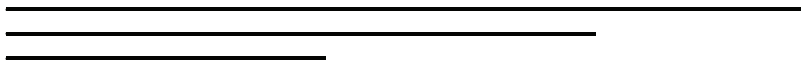


CHAPTER 3

Materials and methods



3.1. Materials

All the chemicals used in this work were of commercially available analytical or guaranteed reagent (AR/GR) grade. Name of the chemicals, their make and purity/grade are given below in the following order: monomers, oxidants, acids, solvents and other chemicals:

Name of the chemical	Grade/Purity	Make
Monomers		
Aniline	AR	Sd fiNE-CHEM LiMiTEd
o-Toluidine	AR	Qualigens
Indole	AR	Sd fiNE-CHEM LiMiTEd
Oxidants		
Ammonium perdisulphate	AR	Sd fiNE-CHEM LiMiTEd
Potassium persulphate	AR	Sd fiNE-CHEM LiMiTEd
Ferric chloride	AR	Qualigens
Acids		
Sulphuric acid	AR	Fischer
Hydrochloric acid	AR	Qualigens
Phosphoric acid	AR	Qualigens
Nitric acid	AR	Qualigens
Solvents		
Acetone	AR	Qualigens
Ethanol	Pure	Sd fiNE-CHEM LiMiTEd
Ethylene glycol	AR	Sd fiNE-CHEM LiMiTEd
O-cresol	AR	Qualigens
N-methyl-2-pyrrolidone	AR	Merck

Chloroform	AR	Qualigens
Acetonitrile	AR	Merck
Methanol	AR	Sd fiNE-CHEM LiMiTEd
Other chemicals		
Cadmium acetate	AR	Sd fiNE-CHEM LiMiTEd
Zinc acetate	AR	Sd fiNE-CHEM LiMiTEd
Sodium hydroxide	AR	Sd fiNE-CHEM LiMiTEd
Urea	AR	Sd fiNE-CHEM LiMiTEd
Thiourea	AR	Sd fiNE-CHEM LiMiTEd
Copper nitrate trihydrate	AR	Sd fiNE-CHEM LiMiTEd
Ammonium molybdate tetrahydrate	AR	Sd fiNE-CHEM LiMiTEd
Silver nitrate	AR	Sd fiNE-CHEM LiMiTEd
Zirconium oxychloride octahydrate	AR	Sd fiNE-CHEM LiMiTEd
Sodium metavanadate	AR	Sd fiNE-CHEM LiMiTEd
Potassium iodate	AR	Sd fiNE-CHEM LiMiTEd
Ammonium hydroxide	AR	Sd fiNE-CHEM LiMiTEd
Sodium tungstate	AR	Sd fiNE-CHEM LiMiTEd
Sodium chloride	AR	Sd fiNE-CHEM LiMiTEd
Lithium chloride	AR	Sd fiNE-CHEM LiMiTEd
Potassium chloride	AR	Sd fiNE-CHEM LiMiTEd
Lithium hydroxide	AR	Sd fiNE-CHEM LiMiTEd
Potassium hydroxide	AR	Sd fiNE-CHEM LiMiTEd
Lead nitrate	AR	Sd fiNE-CHEM LiMiTEd
Cobalt nitrate	AR	Sd fiNE-CHEM LiMiTEd
EDTA	AR	Sd fiNE-CHEM LiMiTEd

3. 2. Purification of materials

3.2.1. Aniline

Aniline was purified by distillation over zinc dust to remove all oxidized products formed during storage [1]. The fractional distillation of aniline with zinc dust was carried out with a water condenser. The initial and final fractions were discarded while the middle fraction containing the colourless aniline, boiling constantly at 184°C was collected and stored in an air-tight bottle. Whenever aniline was required for polymerization, the commercial aniline was distilled and used afresh.

3.2.2. o-Toluidine

All oxidized products formed during storage of o-toluidine were removed by distillation over zinc dust. The fractional distillation of o-toluidine was carried out with a water condenser. The middle fraction containing the colourless o-toluidine boiling constantly at 199°C was only collected and stored in an air-tight bottle. The commercial o-toluidine was distilled freshly as and when it was required for polymerization.

3.2.3. Indole

The commercial indole was recrystallized repeatedly from methanol till a constant melting point was reached [2]. The recrystallized sample has a melting point of 52°C.

