Experimental Techniques

This chapter described the theory of instrumentation and different experimental methods used for characterizations of prepared materials. The nanomaterials and coordination polymers are extensively characterized by several characterization techniques. The characterization techniques include UV-visible spectroscopy, X-ray Diffractometer (XRD), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDX), Scanning Electron Microscopy (SEM), and Atomic Force Microscope (AFM). UV-visible spectrophotometer has been used for optical sensing of different analytes and cyclic voltammetry (CV) setup has been used for electrochemical characterization. The core background of each technique is covered in this proceeding chapter.

2.1 Characterization Techniques

2.1.1 Ultraviolet-Visible (UV-Vis) Spectroscopy

Spectroscopy deals with the study of interaction of electromagnetic radiations with matter. The interaction of atom/molecule with electromagnetic wave result into the some change occurs within the atom/molecule can be rationalized.

There are two type of light illuminating source used in UV visible spectroscopy. First one is hydrogen-deuterium lamps as they cover the whole UV region (200- 400 nm) and other is tungsten filament lamps, as specifically it emit the radiations above to 375 nm (375-2500 nm), hence used in visible region. Ultraviolet and visible spectrometers have become the most significant analytical instrument in laboratory [Perkampus, 1992]. In several applications other methods could be applied but none equal UV-Visible spectrometry for its versatility, simplicity, speed, cost-effectiveness and accuracy.

UV-Vis spectroscopy involves the spectroscopy of photons in the UV-Visible region of the electromagnetic spectrum. The materials like highly conjugated organic compounds, biological macromolecules and transition metal ions, can absorb light in UV or visible range of electromagnetic spectrum depending upon their electronic structure.

Molecules containing non-bonding electrons or π-electrons can absorb energy in the form of visible or ultraviolet light to excite the electrons to higher energy anti-bonding molecular orbitals. If easily electrons excited, the longer wavelength of light can absorb. UV-Vis spectrum is a graph of wavelength in UV or visible regions versus light absorbed. UV-Vis spectrophotometer produced the Spectrum. It measures intensity of light passing through a sample (I) and compares it to intensity of light before it passes through sample (Io). The ratio I/Io are termed as the transmittance and is generally written as percentage transmittance (%T). The relation between % transmittance and absorbance, A, is given by Eq. 2.1

$$A = 2 - \log (\%T) \qquad \text{Eq. 2.1}$$

Electron transfers from ground state to excited state after absorption of energy leads to transition. So, absorption maxima value for any molecule depends on energy difference between ground and excited state level; larger difference of energies leads to larger absorption frequency and thus smaller will be wavelength. Band position (depends on energy difference of electronic levels) and intensity (depends on both energy difference between the ground and excited states and interaction between the radiation with electronic system) are two important characteristics of absorption band. A spectrophotometer contains a sample holder, light source, monochromator or a diffraction grating to separate characteristic wavelengths of light, and a detector. The radiation source is deuterium arc lamp, tungsten filament, and in recent times xenon arc lamps and light-emitting diodes. Detector is charged coupled device (CCD) or

