 14:30 during the months of October 2017. The average intensity of natural sunlight was measured using digital lux meter and was found to be $8.95 \times 10^4$ lux. At a consistent time interval sample aliquots were withdrawn from the reaction suspension, the mixture was centrifuged to determine the dye concentration of residual solution during the degradation was determined by colorimetry using a Shimadzu UV-2500 spectrophotometer. Concentration of Rhodamine B changes from its characteristic absorption band at 553 nm was observed. The efficiencies of decolorization of the dyes were evaluated by the equation:

$$\eta = \frac{(C_i - C_f)}{C_i} \times 100$$

(2.3)

Where $C_i$ and $C_f$ symbolize concentration of dye in solution prior to and after irradiation, respectively. Effect of various parameters such as the initial concentration, irradiation time of Rhodamine B, decolourization efficiency were also investigated.

2.7 Characterization techniques:

2.7.1 Thermal analysis:

It is a characteristic material property that represents the stability of the material as function of temperature. The crucial parameters for this experiment includes the atmosphere,
sample vapor pressure, gas flow rate, heating rate, thermal contact of sample with crucible and sensor, etc. As an effect of temperature, the sample undergoes physical conversion like phase transitions that requires more/less heat flow in comparison to reference to maintain same temperature in both working and reference. The flow of heat depends on the exothermic or endothermic nature during the process. When the sample withstands absorption of heat followed by phase transitions, it is endothermic process. On the other hand, heat required is less during exothermic processes to increase the sample temperature. The heat flow difference between the reference and sample measures the quantity of heat released and absorbed. Thermogravimetry (TG) and Differential Scanning Calorimetric (DSC) analyses of the WO₃ nanopowders were carried out up to 1000°C in a METTLER model TGA 1 SF/1100/358, thermal analyzer with heating rate of 2°C.

**Thermogravimetry / Differential Thermal Analysis (TG-DTA):**

Thermogravimetric curves are distinctive for a specified compound or systems because of the exceptional series of physiochemical reactions, which take place over specific temperature ranges and at rates which are function of molecular structures. Difference in weight are due to rupture or formation of different physical as well as chemical bonds at high temperatures which lead to the formation of volatile products or the formation of massive reaction products. From these curves data is obtained with reference to the thermodynamics and kinetics of the various chemical reactions, reaction mechanism and the intermediate and final reaction products. The typical temperature range is from room temperature to 1200°C with inert or reactive atmospheres. The alteration in weight process is due to release or absorb of energy which is measurable by DTA but not all energy-alteration process is accompanied by change in weight. This variation in two techniques allows a clear difference between physical and chemical changes when the samples are exposed to both DTA and TGA tests.

In general, each substance will give a DTA graph whose shape, number and position of the various endothermic and exothermic features serve as a means of qualitative and quantitative identification of the substance. The sample temperature lags behind the reference temperature while an endothermic change arises because of the heat absorbed in the sample.
The commencement point for a phase alteration or chemical reaction is the point at which the curve first diverge from the base line. When the transition is complete, thermal diffusion brings the sample back to equilibrium quickly. The temperature at which the reaction is completed is called as peak (or minimum) temperature. Endotherms commonly represent physical rather than chemical changes, sharp endotherms are investigative of crystalline rearrangements, fusion, or solid-state evolution for comparatively pure materials. Exothermic behavior (without decomposition) is associated with the reduction in enthalpy of a phase or chemical system. Narrow exotherms usually designate crystallization (ordering) of a metastable system, whether it is super cooled organic, inorganic, amorphous polymer or liquid, or annealing of stored energy ensuing from mechanical stress. Broad exotherms indicate chemical reactions, polymerization or curing of thermosetting resins. Exotherms with decomposition may be either narrow or broad conditional on kinetics of the behavior. The area of exotherms or endotherms can be utilized to determine the heat of reaction or the heat of phase formation [14].

Figure 2.7: Schematic diagram of the TGA-DTA.
Differential Thermal Analysis (DTA):

DTA may be explained as a technique for obtaining the temperature difference in between a sample and a reference material, as both the specimens are subjected to similar temperature regimes at a controlled rate, in a hot or cool environment. In DTA, the reference material is thermally inert the temperature of a sample and reference material are measured as a function of temperature (usually sample temperature). The sample undergoes phase transition which results either liberation or absorption of energy with corresponding variation of its temperature from that of reference. This differential temperature (ΔT) against the programmed temperature (T) at which the whole system is being changed yields the temperature of transitions and the nature of the transition such as exothermic or endothermic [15]. Using TG/DTA studies, melting point, crystallization behavior, glass transition temperature, thermal stability, dehydration, oxidation, phase-transition, specific heat, reaction kinetics etc. are usually determined.

2.7.2 X-Ray powder Diffraction analysis (XRD):

The characteristic property of the synthesized nanopowders and mixed oxide nanocomposites was determined the different analytical techniques. A brief working principle and their utilization for the aforesaid materials are given systematically.

