Chapter 2

Characterization Techniques

This chapter deals with the various instrumentation techniques we utilized to confirm the synthesis of our samples, its various features viz. composition, morphology, elements present along with optical properties. Most of the characterization techniques, we deployed are based on light-matter interaction in simple terms that reveal the internal information. A short description of the tools used to explore the application part of the samples and related terminology is also mentioned.

Generally, the first step after the preparation of the materials is to confirm its successful synthesis, X-ray diffraction (XRD) along with Fourier-transform infrared spectroscopy (FTIR) is a prominent tool for this purpose. Besides this, if synthesized samples have any optical features, it is confirmed by UV-visible and Fluorescence spectroscopy. Morphological analysis tools such as SEM, FE-SEM and TEM are required to find out the surface topology, texture, and size information as all the catalytic activities are surface-based phenomena. Identification of elements, its valence states along and the presence of dopants is performed very precisely by X-ray photoelectron spectroscopy- a very sensitive surface analysis tool. Energy Dispersive X-ray Analysis (EDX/EDS) along with elemental mapping also provides useful supporting data to identify the surface elements as well as uniform-nonuniform distributions of elements in the prepared samples. Surface area analysis is usually performed for samples having catalytic properties and porous nature, Brunauer–Emmett–Teller (BET) theory is used for evaluation of the specific surface area. A short description of all these techniques is provided under the following headings and sub-headings.

2.1 Structural Characterization

The tools utilized for structural characterization are X-ray diffraction, Raman and Fourier-transform infrared spectroscopy (FTIR). Raman study is carried out mainly for 2D materials to quantify structural defects. UV-visible spectroscopy and Fluorescence spectroscopy chiefly provide optical information which play role in the structural organization of the samples under study.

2.1.1 X-ray Diffraction

The XRD technique, a non-destructive tool, provides insight about the structural details, phases, crystallinity, and other useful information such as average grain size, crystallite size, strain, and crystal defects. The source of X-ray in XRD analysis is Cu Kα radiation (λ = 1.5406 Å). The various controlling parameters in XRD measurement are scan rate, step size, 2θ range, tube voltage and current. A standard database - JCPDS database, is used for the identification of phases in the crystalline material among a large variety of crystalline phases reported. [95,96] The diffraction of X-ray into a crystal structure takes place in accordance with **Bragg's equation**. [97] The well-known Bragg's equation relates the 'interplanar spacing' (d) in the crystal to wavelength (λ) of the X-ray radiation and its angle of incidence (θ) (*n* is an integer) as follow

$$2d\ sin\ \theta = n\lambda \quad \text{.....(Eq. 2.1)}$$

The Bragg Brentano geometry of constant distance from the sample to the detector is set into the measuring instrument. All the XRD pattern in our study was recorded on Rigaku Mini Flex BENCHTOP 600 X-ray diffractometer shown in Figure 2.1.

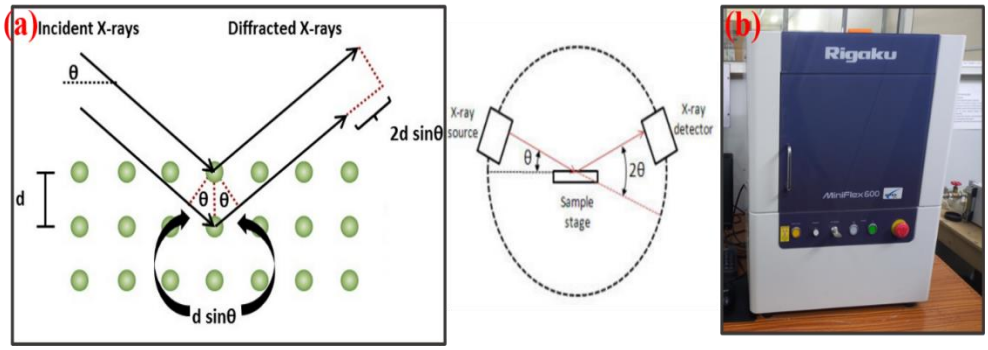

Fig. 2.1 (a) Diffraction pattern of X-ray into the sample and 2.1 (b) Photograph of the Diffractometer. (Courtesy: CIF, IIT (BHU))

2.1.2 Raman Spectroscopy

This analytical technique provides insights about the level of crystallinity, phase, chemical structure, polymorphy and molecular interactions. It is a non-destructive method based on the interaction of laser light with the chemical bond of material. In Raman study, material or sample scatters incident beam of high-intensity laser light, the scattered beam are categorized into Rayleigh scattering and Raman Scattering. If the scattered beam has the same wavelength as of incident laser source viz. $\lambda_{scatter} = \lambda_{laser}$, it is called Rayleigh scattering. The majority of scattering is Rayleigh and it does not provide any useful information. Only a small portion of the scattered beam has a wavelength higher to the laser source ($\lambda_{scatter} > \lambda_{laser}$) which gives insight into the material, it is called Raman scattering (*see* Fig. 2.2) further divided into Stokes and Anti-stokes.

