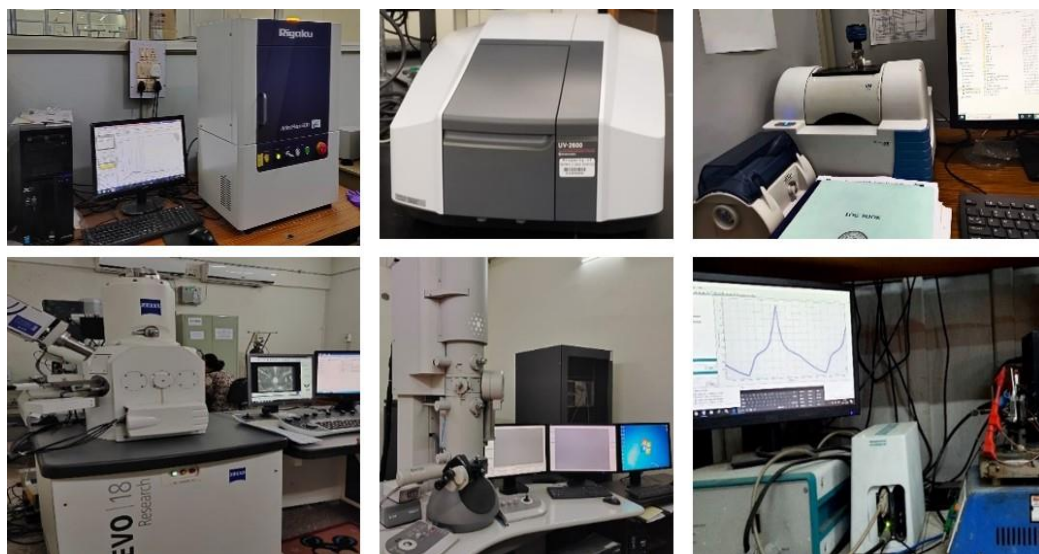


Chapter 2

Characterization techniques



This chapter provides the theory of the many experimental methods and their associated instrumentation to characterize the synthesized materials. The synthesized polymers and their nanocomposites are characterized with the help of various tools for structural, morphological and electrochemical measurements. The theoretical background of these techniques is discussed in detail in this chapter.

Characterization techniques

The initial step after preparing the materials is commonly to confirm the successful synthesis. XRD and FTIR, along with UV-Visible spectroscopy, are the main techniques for the structural characterization of materials. SEM and TEM are used for morphological characteristics such as texture, shape, topology, and size information since the electrochemical processes are surface-based phenomena. Identification of elements and their valance states were precisely performed by X-ray photoelectron spectroscopy (XPS). EDX/EDS, along with elemental mapping, gives an idea of surface elements and their uniform-nonuniform distribution in synthesized samples. Brunauer-Emmett-Teller (BET) theory is used to analyze the surface area and pore size of materials having electrochemical properties. Electrochemical measurements are done on CHI7044 instruments for electrocatalytic and charge storage applications.

2.1 Structural characterization

2.1.1 UV-Visible spectroscopy

The branch of science known as spectroscopy deals with the interaction of electromagnetic waves with matter. UV-visible spectroscopy is useful for identifying the absorption or reflectance band of species like biological molecules, macromolecules, metal ions, and organic compounds present in a solution by exposing the sample to monochromatic UV or visible light. This spectroscopic method obeys Beer-Lambert-law, which states that when monochromatic radiation travels through a solution of light-absorbing species, the rate of depletion in the intensity of incident radiation with the test solution's width is proportional to the incident radiation's intensity and concentration of the solution. Therefore, UV-visible spectroscopy can also be used to determine the concentration of the absorbing species present in the test solution

for a definite path length of the absorbing medium. Beer-Lambert's law is given in the equation as follows:

$$A = \log_{10} (I_0/I) = \epsilon cl \quad (\text{eq. 2.1})$$

where A stands for absorbance, I_0 represents the incident light's intensity, I stands for transmitted light intensity, ϵ is the molar absorptivity (unit $\text{l mol}^{-1} \text{ cm}^{-1}$), c represents the concentration of the test solution, l denotes path length of the light in solution,

The basic principle of UV-Visible spectroscopy is the extent of light absorption increases with the number of light-absorbing species. The specific wavelengths of an absorption spectrum can also help identify the functional groups present in a molecule by providing details on the type of bonds present in given conjugated organic compounds. Additionally, this method is frequently used to characterize nanoparticles because their optical characteristics are closely related to their size, shape, concentration, and dielectric environment [69], [70]. A UV-visible spectrum is a graph that shows the amount of light absorbed with its wavelength in this spectrum, which is recorded by a UV-visible spectrophotometer. It determines the ratio I/I_0 , which is known as transmittance (T) (recorded in terms of percentage transmittance (%T)), by recording the light intensity before passing through the sample (I_0) and after passing through the sample (I). The %T and absorbance A is related as follows:

$$\text{Absorbance } A = 2 - \log_{10} \%T \quad (\text{eq. 2.2})$$

The components of the UV-visible spectrophotometer include a light source, a monochromator or diffraction grating for isolating a specific wavelength, a sample holder, and a detector. It is of two types single beam and double-beam spectrophotometer. The block diagram and photograph of the UV-Visible spectrophotometer as displayed in figure 2.1.