X-ray powder diffraction (XRD) is a non-destructive analytical technique typically applied for the characterization of crystalline materials [16-19]. By this method quantitative analysis, phase identification and the evaluation of structure imperfections of powdered solid samples are successfully determined. Identification of unknown substances can be achieved by powder diffraction, by comparing diffraction data with the data from an international data base. In fact each crystalline solid produces distinctive diffraction patterns. The technique may be also useful to distinguish heterogeneous solid mixtures, to determine comparative abundance of crystalline powders and, if coupled with one of the refinement techniques (e.g. the Rietveld refinement), can provide quantitative structural information.

X-ray diffractions are produced based on the constructive interference between monochromatic x-ray radiations and a powdered sample. X-ray diffraction works on the principle of Bragg’s Law. Mathematically, let us assume an X-ray beam incident on P1 and P2,
a pair of parallel planes which is separated by distance ‘d’ (interplanar spacing). Both of the incident rays makes an angle of θ with these planes. As a result, maximum intense reflection of beam is observed if the waves observed remain in phase and also the path length of each one of these waves equals the integral multiple ‘n’ of the wavelength ‘λ’

Figure 2.8: Schematic representation of constructive interference in Bragg’s Law.

The intensity of interference is because of the cumulative effect of reflections onto crystallographic planes of the crystal lattice denoted as Miller indices (h, k, l). A schematic representation of Bragg’s Law has been shown in Figure 2.8 that narrates the condition on θ to be strongest for constructive interference. The mathematical expression of this is given as follows:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

Where, \( \lambda \) = incident light wavelength.

\( n \) = integer positive number (0, 1, 2, 3, etc.).

\( d \) = interplanar spacing.

\( \theta \) = angle between an incident radiation and the planes (h k l).

The incident angle is chosen by crystal rotation, relative to the ray, the wavelength is fixed and thus the interplanar spacing \( d \) is obtained. The conclusion is that an X-ray beam will reflect any set of planes in a crystal if the set of planes is at ninety degrees to the incident beam. But there arises another question, whether the planes will reflect the beam strongly or not.
The intensity of the reflected beam is proportional to the product of the intensity of the incident beam and electron concentration in the reflecting plane. Thus if the unit cell dimensions and, subsequently, the atomic number of each of the atoms are known, it is possible to calculate concentration of electrons and hence the reflected beam intensity.

Now considering the reverse situation, if the size of unit cell and the intensities of the reflections are known, the positions of atoms and also the relative number of electrons per atom are found. It is apparent that all compounds with different unit cells have different intensities of reflections and different collections of d-spacing. The discovered patterns of spacing and intensities can be utilized to identify an unknown compound in a specific crystalline phase.

In powder diffraction it’s important that the samples have smooth plane surface, with the crystallites randomly distributed. The analysis equipment contains small disc placed inside, which is filled by the powder sample. The monochromatic X-ray source is positioned on a rotating arm, in order to light the sample with variable angle $\theta$. The reflected radiation is collected by the detector, even fixed on a rotating arm, placed at twice this angle. As $2\theta$ is the angle measured between the detector and the incident beam, as given in Fig. 2.9, the diffracted radiation is collected by the detector at the very same incident angle $\theta$.

A characteristic diffraction pattern is made up of a plot of reflected intensities against the detecting angle $2\theta$. Comparing the results with the database of organic and inorganic spectra leads to the determination of the analyzed species.

![Schematic diagram of an X-ray diffractometer.](image)

**Figure 2.9:** Schematic diagram of an X-ray diffractometer.
In particular in this work XRD patterns of all investigated WO₃ nanocrystalline structures were collected using a D/max 2550 V X-ray diffractometer (Rigaku, Tokyo, Japan) with monochromatized Cu Kα radiation (\(\lambda = 1.54056 \, \text{Å} \)) incident radiation. The recording of diffractograms is taken by scanning between 10° and 80° (2θ) angles continuously, with a step of 0.01° s⁻¹. Moreover from XRD patterns, crystallite sizes can be calculated.

The reference powder diffraction data from JCPDS (Joint Committee on Powder Diffraction Standards) was compared and matched for relevant peak position, phase purity, peaks of different atomic planes and pattern of relative intensities of the given sample powder. Generally as the crystallite size decreases, the angular spread of the reflection increases. In this thesis the value of the FWHM (full width at half maximum) of the most intensive line of each phase was used in order to measure the mean particle (crystallite) size, calculated by the Scherrer formula:

\[
d_{(hkl)} = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

Where,
- \(d_{(hkl)}\) = size (nm) of particles in the direction vertical to the corresponding lattice plane.
- \(\lambda\) = X-ray incident wavelength.
- \(\beta\) = line broadening at half maximum intensity (FWHM) expressed in rad.
- \(\theta\) = incident angle.

