

## Chapter 3

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This chapter presents the introductory idea on the method of preparation of Polyaniline based composites and brief description of instrumental techniques used for evaluating structural, electrical, redox properties of the prepared samples. The material was used to fabricate electrochemical sensors, tools and techniques used to evaluate the performance of the developed sensor have also been discussed briefly in the sections to follow.

### 3.1 Introduction:

A multicomponent composite material is a complex system and its component interacts with each other. Combined effect of constituents is realized as improved properties, which can be evaluated by different characterization technique. As described in the previous chapters, composite materials have been extensively explored for various technological applications including sensors. In this research work, we have prepared some binary and ternary composite materials using polyaniline, polysaccharides and MWCNTs. For hybrid materials, it is necessary to correlate different technical data obtained by instrumental analysis and established the characteristics of a material for desired application. Development of new materials should be tailored by considering the effect of each individual constituent by comparing it with a set of composite materials. This chapter deals with the details of the techniques used in this work and additional information has been given in the respective chapters, wherever required.

Over the past several years, automated instrumental analysis has been extensively used to characterize nanocomposite materials. Numerous techniques have been developed and employed for characterization of composite material and nanomaterials. A large number of research papers have been reported in the literature, about the material characterization. A specific technique provides particular information about the nature and structure of the material. Selection of a specific technique depends upon the type of

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material, information need to be explored. Some general characterization techniques developed for material characterization are highlighted given below.

- a. **For crystallinity of the material:** XRD (X-ray powder diffraction), TEM, STM.
- b. **For particle size determination:** DLS (Dynamic light scattering), XRD, TEM.
- c. **For chemical composition:** RBS (Rutherford backscattering spectrometry), XPS.
- d. **For chemical bonding:** XPS, IR, Raman, NMR.
- e. **For compound identification:** Mass spectroscopy, UV-visible, PL, IR and Raman.
- f. **For elemental analysis:** Energy-Dispersive X-ray spectroscopy (EDX), Wavelength Dispersive X-ray spectroscopy (WDX), Mass spectrometry, Impulse excitation technique (IET), Secondary Ion Mass spectrometry (SIMS), Electron Energy Loss Spectroscopy (EELS), Auger electron spectroscopy, X-ray photoelectron spectroscopy (XPS).
- g. **For Magnification and internal visualization:** Optical Microscope, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Field Ion Microscope (FIM), Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM).
- h. **For electrochemical and electrical behavior of material:** Voltammetry (Linear sweep voltammetry, Staircase voltammetry, Square wave voltammetry, Cyclic voltammetry, Anodic stripping voltammetry, Cathodic stripping voltammetry, Adsorptive stripping voltammetry, Alternating current voltammetry, Polarography, Rotated electrode voltammetry, Normal pulse voltammetry, Differential pulse voltammetry, Chronoamperometry, impedance measurement, conductance and capacitance measurement).

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### 3.2 Method of Composite Formation:

Polyaniline based composites can be prepared by different methods i.e. insitu chemical oxidative polymerization, insitu electropolymerization, interfacial polymerization, solution mixing, self assembly, pickering emulsion polymerization, casting, solid state synthesis, melt mixing, mill mixing, solution/dispersion mixing, and thermal reflux.

#### **In-situ Chemical Polymerization:**

In this research work, Polyaniline/polysaccharide composite materials have been prepared by in situ polymerization, means "in the polymerization mixture. Chemical reaction leads to the formation of a fine and thermodynamic stable reinforcing phase within a matrix. A uniform dispersion of Aniline, polysaccharide and MWCNTs was uniformly dispersed in dilute HCl solution. Polymerization was initiated with the dropwise addition of ammonium peroxydisulphate, as oxidizing agent, in the reaction mixture. On completion of polymerization, dark green precipitate was obtained. The precipitate was separate out and washed with appropriate solvent. Washing removed the residual oxidizing agents, unused monomers and small oligomers. Finally the sample was dried in a vacuumed oven at 50-60° C and stored in the desiccators. Different samples have been prepared by following the same procedure.

### 3.3 Characterization of the Prepared Samples:

The prepared samples were characterized by different spectroscopic, microscopic, thermal and electrochemical techniques using following instruments.