photodiode. A spectrophotometer can either be based on the single beam or double beam. In a single beam spectrophotometer, a continuous source or fixed wavelength light source is utilized. The dual beam simplifies this process through simultaneously detection of I and *Io* of sample and reference cells, respectively as shown in Figure 2.1[Bordoloi, 2018]. We performed optical measurements with Epoch 2 microplate reader Biotech (USA) spectrophotometer in quartz cuvette of 1 cm optical path length.
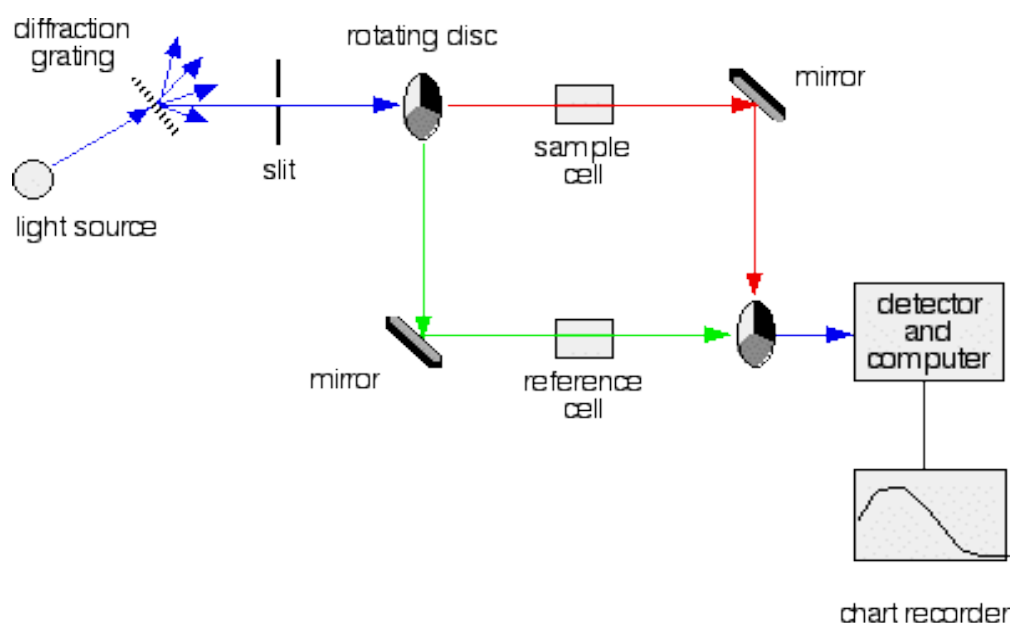

Figure 2.1 Schematic representation of dual beam UV-Vis spectrophotometer [Bordoloi, 2018].

2.1.2 Fourier transforms infrared spectroscopy (FT-IR)

Functional groups attached to the nanomaterials surface show different FT-IR pattern than those of free groups, hence FT-IR provide information about the surface chemistry of nanomaterials. Identification of particular types of functional groups or chemical bonds is possible by infrared spectroscopy. Infrared radiation does not have enough energy to induce electronic transitions as UV-visible, hence bond stretching and bending is possible by absorption of energy. Absorption of Infrared radiation is limited for compounds with small energy differences in achievable rotational and vibrational

states. Net change in dipole moment of molecule is essential for IR absorption. If the vibrational frequency matches with radiation frequency of molecule then radiation will be absorbed, resulting a change in molecular vibration amplitude. The most useful Infrared radiation region for the spectrum interpretation lies between ranges 400-4000 cm^{-1}. When a molecule absorbs infrared radiation, one of its bonds experiences a change in characteristics vibrational energy which reflects in the typical IR spectrum. Each bond has a characteristic frequency in the infrared part of the electromagnetic spectrum. Infrared spectrometers employing an interferometer and having no monochromator is used now a days. These non-dispersive instruments, known as Fourier transform (FT) spectrometers, have increased sensitivity and can document spectra much more rapidly than the dispersive type [Skoog et al., 2010; Harvey et al., 1956]. Particular frequency which matches the characteristic frequency of a specific bond will be absorbed, get reflected in a spectrum. Typical block diagram of FT-IR instrumentation is shown in Figure 2.2 [Mahalingam, 2018].
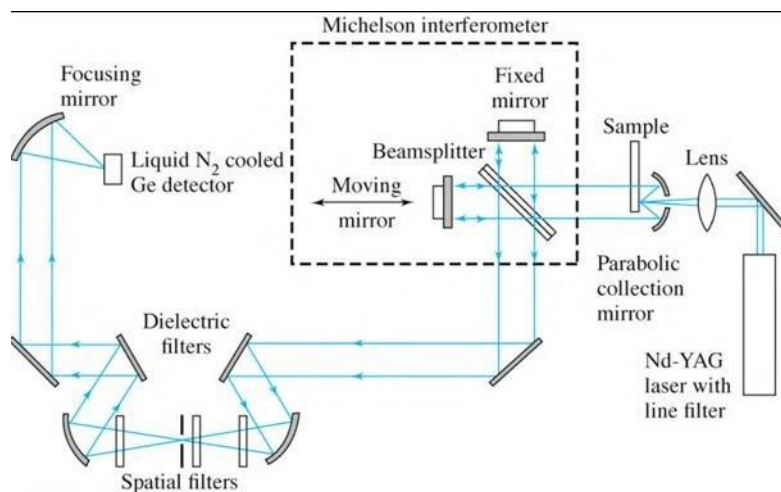