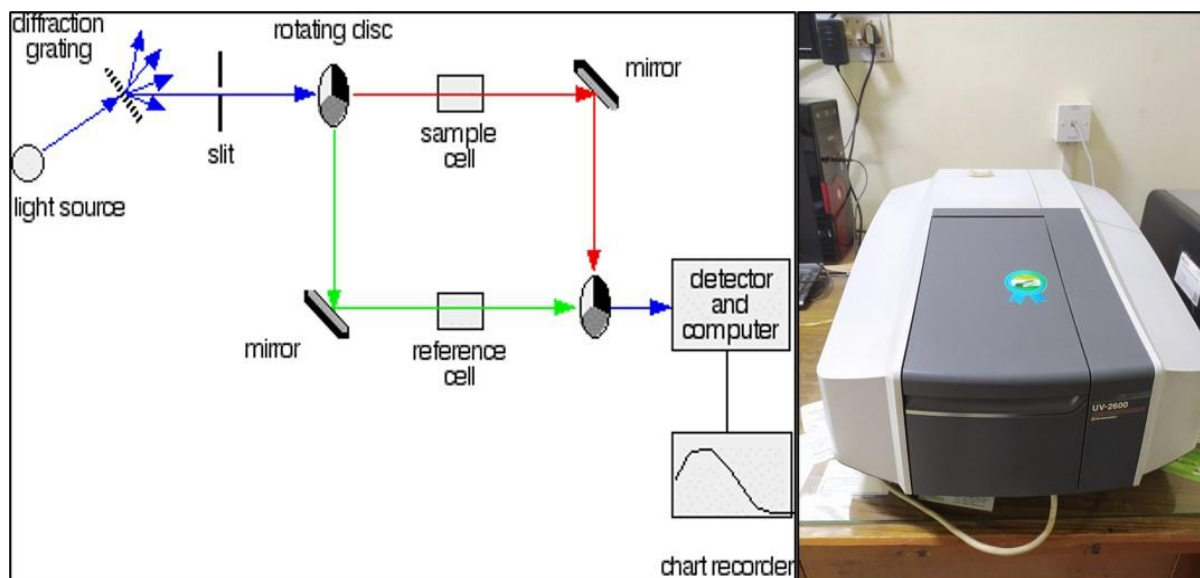


Figure 2.1: Schematic diagram and photograph of a UV-Visible spectrophotometer. (Courtesy: In our lab SMST, IIT(BHU))

2.1.2 X-ray diffraction

XRD is a basic and important non-destructive analytical tool for examining the materials' structural details, such as crystallinity, phases, grain size, strain, crystallite size, and crystal defects. When an X-ray beam is impacted on the sample, the constituent atoms produce an interference pattern of waves due to their regular arrangement in a crystal, which is the fundamental basis for characterizing the materials. The X-ray source of XRD analysis is Cu K-alpha ($\lambda = 1.5406 \text{ \AA}$) radiation. Various parameters in XRD, such as 2θ range, step size, scan rate, tube voltage, and current, play a key role in measurements. The identification of phases of crystalline materials is carried out with the help of a standard database known as the JCPDS database. The X-ray diffraction in a crystal structure occurs under **Bragg's equation**. It relates to the crystal's interplanar spacing (d) with the wavelength of radiation and its incidence angle (θ) as follows

$$2d \sin \theta = n \lambda \quad (\text{where } n \text{ is an integer}) \quad (\text{eq. 2.3})$$

The pattern that forms when the angular positions are plotted against the intensities of the radiation's diffraction peaks serves as the material's characteristic signature. The structural characterization of XRD of synthesized materials was examined in our thesis study using a Rigaku min flex 600 X-ray Diffractometer (figure 2.2).

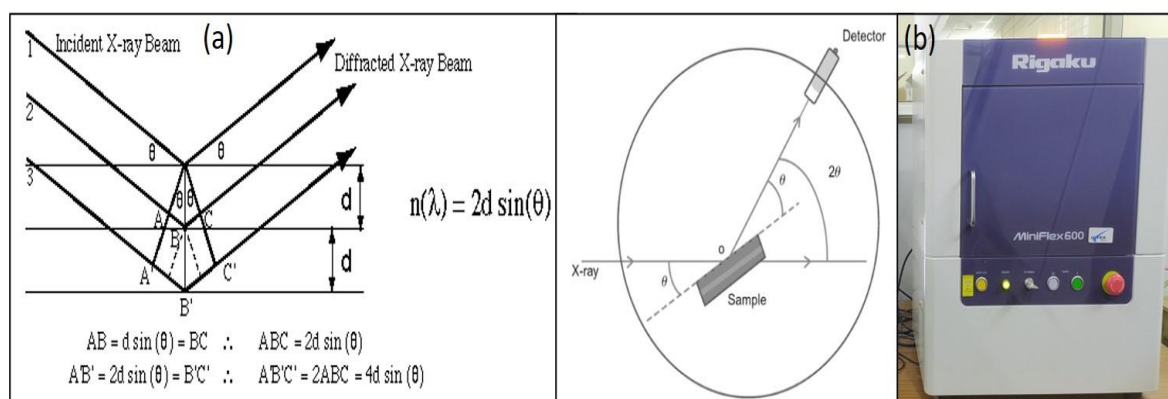


Figure 2.2: (a) Block diagram of the diffraction pattern of X-ray, and (b) Diffractometer photograph. (Courtesy: CIF, IIT(BHU))