#### **3.3.1 Fourier Transform Infrared Spectroscopy:**

Perkin Elmer Spectrum Version 10.03.05 FT-IR spectroscope was used to investigate structural information and interaction among the various components in the spectrum

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range of 4000-500  $\text{cm}^{-1}$  using potassium bromide (KBr) pellets. In FTIR analysis, IR radiation is passed through the sample. Different functional group give specific signal in the spectra due to vibrational motions (bending, twisting, rotating and stretching) associated with absorption of IR radiation by a specific group leads to the vibration bonds. The size of the peaks informs us about the amount of each material present in the substance FTIR is considered as a finger print of the material. A single compound gives a unique fingerprint which cannot be same for any other molecule. FTIR used for the quantitative measurements to identify unknown material (Silverstein et al. 2014; Peter et al. 2007; Smith et al. 2012).

### 3.3.2 Ultraviolet-Visible Spectroscopy:

Varian Carry 100 Bio dual beam spectrophotometer was used to investigate optical absorption spectrum in the wavelength region 200 to 800 nm with a scanning speed of 400 nm/min. The measurement was done using paste of 0.05 g sample and 4 g  $\text{BaSO}_4$ . UV-Vis spectroscopic analysis of composite materials provides key information about the electronic structure of the material. UV-Vis spectroscopy based on the principle Lambert and Beer's law ( $A = abc$ , A is absorbance, a is absorption coefficient, b path length and c is the concentration). In a double beam spectrophotometer, a monochromatic light source produce a beam which split into two beams, one of them is passed through the sample, and the second beams of light passes through a reference samples. When the beams passes through the reference and samples, the two beams are returned back to the detectors where they are compared in form of their intensity. These measurements can be performed at single wavelength or over an extended range of spectrum. This makes the basis of measurement which is the difference produced between the two signals. UV-Visible spectrum used for quantitative and qualitative analysis of coloured compounds,

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and important information about the electronic structure and band gap energy obtained (Perkampus et al. 1992; Clark et al. 1993; Sahoo et al. 2012).

### **3.3.3 Raman Spectroscopy:**

Olympus (Model: MX50 A/T; Olympus, Hamburg, Germany) Raman spectrometer was used to obtain Raman spectra. Raman spectroscopy is used to determine the vibrational, rotational and other low-frequency modes in a system based upon the inelastic scattering of monochromatic light wave with synthesized material. Raman spectroscopy is helpful for analyzing molecules without a permanent dipole moment which are IR inactive. The energies associated with the scattered photons and incident beam are dissimilar. The frequency of scattered photon is very much depending on the functionality of the material. Raman spectroscopy is frequently used in chemistry to give a structural fingerprint by which one can recognize its constituent molecules, molecular structure and functional groups (Ferraro et al. 200; Szymanski et al. 1970).

### **3.3.4 Scanning Electron Microscope:**

Quanta 200 FEI scanning electron microscope, the observations were made at suitable voltages and magnifications. In the present investigations, the SEM was used in its most common mode, the emissive mode. Electron microscopy is an imaging technique like optical microscopy but here a beam of highly energetic electrons is used in place of light. Important components of scanning electron microscope are electron gun, magnetic condenser, scanning coil, detector, and output device. When the accelerated primary electrons strike the sample, it produces secondary electrons. The electron detector (Scintillator) is used to collect the secondary electrons and can be converted into electrical signal. These signals fed into CRO through video amplifier, which in turn gives

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a 3D image of the sample. Electron beam accelerate by the grid and the anode. When the electron beam impinges on the sample various types of signals are produced viz. secondary electrons, back scattered electrons, characteristic X-rays, Auger electrons and photons of various energies. SEM images provide valuable information about morphology, topography, phase distribution, and surface structure of the material. EDX facility used for the elemental composition some SEM instruments have attached EDS facility. High resolution SEM have been developed for the determination of chemical structure and morphology of the composites materials. HRSEM uses highly sensitive electromagnetic radiation, and it provides very high magnification images of the materials (Zhou et al. 2006; Reimer et al. 1998).

### **3.3.5 Transmission Electron Microscopy:**

Tecnai 20G2 FEI transmission electron microscope was used to investigate the morphology of the materials at nanoscale resolution. TEM can be used to observe particles at a much higher magnification and resolution than can be achieved with any other microscope because wavelength of an electron is much shorter than that of a photon. It also provides higher resolution images than a SEM, which can only be used to scan and view the surface of a sample. TEM can be used to view specimens to the atomic level, which is less than 1 nm. In this technique the position of detector is in different position and SEM, the electron beam passes the sample to be analysis, in this way internal structure of the material could also examined by this technique. Recently, TEM has gained much popularity among the scientific community for determination of size and shape of chemical compounds, especially nanomaterials (Zhnag et al. 2001; Kuo et al. 2007).

### 3.3.6 Atomic Force Microscopy:

DI Nanoscope IIIa microscope of the LNLS, in non-contact mode was used for topographic images. (NT-MDT) AFM provides a 3D image of the surface on a nanoscale by measuring forces between a sharp probe and the surface of material at very short distance. AFM is relatively a new technique developed in 1980s. 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. The probe is supported on a flexible cantilever. The AFM tip gently touches the surface and records the small force between the probe and the surface. The dominant interactions at short probe-sample distances in the AFM are Van der Waals interactions. However long-range interactions are significant further away from the surface. During contact with the sample, the probe predominately experiences repulsive Van der Waals forces (contact mode). This leads to the tip deflection described previously. As the tip moves further away from the surface attractive Van der Waals forces are dominant (non-contact mode) (Eaton et al. 2010; Haugstad et al. 2012).

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### 3.3.7 X-ray Diffraction:

Ultima IV X-ray diffractometer was used to investigate crystalline properties of materials using Cu K $\alpha$  radiation. X-ray diffraction (XRD) is a powerful nondestructive technique for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. It is based on the Bragg's law. It provides information about structure, phase, preferred crystal orientations and other structural parameters such as average grain size, crystallinity and crystal defects. This technique can also be used to determine the crystal properties namely lattice constants, micro strain, dislocation density and so on of a material with high degree of precision and accuracy in the order of 0.001 to 0.0001 Å. The data collection and analysis were carried out using the software supplied with the diffractometer. By applying Scherrer equation on the XRD pattern, the particle size can be calculated:

$(D = K\lambda / (\beta \cos \theta))$ , Where D is the mean size of crystallites (nm), K is crystallite shape factor a good approximation is 0.9,  $\lambda$  is the X-ray wavelength, B is the full width at half the maximum (FWHM) in radians of the X-ray diffraction peak and  $\theta$  is the Bragg's angle (deg.) (Waseda et al.2011; Suryanarayana et al. 1998).

### 3.3.8 Thermal Gravimetric Analysis:

Thermal analyser (STA 449, NETZSCH) used to investigate the thermal analysis. In TGA, the specific amount of the specimens were first heated from ambient temperature to 350°C under a constant heating, which lead to changes in the weight of a sample as a function of temperature and/or time. TGA provide valuable information about polymer degradation temperatures, absorbed moisture content, residual solvent levels and the amount of inorganic filler in polymer or composite material compositions. It assists in the de-formulation of complex polymer products. From the knowledge of information of both

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the glass transition temperature and crystalline melt properties regarding the degree of crystalline miscibility of blends and alloys and the processing conditions for component manufacture can be gained. The technique is also used to determine the thermal stability of polymers through determination of the oxidation induction time/temperature (Gabbott et al. 2007; Haines et al. 1995).

### **3.3.9 Differential Scanning Calorimetry:**

DSC is a thermo-analytical tool in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. DSC consists of two sealed pans: a sample pan and a reference pan. During the experiment, the instrument identifies differences in the heat flow between the sample and the reference. This information is treated and results in a plot of the differential heat flow between the reference and sample cell as a function of the temperature. An exothermic or endothermic process within the sample results in a deviation in the difference between the two heats flows (Hohne et al. 2003; Bershtein et al. 1994).

### **3.3.10 BET-Surface Area Analyzer:**

Micromeritics ASAP-2020, USA: The surface area and porosity were determined from nitrogen adsorption/desorption isotherms using the BET equation to estimate the overall surface area. Surface area analyzer is useful to characterize porous materials for the determination of their specific surface area, pore volume and pore size distribution. This is a frequently used method of measuring the surface area of a solid material using nitrogen as the adsorbent was introduced by Brunauer, Emmett and Teller. On the basis of BET analysis the porosity in materials are classified as micro, meso, and macro porosity (Gregg et al. 1991; James et al. 2006).

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### 3.3.11 Electrochemical Studies:

CH-630C series (CH instruments, USA) electrochemical workstation was used to investigate the electrochemical experiments. Electroanalysis is the interplay between electricity and chemistry in which a quantity of electricity such as current, potential, or charge is measured and it is related to chemical parameters. In electrochemical sensors, the analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer. Electroanalytical methods such as cyclic voltammetry, stripping voltammetry, differential pulse voltammetry, and chronoamperometry are not only capable of assaying trace concentrations of an electroactive analyte, but supply useful information concerning its physical and chemical properties. Quantities such as oxidation potentials, diffusion coefficients, electron transfer rates, and electron transfer numbers are readily obtained using electroanalytical methods, and difficult to obtain using other techniques. Electroanalytical methods can also be combined with spectroscopic techniques in situ to provide information concerning molecular structures and reaction mechanisms of transient electroactive species.

### 3.3.12 Cyclic Voltammetry:

We have used the most popular electroanalytical technique “cyclic voltammetry” for analyzing the electrochemical behavior of composite material which we have prepared. It is an effective tool to study the different electrochemical processes (Faradaic and non-faradaic) associated with an electrode material provide a rapid location of redox potentials of the electroactive species. It gives the valuable quantitative information about oxidation and reduction (redox) reactions, intermediate formation, thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions and of coupled chemical reactions or adsorption processes. It involves the process of linearly scanning

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the potential of a stationary working electrode (usually in an unstirred solution), using a triangular potential wave form. We have used phosphate buffer solution as electrolyte throughout the work and convention three electrode system.

The reaction of electrode generally involves electron transfer reaction which is influenced by electrode potential. CV is also used to study the electrochemical behavior of species diffusing to an electrode surface, interfacial phenomena at an electrode surface, and bulk properties of materials in or on electrodes. During the potential sweep, the current resulting from the applied potential is measured. The current and potential are then both plotted on a diagram called a cyclic voltammogram. It is a complicated, time-dependent function of a large number of physical and chemical parameters. CV measurement was performed by using three electrode systems are in common practice although two electrode systems can also be used. This is the three electrode systems in which the potential is applied between working electrode and reference electrode while the current is measured in between the working electrode and the counter electrode. To tackle with large currents, normally counter electrode will be with very high surface area (Zoski et al. 2007; Wang et al. 2006).

### **3.3.13 Chronoamperometry:**

In this electrochemical technique the potential of the working electrode is stepped and the resulting current from faradic processes occurring at the electrode (caused by the potential step) is monitored as a function of time. Limited information about the identity of the electrolyzed species can be obtained from the ratio of the peak oxidation current versus the peak reduction current. However, as with all pulsed techniques, chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit. The Faradaic current is due to electron transfer events and is most often the current

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component of interest. In most electrochemical cells this decay is much slower than the charging decay; cells with no supporting electrolyte are notable exceptions. Most commonly investigated with a three electrode system. Since the current is integrated over relatively longer time intervals, chronoamperometry gives a better signal to noise ratio in comparison to other amperometric technique.

### 3.3.14 Sensor Fabrication:

Sensor application was fabricate modified carbon paste electrode using a glass capillary, Nujol oil as binder, and clean copper wire for connection. In this work the response of the analyte was measured by cyclic voltammetry, the peak current increase with the successive addition of analyte in the test solution. A calibration plot was obtained by measuring current signal with respect to the concentration of the analyte. The sensor performance was evaluated by measuring limit of detection, sensitive, selectivity, linear range, and effect of interference.

**Limit of Detection:** It is defined as the lower concentration of analyte that can be detected, it is measured by the formula;  $3 \times \text{SD} / m$ , where SD is the standard deviation of blank reading, m is the slope of the calibration.

**Sensitivity:** It is an absolute quantity, the smallest absolute amount of change that can be detected by a measurement. It is defined as the ratio between the output signal and measured property. Sensitivity is normally calculated from the slope of the linear calibration curve.

### **Linear Range:**

The linear range is that range of input or output values for which an electronic amplifier produces an output signal that is a direct, linear function of the

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input signal. That is, the output can be represented by the equation;

$$\text{Output} = \text{Input} \times \text{Gain}.$$