3.2.4. Ethanol

The literature procedure [1] was adopted for the purification of ethanol solvent. The commercially available ethanol was refluxed and distilled over anhydrous calcium oxide. The flask containing ethanol and calcium oxide was fitted with double surface water condenser carrying calcium chloride guard-tube and subjected to reflux gently for 6 hours and allowed to stand overnight. Then it was distilled and the fraction boiled at a constant temperature of 78.3°C was collected.

3.2.5. Methanol

The literature procedure [1] was adopted to purify methanol. First 50-75 ml of the methanol was refluxed with 5 g of magnesium turnings and 0.5 g of iodine in a RB flask fitted with double surface condenser carrying calcium chloride guard-tube until the iodine has disappeared. Heating was continued until all the magnesium was converted into methanolate. Further 900 ml of methanol was added and the mixture was subjected to reflux for 30 minutes. The methanol is then fractioned through an efficient column, the first 20 ml of distillate was discarded and the following fraction boiling constantly at 65°C was collected.

3.2.6. Water

The water was first distilled with stiller distillatory plant and then it was distilled over alkaline potassium permanganate in an all glass setup. The double-distilled water thus collected was stored in amber-colour glass bottles. This double-distilled water was used in all the experimental study for the preparation of solutions.

All other solvents viz., acetone, ethylene glycol, o-cresol, N-methyl-2-pyrrolidone, chloroform and acetonitrile are of AnalaR grade and were used as such without further purification.

3.3. Synthesis of inorganic nanoparticles

3.3.1. Zinc oxide

1.1 g of zinc acetate (0.1 M) in 50 ml of ethylene glycol was mixed with 0.9 g of urea (0.3 M) in 50 ml of ethylene glycol and to this solution 0.5 g of sodium hydroxide (0.125 M) was added. Microwave irradiation was carried out till the solvent was evaporated completely from the system. The particles obtained were cooled and washed several times with distilled water, acetone and then dried [3].

3.3.2. Cadmium sulphide

1.1 g of thiourea (0.3 M) was mixed with 0.13 g of cadmium acetate (0.1 M) dissolved in 50 ml of ethylene glycol and to this 0.5 g of sodium hydroxide (0.125 M) was added. Microwave irradiation was carried out till the solvent evaporated completely. The precipitated nanoparticles were cooled and washed several times with distilled water and dried [4].

3.3.3. Cadmium oxide

0.13 g of cadmium acetate (0.1 M) and 0.9 g of urea (0.3 M) were dissolved separately in 50 ml of ethylene glycol and the two solutions were mixed thoroughly at room temperature. To the above mixture 0.5 g of sodium hydroxide (0.125 M) was added with stirring and continued for 12 hours. The product obtained was first washed with distilled water and then with acetone and dried at 50°C under low pressure [5].

3.3.4. Copper oxide

2.52 g of copper nitrate trihydrate (0.14 M) was dissolved in 180 ml of ethylene glycol in a 250 ml conical flask with a continuous magnetic stirring for about 10 minutes. Then the mixture in the conical flask was placed in an oil bath heated around 180°C for about 10 minutes, precipitate of copper oxide nanoparticles were formed. The precipitate was centrifuged, washed with double distilled water and finally with methanol and then dried in vacuum for 2 hours [6].

3.3.5. Silver molybdate

The solutions containing 0.61 g of ammonium heptamolybdate tetrahydrate (0.05 M) dissolved in 10 ml of distilled water and 0.08 g of silver nitrate (0.05 M) in 10 ml distilled water were prepared. The silver nitrate solution was slowly added into ammonium molybdate solution under magnetic stirring to form a homogeneous greenish-yellow precipitate. The resulting precipitate was transferred into a sealed autoclave maintained at

140°C. After 12 hours, the autoclave was cooled and the resulting greenish-yellow product was retrieved from the solution by centrifugation, washed with distilled water followed by ethanol and finally dried in air [7].