This formula is relatively suitable for comparative studies when there are number of samples belonging to a related series, but it should be used with caution when best accuracy of sizes are needed. In this regard the Scherrer equation shows two main limitations:

1. The numerical value of K (shape factor) for spheres has been approximated to 0.9.

Finally a few critical aspects related to the use of XRD analysis in gas sensing and photocatalysis field of research merit to be outlined. One of the limitation of XRD analyses is that only crystalline phases can be detected, while the amorphous component, if present in samples, exhibits no diffraction peaks. Actually there are no reports showing a quantitative examination of the amorphous content. Thus, the amorphous content should be determined as a residual of the crystalline part and therefore an accurate examination of the crystalline content is necessary. In principle, peak intensity of XRD is proportional to the content of the corresponding crystallites, but obtaining universal standard samples of each crystalline phase has become a problem, because crystallites having smaller size may exhibit lower peak
intensity. In this regard a precise analysis of crystalline content (including amorphous component determination) can be assured when crystalline particles in a sample are chemically extracted (from the original sample) and used for creating an XRD calibration graph based on the assumption that crystallites and amorphous particles are separated, i.e. not in the form of, for example, a core–shell structure. In fact, if a sample particle is made by a core–shell structure, it is very difficult to determine the crystalline content very precisely.

Misunderstanding regarding the phrase “crystallinity” arises as the term is described on the basis of sharpness of an XRD peak, e.g. “Sharpness of the peak indicates higher crystallinity of a nanocrystallites.” Since peak width of an XRD reflects the size of particle, as previously described for the Sherrer equation, size of crystallites is shown by peak sharpness. In this sense, “crystallinity” is used to show how crystallites grow to be larger sized particles.

Another use of the phrase “crystallinity” is to demonstrate perfectness of crystals, i.e. higher crystallinity means crystalline defects are of lower density. Assuming that larger crystallites are expected to contain crystalline defects of a lower density, the sharpness of XRD peaks can also be a relative/indirect measure of this second meaning of “crystallinity”.

2.7.3 Electron microscopy:

Since its invention, the electron microscope is became an important tool in the development of methodical theory and it has greatly contributed to medicine, biology and material sciences. This extensive application of electron microscopes is based on the reality that they allows an observation and characterization of materials on a nanometer (nm) to micrometer (μm) scale. The fundamental theory for electron microscopy are here shortly presented, concentrating on the two main types of electron microscopes; SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope).

Electron microscopes are technical instruments which use a beam of extremely energetic electrons to observe objects on a very superior scale. This analysis can yield topographic information (surface information of an object), morphology (particle’s shape and size that makes the object), composition (the configuration of elements and compounds that the object and the relative data of them) and crystallographic information (arrangement of the atoms in the object).
Light microscopes have limitations due to the physics of light to 500x or 1000x magnification with a resolution of 0.2 mm to conquer this problem, electron microscopes were developed. In the early 1930’s there was a scientific desire to observe the fine details of the internal structures of organic cells (mitochondria, nucleus...etc.) and this essential theoretical limit had been 10,000x plus magnification which was not achievable using light microscopes.

The first type of Electron Microscope in practical use was Transmission Electron Microscope (TEM) which was assembled and patterned exactly on the Light Transmission Microscope excluding a focused beam of electrons is used as an alternative of light to "see through" the specimen. It was designed by Ernst Ruska and Max Knoll from Germany in 1931. The Scanning Electron Microscope (SEM) was debuted in 1942, and the first instrument was marketed in 1965. Its delayed progress was due to the electronics concerned in "scanning" the beam of electrons across the sample.

The function of Electron Microscopes (EMs) is exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition.

2.7.3.1 Electron-matter interactions:

An individual incident electrons undergo elastic and inelastic types of scattering when there is an interaction of an electron beam with the atoms in a sample. In the past, only the trajectory changes and the velocity and the kinetic energy remains constant. In an inelastic scattering, from the incident electrons some electrons actually collides with each other and displace different kind of electrons from the specimen, thus losing their kinetic energy. This kind of interaction produces the large amount of information by considering this information efforts are taken to amplify every single by using different kinds of instrumentation. In this regard the first main difference between SEM and TEM, mainly concerning the sample location in the microscope, can be outlined.

In particular SEM studies the information related to secondary and backscattered electrons, detected on the same side with respect to an incident electrons beam. In this case the sample holder is located at the end of microscope’s column. On the contrary TEM deals with transmitted, elastically or inelastically scattered electrons, detected on the opposite side with
respect to the incident electrons beam. In this case the sample holder is situated in the middle of the microscope’s column.

Both SEM and TEM instruments must work under ultra-high vacuum conditions (10^{-7}-10^{-8} \text{ Pa}) in order to avoid any kind of collision between the electrons beam and atoms, which are not those contained in the sample to be investigated.

Moreover there are essential instrumental components which are common to SEM and TEM systems: electron guns, which can be divided into thermoionic and field-emission types, and to confine and focus the electron beam towards the specimen magnetic lens and metal apertures are necessary.