Figure 2.2 Block diagram for FT-IR [Mahalingam, 2018].

We have utilized FT–IR technique as preliminary studies to interpret the interaction of metal and functional groups (S–Ag, N–Ag, S–Pd and N–Pd). Nano silver /gold interacts

with nitrogen or sulphur atom present in the molecule, thereby electron density get transferred from organic functionalities to metal surface hence the characteristics vibrational stretching (C–H, N H, S–H, C–N, C–S) frequency get changed.

FT-IR plot is (%) transmittance Vs vibrational frequency in wave numbers (cm^{-1}). The FT-IR measurements of film and powder samples were conducted in transmission mode. We performed optical measurements with Perkin- Elmer 783 spectrometer.

2.1.3 X-ray Diffractometer (XRD)

X-ray Diffractometer (XRD) is a flexible technique that provides detailed information about the crystallographic structure as well as chemical composition of natural and synthesized materials.

It works on the theory when a monochromatic X-ray beam with wavelength λ is projected onto a material at an angle θ, diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number of wavelengths. The atoms are in order such a manner that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the particular material. In any crystal, planes exist in a number of different orientations, each with its own specified-spacing.

W. H. Bragg and his son W. L. Bragg establish a relationship to describe cleavage faces of crystals to reflect X-ray beams at certain angles of incidence θ and the variable λ is the wavelength of the incident X-ray beam and n is an integer and d is distance between atomic layers in a crystal. This observation is an example of X-ray wave interference, commonly known as X-ray diffraction and was direct evidence for the periodic atomic structure of crystals (Figure 2.3) [Barcikowski et al., 2016].
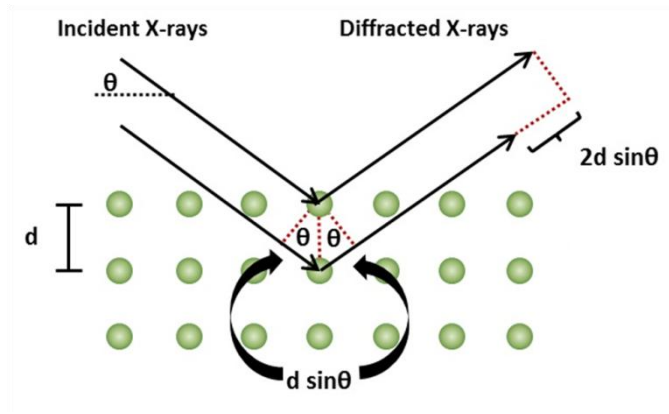
Figure 2.3 Schematic representation of X-ray beam incident on a crystallographic material [Barcikowski et al., 2016].

Bragg's law is given by,

$$n\lambda = 2d\sin\theta \qquad\qquad \text{Eq. 2.2}$$

Where, d is the spacing of the layers, θ is the incident angle of the photons and λ is wavelength of the X-rays,

Bragg's Law conditions are satisfied by varying angle θ, in polycrystalline materials (different d-spacing). Plotting intensities and angular positions of resultant diffracted peaks results a pattern, is characteristic of particular sample. When various phases are present, resultant diffractogram is plotted by the sum of individual patterns.