2.1.3 FTIR spectroscopy

FTIR spectroscopy is utilized to analyze various organic functional groups, polymers, biological samples and inorganic materials in their thin film, solid powder, pellet form, liquids and other forms. FTIR spectroscopy deals with infrared (IR) radiation ranging from 450 and 5000 cm^{-1} . IR radiation generates enough energy to cause the chemical bonds of a molecule to vibrate (stretching or bending). When IR radiation strikes a molecule, it only absorbs wavelengths with energy sufficient to trigger a specific vibration in a bond while transmitting all other wavelengths. In other words, the IR radiation of a particular frequency that matches a molecule's bond frequency is absorbed and visible in the resulting spectrum [69]. The FTIR spectra of the functional groups that are already present on the surface of nanomaterials differ from those of the corresponding free groups. To characterize and identify the functional groups,

the surface chemistry of these materials can be studied using FTIR spectroscopy and bonding patterns [69], [70]. A typical block diagram and photograph of the spectrophotometer are displayed in figure 2.3.

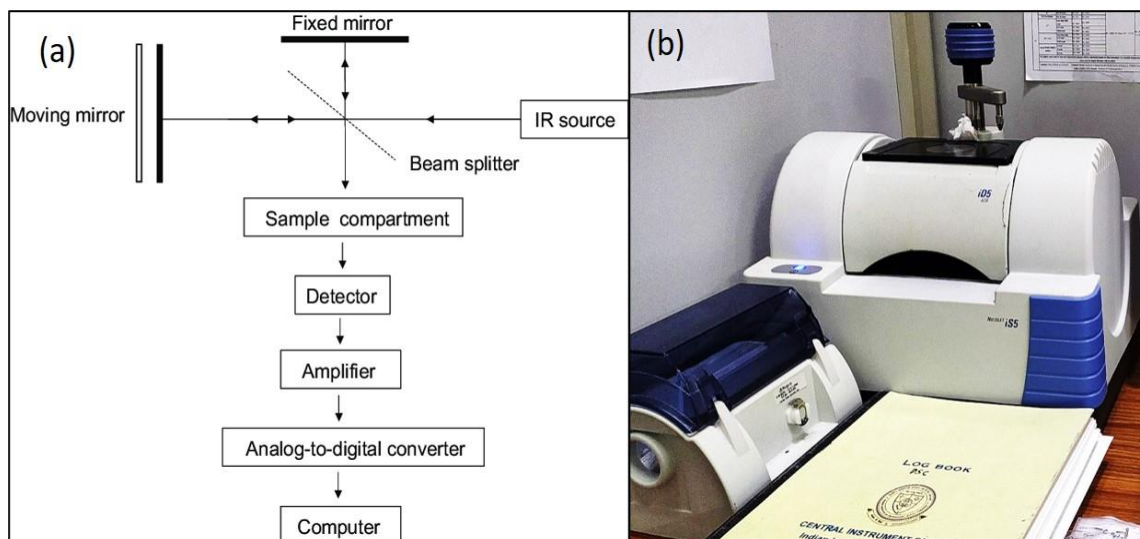


Figure 2.3: (a) Block diagram (b) photograph of FTIR spectrophotometer. (Courtesy: CIF, IIT(BHU))

A conventional FTIR spectrophotometer consists of a light source, sample cell, interferometer, detector, signal amplifier, and display unit. The sample is exposed to IR radiation from the light source, which travels through the interferometer and is detected by the detector. The received signal is then amplified and transformed into a readable form, known as an interferogram, and displayed in the display unit.

2.2 Morphological characterization

It covers the surface analysis of synthesized materials in the scale range of micrometer to the nanometer range. The instruments used for the surface analysis are as follows

2.2.1 Scanning electron microscopy (SEM)

SEM is an essential characterization tool that scans a specimen's outer surface with a focussed electron beam to provide enlarged, high-resolution images of the sample. It provides information on the material's topography, microstructure, and chemical composition. A typical SEM instrument is composed of the following essential components:

- i. Electron Gun
- ii. Apertures
- iii. Electron lenses (Condenser and objective)
- iv. Scanning coils
- v. Detector (different for SEs and BSEs)

Electrons are produced from a source, such as lanthanum hexaboride (LaB₆) single crystals or a heated tungsten filament, and are then accelerated by a voltage and pointed toward the centre of an electron optical column that contains various magnetic lenses to create a focused electron beam that will strike the surface of the material. Scanning coils positioned above the objective lens control the focus of the electron beam, allowing it to scan over the specimen surface. The interaction between the incident electron and the sample is crucial for image generation. These interactions fall into two categories: elastic interactions (Backscattered electrons, BSEs) and inelastic interactions (secondary electrons, SEs), as displayed in figure 2.4.