3.3.6. Zirconium vanadate

1.61 g of zirconium oxychloride octahydrate (0.1 M) was dissolved in 50 ml (0.04 N) hydrochloric acid and mixed with 1.5 g of urea. Then 2.44 g of sodium meta vanadate (0.4 M) dissolved in 50 ml of water was added drop wise to the above solution with constant stirring. After complete addition, the resulting solution was heated on a hot plate, until yellow precipitate of zirconium vanadate was formed. The reaction mixture was diluted with water and allowed to settle for 24 hours. The precipitate was washed several times with distilled water, filtered and again washed with hot water. The washed solid was dried and preserved in a desiccator [8].

3.3.7. Zirconium(IV) tungstiodophosphate

Zirconium(IV) tungstiodophosphate ion-exchanger was prepared by mixing 1.61 g of zirconium oxychloride octahydrate (0.1 M) in 50 ml of 4 N hydrochloric acid solution. This was added to a solution containing 5.4 g of potassium iodate (0.5 M) and 8.3 g of sodium tungstate (0.5 M) in 100 ml of water at the flow rate at 0.5 ml minute⁻¹. To the resulting mixture, 50 ml of 1 M ortho phosphoric acid was added by maintaining the pH as 1 with constant stirring using a magnetic stirrer at room temperature. The white gel obtained was filtered off, washed thoroughly with distilled water to remove excess acid and was dried in an electric oven at 60°C [9].

3.4. Synthesis of conducting polymers

3.4.1. Polyaniline-Cl⁻

Polyaniline was prepared from aniline by *in-situ* chemical oxidative polymerization technique using ammonium perdisulphate (APS) as oxidant in a similar

procedure as described by Trivedi [10]. Polymerization was effected at room temperature by drop-wise addition of oxidant (0.1 M) in water to the continuously stirred solution of aniline (0.1 M) in hydrochloric acid for an hour. After the addition of APS, polymerization was allowed to proceed further for overnight in a refrigerator. The formed precipitate was filtered, washed with distilled water, methanol and acetone repeatedly until the filtrate became colourless and was dried in an air oven at 80° C for about 4 hours. The dried polymer sample was ground into a fine powder. The greenish black powder of polyaniline-Cl⁻ was dedoped with 100 ml of 2 M ammonium hydroxide to get the blue coloured emeraldine base of the polymer.

3.4.2. Poly(o-toluidine)-Cl⁻

Poly(o-toluidine)-Cl⁻ was prepared by *in-situ* chemical oxidative polymerization technique [10]. Polymerization was effected by drop-wise addition of 0.1M potassium persulphate oxidant in water to the continuously stirred solution of 0.1 M o-toluidine in hydrochloric acid for an hour at room temperature. After the addition of potassium persulphate, polymerization was allowed to proceed further for overnight in a refrigerator. The precipitate formed was filtered, washed with distilled water, methanol and acetone repeatedly until the filtrate became colourless. The polymer thus obtained was then dried in an air oven at 80° C for about 4 hour. The greenish black powder of poly(o-toluidine)-Cl⁻ was dedoped with 100 ml of 2 M ammonium hydroxide to get blue coloured emeraldine base of the polymer.

3.4.3. Polyindole

The chemical oxidative polymerization of indole monomer was carried out in the presence of either ferric chloride or ammonium perdisulphate [11]. About 1.17 g of indole (0.05 M) was dissolved in 180 ml of acetonitrile. About 1.6 g of anhydrous ferric chloride (0.5 M) dissolved in 20 ml acetonitrile was added to the monomer solution under vigorous

stirring at room temperature. After 4 hours, the polymerization was stopped and the reaction mixture was filtered and washed with distilled water. A brown coloured product was obtained. In another experiment, instead of anhydrous ferric chloride, about 7.85 g of ammonium perdisulphate (1.7 M) dissolved in 20 ml water was added to 1.17 g of indole (0.05 M) in 180 ml acetonitrile and the polymerization was carried out as before.

3.5. Synthesis of organic-inorganic nanocomposites

3.5.1. Polyaniline–zirconium vanadate

A modified procedure as described by Trivedi [10] was adopted for the preparation of polyaniline-zirconium vanadate nanocomposites. Zirconium vanadate (4 g) dissolved in 20 ml of distilled water was dropped slowly into a solution of 5 ml aniline dissolved in 70 ml of 1 N hydrochloric acid under constant stirring. The flask was left for 30 minutes, during which the temperature was kept constant at 25°C. The nanocomposites were filtered and washed with distilled water until the filtrate became colourless. Finally, it was dried at 60°C for 24 hours under vacuum to obtain a fine dark green powder, namely doped polyaniline resin.

3.5.2. Polyaniline-silver molybdate

Polyaniline-silver molybdate nanocomposites were prepared by *in-situ* chemical oxidative polymerization of 0.1 M aniline monomer in 100 ml of 1 N hydrochloric acid in the presence of 100 mg of silver molybdate using 0.1 M ammonium perdisulphate in 100 ml distilled water as oxidant [10]. Polymerization was effected by drop-wise addition of oxidant to the continuously stirred solution of aniline for an hour. After addition of ammonium perdisulphate, polymerization was allowed to proceed further for overnight in a refrigerator. The product was filtered, washed with distilled water, methanol and acetone until the filtrate became colourless and dried in an air oven at 80°C for about 4 hours. The dried polymer sample was ground into a fine powder. Similar procedure and conditions

were followed in the absence of silver molybdate to prepare the polyaniline hydrochloride salt. The greenish black powder of polyaniline-silver molybdate was dedoped with 100 ml of 2 M ammonium hydroxide to get the blue coloured emeraldine base of the polymer.

3.5.3. Polyaniline-copper oxide

Polyaniline-copper oxide nanocomposites were prepared by *in-situ* chemical oxidative polymerization of 0.1 M aniline monomer in 100 ml of 1 N hydrochloric acid in the presence of 100 mg of copper oxide using 0.1 M ammonium perdisulphate in 100 ml distilled water described by Trivedi [10]. Polymerization was effected by drop-wise addition of ammonium perdisulphate oxidant to the continuously stirred solution of aniline and copper oxide for an hour. After all the addition, polymerization was allowed to proceed further for overnight in a refrigerator. The precipitated nanocomposites were filtered, washed with distilled water, methanol and then with acetone until the filtrate became colourless and dried in an air oven at 80°C for about 4 hours. The dried polymer sample was ground into a fine powder.

3.5.4. Polyaniline-zirconium(IV) tungstiodophosphate

The composite ion-exchanger was prepared by the sol-gel mixing of polyaniline, an organic conducting polymer with the inorganic precipitate of zirconium(IV) tungstiodophosphate [12]. In this process, *in-situ* polymerization of aniline (0.1 M) in the presence of 100 mg of zirconium(IV) tungstiodophosphate by using 0.1 M potassium persulphate as oxidant. Polymerization was effected by drop-wise addition of 5.7 g of oxidant in 100 ml of water to the continuously stirred solution of aniline and zirconium(IV) tungstiodophosphate in 1 N hydrochloric acid for an hour. After addition of all potassium persulphate, polymerization was allowed to proceed further for overnight in a refrigerator. The resultant mixture was turned slowly into greenish black coloured slurry and it was kept for 24 hours at room temperature. The polyaniline composite gels

were filtered off, washed thoroughly with distilled water to remove the excess acid and any adhering trace of potassium persulphate. The product was dried in air oven. The dried gel was put into the distilled water to obtain granules of uniform size. The dried granules were converted into the H^+ form by keeping them immersed in 1 M nitric acid for 24 hours with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The material thus obtained was then washed with distilled water to remove the excess acid before drying finally at 50 °C.

3.5.5. Poly(o-toluidine)-cadmium sulphide

Poly(o-toluidine)-cadmium sulphide nanocomposites were prepared by *in-situ* chemical oxidative polymerization technique [10]. In this method 0.1M o-toluidine monomer in 100 ml of 1 N hydrochloric acid in the presence of 100 mg of cadmium sulphide nanoparticles, prepared by microwave assisted wet chemical synthesis, was oxidative polymerized by using 0.1 M ammonium perdisulphate oxidant in 100 ml distilled water. Polymerization was effected by drop wise addition of oxidant to the continuously stirred solution of o-toluidine for an hour. After addition of ammonium perdisulphate, polymerization was allowed to proceed further for overnight in a refrigerator. The material formed was filtered, washed with distilled water, methanol and acetone until the filtrate became colourless and dried in an air oven at 80°C for about 4 hours.

3.5.6. Polyindole-zinc oxide

Polyindole-zinc oxide nanocomposites were prepared by mixing 1.6 g of anhydrous ferric chloride (0.5 M) in 20 ml acetonitrile with a solution containing the indole monomer (1.17 g, 0.05 M) and 100 mg of zinc oxide nanoparticles, prepared by microwave assisted route in 180 ml acetonitrile under stirring. The solution was stirred continuously for 4 hours. Then the supernatant solution was decanted and the sediment,

polyindole-zinc oxide nanocomposites were washed with acetonitrile and water and dried at 50°C [13].

3.5.7. Polyindole-cadmium oxide

1.17 g of the indole monomer (0.05 M) was dissolved in 180 ml of acetonitrile. Cadmium oxide nanoparticles (100 mg) prepared by polyol method were added to the monomer solution under stirring. After 1 hour of stirring 1.6 g of anhydrous ferric chloride in acetonitrile (20 ml) was added, and the solution was stirred continuously. After 4 hours, the supernatant solution was decanted, and the sediment polyindole-cadmium oxide nanocomposites were washed with acetonitrile followed by water [13].

3.5.8. Polyindole-copper oxide

The indole monomer (1.17 g, 0.05 M) was dissolved in acetonitrile (180 ml). 100 mg of copper oxide nanoparticles prepared by polyol method was added to the monomer solution under stirring. After 1 hour, 1.6 g of anhydrous ferric chloride (0.5 M) in 20 ml acetonitrile was added, and the solution was continuously stirred for 4 hours. Pure polyindole-copper oxide nanocomposites were obtained after decanting supernatant solution and washed the sediment with acetonitrile and water [13].

3.6. Characterisation

3.6.1. DC conductivity measurements

The powdered polymer samples were pressed into pellets of 13 mm diameter and 1 mm thickness in a hydraulic pellet press by maintaining 3 ton metric pressure. These pellets were subjected to conductivity measurements in a four-probe set-up. Current (I) – Voltage (V) measurements of the pellet were made at different positions of the pellet, which yielded more or less the same value within the experimental error. Conductivity was measured by using Ohm's law,

$$V = RI$$

Where I is the current (in amperes) through a resistor, R (in ohms) and V is the drop in potential (in volts) across it. The reciprocal of resistance (R^{-1}) is called conductance. The I and V values were plotted according to Ohm's Law and the resistances were obtained from the slope of the plot. Conductivity values were then computed from the values of resistance and dimensions of the pellet using the following equation,

$$\text{Conductivity } (\sigma) = (1/2\pi sR)$$

Where R is the resistance and s is the distance between the two probes (2 mm).

3.6.2. AC conductivity measurements

AC electrical conductivity measurement was done by using Digital LCR meter (Pacific, model: PLCR 8C). The various nanocomposite materials were finely ground in a mortar pestle and pellets were made at room temperature with the help of hydraulic pressure instrument at 25 KN pressure for 20 minutes. The thickness of the pellet as well as diameter of pellet was measured by using screw gauge. The AC electrical conductivity of the solid samples can be calculated using the following equation.

$$\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$$

$$\epsilon_r = C/C_0$$

$$C_0 = A\epsilon_0/d; A = \pi r^2$$

Where,

σ_{ac} – AC electrical conductivity (S/cm⁻¹)

f – frequency (Hz)

ϵ_0 – permittivity in free space (8.85×10^{-12} f/m)

ϵ_r – relative permittivity (f/m)

$\tan \delta$ – tangent loss (or) dielectric loss

C – capacitance at particular temperature (Faradays)

C_0 – capacitance at absolute temperature (Faradays)

- A – area of the sample (m^2)
- D – thickness of the sample (m)
- R – radius of the sample (m)

The capacitance and conductance of the material over a range of temperature and frequency are then calculated from the relationship between the applied voltage, measured current and are related to relative permittivity (ϵ_r) and the dielectric loss factor ($\tan \delta$) respectively. Dielectric loss tangent (dissipation factor) is the tangent of the loss angle when a dielectric is subject to a sinusoidally varying applied electric field. Since $\tan \delta$ equals to the ratio of the imaginary loss to the real (storage) relative permittivity, it is also the ratio of the energy dissipated to the energy stored for each cycle. $\tan \delta$ is high frequency and temperature dependent, reaching a maximum value as a dielectric relaxation is passed. Dielectric permittivity is a measure of the energy stored in a material subjected to electrical stress i.e., the ability of an insulator or semiconductor to resist the passage of alternating current or serve as a capacitor.

AC electrical conductivity measurement was also done by using impedance analyzer (IM6 ZAHNER) for various nanocomposite materials in the frequency range of 100 mHz to 1 kHz available at PSN Engineering College, Tirunelveli. Impedance methods are widely used for investigating the electrical behaviour of the materials over a wide range of frequency and temperature which helps to separate the real and imaginary components of the electrical parameters and hence provide a better understanding of material characteristics. The impedance data were plotted in the complex plane, a representation based on the plot of the imaginary component z'' versus the real component z' . In complex impedance plane, each effect viz., grain, grain boundary, or grain – electrode effect, appears as a semicircle, whose center lies on a line below the real axis.

Nyquist plots i.e., z'' versus z' also called cole – cole plots of the compounds under investigation were measured at different temperatures. A representative Nyquist plot for PIn-CuO nanocomposites is given below (Figure 3.1).

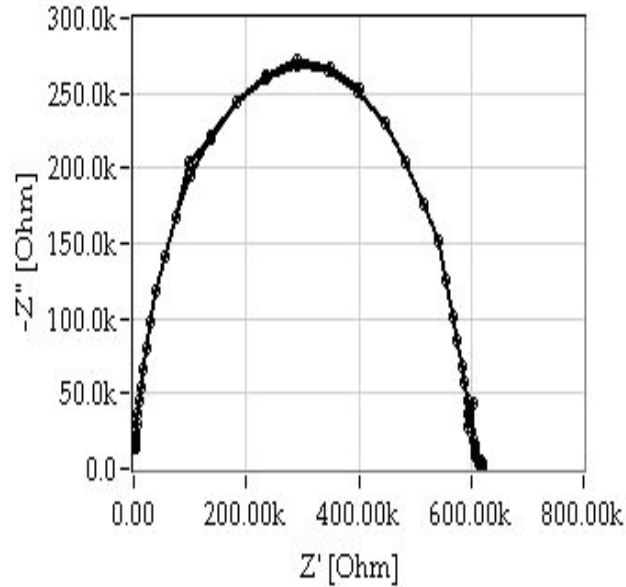


Fig. 3.1. Nyquist plot of PIn-CuO

The point where the semi-circle intersects the real axis (Z') gives the value of bulk resistance (R_b). By knowing the value of bulk resistance along with the dimensions of the sample, the conductivity of the sample has been calculated by using the relation

$$\sigma_{ac} = t / R_b A$$

$$R_b = (R_{\Omega} + R_b) - R_{\Omega}$$

Where,

σ_{ac} - AC electrical conductivity (S/cm^{-1})

t - thickness of the sample (cm)

A - area of the sample (cm^2)

R_{Ω} - ohmic resistance (ohms)

R_b - bulk resistance (ohms)

3.6.3. UV-visible spectroscopy

Ultraviolet-visible absorption spectroscopy is the measurement of the attenuation of the beam of light after it passes through a sample or after reflection from a sample surface. UV-visible spectroscopy includes transmittance, absorption and reflection measurements in UV, visible and near infra-red region. The absorption of UV radiation by organic compounds in the visible and ultraviolet region involves promotion of electrons in σ , π and n-orbitals from the ground state to higher energy states. The electronic transitions that are involved in the UV and visible regions are associated only with unsaturated centers in the molecule. Compounds containing isolated double bond absorb in the range 162 nm to 190 nm, while molecules containing conjugated double bond absorb above 210 nm. Extension of conjugated systems intensifies the absorption peaks and shifts them to the higher wavelengths, towards the visible spectrum. This technique not only provides information about the different bonding but also is an excellent tool for determining the band energy, which is an important parameter used in investigating the conduction mechanism in the organic conductors. UV-visible spectra of the synthesized samples were recorded at room temperature in different solvents viz., NMP, chloroform, o-cresol, DMSO in 300-900 nm range with Elico model SL-164 Double Beam UV-visible spectrophotometer available in our laboratory. The solutions were taken in a quartz cell of 10 mm path length.

3.6.4. Photoluminescence spectroscopy

Photoluminescence spectroscopy has emerged as an important tool for studying the optical and electronic properties of solid state nanomaterials. A spectrophotometer (Hitachi F-7000) available at Madurai Kamaraj University, Madurai was used to record the photoluminescence spectra of some nanoparticles and conducting polymeric nanocomposites.

3.6.5. FT-IR spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility over the other usual method of structural analysis is that it provides useful information about the structure of the molecules and bonding quickly without tiresome evaluation method. The Fourier transform spectrometer is just a Michelson interferometer with a movable mirror. This device generates the Fourier transform of the infrared spectrum, which is converted to spectrum itself by a computer. FT-infrared spectra can yield valuable evidence concerning the electronic structures of the samples. FT-IR spectra of conducting organic polymers, nanoparticles, conducting polymeric nanocomposites, inorganic ion-exchangers, conducting polymer-inorganic hybrid ion-exchangers were taken by KBr disc method at room temperature performed on NEXUS-670 FT-infrared spectrometer available at CECRI, Karaikudi. The FT-IR spectrum is mostly used to identify the functional group present in the compounds.

3.6.6. X-ray diffraction studies

The powder X-ray diffraction technique has been employed to identify the crystalline phases of the samples using monochromatized Cu- K_{α} ($\lambda = 1.5056 \text{ \AA}$) on X-ray diffractometer (Model: PW3040/60 X' pert PRO) available at CECRI, Karaikudi. The data collection was over the 2-theta range of 3° - 80° in steps of 0.1° /sec. The particle size was measured from X-ray broadening by employing the well-known Scherrer equation,

$$D = 0.96\lambda / \beta \cos \theta$$

Where, D - particle size of the sample (nm)

λ - wavelength of the X-ray (1.5056 \AA)

β - width of the XRD pattern line at half peak-height (Rad)

θ - angle between the incident and diffraction beam ($^{\circ}$)

3.6.7. Scanning electron microscopy

Scanning electron microscopy (SEM) is a method for high resolution surface imaging. The SEM uses an electron beam for surface imaging. The advantages of SEM over light microscopy are greater magnification and much larger depth of field. SEM was performed on ground materials by an electron microscope JEOL Model JSM-6390LV at various magnifications ($\times 5$ to $\times 300,000$) available at STIC, Cochin University and HITACHI Model S-3000H with maximum magnification $\times 300,000$, available at CECRI, Karaikudi.

3.6.8. Thermogravimetric analysis

TGA studies of the conducting polymeric composite materials in original form were carried out by an automatic thermo balance on heating the material from 30°C to 1000°C at a constant rate of $10^{\circ}\text{C min}^{-1}$ in the nitrogen atmosphere with Perkin Elmer, Diamond Thermo gravimetric analyzer at STIC, Cochin University, Cochin and TGA Instrument Model SDT Q600 at CECRI, Karaikudi.

3.7. Studies on ion-exchange properties of PANI ZTIP

3.7.1. Ion-exchange capacity

For the determination of ion-exchange capacity (IEC), one gram (1.0 g) of the dry cation-exchanger in H^+ form was taken into a glass column. The bed length was approximately 1.5 cm long. 1 M alkali metal chlorides (LiCl, NaCl and KCl) were used to elute the H^+ ions completely from the cation exchange columns maintaining a very slow flow rate. The effluents were titrated against standard 0.1 M NaOH solution for the total ions liberated in the solutions using phenolphthalein indicator.

3.7.2. Effect of eluent concentration on IEC

To find out the optimum concentration of eluent for complete elution of H^+ ions, a fixed volume (250 ml) of LiCl, NaCl and KCl solutions of varying concentrations

(0.2 – 1.8 M) were passed through a column containing 1 g of the exchanger in H^+ form with a flow rate of $\sim 0.5 \text{ ml min}^{-1}$. The effluent was titrated against standard alkali solution of 0.1 M NaOH for the H^+ ions eluted out for the determination of optimum concentration of eluent using phenolphthalein as an indicator.

3.7.3. Elution behaviour

A column containing 1 g of the exchanger in H^+ form was eluted with different 10 ml fractions of LiCl, NaCl, KCl solutions of concentrations 1.4 M, 1.4 M, and 1.2 M respectively with minimum flow rate of 0.5 ml min^{-1} . Each fractions of 10 ml effluent was titrated against standard NaOH (0.1 M) solution to determine the strength of H^+ ions eluted out.

3.7.4. Effect of time on IEC

The optimum shaking time of ion-exchanger with LiCl, NaCl and KCl solutions for complete elution of H^+ ions was also determined. 0.25 g of ion-exchanger was shaken with 25 ml of alkali metal chloride solutions (LiCl, NaCl and KCl) and the amount of liberated H^+ ions was titrated against the standard NaOH solution at different time intervals.

3.7.5. pH titration

The pH titration studies of PANI-Zr(IV) tungstiodophosphate was performed by the method of Topp and Pepper [14]. A total of 200 mg portions of the cation-exchanger in the H^+ form were placed in each of the several 250 ml conical flasks followed by the addition of equimolar solutions of alkali metal chlorides (LiCl, NaCl and KCl) and their hydroxides (LiOH, NaOH and KOH) in different volume ratios by maintaining the final volume as 50 ml and the ionic strength as constant. The pH of the solution was recorded every 24 h until equilibrium was attained which needed 5 days.

3.7.6. Selectivity (sorption) studies

The distribution behaviour of metal ions plays an important role in the determination of selectivity of the material. The distribution coefficient (K_d values) of various metal ions on cation-exchangers can be determined as follows. 200 mg of the composite cation-exchanger beads in the H^+ form were equilibrated with 20 ml of different metal nitrate solutions ($PbNO_3$, $Co(NO_3)_2$, $Cu(NO_3)_2$) of 0.005 M concentration and kept for 24 hrs. after initial shaking for 6 hrs. in a shaker at $25 \pm 2^\circ C$ in the required medium to attain equilibrium. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solutions of EDTA [15]. The distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and mathematically calculated using the formula

$$K_d(m/g)^{-1} = (I-F) / F \times V/m$$

Where, I = initial amount of metal ion in aqueous phase (M)

F = final amount of metal ion in aqueous phase (M)

V = volume of the solution (ml) and

m = amount of cation exchanger (g).

3.8. References

1. Furniss B S, Hannaford A J, Smith P W G and Tatchell A R, (1989) A. I. Vogel's Textbook of *Practical Organic Chemistry*, Fifth Edn. (London: ELBS with Longman Group) p.893.
2. Syed Abthagir P and Saraswathi R, (2004) *Thermochim. Acta.*, **424**, 25.
3. Ghule L A, Shirke B S, Sapnar K B, Dhole S D, Hankare P P and Gardkar K M, (2011) *J. Mater. Sci.*, **22**, 1120.
4. Oliveira J F A, Milao T M, Araujo V D, Moreira M L, Longo E and Bernardi M I B, (2011) *J. Alloys Compds.*, **509**, 6880.
5. Meenakshi Sundar S, Mahadevan C K and Ramanathan P, (2007) *Mater. Manufact. Procs.*, **22**, 400.
6. Wang H, Xu J Z, Zhu J J and Chen H Y, (2002) *J. Cryst. Growth*, **244**, 88.
7. Cui X, Yushu H, Li L, Biao L, Li H, Mo M and Liu X M, (2004) *Chem. Eur. J.*, **10**, 218.
8. Lahiri S, Roy K, Bhattacharya S, Maji S and Basu S, (2005) *Applied Radiat. Isotopes*, **63**, 293.
9. Siddiqui W A and Khan S A, (2007) *Bull. Mater. Sci.*, **30**, 43.
10. Trivedi D C, (1997) *Polyanilines in Conductive Polymers: Synthesis and Electrical Properties, Vol.2, Handbook of Organic Conductive Molecules and Polymers* (Ed.) Nalwa H S (John Wiley and Sons Ltd., Chichester) p.505.
11. Rajasudha G, Rajeswari D, Lavanya B, Saraswathi R, Annapoorni S and Mehra N C, (2005) *Colloid Polym. Sci.*, **283**, 575.
12. Khan A A and Akhtar T, (2008) *Electrochim. Acta.*, **53**, 5540.
13. Rajasudha G, Shankar H, Thangadurai P, Boukos N, Narayanan V and Stephen A, (2012) *Polym. Bull.*, **68**, 181.
14. Topp N E and Pepper K W, (1949) *J. Chem. Soc.*, 3299.
15. Reilly C N, Schmidt R W and Sadek F S, (1959) *J. Chem. Educ.*, **36**, 55.