By X-ray diffraction, chemical, physical and structural, information about material can be investigated.

Powder XRD uses X-rays to examine and measure nature of materials by measuring the X-rays diffraction from atoms planes within the provided material. It is depends on both the length scale of crystalline order persists as well as type and relative position of atoms. So, it determine the spacing between lattice planes, crystalline nature of materials, crystalline phases, the length scales, preferential ordering and epitaxial growth of crystallites.

The prepared, mechanically milled and rapidly solidified samples were characterized by using Rigaku Smart Lab X-ray Diffractometer (Figure 6). The latter is attached to an X-ray generator operated at 45 keV and 40 mA in most of the cases. In the present investigation Cu-Kα (λ=1.5405Å) has been used. The diffractometer was calibrated using silicon powder. Single crystal silicon was used as standard for obtaining the accurate value of 2θ for calculation of the quasi lattice parameter. The XRD patterns collected from cross section of as-cast, powder and ribbon samples typically over 10-80° in 2θ; using a step size of $0.05°$ (These parameters were also varied as per need). The XRD characterization was used routinely to identify the structural phases present in the samples (DCB., 1967; LV A., 1968; SR CBaS, 2001).

2.1.4 X-ray Photoelectron Spectroscopy (XPS)

Irradiation of the surface of sample by monochromatic X rays is called as X-ray photo electron spectroscopy (XPS). It is also termed as electron spectroscopy for chemical analysis (ESCA). Figure 2.4 representing the schematics of physical process of XPS. It is based on principle of photoelectric effect. The three lower lines mark as Eb E`b E``b stand for energy of the inner shell K and L electron of an atom. The upper lines are outer shell/ valance electron energy level. One photon of monochromatic X rays beam (known energy hυ) ejects an electron from the K orbital of an energy E_b, represented as

$$A + h\upsilon \longrightarrow A^{*+} + e$$
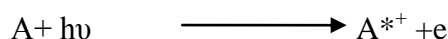
A is an ion or molecule and A^{*+} is excited state. An electron spectrometer is used for the measurement of kinetic energy of an emitted electron (E_K), so the binding energy of electron (E_b) can be measured by the following equation where, W is work function of the spectrometer.
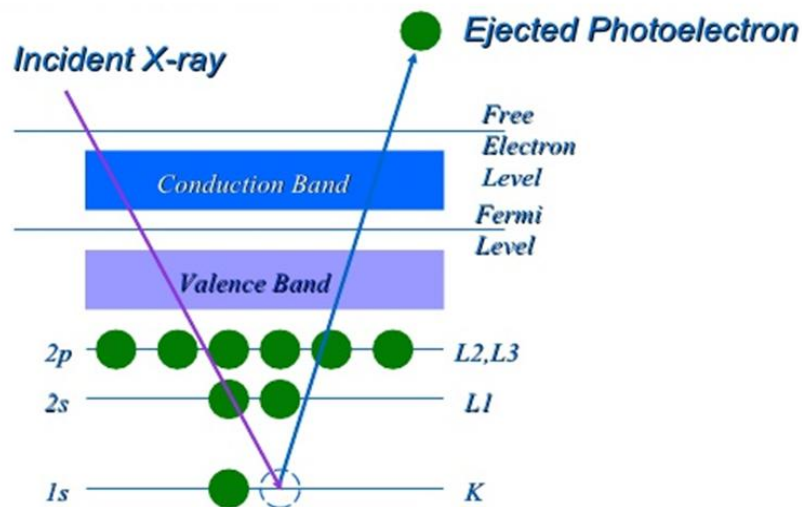
$$E_b = h\upsilon - E_K - W$$

Figure 2.4 Physical process involved in XPS [Embong, 2011].