### 2.7.3.2 Field Emission-Scanning Electron Microscopy (FE-SEM):

This analytical technique is used to explore the surface structures using electrons instead of light. It provides the information about the surface or near the surface region. The electrons are ejected from a field emission source and accelerated in a high electrical field gradient are primary electrons. These electrons are allowed to focus and deflected by electronic lenses to produce a beam for bombardment with the object that emits secondary electrons as shown in Figure 2.10.

There are many advantages in using FESEM microscopy. The FESEM has great depth of field, that so that operator can focus on large amount of the sample under investigation at a time. The images produced are having high resolution so that we can examine the closely spaced features magnifying at particular point. The combination of magnification and the depth in focusing with high resolution we can easily observe the sample at particulate level which makes FESEM as the most heavily used instruments while doing research today. For any of the microscope, the main objective is having higher magnification and clear focusing. An optical microscope lenses are used to bend the light waves and then these are tuned for focus. whereas in the SEM this work has been done by the electromagnets and the electromagnets bend an electron beam, to produce an image on the screen. Benefit of electromagnets is an observer had more control on the required magnification. Moreover the electron beam facilitates great clarity in the image produced [20-21].
In a very brief way FESEM works under vacuum in a column where an electron gun (‘Virtual Source’) emits a beam of high-energy electrons. This high energy electron beam travels through magnetic lenses arranged in series and designed to focus to a very fine spot. The set of scanning coils is situated near the bottom which moves the focused beam back and forth across the sample specimen, row by row. Secondary electrons are emitted from the surface when the electron beam bombards on every spot of the sample. Counting of these electrons is progressed by the detector resulting in sending the signals to an amplifier. An ultimate image is obtained from the number of electrons ejected from every spot on the sample.
The surface of the object decides the nature of the secondary electrons. These secondary electrons are caught to produce electronic signal that is amplified to a scan image and saved. The EDAX (Energy dispersive X-ray analysis) along with elemental mapping system provides the qualitative as well as quantitative elemental analysis of in a sample where the matter interacts with the electromagnetic radiation. As each of the elements possesses unique atomic structure thus, X-rays distinguish each element in a distinctive manner. FESEM images for all WO$_3$ as prepared samples were obtained by using NOVA NANOSEM FEI 450 system. Double-sided carbon tape was stick to SEM stub, the powder was sputter coated with gold for 2 min before mounting on the stub. The EDAX and elemental mapping has been done for pristine and doped WO$_3$ nanocomposites

2.7.3.3 Energy Dispersive X-ray Spectroscopy (EDS or EDAX):

Energy Dispersive analysis of X-rays (EDAX) is a chemical analytical technique. It uses X-rays that are ejected from the sample at the time of bombardment by the high energy electron beam. These are used to describe the elemental composition of the sample under investigation. Features or phases as small as about 1 μm can be analyzed using EDAX [22]. When a metal target present in an X-ray tube is bombarded with electrons of sufficiently high energy, emit characteristic X-rays. This is the basis of Energy dispersive X-ray spectroscopy, When the electron beam is bombarded on the specimen, electrons are expelled from the atoms containing the sample’s surface. A resulting position of electron is filled from higher shell electron, and To balance this energy difference X-ray photon is emitted. The measurement of the number of emitted X-rays against their energy is detected by detector. The energy of the X-ray is characteristic of the elements of the specimen from which the X-ray was emitted. These X-rays from the specimen bombarded by high-energy electron beam are analyzed in an X-ray spectrometer, and the elements present in the sample are qualitatively identified by their characteristic wavelengths. Quantitative estimation is also possible by measuring relative intensities in the X-ray spectra. For compositions greater than or about 1 % and elements separated by few atomic numbers, EDAX is very useful because the intensities are increased by about 100-fold [23]. Due to limitations of resolution overlapping of lines from nearby elements may occur. The specimen should be either electrically conducting or made so by evaporating a metallic layer on it.
2.3.3.4 Transmission Electron Microscopy (TEM):

TEM is an investigative technique that helps in studying the high resolution morphology, crystallinity of materials and lattice fringe. In this technique, a beam of electrons is transmitted through the ultra-thin specimen where the specimen interacts with the electrons. An image is progressed from the interaction of electrons transmitted through the specimen. It operates like a slide projector, this beam of electrons shining from projector gets transmitted through the slide. The patterns on the slide allow certain parts of the light beam to pass through. As a result, the replicated pattern from the slide forms an enlarged image upon falling on the phosphor screen as shown in Figure 2.11. The particle size, morphology, particle growth direction and lattice parameters like d-spacing of the as synthesized nanopowder and nanocomposite were studied by TEM, HR-TEM and SAED pattern, respectively. For the TEM sample preparation small amount of powder is dispersed in ethanol by using 20 kHz and 500W ultrasonic energy for 30 min. A carbon coated copper grid was used as substrate. A well dispersed suspension was dropped onto the substrate and dried for evaporation of the solvent. The powder morphology was observed under bright field mode transmission electron microscope (JEOL JEM-2100, TEM).