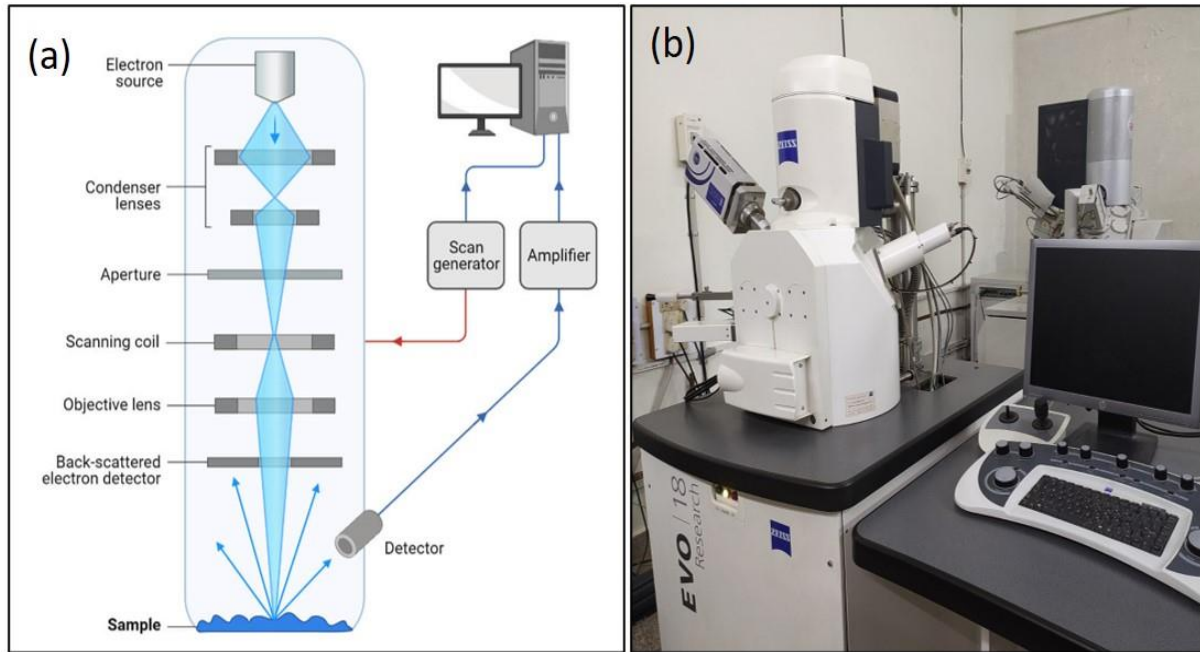


Figure 2.4: (a) Block diagram (data extracted from microbe notes) and (b) photograph of SEM microscope instrument. (Courtesy: CIF, IIT(BHU))

The BSEs generated from the deeper portion of the sample provide information about the sample's topography and constituents. The SEs generated from the sample's surface area provide topographic contrast data and a visual representation of the outer surface roughness. Conducting samples was investigated by directly placing them over carbon tape. Before the examination, the metal coating is applied to non-conducting samples using metals like gold, platinum, silver, etc. The SEs and BSEs eventually influenced the formation of the SEM image. [69], [70]

2.2.2 Transmission electron microscopy (TEM)

TEM is a powerful and sophisticated characterization tool that examines the interaction of a beam of highly energetic electrons (60–300 keV) with a thin sample (<100 nm) as it is transmitted through the sample. Images of the highly resolved and enlarged sample are

produced due to this interaction. This technique helps in examining the distribution, chemical make-up, electrical characteristics, and microstructure of the nanomaterials in the sample.

The key components of a TEM instrument in the column structure are:

- i. Electron Gun
- ii. Scanning and condenser lenses
- iii. Sample holder
- iv. Objective lenses
- v. Signals detections

A heated tungsten filament is most frequently employed as an electron gun, which acts as the electron source. It emits electrons that move down a column where a high aperture condenser lens concentrates them into a very narrow beam and filters out the high-angle electrons. This beam of high-speed electrons illuminated the specimen mounted on a sample holder. A few electrons scatter and disappear from the beam depending on the density of the material. Now, an image of the sample is created on a phosphorescent screen by the electron beam being focused on it. All of these images of the sample are either digitally taken by a CCD camera positioned behind the screen or immediately exposed over a photographic emulsion. One of the significant advantages of this method is the capability to inspect the materials in reciprocal and real space, as well as diffraction and imaging modes. In traditional microscopy, the imaging is done by selectively allowing the transmitted beam (also known as bright-field imaging) or the diffracted beam (also known as dark-field imaging) to descend to the microscope column. The fluctuation of the transmitted beam and diffracted beam, which results from variation in diffraction circumstances and relies on the microstructural feature of the electron route,

determines the level of picture contrast [71]. A schematic diagram and photograph of a typical TEM are displayed in figure 2.5.