Commonly surface measurement includes irradiation of sample with a primary beam of electrons, photon and impact on surface result in generation of secondary beam from substrate which is detected or measured by spectrometer represented in Figure 2.4 [Embong, 2011]. XPS spectrum is plot of Binding energy (eV) vs intensity (count/sec). XPS spectrum normally scans the binding energy from 0 to 1200 eV. In this thesis we used XPS spectrum for identification of oxidation state and elemental analysis of the synthesized coordination polymers and nanomaterials [Skoog et al., 2010; Harvey et al., 1956]. We performed XPS measurements by using Kratos Analytical Instrument, Shimadzu, Amicus XPS, UK.

2.1.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is electron microscope able to generating high resolution images of the sample surfaces by scanning it through a beam of electrons in a the raster scan pattern. After interaction of electrons with atoms of the sample generating signals that have information of sample's surface topography, sample

composition, and properties such as electrical conductivity etc. (RBG., 1970; Heal J. W. SJaCP. 1972). For obtaining SEM image a finely focused beam of electron incident on the surfaces of the specimens. The beam of electron is scanned across the sample in a raster fashion by raster coils. The obtained scanning pattern is analogous to used cathode ray tube (CRT) of television set in which the electron beam is (1) swept across sample surface in the X direction, (2) returning to its starting position, (3) shifting downwards in the Y direction with standard increment. This process is repeated until a required surface area has been scanned. In a digital system signal is received from the Z direction and stored in a computer, ultimately converted to an image. In SEM instrument back scattered and secondary electron are used to construct an image [Skoog et al., 2010; Harvey et al., 1956].

Electrons generated from Lanthanum hexa boride (LaB_6) or heated tungsten filament single crystals are accelerated by voltage in range of 20 V to 30 kV and directed down centre of an electron. Electrons produced into fine electron beam by magnetic lenses and follow it onto sample surface of solid specimen (SS) and scan on a raster on surface by a deflection system comparable to television techniques. For chemical analysis purposes modern SEM utilizes the X-ray detectors that allow qualitative and quantitative determination of the sample by means of X-ray (EDAX). Measuring energy of emitted characteristic X-rays allows the identification of element composing the area of sample analyzed.

2.1.6 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a electron microscopy technique in which high resolution images of the thin samples. It provides an approach to investigating sample's dimensions, morphology, distribution and crystalline phases of provided sample. The emission source is electron gun emits electrons that travel over a column

and focused by condenser lens into thin beam. By using objective lens transmitted electrons are focused into an image, followed by projective lens into magnify image. The electron distribution of specimen is magnified with three/four stage lens scheme and viewed on fluorescent screen. The image obtained by direct introduction of photographic emulsion or digitally by a CCD camera or an image plate. In a typical TEM a static beam of electrons at 100 – 400 KeV accelerating voltage passes through in a region of an electron transparent specimen which is immersed in the objective lens of the microscope [Williams et al., 2010; Skoog et al., 2010]

One of significant advantages of TEM is exploring materials in reciprocal space and in real space also i.e. in imaging and diffraction modes. We have utilized transmission electron microscope (TEM)-FEI-Tecnai 20 U Twin with EDX and Tecnai 20 G2 operated at 200 KeV, for the structural characterization of different nanomaterials.

2.1.7 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a technique that can reveal information down to atomic scale by using a sharp probe to scan across the surface of a sample. Depending on the different operational conditions of the probe during scanning, there are three operation modes for AFM, namely contact mode, tapping mode and non-contact mode. During contact mode measurement, a tip mounted at the end of a cantilever scans across the sample while contacting the surface. The deflection of the cantilever is monitored using a laser shining on the tip and redirect the laser to a split photodiode, which measures the signal variation coming from the vertical movement of the cantilever. A feedback control loop maintains a constant deflection of the cantilever by adjusting the vertical position of either the piezoelectric scanner or the sample. This position change is monitored and converted to the surface morphology of the sample. In tapping mode, the cantilever oscillates at or slightly below its resonance frequency at a position very

close to the sample surface. Instead of direct contacting the sample surface, the tip only taps on the sample surface. The root mean square (RMS) of the oscillation signal is maintained by the feedback control loop by adjusting the positions of the scanner of the sample and the position change is converted to morphology. For non-contact mode, the tip oscillates close to the surface but never touches the sample surface. The oscillation amplitude and frequency will be changed by the Vander Waals force, which extends a few nano-meters above the sample surface. The feedback control loop maintains a constant oscillation amplitude and frequency by vertically moving the scanners and this movement is converted to surface morphology.

Contact mode AFM has high scan speed and good resolution, but the lateral forces exert on the sample surface may damage soft samples. Non-contact mode AFM exerts little force on the sample surface and is not likely to scrap the sample, but the scan speed is low and the sample should be extremely hydrophobic to prevent the tip from getting stuck by the adsorbed fluid layer on the sample surface. Tapping mode AFM has less surface damage than contract mode AFM and can be used on most samples comparing to non-contact mode AFM. AFM study was conducted by using Molecular Imaging; USA made AFM equipment in non-contact, acoustic AC (AAC) mode. Phase image can also obtain in AAC mode besides topography image. Phase imaging additional characteristic of AAC mode AFM which provide information about existence of other phases. Cantilever interacts with sample surface which is mapped by measuring change in the phase angle between approach and retraction, in phase imaging AFM. For stress free surfaces, phase contrast is due to change in chemical composition or change in structure. Thin film samples were exposed in white light by using 100 watt quartz tungsten halogen (QTH) lamp in spectral range from 450 to 850 nm in distance of 10 cm for some hrs at room temperature. For exact structural measurement,

characterization were done under the ambient conditions by micro cantilever probe, tip radius and probe spring constant in ranges between 5-10 nm and 4-5 N/m, respectively. We performed AFM measurements with NT-MDT, Russia.

2.1.8 Cyclic Voltammetry (CV)

In the present work, the electrochemical characterizations of the fabricated electrodes and the electrochemical response have been done by using cyclic voltammetry (CV) Autolab (PGSTAT101, Metrohm, Netherlands) and Ω Metrohm, 797 VA, Computrace trace analyzer, Switzerland, using three electrode assembly and Measuring the current potential.

The potential of one of the electrodes is sensitive to analyte's concentration & upon which electrochemical redox reaction take place so called working or indicator electrode. The second electrode, which is called the counter electrode, serves to complete the electric circuit. The third electrode, which is called the reference electrode whose potential is known w.r.t. standard hydrogen electrode (0.00 V) and measure the potential of working electrode w.r.t. reference electrode & which is irrespective of analyte concentration [Bockris et al., 2000; Skoog et al., 2010].

Cyclic voltammetry (CV) is a multipurpose potentio dynamic electroanalytical technique which has been used to investigate the electrochemical properties of electroactive species. In cyclic voltamogram, the corresponding spectrum of a CV is a measure of the change in current measured corresponding to changing voltage in the solution. The microelectrodes and an unstirred solution are used in this electrolytic method; thereby the measured current is limited by analyte diffusion at the electrode surface.

The current response over a range of potentials is measured in a CV experiment, starting at an initial value and varying the potential in a linear manner to a pre-defined limiting

value. As in CV measurements until the voltage reaches the oxidation potential of the analyte, the current increases and after that it falls off as the concentration of the analyte depletes close to the electrode surface. At this switching potential, the direction of the potential scan is reversed in which the same potential window is scanned in the opposite direction (thereby the term cyclic). When reversing the applied potential, a potential will be reached where the reduction of product resulted during the forward scan starts producing a current which is of reversed polarity. The reduction peak also usually has the similar shape as that of an oxidation peak in the other direction. Further in case of some non-symmetric peaks are generated, which may attribute to the quasi-reversible reaction. Along with if the process is completely irreversible, then the anodic peak does not appear in the potential region. These all result the information regarding the redox potential and the nature of the electrochemical reactions.