TEM is a microscopic technique where an electron gun emits a beam of electrons which is generally fitted with filament (tungsten) cathode as the electron source. Anode accelerates the electron beam usually at 100 keV with respect to the cathode. focusing is done by electrostatic and electromagnetic lenses, which is transmitted through the specimen containing grid. It interacts with the specimen when it passes through it (Figure 2.11). The TEM lenses permits beam convergence, where angle of convergence is a variable parameter. This gives the ability to alter the magnification just by modifying the amount of current flowing through the coil. The TEM analysis have lenses in three stages. These lenses are the condenser lenses, the objective lenses, and the projector lenses. Primary beam formation is executed by the condenser lenses, whereas focusing of the beam on the sample itself is progressed by the objective lenses. The imaging on to the phosphor screen or other imaging device is done by projector lenses by expanding the beam. We get maximum magnification image (to atomic level) due to the ratio of the distances between the specimen and the objective lens' image plane. An image is produced from the interaction of the electrons transmitted through the
specimen, the magnified image can be focused on different imaging devices, like a fluorescent screen, or photographic film, or by a sensor such as a CCD camera.

**Figure 2.11: A schematic diagram of the transmission electron microscope.**

Imaging at higher resolution than light microscopes can be achieved significantly in TEM is because of small de Broglie wavelength of electrons. The instrument's user is enabled to examine minute details of the specimen even up to a single column of atoms, which is very much smaller than the least resolvable specimen in a light microscope. All these extraordinary features made TEM as an important analysis tool in a variety of scientific fields, in chemical physical and biological sciences. It is most required equipment in cancer research, materials science, virology and semiconductor research [24].

There is difference in the imaging at smaller and higher magnifications image is contrast at lower magnification due to absorption of electrons, thickness and composition of the material. Complex wave interactions change the intensity of the image which requires expert
analysis of obtained images. Different modes of utilization are available in TEM analysis to observe modulations in crystal orientation, electronic structure, chemical identity and phase shift induced by sample electron with regular absorption based imaging.

There are basically three different imaging modes in TEM, these modes are selected by changing an appropriate apertures of the rear focal plane (after the objective lens) (Fig. 2.12).

1) **Bright field mode**: the aperture selects only transmitted electrons. In this case, factors such as mass and thickness of the sample influence the formation of the image.

2) **Dark field mode**: in this case only diffracted electrons, which gave strong interaction with the sample, are selected. The image obtained can give information about the existence of defects or different phases of the specimen.

3) **High resolution (HR-TEM)**: in this case both transmitted and diffracted electrons are selected. Using proper corrections for spherical aberration, special high resolution TEMs can generate images with a resolution below 0.1 nm; it’s thus possible observe reticular planes and get crystallographic information of the examined sample. By considering that for TEM analysis the analyzed electrons should pass through the sample, the specimens have to be rather thin, less than 100 nm.

![Different imaging modes in TEM](image)

**Figure 2.12: Different imaging modes in TEM**

### 2.7.3.5 Selective Area Diffraction Pattern (SAED)

Diffraction patterns can be observed due to an angular distribution of scattering in the form of scattering patterns, generally mentioned as Selected Area Electron Diffraction (SAED).
Spatial distribution of scattering can be viewed as contrast in images of the specimen. The benefit of this arrangement is the feasibility of directly viewing the part from which the diffraction pattern arises. Virtually, TEM is useful for determining size, arrangement of the particles and shape of the specimen. Moreover, for the determination of the lattice planes is possible with the detection of defects in the samples in areas measures in nanometers by using selected area electron diffraction (SAED) technique [25, 26]. The $d$-spacing between lattice planes of crystalline materials can be calculated from a SAED pattern using the relationship:

$$dr = \lambda L$$  \hspace{1cm} (2.6)

Where $L$ is the distance in the photographic plate and specimen, $L$ is known as the camera constant and $r$ is the radius of diffracted rings. It is easy to measure directly from the photographic plate, and $\lambda L$ can be established from the instrument by calibrating it with a standard material (usually Ag), and hence one can easily get $d$ values. Since each $d$ value corresponds to a specific lattice plane for a specific crystal structure, a minimum description of crystal structure of a crystalline specimen can be obtained from a SAED pattern.

In selected area electron diffraction (SAED), an aperture is utilized to identify the area. From this area a diffraction pattern is produced in a TEM specimen. The obtained pattern consists of the data which states the phases present (lattice spacing measurement) and sample orientation.

2.7.3.6 High Resolution Transmission Electron Microscopy (HRTEM):

HRTEM (high resolution transmission electron microscopy) is the extension of TEM in which further more resolution (<10 nm) is possible in such a manner that interplanar spacing can be directly seen in the image as a series of fringes. Conventional TEM detects only the transmitted electrons. HRTEM (High Resolution TEM) can detect electrons diffracted at wide range of angles. By using this technique we can obtain images of the atomic structure of the materials under investigation.