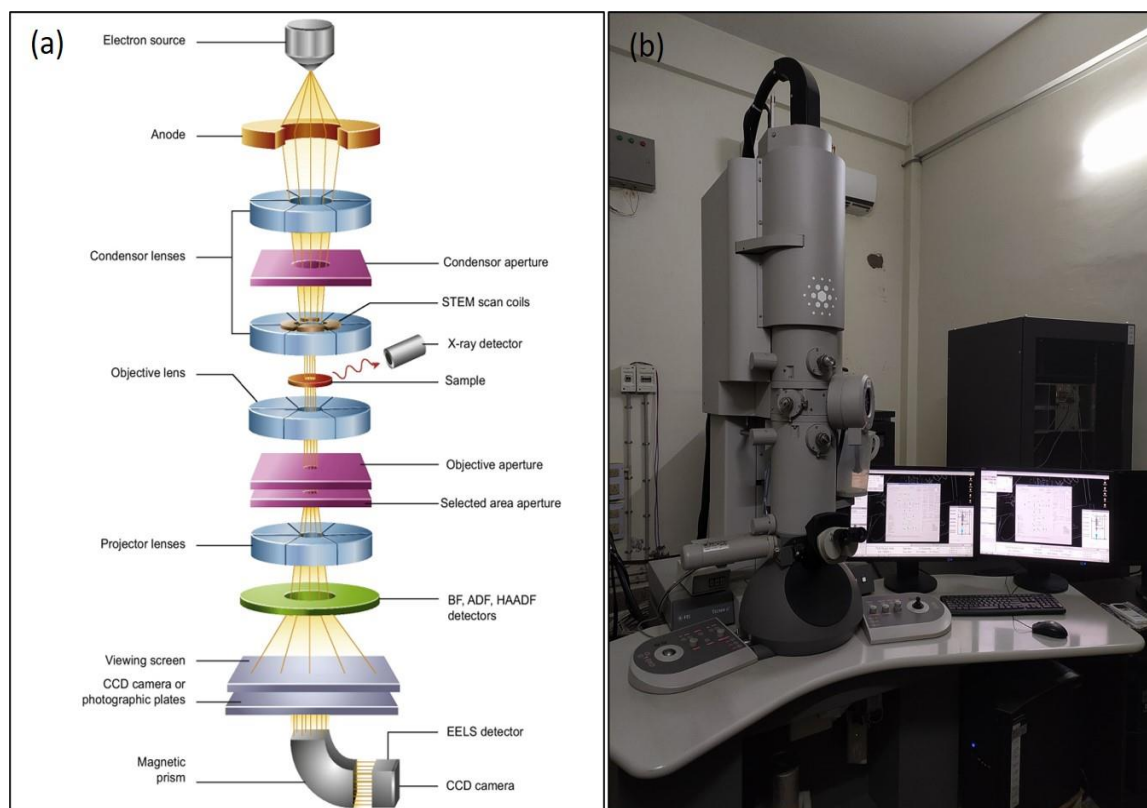


Figure 2.5: (a) Schematic diagram [71] and (b) photograph of a typical TEM microscope instrument. (Courtesy: CIF, IIT(BHU))

Our samples were prepared on a copper grid covered with carbon, and transmission electron microscopy (TEM)-FEI-Tecnaï 20 U Twin with EDX and Tecnaï 20 G2 were taken for TEM micrographs investigation (figure 2.5(b)).

2.3 Elemental analysis

2.3.1 X-ray photoelectron spectroscopy (XPS)

XPS is the name of a particular type of electron spectroscopy used for chemical analysis. This method directs a monochromatic X-ray beam of known energy toward the sample surface, knocking out one of the core electrons with computed kinetic energy (KE). The physical

procedure used in XPS is illustrated in Figure 2.6 using the photoelectric effect. The following equation can be used to calculate the binding energy of an electron (BE):

$$KE = h\nu - BE - \Phi_s \quad (\text{Eq. 2.4})$$

where h = Planck's constant, ν = frequency of x-rays, and Φ_s = work function

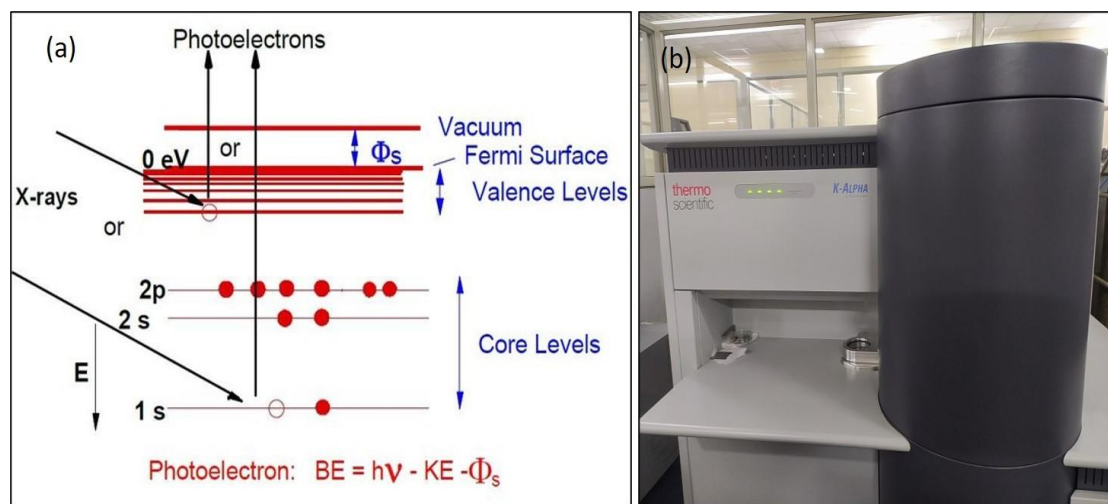


Figure 2.6: (a) Basic principle (data extracted from researchgate) and (b) photograph of XPS spectrophotometer. (Courtesy: CIF, IIT(BHU))

A typical XPS approach exposes a sample to a primary beam of photons and electrons. As a result of the primary beam's impact on the sample surface, a secondary beam is produced from the sample, which is then examined or detected by a spectrometer. XPS is a surface-sensitive method that can identify the elements present in a material and its electronic state. All elements may be identified using this method except hydrogen and helium. In the existing thesis, we used this method to analyze the elements and determine their oxidation states in the synthesized nanocomposites.

2.3.2 Energy dispersive X-ray analysis (EDX)

EDX is an essential supporting tool to analyze the elements and their relative percentage in the sample, i.e., quantitative and qualitative analysis of elements. It is associated with both SEM

and TEM instruments. It shows the relative peak intensity of elements, and their distribution is given by elemental mapping up to a depth of 100 nm.

2.4 Surface area analysis: Brunauer-Emmett-Teller (BET) theory

Using probing gas and the physical multilayer adsorption hypothesis put forward by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938, it is possible to measure the surface area of any electrochemically active substance [72]. The sample serves as the adsorbent while the probing gas, typically nitrogen (N₂), acts as adsorbate and the measurement is carried out at 77 K. The BET theory, which is for multilayer adsorption, is modified Langmuir's Theory of adsorption of the monolayer. The calculation of surface area using N₂ adsorption-desorption isotherm was carried out with the help of a well-known BET equation as follows

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \left(\frac{P}{P_0} \right) \quad (\text{eq. 2.5})$$

where X is the volume of adsorbed gas, X_m is the volume of monolayer adsorption, P/P₀ is the relative pressure at adsorption temperature and C is the adsorption constant which should be positive.

A plot between $1/X[(P_0/P)-1]$ on the y-axis and relative pressure (P/P_0) gives the BET plot. The slope and y-intercept are obtained from a linear relationship in the relative pressure area of 0.05 to 0.35; from there, C and X_m can be calculated, determining materials' total and specific surface areas. Barrett, Joyner and Halenda's (BJH) theory is used to determine pore size distribution (and hence pore volume) from adsorption isotherm using the Kelvin model of pore filling. This is only valid for small micropore and mesoporous range sizes. The BET measurement in this thesis was done using the BELLSORP MAX II model Microtrac Corp as displayed in figure 2.7. The sample is pre-treated with heat to remove any volatile

contamination for approximately 4 hours before putting it in the sample tube for surface area measurements.

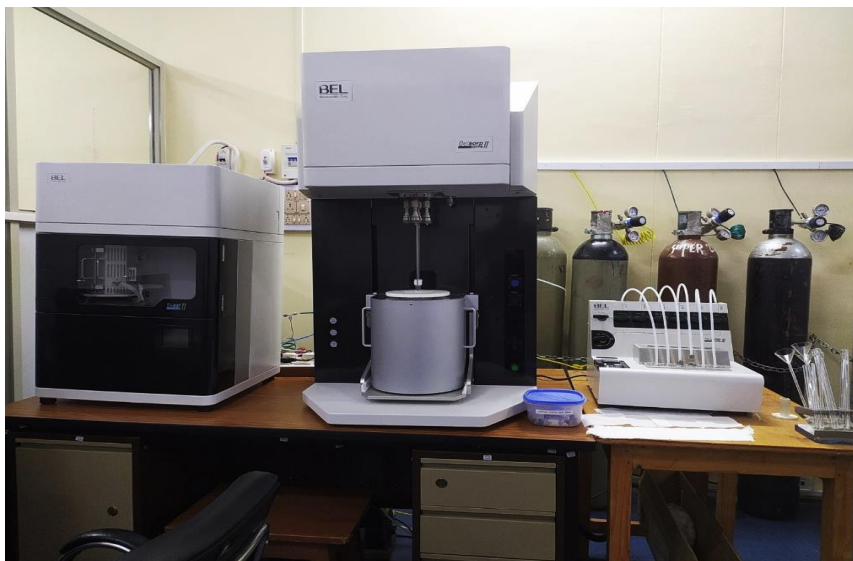


Figure 2.7: Photograph of BET instrument for surface area measurement. (Courtesy: CIF, IIT(BHU))

2.5 Electrochemical analysis

The measurement of electrochemical properties and application of materials was done on the CHI7044 workstation using the following techniques:

2.5.1 CHI7044 electrochemical workstation

The working principle and essential components are discussed in this section. The CHI7044 electrochemical workstation, made in the USA, is used for all electrochemical measurements, as shown in figure 2.8.