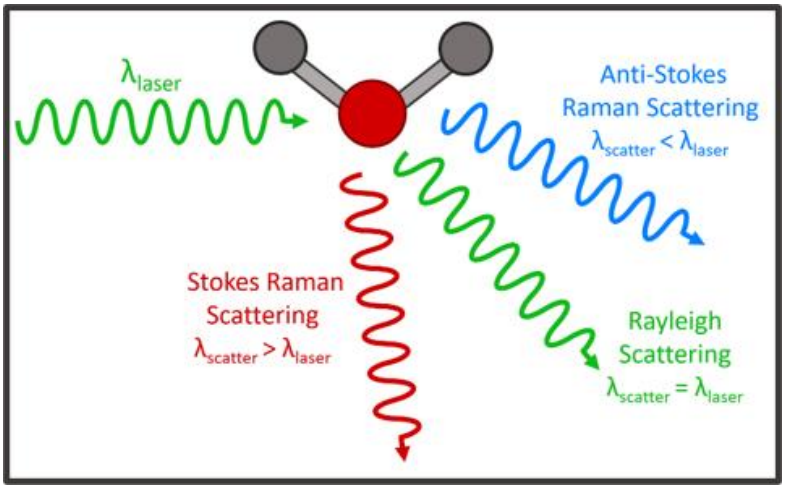

Fig. 2.2 Rayleigh and Raman scattering by molecule upon irradiating with the laser of wavelength λ. (Courtesy: Edinburgh Instruments)

Raman spectrum consists of a series of peaks of variable intensity and wavelength position corresponding to Raman scattered light. In Raman spectrum of 2D material viz. graphene, g-C_3N_4, hBN, peaks of interest are D peak (disorder in structure), G peak (in-plane vibration in structure) and 2D peak (helps in determining the number of layers). The ratio of I_D/I_G reveals the level of the defect and other valuable information in the structure. Different kinds of samples can be analyzed using this technique, viz. solid, powder, organic, inorganic, biological, alloys materials, etc. [96,98]

2.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is used to analyze many organic functional groups, biological samples, polymers, inorganic materials, thin films, liquid, solid (powder) fibers and other forms, etc. FTIR abbreviated as **"**Fourier Transform Infrared Spectroscopy", the invention of the third-generation IR Spectroscopy marked the renunciation of monochromator and the success of interferometer, which resulted in exceptionally powerful IR spectroscopy. It is concerned with the vibration of molecules. It takes advantage of how IR radiation changes the dipole moments in molecules that correspond to specific vibrational energy. Each functional group has its own discrete vibrational energy which can be used to identify a molecule. [95,96] Vibrational energy corresponds to two variables: 'reduced mass' (inversely proportional, μ) and 'bond spring constant' (directly proportional, k). The Frequency of absorbance characteristics of a functional group is expressed as wavenumber (ṽ)

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad \text{.....(Eq. 2.2)}$$

Where 'c' stands for the speed of light, 'k' for the spring constant of the bond and 'μ' for the reduced mass. A linear molecule (for e.g., CO_2) possesses 3N−5 vibrational degrees of freedom, while non-linear molecule (for e.g., H_2O) possesses 3N−5 vibrational degrees of freedom, N stands as the number of atoms in the molecule).

The three major components of FTIR instruments are a light source, interferometer and detector as depicted in the block diagram in Figure 2.3 (a). The interferometer is the heart of FTIR instrument consisting of a beam splitter, a stationary mirror, a moving mirror and an IR laser. The range of Infrared radiation is 12800 ~ 50 cm^{-1}, that further categorized into three regions viz. near-infrared region (12800 ~ 4000 cm^{-1}), mid-infrared region (4000 ~ 200 cm^{-1}) and far-infrared region (50 ~ 1000 cm^{-1}).

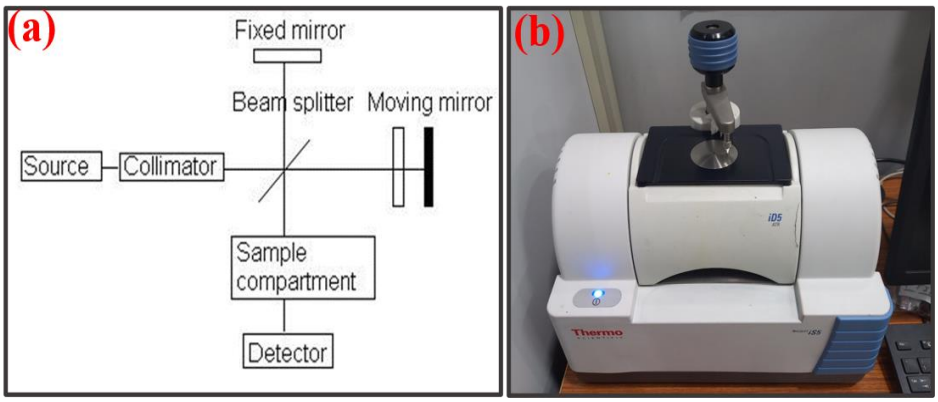

Fig. 2.3 (a) Block-diagram and (b) Photograph of FT-IR Spectrophotometer. (Courtesy: CIF, IIT (BHU))

The FTIR spectrum is a spectrum of molecular vibrational. The absorption of IR radiation appears as vibration peak, the number of peaks observed in the spectra is

related to the number of vibrational freedoms of the molecule. The IR absorption (A) is converted into % transmittance (T) using the following formula (Eq. 2.3) and plotted against wavenumber (in cm^{-1}).

$$A = -log_{10}T \text{.....(Eq. 2.3)}$$

2.1.4 UV-visible Spectroscopy

A UV-vis spectroscopy also known as the optical absorption spectroscopy, is the low-cost, facile characterization technique used for the capture of absorbance or reflectance band of an analyte such as biological macromolecules, conjugated organic compounds, the functional group-containing species and transition metal ions, present in liquid medium by passing monochromatic radiation of UV or visible light through the sample. Figure 2.4 (a) shows the block diagram of the spectrophotometer.

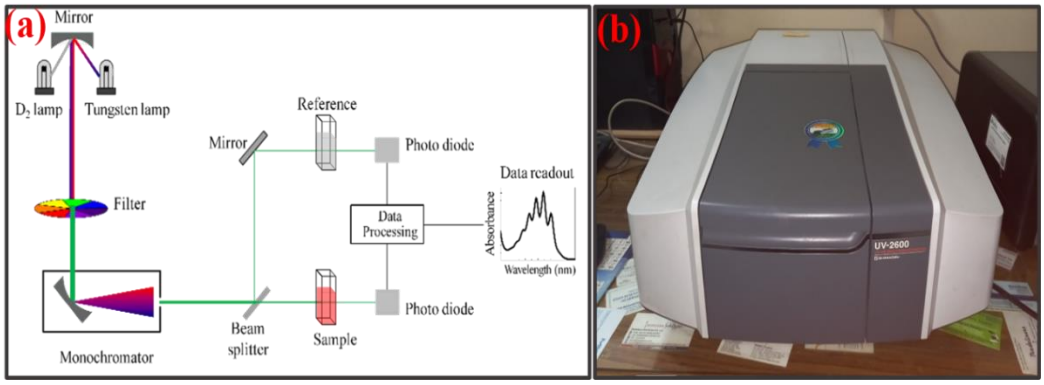

Fig. 2.4 (a) Schematic diagram of the UV-visible spectrophotometer (Courtesy: Wikimedia Commons) and (b) Photograph of the Spectrophotometer. (Courtesy: CIF, IIT (BHU))

The absorption of monochromatic radiation by the analyte follows the Beer-Lambert law's law.[99] According to Beer-Lambert's law, the absorbance by an analyte in the solution is proportional to the concentration of the absorbing species into the solution and the path length of light in the solution. Thus, a constant path length (l) value helps for the determination of the concentration of the absorbing species into the solution. The Beer-Lambert's law can be expressed as

$$log_{10}\ \frac{I_0}{I} = A = \varepsilon cl \text{.....(Eq. 2.4)}$$

Where 'I_0' is the incident intensity, 'I' is the transmitted beam intensity through given sample solution, 'A' is measured absorbance, 'ε' is known as the molar extinction coefficient (unit l mol^{-1} cm^{-1}), 'c' is the conc. of the absorbing analyte and 'l' is the path length of light through the sample. The absorb wavelengths can be associated with the conjugation bond as well as the functional groups within a molecule or nanomaterial.

In the case of solid samples (insoluble in any solvent), reflectance spectra are recorded using $BaSO_4$ as reference material and a thin film of sample is smeared over the reference $BaSO_4$ for reflection measurement. The reflectance spectrum is converted into a corresponding absorbance spectrum using the Kubelka-Munk function. We utilized the UV-2600 model of Spectrophotometer of Shimadzu Corp. Japan (see Fig. 2.4 b); its wavelength range can easily be expanded to the near-IR region of 1400 nm using the optional integrating sphere.

2.1.5 Fluorescence Spectroscopy

This Spectroscopic method is used to obtain information about surface features of nanomaterial by light-matter interaction and is widely utilized in the biological

research field. This technique is based on the light-emitting process triggered by the absorption of an appropriate excitation wavelength on the surface of the nanomaterial or quantum dots. The excitation wavelength is usually in the UV range, which is further optimized to achieve the best emission profile. The transition (both allowed and forbidden) process follows the well-known Jablonski diagram (*see* Figure 1.20 in Chapter 1) as described in section 1.4 of chapter 1.

2.2 Morphological Characterization

It covers the surface features of prepared samples at micrometer (μm) and nanometer (nm) scale (up to atomic scale). The used techniques are as follow

2.2.1 Scanning Electron Microscopy (SEM) and Field-emission Scanning Electron Microscopy (FE-SEM)

Scanning Electron Microscopes can scan the samples with a focused electron beam to get knowledge about surface topography as well as composition. The raster scan pattern is followed for scanning by the electron beam. Structural information of the prepared materials/composites was obtained up to 200 kX magnification, at the scale of up to 0.1 μm (100 nm) and accelerating voltage of up to 20.0 kV using Carl Zeiss, Supra 40, Germany instrument (*see* Fig. 2.5).

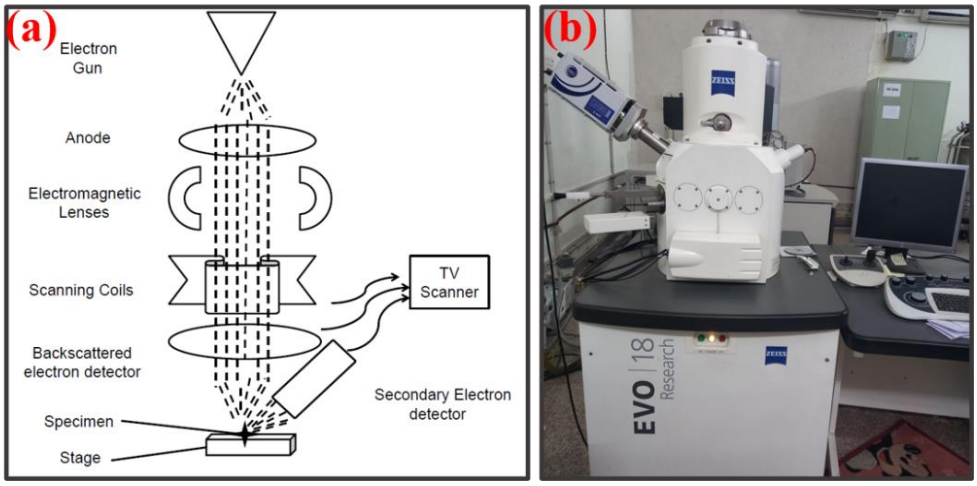

Fig. 2.5 (a) Schematic diagram of the components of SEM microscope and (b) Photograph of the SEM instruments. (Courtesy: CIF, IIT (BHU))

FE-SEM technique provides information about the surface features at higher resolution and broader energy range. Similar to conventional SEM, in FESEM, the surface of the species is scanned with the focused electron beam, but the difference between the two is in the electron generation system. The FESEM instrument is fitted with a field emission gun generating extremely focused high and low-energy electron beams, it improves the spatial resolution of the species. In FESEM, work can be carried out at a very low value of potential (0.02–5.0 kV). Such sophistication helps to lower the damage of non-conductive specimens by charging.[100] FESEM uses an in-lens detector which gives high-resolution images at very low accelerating voltage. Figure 2.6 shows the FESEM instrument utilized in the study of our samples. It is FEI NOVA NANO SEM 450 model, made in the USA.

SEM and FESEM instruments incorporate the following detectors

2.2.1 (a) Secondary Electron Detector (SE2)

It is primarily used to obtain the specimen image at a large depth of field. It suits to get information of sample topography at low magnification with high acceleration potential.

2.2.1 (b) Secondary Electron In-Lens Detector

It functions with low energy secondary electrons and provides images with a resolution of higher order. It works at low acceleration potentials (<5 kV), hence suitable to minimize the charging effect on non-conductive samples.

2.2.1 (c) Backscattered Electron Detector (AsB)

It is highly sensitive to elements of the different atomic numbers present in the sample; it is suitable for the study of changes in the chemical composition of the sample.

2.2.1 (d) Backscattered Electron In-lens Detector (EsB)

It provides a large value of Z-contrast than any other backscattered detector, and it has the ability to select the electrons according to their energy. It enables the differentiation of the elements that are only distinguished by a few atoms.

2.2.1 (e) An X-Ray Dispersive Energy Detector (EDS)

It detects x-rays from each surface point the electron beam scans over, since the energy of each scattered x-ray is specific to elements, this detector gives qualitative as well as quantitative analytical information about the selected points, lines, or areas on the surface of the sample. [101]

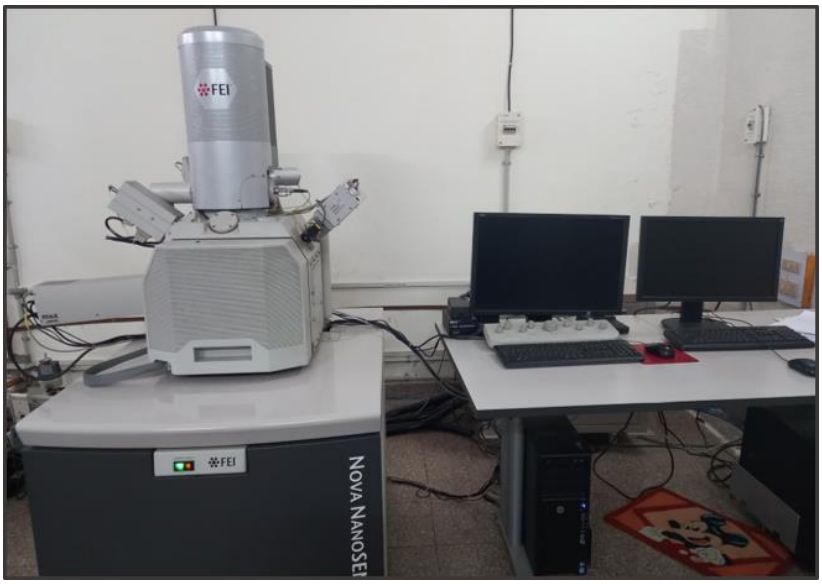

Fig. 2.6 Photograph of the FESEM instruments. (Courtesy: CIF, IIT (BHU))

2.2.2 Transmission Electron Microscopy (TEM) and High-resolution TEM (HR-TEM)

In the transmission electron microscope, a beam of high-energy electrons transmits through an ultra-thin object and interacts with the specimen as it travels through. The interaction of transmission electrons, while passing through the specimen produces an image, which is magnified and focussed over an imaging device, generally a fluorescent screen or a layer of photographic film, or a sensor. Due to the lower de Broglie wavelength of electrons, TEMs offer images with substantially higher resolution than optical microscopes. These electrons enable the examination of finer details that are thousands of times more detailed to the greatest resolution offered by an optical microscope. Nonetheless, the magnification provided by a TEM image contrast with electron absorption in the material, which is mostly attributable to the thickness or composition of the material.

TEM uses an electron beam accelerated at high voltage. These electrons are generated by an electron gun fitted at the top of the TEM machine and goes through the vacuum tube of the microscope. The TEM instrument has a condenser lens to concentrate the generated electrons into the beam of small thickness. These electrons either scatter or strike the fluorescent screen at the bottom of the microscope after passing through the thin object. On the fluorescent screen, the image of the specimen appears with its various detail components differentiated depending on their density. [102]

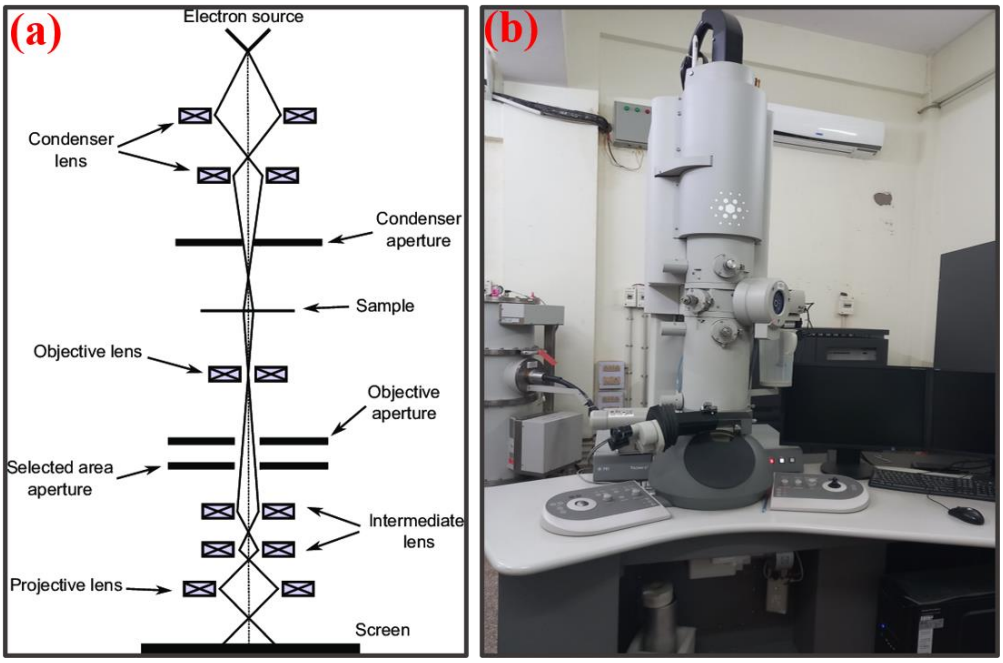

Fig. 2.7 (a) Schematic diagram of the components of TEM microscope (Courtesy: Research Gate) and (b) Photograph of the TEM instruments. (Courtesy: CIF, IIT (BHU))

Sample preparation is a very important aspect in any characterization technique and the same is in TEM analysis. In TEM, sample dispersed in a suitable (organic) solvent is drop cast in carbon film coated copper grid (mesh size 100/150/200) to

make the thinnest possible film enough to transmit electrons coming from the electron gun to form an image with minimum loss of energy and dried well. Figure 2.7 (a) and (b) shows the schematic diagram of various components of the TEM instrument and a photograph of the instrument.

2.3 Elemental Analysis

2.3.1 X-ray Photoelectron Spectroscopy (XPS)

It is a surface-sensitive chemical analysis method used to identify the elements present, their chemical states, overall electronic structure as well as composition. It is also called ESCA (Electron Spectroscopy for Chemical Analysis). It is based on the photoemission phenomenon initiated by irradiating the sample's surface using a beam of X-ray and the kinetic energy of emitted electrons ($E_{kinetic}$) are measured (*see* Fig. 2.8). The binding energy of these emitted photoelectrons ($E_{binding}$) is determined using the photoelectric effect equation

$$E_{binding} = E_{Photon} - (E_{kinetic} + \phi) \text{.....(Eq. 2.5)}$$

'E_{photon}' is the energy of X-ray photon used and 'Φ' is the work function. This technique detects all elements except H and He, and it requires ultra-high vacuum (UHV) of $10^{-6 \text{ to } -7}$ Pa. XPS spectrum has binding energy vs intensity (count per second) plot and obtained data is standardized at 284.8eV (binding energy of sp_3 carbon) by default. The wide scan survey spectrum ranges from 0 to 1200 eV binding energy. The penetration depth of XPS analysis is ~20 nm into the sample. [103]

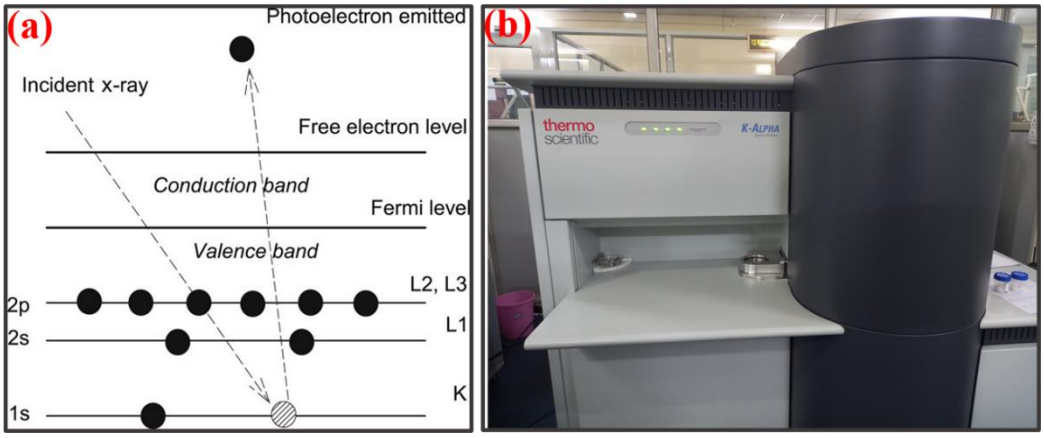

Fig. 2.8 (a) Photoelectron effect in XPS [103] and (b) Photograph of the XPS spectrophotometer. (Courtesy: CIF, IIT (BHU))

The powder sample in form of a pellet is loaded in the ultra-high vacuum chamber (UHV) of the instrument. Sample containing a volatile element such as iodine, sulfur is avoided as it contaminates the chamber at UHV in the machine.

2.3.2 Energy Dispersive X-ray Analysis (EDX)

It acts as an important supporting technique to find out the elements and their relative percentage into the specimen i.e., qualitative and quantitative elemental analysis. EDX systems are attached to the SEM and TEM instruments. EDX spectra show elements with relative peaks intensity and elemental mapping of each individual element is also obtained. It gives the bulk concentration of elements at 50 to 100 nm depth.

2.4 Surface Area Analysis: Brunauer–Emmett–Teller (BET) Theory

The determination of the surface area of any (hetero)catalytic active sample is done using a probe gas with help of the theory proposed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938 for physical multilayer adsorption. [104] The

probe gas is usually Nitrogen (N_2) acting as adsorbate, while the sample acts as adsorbent and measurement is conducted as 77K (boiling point of liquid N_2).

The BET theory is a further modification of Langmuir's Theory of monolayer adsorption, but it's for multilayer adsorption. The well-known form of **BET equation** used for specific surface area calculation from N_2 adsorption-desorption isotherm is as follow

$$\frac{1}{\upsilon[(p_o/p)-1]} = \frac{c-1}{\upsilon_m c}\left(\frac{p}{p_0}\right) + \frac{1}{\upsilon_m c} \text{.....(Eq. 2.6)}$$

Here, 'p' and 'p_0' are equilibrium and saturation pressure of adsorbate (N_2 here) at adsorption temperature, respectively, 'υ' is adsorbed gas volume, 'υ_m' is the volume for monolayer adsorption. The 'c' is the BET constant, it should be positive.

Fig. 2.9 Photograph of the Surface area measurement instrument. (Courtesy: CIF, IIT (BHU))

The plot of relative pressure (p/p_0) on the x-axis and $1/\upsilon[(p_0/p)-1]$ on the y-axis is called a BET plot. By making a linear relationship in the relative pressure area of 0.05 to 0.35, the slope and y-intercept are obtained which are further used to calculate c (BET constant) and υ_m (monolayer adsorption volume), hence the total and specific surface area of the material.

The determination of pore size distribution (and pore volume distribution) is made using Barrett, Joyner, and Halenda's (BJH) theory from adsorption isotherm with the help of Kelvin model of pore filling. It is applicable only for the mesopore and small macropore size range. The t-plot is used in the case of the microporous material.

Figure 2.9 shows the BELLSORP MAX II model of Microtrac BEL Corp., we utilized for performing N_2 adsorption-desorption measurements. There is pre-treatment of sample for a minimum of 4 h to remove any vapourable contamination along with heating, prior to transferring it into the sample tube at liquid N_2 temp.

2.5 Electrochemical Workstation: CHI7044 and Electrochemical Methods

In this section, the basic components of the electrochemical workstation and its working principles have been discussed. We used an electrochemical analyzer/workstation CHI7044, Made in the USA, for purpose of all electrochemical measurements. The block diagram of the instrument is shown in Figure 2.10.

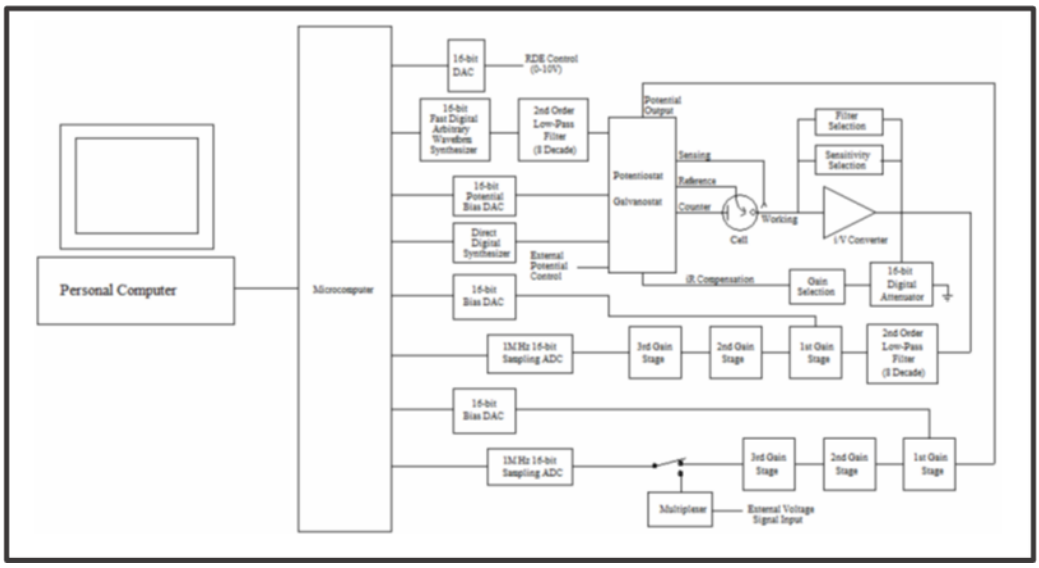

Fig. 2.10 Block Diagram of the CHI7044 instrument. (Courtesy: CH Instruments)

This instrument is utilized for Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Galvanic Charge Discharge (GCD), Impedance measurement, Open Circuit Potential (OCP) measurement, Tafel slope, etc. As a potentiostat, it measures the current between the working and counter electrode as a function of potential. The controlled parameter in a potentiostat is the cell potential, while the measured parameter is the cell current. All the measurements are performed in the electrochemical cell using three electrodes set up, working, counter and reference electrode.

2.5.1 Working Electrode

At the working electrode, the applied potential is the controlling parameter and output current is measured. Generally, gold, platinum or glassy carbon is used as working electrodes, at their surface material of interest is coated for electrochemical study.

2.5.2 Reference Electrode

It should have a constant electrochemical potential when no current passes through it. It is used to measure working electrode potential. Saturated calomel electrode (SCE) and Ag/AgCl electrode are common reference electrodes used in the lab.

2.5.3 Counter (Auxiliary) Electrode

It balances the redox reaction taking place at the working electrode and completes the cell circuit. The counter electrode should have a high surface area. Platinum wire electrode is a common electrode used for this purpose.

These electrodes are immersed into electrolytes (aqueous or non-aqueous electrolytes) kept into the electrochemical cell. [105,106] A representative image of the electrochemical cell setup is shown below (Fig. 2.11)

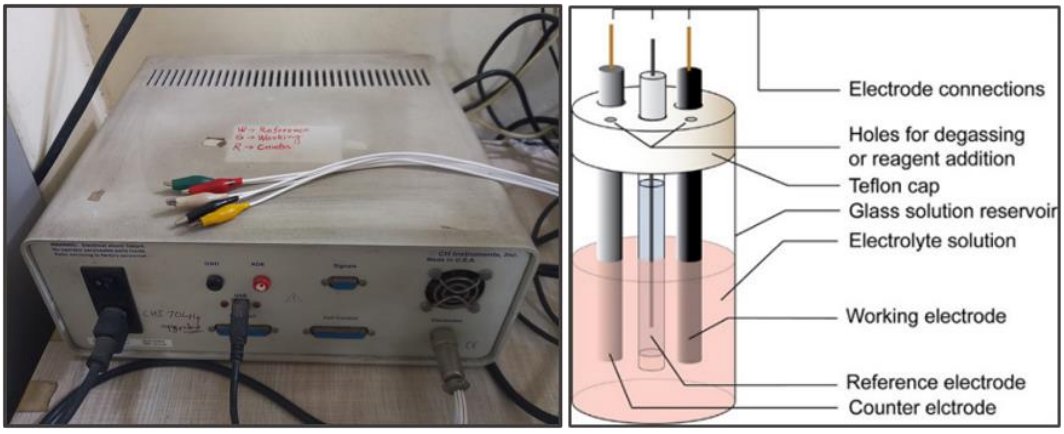

Fig. 2.11 CHI7044 electrochemical workstation (in our lab) and a representative electrochemical cell. Reprinted with permission from Ref. [106] Copyright@2017 The American Chemical Society and Division of Chemical Education, Inc.

A short description about associated terms CV, LSV, amperometry, chronoamperometry, Faradic-nonfaradic and Capacitive current is as follow

2.5.4 Cyclic Voltammetry and Linear Sweep Voltammetry

CV is a potentiodynamic electrochemical measurement to study the redox features of samples/materials. In CV, the potential of the working electrode varies according to an input scan rate (mV/sec) and current output is measured. The electrode potential ramps linearly versus time in the cyclic phase as in waveform Figure 2.12 (b). The applied potential on reaching its final input value, returns back to its initial input value giving response of output current in cyclic form, hence called cyclic voltammetry. In the Cyclic voltammogram, at the upper half, we get oxidation peak (positive current) and at the lower half, reduction peak (negative current) as shown in Figure 2.12 (c). [107, 109] It is to study the electron transfer properties and redox reactions of an analyte in a solution or material coated on a working electrode surface.

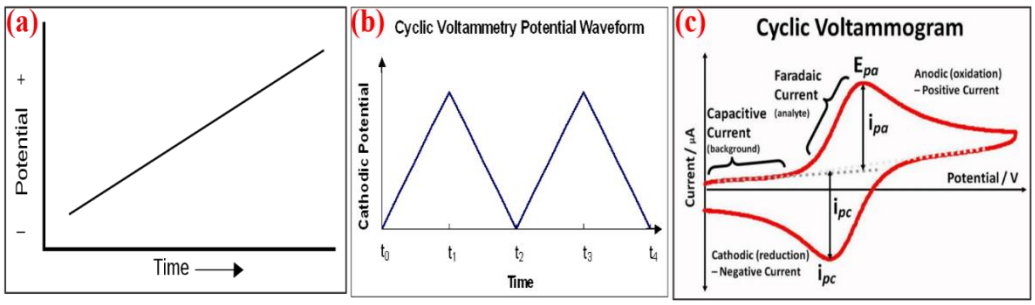

Fig. 2.12 LSV waveform, CV waveform and Cyclic Voltammogram. (Courtesy: Wikimedia Commons)

In Linear Sweep Voltammetry, the potential of the working electrode is varied linearly with respect to time (at a given scan rate) and reaches its final value (Fig. 2.12 (a)). It does not make a cycle. The current output is measured. Either oxidation

or reduction peak is obtained depending on the material's nature and potential range. LSV is performed for HER, OER and ORR studies.

The peak current (i_p) in cyclic voltammogram depends on scan rate as described by **Randles–Ševčík equation** as following

$$i_p = 0.4463\, nFAC \left(\frac{nFvD}{RT}\right)^{1/2} \text{.....(Eq. 2.7)}$$

Where 'i_p' stands for peak current, 'n' stands for the number of electrons transferred in the redox process, 'F' is Faraday constant, 'A' is the electrode area, 'C' is concentration, 'υ' is scan rate, 'D' is diffusion coefficient, 'R' is gas constant and 'T' is the temperature in kelvin.[108] Hence, the peak current (i_p) is directly proportional to the square root of the scan rate, as the scan rate increases, the peak current increases proportionally (also *see* Fig. 2.13)

$$i_p \propto \sqrt{v} \text{.....(Eq. 2.8)}$$

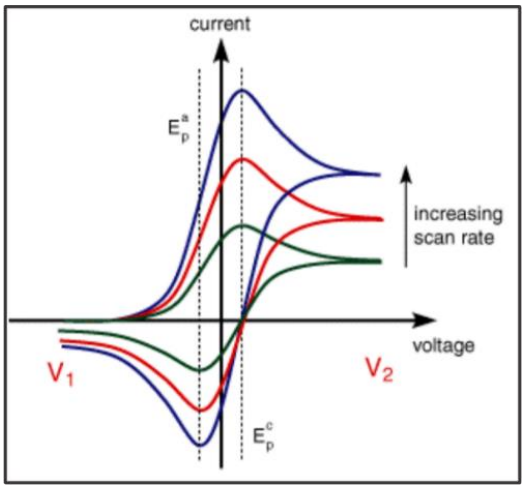

Fig. 2.13 Variation of peak current in cyclic voltammogram as a function of scan rate. [107]

In a diffusion control process, the change of current as a function of time in a step potential experiment is described by the **Cottrell equation** as following

$$i = \frac{nFAC_j^0\sqrt{D_j}}{\sqrt{\pi t}} \text{.....(Eq. 2.9)}$$

Here, 'I' stands for the current, 'n' stands for the number of electrons involved in a redox process, 'F' stands for Faraday constant, 'A' stands for the area of the electrode, 'c_j^0' for the initial concentration of the analyte, 'D_j' for the diffusion coefficient and 't' stands for time. here, current (i) is indirectly proportional to the square root of time. [109]

2.5.5 Amperometry, Chronoamperometry and Chronopotentiometry

In the Amperometry technique, a fixed potential is applied at the working electrode and output current is measured as a function of time. It is used for stability measurement in the case of energy conversion electrode materials and for the detection of redox-active species in bioanalysis.

In the Chronoamperometry technique, a potential is stepped up at the working electrode and current output due to the faradic process is measured as a function of time. It can be used to measure the current–time dependence of a diffusion-controlled process taking place at the electrode. It has implications for the stability and electrochemical activity of electrocatalysts. [109]

In chronopotentiometry, a fixed current is applied at the working electrode for a given period of time and the potential of W.E. is recorded as a function of time. This method is deployed to study chemical reaction mechanisms and kinetics as well as electrodeposition.

2.5.6 Faradic and Capacitive Current

In the faradic process, charged particles transfer from one bulk phase to another across the electrode via diffusion and involve electron transfer in form of a peak. The nature of species can be anticipated from the position of peak current (or peak potential).

In a Non-faradic process, charged particles are progressively stored at the electrode interface leading to capacitance at changing potential. It does not involve any chemical reactions i.e., charge transfer, only involves accumulation or removal of charges at the interface. It is also called 'capacitive current' or 'double layer current'. As the potential of an electrode varies, there is always the flow of some capacitive current. [109]

The total current is given as the sum of faradic ($i_{faradic}$) and capacitive current ($i_{capacitive}$) as following

$$i_{total} = i_{faradic} + i_{capacitive} \quad \text{(Eq. 2.10)}$$