2.7.4 Ultra-violet Visible Spectrometer (UV-Vis):

Absorption spectroscopy in the UV and visible region has long been an essential tool to the analyst [27]. It measures the strength of absorption of near-ultraviolet and visible light (wavelength region from 200-800 nm) by a sample. The transitions occurs due to molecular
and structural changes in the specimen under examination, that leads to match changes in the capacity of the sample to absorb light in the UV and visible region of the electromagnetic spectrum. UV and visible light are enough energetic to promote the outer electrons in an atomic, molecular or material system to next energy levels depending on the specific nature of the electronic states of a given material. Absorption of energy leads to a transition of electron from ground state to excited state. In semiconductors, when the event photon energy more than or equal to band gap energy of the material then absorption takes place and signal is recorded by the spectrometer. This spectrometer can operate in two modes (i) transmission and (ii) reflection mode. In transmission mode usually thin films and well-dispersed nanoparticles in the solvent are used. The optical measurements for those nanoparticles which are not dispersible in solvents are done in diffuse reflectance spectra (DRS) mode. Reflectance spectra provide information about the scattering and absorption coefficient of the samples and hence their optical properties. Schematic of UV-Vis spectrometer is drawn schematically in Fig 2.13.

![Figure 2.13: Schematics of UV- VIS spectrophotometer](image)

For photocatalytic applications of materials, the Ultra-violet Visible (UV-Vis) spectrometer is fundamental instrument. The UV-Vis spectra not only uniquely define the material, but also identity the possibility of using the materials for photocatalytic studies either in the UV or visible light range. To be more specific, the UV-Vis Spectra give the information
necessary to decide the maximum wavelength (minimum frequency and energy) required in the incoming light source in order to excite the photocatalyst. The spectra generated here is because of an optical transitions from ground state to an excited state of the catalyst molecules, i.e. a transition of electrons from valence band to conduction band. The UV-Vis spectra is also a signature for a molecule with conjugated pi-electrons such as rhodamine B dye, the test dye we used to evaluate the photocatalytic properties of WO$_3$ nanostructures in this project. From the spectra, we can decide important information like the maximum absorption wavelength of the test dye solutions, and evaluate any change in the absorbance of the dye after irradiated for a definite period of time. In this project, the UV-Vis transmission spectra of the prepared WO$_3$ nanostructures were recorded by the Cary UV-60 Spectrophotometer, Agilent technologies, in wavelength range of 200-800nm, in order to determine the proper wavelength of the incoming light source. The UV-Vis absorption spectra of RhB solutions before and after sunlight irradiation were also obtained using the same equipment, as described in detail in the photocatalytic experimental section.

The detector, which is often a photodiode, alternates among measuring the sample and the reference beam (see schematic Fig. 2.14). Some double beam instruments have obviously two detectors, and the sample and reference beam are calculated at the similar time. In other instruments, there are two beams that pass through from that one beam is blocked at a time by the chopper. The source used for the UV plus visible light are deuterium and tungsten lamps respectively and the detector used is PMT (Photo Multiplier Tubes).

UV-Vis spectroscopy can successfully applied inorganic ions or complexes and molecules in the solution. Actually UV-Vis spectra is having extensive features, the uses are restricted for sample identification but these are more useful for quantitative measurements. By measuring the absorbance wavelength, concentration of an analyte in solution is calculated by applying the Beer-Lambert law.

The equilibrium charge carrier distribution in any material (conductor, semiconductor or insulator) can be disturbed by its exposure with electromagnetic radiation of suitable energy. The photons incident on any material may be reflected, transmitted or absorbed. The quantity of radiation of wavelength $\lambda$ absorbed by a material slab of thickness $t$ is measured in terms of optical density ($\alpha t$). Assuming negligible reflection, the energy absorbed can be given by Lambert’s equation,
Figure 2.14: Schematic of Beer-Lambert’s Law.

\[ I = I_0 \exp (-\alpha t) \]  

(2.7)

Where \( I_0 \) is incident intensity and \( I \) is transmitted intensity. In other words, optical absorption coefficient of films is evaluated from transmittance as [28],

\[ T = A \exp (-\alpha t) \]  

(2.8)

Where \( A \) is a coefficient related to the refractive index, at the absorption edges \( A \) is nearly equal to unity, \( T \) is transmittance, \( t \) is thickness of film, and \( \alpha \) is the absorption coefficient.