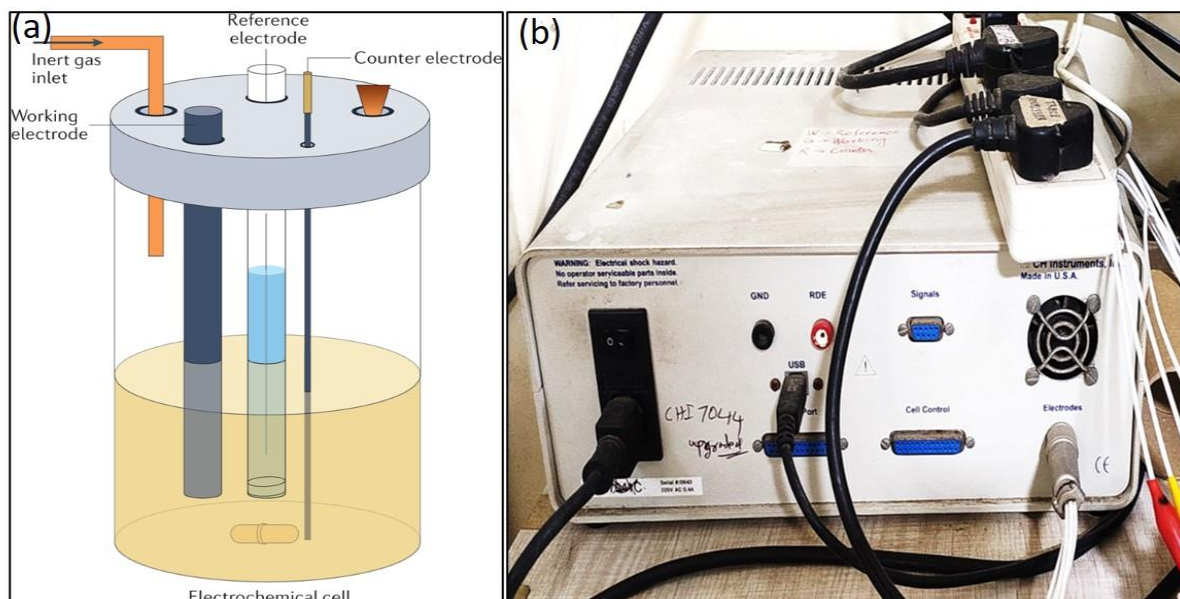


Figure 2.8: (a) A typical three-electrode system of an electrochemical cell (data extracted from ref. [73]) and (b) CHI7044 electrochemical workstation (in our lab).

The measurements of various procedures like cyclic voltammetry (CV), differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), galvanic charge-discharge (GCD), and Amperometry were done on the CHI7044 electrochemical workstation and are discussed later. The current is measured between the working and the counter electrode as a function of the potential. The electrochemical measurements were performed on a three-electrode system having a reference electrode, a working electrode, and a counter electrode.

2.5.1 CV and LSV techniques

Researchers typically employ the effective and well-known electrochemical technique known as cyclic voltammetry (CV) to investigate how molecular species are reduced and oxidized. In a CV measurement, the working electrode's potential is swept linearly with respect to time. (figure 2.9). In a CV experiment, after reaching the target potential, the working electrode's

potential ramps in the opposite direction to return to the initial potential. The working electrode current vs. applied voltage plot produces the cyclic voltammogram trace [45]. CV is also significantly valuable for studying chemical reactions initiated by electron transfer, such as catalysis and charge storage.

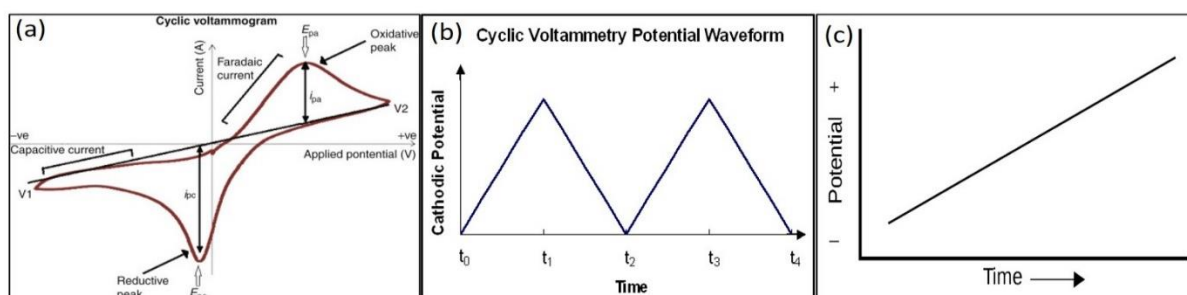


Figure 2.9: (a) A typical cyclic voltammogram (data extracted from ref. [74]), (b) CV waveform and (c) LSV waveform. (data extracted from Wikipedia)

A voltammetric technique named LSV measures the working electrode current while linearly sweeping the potential between the reference and the working electrode over time. Oxidation or reduction of a species is reflected as a peak or trough in the current signal at the potential at which it begins to occur. It does not complete a cycle. This technique is used for the HER, OER, ORR and other applications.

The **Randles–Ševčík equation**, used in CV, explains how the scan rate affects peak current (i_p). The **Randles–Ševčík equation** [45] can be written as follows

$$i_p = 0.4463 nFAC (nFvD/RT)^{1/2} \quad (\text{eq. 2.6})$$

where n is the number of electron transfers, F represents the Faraday constant, electrode area is represented by A , C stands for concentration, v represents scan rate, D represents diffusion coefficient, R denotes the gas constant, and T is the temperature (Kelvin). Thus, the peak current (i_p) is proportional to the square root of the scan rate, i.e., $i_p \propto v^{1/2}$.

In a step potential experiment, the process of changing current as a function of time represents diffusion-controlled and is given by the Cottrell equation [45] as follows

$$i = nFAC_0^*(D/\pi t)^{1/2} \quad (\text{eq. 2.7})$$

2.5.2 DPV technique

DPV is an electrochemical measurement technique that is a derivative of LSV and staircase voltammetry. The potential linear sweep or stairsteps are subjected to a series of regular voltage pulses [45]. The current is measured right before each change in potential in order to plot the current difference as a function of potential. It is possible to decrease the charging current's impact by sampling it shortly before the potential is adjusted. In contrast, the current produced by a sequence of progressively bigger potential pulses is contrasted with the current at a fixed "baseline" voltage in standard pulse voltammetry. These measurements can be used to study the redox properties of extremely low chemical concentrations because of the following two characteristics: 1) electrode reactions are investigated more precisely because it only extracts faradaic current. 2) High sensitivity is attained in these tests by minimizing the impact of the charging current.

2.5.3 EIS technique

EIS is a helpful technique for examining materials' interfacial properties like resistance, electron transfer, and electrode reactions [75]. It is a susceptible characterization method used to assess chemical systems' electrical behavior without causing damage. The temporal response of chemical processes is described by EIS systems using low amplitude alternating current (AC) voltages dispersed over a range of frequencies. A working, reference and counter-electrode configuration are used to transfer a known voltage from the working electrode to the counter electrode using an electrolytic solution. Quantitative measurements produced by the EIS allow

for evaluating small-scale chemical mechanisms at the electrode interface and within the electrolytic solution. EIS is so helpful in determining components' electrical and dielectric properties in research disciplines looking at electrocatalysis, batteries, corrosion, etc.

2.5.8 Galvanic charge-discharge (GCD)

The galvanic charge-discharge (GCD) technique is used to investigate the materials' specific capacitance (C_{sp}) under current controlled conditions [45]. C_{sp} can be calculated using a discharge curve as follows:

$$C_{sp} = i \times \Delta t / \Delta V \times m \quad (\text{eq. 2.8})$$

where i stands for current applied, ΔV represents voltage window, Δt denotes discharge time, and m stands for the active mass of electrode material.

2.5.9 Amperometry: chronopotentiometry and chronoamperometry

Amperometry is a technique in which a constant potential is applied at the working electrode to measure the output current as a function of time. This technique is used to investigate the stability of electrode materials in energy conversion and the detection of redox-active species in the case of bioanalysis.

Chronopotentiometry is a technique in which the potential of the working electrode is measured with respect to time by applying a fixed current at the working electrode for a given time. It is used to study the kinetics and mechanism of chemical reactions and electrodeposition.

Chronoamperometry is a technique in which output current due to the faradic process is recorded as a function of time by a stepped-up potential over the working electrode. It is used to record the current-time response of a diffusion-controlled process. It is used to investigate the electrochemical activity of materials and their stability. [45]

2.5.10 Faradic and capacitive current

In the faradic process, charged particles diffuse over the electrode from one bulk phase to another, transferring electrons in the form of a current peak. The peak position of current or potential is used to interpret the electrochemical nature of species.

The charged particles are gradually accumulated at the electrode interface in the case of a non-faradic process, resulting in capacitance at the varying potential. In this process, there is no chemical reaction (charge transfer) occurs. Only charge accumulation or removal at the interface appears. Thus, it is termed a double layer or capacitive current. There is always some capacitive current flow when the electrode potential varies[45]. Hence the total current is the combination of faradic and capacitive current as follows

$$i_{total} = i_{faradic} + i_{capacitive} \quad (\text{eq. 2.9})$$