A photon absorption by a material is characterized by transition of electron in energy states or energy bands according to quantum rules. An ideal semiconductor, at moderate temperature has small number of holes present in the valence band and electrons in the conduction band. Absorption of photons of adequate energy leads to move the electrons from valence band to conduction band which gives absorption maxima. Thus, the spectrum of optical absorption of pure semiconductor exhibits a fundamental absorption edge at a certain incident photon energy, which can be attributed to the excitation of electrons from valence to conduction band separated by energy equal to the band gap energy \( (E_g) \).
The dependence of photon energy at absorption edge is given by [29],

\[(\alpha h\nu) = B (h\nu - E_g)^n\]  \hspace{1cm} (2.9)

where \(h\nu\) is the photon energy of incident ray, \(B\) is parameter of edge width and \(n\) is an exponent that decides the type of electronic transition causing absorption, which is \(1/2\) for direct allowed, \(3/2\) for direct forbidden, \(2\) for indirect allowed and \(3\) for indirect forbidden transitions. Band gap energy of the powders are obtained by extrapolating the linear region of the graphs \((\alpha h\nu)^n\) to absorption coefficient \(\alpha=0\).

In the present study, UV-Vis spectroscopy measurements of the powder samples at room temperature at wavelength range of 200-1000 nm operated at a resolution of 1 nm.

**2.7.4.1 UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS):**

It uses the light from UV, visible and other near infrared region to detect the transitions taking place due to excitation from ground state to excited state. Penetration of light cannot occurs in solid (opaque) samples, it reflects from surface of the samples. As shown in the below Fig. 2.15, In specular reflection, the light is reflected symmetrically with respect to the normal line while in diffuse reflection incident light is scattered in different directions. The basic principle is that the easy electron excitation causes longer wavelength absorbance due to smaller energy gap in the Highest Occupied Molecular Orbital (HOMO) and lowest occupied molecular orbital (LUMO) of the material. This suggests that the sample may absorb light energy in order to move electrons from valence band having filled energy level to vacant conduction band causing relative decrease in the quantity of light energy with respect to a reference source. In this experiment, the light is allowed to scatter in all directions from the sample followed by collection of scattered light by an optical detector. Surface reflectance is measured by scanning the sample over a series of wavelengths. In other way, the relative change in the amount of light reflected from surface is being measured.

Diffuse reflectance measurements were obtained from JASCO Spectrophotometer (FT/IR-6100typeA) to calculate band gap energy for WO₃, nanopowders and nanocomposites. Diffuse reflection percentage at room temperature was measured in the wavelength region 200-800nm. Barium sulphate was used as the reference for this measurement.
2.7.5 BET (Brunauer, Emmett and Teller) surface area studies:

The phenomena of BET theory is explained to explain the physical adsorption of gas molecules on the powder surface for measurement of the specific surface area of the powder. The theory was a joint invention by Stephen Brunauer, Paul Emmett and Edward Teller in 1938, who perused the surface phenomena of a powder or porous body with the help of gas adsorption method. This theory is an expansion of Langmuir theory which explains monolayer or multilayer adsorption following certain hypotheses. Low pressure adsorption isotherm provides a mean to take the mass of adsorption corresponding to a single gas molecule layer and calculated the surface area from it. BET surface area is then calculated from adsorption behavior under a range of partial pressures. The BET equation is represented as:

\[
\frac{P}{X(P_0 - P)} = \frac{1}{X_mC} \left[ 1 + \frac{P}{P_0}(C - 1) \right]
\]

(2.10)

Where,

\( P \) = Measured partial pressure of adsorbate

\( P_0 \) = Equilibrium or saturation pressure of adsorbate (depends on the gas and temperature),
\[ X = \text{Mass of the gas adsorbed at pressure } P \]
\[ X_m = \text{Adsorption capacity of the powder (the mass of gas necessary to form a saturated surface coating one atomic layer thick)} \]
\[ C = \text{Constant relating to the adsorption enthalpy.} \]

BET equation is a linear equation and valid for measuring surface area of powder when the pressure range \( P/P_0 \) varies from 0.05 to about 0.35. The \( S_{\text{BET}} \) equation can be represented in a general form as:

\[
S_{\text{BET}} = \frac{X_m N_0 A_0}{WM} \tag{2.11}
\]

Where,

\[ M = \text{Molecular weight of the adsorbate}, \]
\[ A_0 = \text{Average occupational area of an adsorbate molecule (nitrogen is the most popular adsorbate gas and it has an average occupational area of } 16 \times 10^{-20} \text{ m}^2), \]
\[ N_0 = \text{Avogadro’s number, and} \]
\[ W = \text{Mass of the sample.} \]

The adhesion of atoms/molecules of gas to a surface is called as adsorption. There should not be confusion in adsorption with absorption, in absorption fluid soaks in a liquid/solid. The quantity of gas adsorbed depends upon the surface area, temperature, gas pressure and interaction between the solid and the gas. The BET surface area investigations widely employs \( N_2 \) gas as it is available with high purity and most of solids interacts with nitrogen. In a typical experiment known amount of \( N_2 \) gas is added stepwise into the sample cell. Vacuum is created in order to maintain the relative pressures lower than atmospheric pressure. Beyond the saturation pressure, adsorption does not occur irrespective of further rise in pressure. Highly accurate or very precise pressure transducers are used to monitor the change in the pressure because of the adsorption process. Once the adsorption layers are produced, the sample is released from the \( N_2 \) atmosphere, heated is done to cause desorption of \( N_2 \). The data is displayed as a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure.
2.7.5.1 Sample preparation:

For removal of water and other contaminants the sample should be degassed in a vacuum environment at elevated temperatures before estimation of surface area. The highest temperature is selected such that it will not damage the sample in order to curtail the degassing time. According to the IUPAC recommendations the samples should be degassed for minimum 16 hrs to ensure that undesirable vapors/gases are removed from the sample surface. Normally, the samples that can withstand at higher temperatures without structural changes have shorter degassing times.

2.7.5.2 Measurement:

![Schematic diagram of the BET instrument.](image)

Figure 2.16: Schematic diagram of the BET instrument.

To analyze the sample for BET, sample is placed in glass cells to be degassed. Generally the glass rods are kept in the container to curtail the dead space in container. Sample cells typically in sizes of 6 mm, 9 mm and 12 mm available in different shapes for larger particles, fine powders, small pellets and large pieces which are unable to reduce further. The cells are sited into heating mantles and joined to the outgas port of the machine. After degassing the sample, the container is relocated to the analysis chamber (Figure 2.16). Liquid
nitrogen dewar is used for sample cooling and to maintain the constant temperature. A temperature maintained must be low to increase the interaction between sample surface and the gas molecule so that measurable amounts of adsorption will occur. The adsorbate is forced into the sample container with the assistance of calibrated piston.

The dead volume in the sample container has to be calibrated before and after every measurement. For this the helium (He) gas is used for a blank run, as helium does not adsorb on the surface of sample.

2.7.5.3 Gas phase adsorption:

For the pure gases, there are different shapes observed in experimental section of physical adsorption isotherms. These isotherms are classified into 5 types as discussed below. Each of these types is observed in practice but the most frequent types are type I, type II and type IV. An intrinsic property of type I isotherms is that adsorption is restricted to the single monolayer completion of an adsorbate at the adsorbent surface. Type I isotherms are noticed for microporous solids having pore sizes not much bigger than the molecular diameter of the adsorbate. When there is complete filling of these narrow pores there is completion of a molecular monolayer. We can observe such type of example in the adsorption of oxygen on carbon black at 183°C. Adsorption the other types does not reach a limit analogous to the fulfillment of a monolayer.

In case of type II isotherms, saturation limit do not exhibit as it exists in type I. Indefinite multilayer formation is progressed after completion of the monolayer is seen in this type of isotherm. This indicates that there is a wide distribution of pore sizes. Close to the initial point of inflexion, a monolayer is accomplished, following with adsorption in successive layers. This type of adsorption is observed in the adsorption of water vapor on carbon black at 30°C.

When the quantity of gas adsorbed increases limitlessly, type III isotherm is observed as its relative saturation approaches unity. An example is when bromine is adsorbed on silica gel at 20°C this type of isotherm is obtained.

Type IV isotherm is a variation of Type II, but with a finite multilayer formation corresponding to absolute filling of the capillaries. Termination of adsorption occurs near to a relative pressure of unity. This type of isotherm is observed by the adsorption of water vapor on
activated carbon at 30°C. Type V isotherm is similar variation of type III obtained when water vapor is adsorbed on activated carbon at 100°C.

Figure 2.17: Schematic of the adsorption of gas molecules onto the surface of a sample

Figure 2.18: Adsorption desorption plots of different types

Uses of adsorption isotherms: Adsorption isotherms are most frequently used to choose the adsorbent or even the adsorption procedure for the adsorptive separation of gases. If the
adsorption isotherm shape is type I, type II or type IV, adsorption can be used to separate the adsorbate from the carrier gas. If it is type III or type V, adsorption will perhaps not reasonable for the separation. Although the effectiveness of an adsorption isotherms are investigative for a particular adsorbate removal, they do not provide data to permit the calculation of contact time or the amount of adsorbent required to reduce the solute concentration below prescribed limits. Various expressions are available to describe the various isotherms.

Figure 2.19 Different types of hysteresis in an isotherm plot.

Steepness of the isotherms decreases from H1 to H4. The hysteresis is usually attributed to the thermodynamic or network effects or the combination of these two effects.

**H1**: Aggregated or spherical particles are quite uniformly arranged, as the pore geometry is cylindrical it indicates that the pore size is relatively high and there is uniformity and facile pore connectivity in the material.

**H2**: In this type of isotherm the pores are having narrow mouths usually called as ink-bottle pores, they form comparatively uniform channel.

**H3**: Aggregates (loose assemblages) of plate like particles forming slit-like pores
**H4:** Narrow slit-like pores, particles with internal voids of irregular shape and broad size distribution, hollow spheres with walls composed of ordered mesoporous silica
2.8 References: