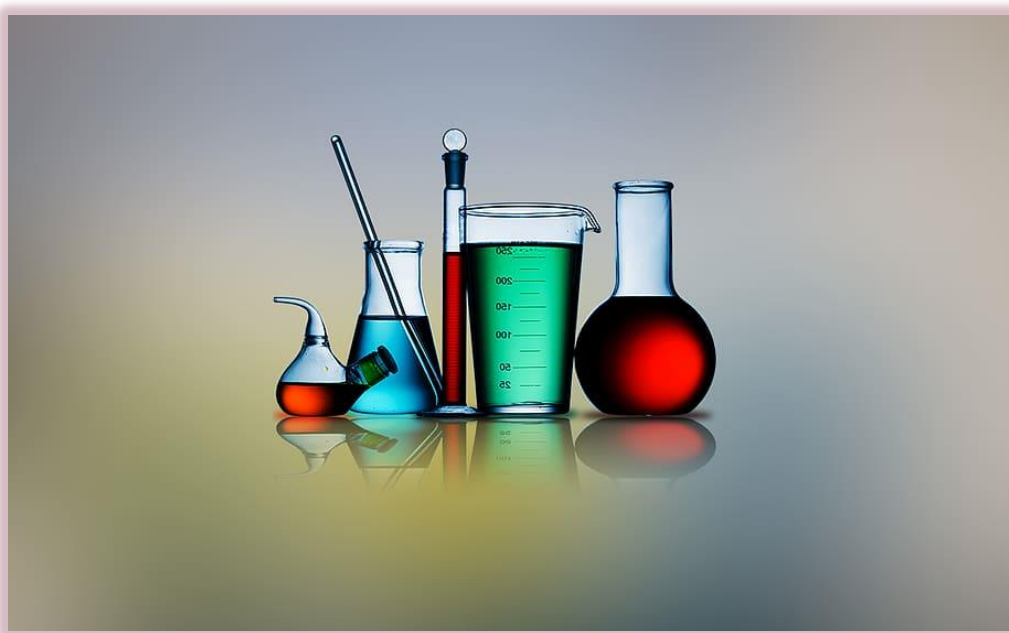


Chapter 2

Experimental Section



2.1 Synthesis of thermoplastic polyurethane and its functionalization

2.1.1 Materials

Hexamethylene diisocyanate (HMDI), Polycaprolactonediol ($M_n = 2000$ g/mol) polycaprolactone diol (PCL-diol) ($M_n = 2000$), Poly(tetra methylene glycol) (PTMG), (sigma – aldrich, $M_n=2900$ g/mol), 1,4 butanediol (BD) (Sigma – Aldrich), different chain length of diamine (ethylenediamine C_2 (EDA) Hexyl diamine C_6 (HDA), Dodecyldiamine C_{12} (DDA), p-phenylenedimine (PDA), Sodium hydride (NaH, 60 % dispersion in mineral oil), γ -propane sultone (PS) all from (Sigma-Aldrich, India), the catalyst dibutyltin dilaurate (DBTDL). The solvent N, N-dimethylacetamide (DMA), N, N- dimethylformamide and N – methyl pyrrolidone were procured from Himedia (India) and Merck (India), respectively. Cadmium nitrate tetra hydrate (Merck, India), Sodium sulfide (Na_2S , Himedia), Ethylenediamine tetraacetic acid (EDTA), Himedia, 3 – Mercaptopropionic acid (MPA) (Sigma Aldrich) and ethanol Merck India] were used for Quantum Dot synthesis.

2.1.2 Synthesis of aliphatic polyurethane

Thermoplastic polyurethanes are synthesized from reaction of diisocyanates (hard segment), Polyetherdiol or polyesterdiol (soft segment) and reactive aliphatic or aromatic diamine (chain extender) under the condition of suitable temperature and atmospheric pressure [115]. Polyurethanes were synthesized through two steps of polymerization technique in a three neck round botton flask. The hard segment content was retained 30% by using predetermined amount of diisocyanates, polyol (polyether or polyester) and chain extender.

$$\text{HSC (\%)} = \frac{\text{Weight of (diisocyanate+diamine or diol)}}{\text{Weight of (diisocyanate+polyol+diamine or diol)}} \quad (2.1)$$

First step involves prepolymerization process which was carried out under nitrogen atmosphere for 4 hours at 70°C while second step; Chain extension (polymerization) was carried out by reaction of diamine or diol and organometallic catalyst (DBTDL; 0.1 mL of

1 w% toluene solution) under same reaction condition for 24 hours [107]. The polymer was obtained through the precipitation in aqueous solvent (distilled water) and procured flake materials was dried under reduced pressure and constant temperature 60°C in vacuum oven for 24 hours.

2.1.2.1. Synthesis of polyurethane by using ethylenediamine as chain extender

In this phase of polymerization, Prepolymerization was carried out by reaction of Hexamethylene diisocyanate and polytetramethylene glycol under Nitrogen purging at 70°C for four hours. The chain extension was carried out by addition of short chain extender (C₂ diamine) reaction condition of polymerization. The polymer was obtained through the precipitation in aqueous solvent (distilled water) and procured flake materials was dried under reduced pressure and constant temperature 60°C in vacuum oven for 24 hours [108, 110].

2.1.3. Functionalization of polyurethane chain

Polyurethane ionomers are prepared through bimolecular nucleophilic displacement reaction followed by ring opening polymerization [116]. Polyurethane was modified chemically using propane sultone to enhance the physical property *i.e.* redox activity and conductivity. In a typical synthesis method, as reported by Banerjee et al. 0.3gm pure polyurethane flake was dissolved in DMA at 130 °C. It was cooled at low temperature (-5°C) followed by the addition of 0.6 gm of pure sodium hydride to abstract proton from under continuous hard segments purging of nitrogen at constant stirring for 1h. Then, 1 mL of 1, 3 propane sultone was added to above reaction mixture at room temperature followed by heating at 65 °C under nitrogen atmosphere with constant stirring for 3h. The ionomer was precipitated by pouring it in toluene. Precipitated ionomer was separated from toluene and washed with ethanol several times to remove unreacted chemicals. Finally, it was dried under reduced pressure at 60 °C.

2.1.3.1. Preparation of functionalized polyurethane ionomer gel electrolyte

20 m/v % of sulfonated polyurethane was stirred and mixed in 1 mL highly polar solvent (mixture of DMA + NMP each in equal proportions) works as plasticizer at 90 °C until solubilized in homogeneous liquid phase further converted into viscous phase and finally approaches to gelatinous like immobile phase commonly referred to as gel. The perfect gel was obtained by cooling the highly viscous matrix. During gel formation a weak intermolecular force of attractions established between polymer-polymer, sulfonated group (pendant group)-solvents (plasticizer) and polymer-plasticizer - polymer gives rise to the formation of a thermoplastic polymer gel electrolyte without any other redox couple or liquid electrolyte. The solvents were encapsulated between interchains of polymer and protect ionic (polar group) moieties from agglomeration. The solvents loading or uptake was maximized through increasing mixing or stirring time. Polyurethane ionomer was obtained as sodium salt. Polar solvent dissociates the ionomer into Na^+ and short chain grafted sulfonate ion. Sodium ion was adsorbed over the polar carbonyl or polyether group of polyurethane backbone. The conductivities of redox active groups were expected to be enhanced due to chemisorption of sodium cation over carbonyl sites. mononegative charge delocalizes equally over the surface sulfonate group (three oxygen atoms tagged with sulfur) due to presence of resonance hybrid structure. Delocalization stabilizes the ionomer and re-creates electron rich chemical environment. The delocalized surfaces were more prone to adsorb organic solvents and liquid electrolyte.

2.2. Synthesis of polyurethane through variation of chain extenders

Polymerization was performed through chemical reaction of hard segment (HMDI), soft segment (PTMG) and chain extender [110]. Prepolymerization was carried out through reaction of HMDI and PTMG at 70°C for 4 hour under continuous stirring in N_2 purged state. The viscous reaction mixture was treated with chain extenders (Short and long chain extender based aliphatic diamine, Butanediol, p-phenylenediamine) followed by addition of

organometallic catalyst (DBTDL; 0.1 mL of 1 w% toluene solution) and N, N dimethyl formamide (DMF) as organic solvent under same reaction condition for 24 hour.

2.2.1. Synthesis of polyurethane using polycaprolactone diol (PCL-diol)

Polyurethane (HMDI+PCL-diol+EDA) was synthesized through the reaction of EDA chain extender with NCO terminated pre-polyurethane residue under same reaction condition of polyurethane synthesis

2.2.2. Sulfonation of different hard segments in polyurethane chains

The chemical tagging of short chain anionic group on urethane–NH sites of polymer chain was carried out with γ -propane sultone, an aliphatic cyclic organic compound. First, 500 mg of polymer flaks was dissolved in 40 mL of non aqueous highly polar solvent (DMA+ NMP) at 100 °C. The dissolved polymer solution was taken in two naked round bottom flask set up with adaptor for the creation of vacuum and N₂ atmosphere and kept on ice bath (-5 °C). Further, 500 mg of NaH solid powder was added to the polymer solution in cold state with fast stirring, since the reaction is exothermic in nature. The reaction of –N-H with sodium hydride NaH produces nucleophile in hard segment with evolution of H₂ gas. Then the reaction mixture was stabilized at room temperature. 1 mL of propane sultone was added to that reaction mixture under continuous stirring in N₂ atmosphere and the reaction system was set up and placed on oil bath keeping the temperature at 60 °C on the hot plate for 3 h. The sulfonated PU ionomer was extracted as precipitate by pouring reaction mixture in toluene. It was washed several times with ethanol to remove unreacted chemical species and dried at 50 °C in air oven. Similarly, structurally different polyurethane ionomers were obtained through same procedure. **Scheme 1b** displays synthetic reaction and functionalization of polyurethanes followed by modification in polyurethane ionomer. Polyurethane (HMDI+PTMG+EDA) was functionalized through the substitution of PTMG with PCL–diol followed by sulfonation under same reaction condition. Polyurethane (PU-PCL-EDA) was

sulfonated in the presence of carbon black (CB) as composite phase under same reaction condition of functionalization.

2.2.3. Preparation of polyurethane ionomer gel electrolyte (Redox active electrolyte)

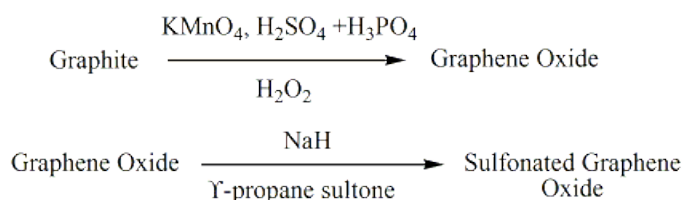
Ionomer gel electrolyte was prepared by dissolving excess amount of sulphonated polyurethane in the mixture of highly polar solvent in equal ratio *i.e.*, mixture of DMAc and NMP (N-methyl pyrrolidone). Ionomer was mixed and dissolved at 90 °C through constant stirring in a magnetic stirrer. The stirring was continued to get a homogenous and gelatinized mixture followed by freezing at lower temperature (5°C) for overnight. The gel contains extensively solvated polyions in swelled state.

2.3. Synthesis of grapheme oxide and its functionalization with γ -propane sultone

The modified Hammer's method is empirical way to develop GO as a oxygenated sheet from graphite flakes at room temperature and pressure. The synthesis consists of highly acidic reaction media of 9:1 concentrated H₂SO₄ and H₃PO₄. Graphite flakes (3.0 g) was added slowly to the reaction media followed by slow addition of KMnO₄(18.0g) under stirred condition. As reaction starts exothermally at room temperature and maintained up to 50°C for 15 hr. Now reaction mixture is cooled to the room temperature and 9mL 30% H₂O₂ in ice water was added to reaction mixture to control the oxidation and reaction rate. In order to settle down the dispersed product, deionized water was added and kept for stability and washed many times until it became neutral. Finally 30% HCl and ethanol was used to complete washing and centrifuged with deionized water at 8000 rpm for 8 min. and dried 70°C under reduced pressure.

0.3g GO was dispersed in 150 mL DMF with ultra sonicator for 1 hr. The dispersed and stable GO was treated with 1.8 g NaH to produce dehydrogenated GO under nitrogenous atmosphere with constant stirring at 65°C for a 4 hr. The residue was reacted with 1.5mL γ - 1, 3-propane sultone at 80°C for 12hr. under N₂ purging with constant string.

Now, residue was stabilized over room temperature. It was collected and separated in test tube with centrifuge machine operated at 8000 rpm for 8min. and finally, washed with mixture of water and ethanol over 10,000 rpm and 8min. The Black brown phase separated in petridish and kept for drying at 70°C in air oven (**Scheme 2.1**).



Scheme 2.1: synthetic reaction scheme of GO and its functionalization.

2.3.1. Synthesis of GO implanted polyurethane and its ionomer

20, 50 and 100 mg GO were dispersed in a beakers containing each 50 ml DMF over ultrasonication bath for 1 hr. The GO monohybrid was synthesized by grafting NCO terminated urethane linkage with hydroxyl moieties. The synthesis protocol consisted of two steps. Firstly, 10 g PTMG was taken in a two necked round bottom flask and equipped with adapter to connect N₂ purging source. The precursor was vacuumed and adjusted over the surface of silicon oil bath maintaining temperature 70°C with rpm 400. The molar ratio of PTMG, HMDI and EDA was maintained 1:6:5 with 30% of HSC. The HMDI was added in Rb flask with syringe and continued the reaction for 3.5 hr. at pre adjusted reaction condition. Now, dispersed GO was added to the vessel having NCO terminated urethane residue. The DBTDL catalyst was added to enhance the reaction dynamics over the surface of GO. Further, reaction was continued for 24 hr. under same reaction condition to complete the polymerization. Thus, NCO- terminated pre-polymer was reacted with 0.2w%, 0.5w% and 1w% GO under same reaction condition to obtain nanocomposite polyurethane. The viscous residue was stabilized at room temperature. The urethane functionalized GO was precipitated in cold distilled water as a nanohybride of block copolymer. The crude precipitate was

washed with distilled water many times to remove unreacted chemicals and DMF. The black flakes were dried at 70°C for 12 Hr. under reduced pressure in the air oven. Finally, product was vacuum dried.

The dried GO implanted polyurethane hard segment contents were reacted with constant weight ratio of sulfonating agents (NaH+Y-propane sultone) in organic solvent as reaction media. The reacted residue was precipitated with toluene. The precipitate was washed with alcohol and dried at 70°C with reduced pressure.

2.4. Synthesis of CdS quantum dot and its surface quantization effect

The CdS QDs were synthesized through solution phase technique by using EDTA, MPA and EDA as surface stabilizing agent.

2.4.1. Synthesis of CdS QDs by using ethylenediamine (EDA)

CdS particle was synthesized through capturing Cd ion with different concentration of EDA molecule at 90°C. The reaction residue was stabilized at room temperature. The fixed concentration of Na₂S solution was added in the reaction vessel and stirred at room temperature to for complete precipitations as CdS particle. The precipitate was separated through centrifugation technique. The residue was washed with alcohols several time to remove unreacted chemicals and kept in freezer to stabilize as nanocrystals.

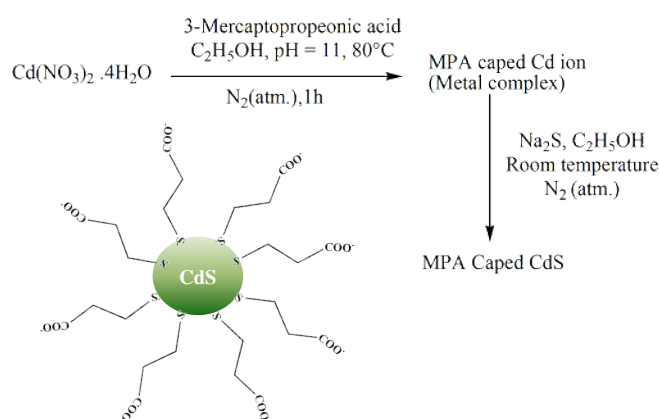
2.4.2. Synthesis of CdS QDs by using ethylenediamine tetraacetic acid (EDTA)

In a typical synthetic process, 1.234 gm (0.4 M) cadmium nitrate was dissolved in 10 mL ethanol to get Cd²⁺ solution and was added to 0.855 gm (0.114 M) of EDTA dissolved in 20 mL deionized water with constant stirring at room temperature. The reaction mixture was further stirred at 100°C keeping the pH ~5.5 for 2 h. EDTA capped Cd²⁺ was stabilized at room temperature. A solution of 0.12gm (0.11 M) sodium sulfide, dissolved in 10 mL ethanol, was added drop wise under vigorously stirring for 30 min until light yellow precipitate was obtained and the suspension was centrifuged followed by washing with water

and ethanol to remove unreacted species. Thus, different size of CdS quantum dots were synthesized by varying the composition of sulfide ion at a constant weight ratio of $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and EDTA under similar reaction condition. EDTA capped CdS were kept in freezer to prevent its agglomeration and further nucleation [25, 27, 33].

2.4.3. Synthesis of CdS QDs by using 3- mercaptopropionic acid (MPA)

3-Mercaptopropionic acid (surface stabilizing agent) is a bifunctional material with thiol group linked on one side of the carbon chain and carboxylic acid to the other end. The alcoholic solution of 0.4M cadmium nitrate was prepared in two necked flask and saturated in N_2 atmosphere followed by addition of 0.65M alcoholic solution of MPA having pH = 11 and stirred continuously at 450 rpm to stabilize the Cadmium ion maintaining the temperature at 60°C for 1h. under same nitrogen atmosphere. The resultant reaction mixture was cooled at room temperature. Then few drops of Sodium sulfide (Na_2S) solution of fixed molarity was added and strired the same for 30 min. to complete the reaction and nucleation of CdS quantum dots. The particles with various size and energy gap were precipitated out by changing the concentration of MPA solution (**Scheme 2.2**). The yellow precipitate was centrifuged at 8000 rpm and washed three times with mixture of water and alcohols to remove unreacted species and kept in freeze at 4°C to stop reaction and coagulation.



Scheme 2.2: Schematic representation of synthesis and surface functionalization of CdS quantum dots

2.5. Fabrication of device

Fabrication involves following steps in the solar cell designing in an ambient condition

2.5.1. Washing and cleaning of FTO

The FTO was washed with soapy water followed by ultrasonication for 30 min. Further, FTO was washed with distil water with constant ultrasonication. The washing process was repeated three times to remove surface impurity. Finally, FTO was cleaned with mixture of ethanol and acetone with ultrasonication. It was dried in air oven at 50°C for half hour. Then, dried FTO was purged with N₂ gas to remove other gases. Finally, it was kept in vaccume oven at room temperature

2.5.2. Preparation of photoanode

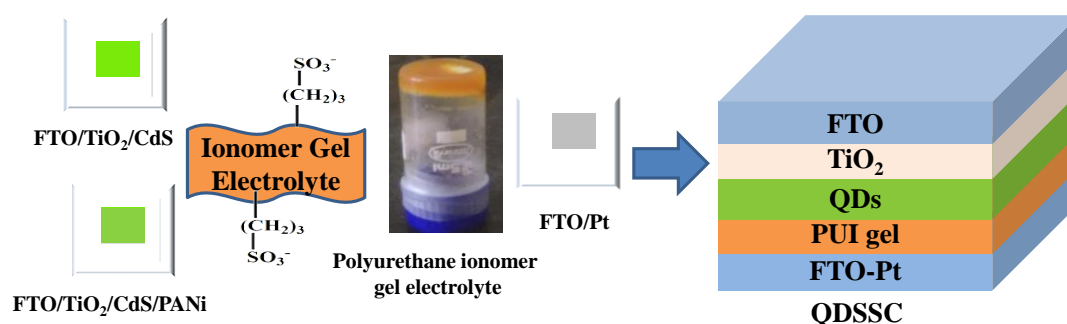
The well cleaned and N₂ dried FTO of size (2.0×1.5) cm² was taken to fabricate anode. The active area 0.25 cm² was defined with thin cello tape over the conductive surface of FTO. The defined conductive surface was printed as a thin film of TiO₂ by using doctor blade technique and after removing cello tape, film residue was kept on hot plate over 80°C for half an hour to vaporize lower boiling solvent. The cohesive forces held the surfaces to organize uniform film thickness. Now, it was annealed over 450°C for half an hour to remove high boiling surfactant, adhesive and binder. Finally, it was crystallized as nanostructures over the surface of FTO with high electrical contact covered by high transparency. The stable active area was spin coated with CdS QDs as photo sensitizer followed by spin coating of surface doping layer and put on hot plate at 150°C to create well connected ET interface layer.

2.5.3. Preparation of counter electrode

Similarly, optimum thickness of Pt paste was printed on conductive surface of another piece of FTO having same size and shape and in continuation, printed screen was annealed at 450°C for half an hour to crystallize the particles as nanostructures.

2.5.4. Fabrication of QDSS cells

The quantum dot sensitized solar cell was fabricated with photoanode and counter electrode followed by sandwiching/ inserting gel polymer electrolyte in between two electrodes. The gel electrolyte inserted electrodes were balanced with binder clip to create interfacial contact. The fabricated device was vacuum dried for saturation.



Scheme 2.3 Fabrication scheme of basic QDSS cell

2.6. Characterization Techniques:

Different characterization methods were used to characterize synthesized polyurethanes, functionalized polyurethanes and CdS quantum dot

2.6.1. ^1H NMR spectroscopy

Nuclear magnetic resonance spectroscopy was used to resolve chemical structure of polymer (polyurethane) and its functionalized matrix. ^1H NMR spectroscopy is used to measure the chemical shift and signal height corresponds to different proton attached on polymer matrix. Different chemical environment affects the peak position and peak height. The technique is also susceptible to measure the degree of functionalization on a particular unit of polymer (polyurethane) framework. ^1H NMR spectra was recorded on a Bruker BioSpin 500 MHz spectrometer after dissolving the sample in d_6 -DMSO solvent. The homogeneous sample was placed in the magnetic field before spectral measurement. The chemical shifts were recorded in ppm unit relative to the reference sample tetramethylsilane (TMS).

2.6.2. Fourier transform infrared spectroscopy (FT-IR)

FT-IR is a most powerful spectroscopic technique for characterization of organic molecule and polymer or functionalized polymer matrix based on chemical moieties or functional groups present on molecule or polymer chain. The infrared range in the electromagnetic radiation is from 700 nm to 1 mm. FTIR collects data over a wide spectral range. The radiation wavelength that a molecule absorbs depends on its atoms and how they are bound together. The sharp (intense) signals were used to measure the position or shifting of peaks. The spectra were recorded in transmission mode by irradiating the solid sample directly. The technique offers high signal to noise ratio for different groups in polymer framework. Thermo-Nicolate 5700-FTIR was used to record the infrared spectra of solid polyurethane and functionalized (sulfonated) polyurethane in the range of 400-4000 cm^{-1} with the resolution of 4 cm^{-1} in ATR mode.

2.6.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is thermal technique used to investigate the thermal stability of the synthesized polyurethane or functionalized polyurethane. The method demonstrates changes in samples weight is as a function of temperature, in a specific atmosphere (N_2 gas). The weight changes are due to presence of specific functionalities or volatile part present in materials. 6 mg of sample was mounted on crucible and scanned at the rate of 20° min^{-1} in the temperature range of 40-600°C. The degradation temperature corresponding to 5% weight loss was taken as standard confident limit. TGA analysis was performed thermo gravimetric analyzer *Mettler-Toledo* (Mettler 832, USA). The material was characterized with a thermal degradation curve at particular temperature.

2.6.4. Differential scanning calorimetry (DSC)

The differential scanning calorimetry is a widely known thermal technique is used to characterize thermal behaviour of materials. The melting temperature, glass transition temperature and gel transition temperature were examined by (Mettler 832, USA) differential

scanning calorimetry. The melting temperature and enthalpy of fusion were calculated from the plots obtained using area under the curve. The measurement was conducted from room temperature to 300° C at scan rate of 10° C/min. The bidirectional (heating and cooling) cycle was carried out to investigate the gel transition temperature for the same sample with same scan rate.

2.6.5. UV-visible absorption spectroscopy

UV-visible spectrophotometer is a powerful technique to characterize the sample both in liquid phase as well as solid thin film. The technique is used to record spectrogram corresponds to broad peaks of different chromophores linked at polyurethane or sulfonated polyurethane. UV-visible spectrum is characterized by electronic transition associated with π - π or π - π^* transition corresponds to particular functional group or unsaturated groups present in molecule or polymer matrix. The UV-visible spectra were performed using JASCO V-650 spectrophotometer in solid state, in the range of 200-800 nm wavelengths. The wavelength λ_{\max} is due to absorption of photon energy associated with extent of intermolecular or intermolecular interaction.

2.6.6. X-ray diffraction (XRD)

X-ray diffraction of synthesized polyurethane/ sulfonated polyurethane sample was investigated using Rigaku Miniflex 600 wide angle X-ray diffractometer integrated with a multi-temperature chamber and a graphite monochromator using a Cu K α source with a wavelength of 0.154 nm. The generator were operated at 45 Kv and 200 mA The thin film of sample holder and scans were done at diffraction angle from 10 to 100 °, keeping the scanning rate 3° min⁻¹

2.6.7. Dynamic light scattering (DLS)

The particle size was analyzed through ultrafine alcoholic dispersion using dynamic light scattering (DLS). The Horiba Scientific Nanoparticle analyzer SZ-100 was used to record the particle size (in solvated phase) in ultra diluted solution at the scattering angle of 90° at room temperature.

2.6.8. Atomic force microscopy

It is a powerful non optical imaging technique which is used to characterize all type of surfaces and textures via contact mode. The NT-MDT multimode AFM (Russia) regulated by solver scanning probe microscope controller is used to investigate the bulk morphology of sample

2.6.9. Scanning electron microscopy (SEM)

Scanning electron microscopy is a technique used to characterize surface morphology (shape, size, volume) for aggregated or segregated structure. The sample image was produced by scanning the surface with a focused beam of electrons, with energy between 1 and 50 keV. The electron beam is generated from lanthanum hexaboride (LaB6) filament. These electrons interact with the atoms in the sample and produces signals that contains information about sample surface morphology and composition (capping level of particle). A *Supra 40, Zeiss FESEM* was used to obtain the surface morphology of the samples.

2.6.10. Transmission electron microscopy (TEM)

TEM is a microscopy technique for imaging nanomaterials with sub-nanometer resolution. In this technique a beam of electron is transmitted through a specimen for image. The typical acceleration voltage is 80-200 kV. The electrons are emitted from a field emission or thermionic electron guns. The specimen is an ultrathin section of thickness less than 100 nm or a suspension on carbon coated copper grid. The capping level of the nanoparticles and crystallites in the polymer matrix was examined with FEI Technai 20 TEM operating at a voltage of 200 kV. The particle size was analyzed with ImageJ software.

2.6.11. Cyclic voltammetry (CV)

Cyclic voltammetry is an electrochemical technique used to study of electrochemical behaviour (redox activity). Cyclic voltammetry experiments were conducted to measure its redox potential (oxidation and reduction potential). It is equipped with Pt disc (2 mm diameter) electrode as a working electrode, Pt wire (1 mm diameter) as counter electrode and Ag/AgCl a reference electrode saturated with 3M KCl solution operated at room temperature for obtaining CV profile of diluted solution of different sample in the potential range of -2.0 eV to +2.0 eV of N-methyl pyrrolidone. The cyclic voltammogram was obtained by NOVA 2.1 software at room temperature with scan rate of 20 mV/s.

2.6.12. Linear sweep voltammetry (LSV)

LSV is carried out to examine the electrochemical stability window in solution phase of sample with CV assembly at room temperature with a fixed scan rate.

Electrochemical impedance spectroscopy

2.6.13. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is an powerful tool to study the charge transfer resistance of solution based on frequency response analysis. The spectra was recorded in the frequency range of 0,01Hz to 1 MHz. Electrochemical impedance spectroscopy (EIS) studies were widely used to investigate the intrinsic interfacial charge transfer and to understand the transport kinetics of electrochemical and photo electrochemical processes occurring at the electrode electrolyte interface. The electron transport, recombination and lifetime were evaluated through spectrogram both for materials in solution phase as well as photonically irradiated device. Two semicircles including a small semicircle at high frequency and a large one at low frequency were observed in the Nyquist plots. The smaller semicircles at high frequency region represent the charge transfer at the Pt/electrolyte interface, whereas the large semicircle in the middle to low frequency region represents charge transfer at the TiO₂ /

QDs interface and the resistance of charge transfer from TiO₂ to the electrolyte (back recombination resistance).

2.7. Measurements and calculations

2.7.1. Degree of sulfonation on hard segment content into polyurethane ionomer

Degree of sulfonation (DS) as a function of weight ratio of the sulfonating agent to the urethane linkage of polyurethane. The DS was observed to increase with increasing the concentration of the sulfonating agent. The degree of sulfonation over urethane linkage was determined by using following expression:-

$$DS(\%) = \frac{b/2}{a+b/2} \times 100 \quad (2.2)$$

Where, a is the peak intensity or area of the signal corresponding to the hydrogen atoms of -NH group of polyurethane hard segment content and b is the peak height or area of the signal corresponding to hydrogen atoms of -CH₂ groups of pendant group (propane sultone group) attached on hard segment content or urethane linkage of polyurethane ionomer.

2.7.2. Calculation of % crystallinity

$$\text{Crystallinity (\%)} = \frac{\Delta H_{\text{ionomer}}}{\Delta H_{\text{PU}}} \times 100 \quad (2.3)$$

2.7.3. Calculation of optical band gap and HOMO-LUMO energy levels

The size quantization effect or optical band-gap (E_g) of the nanoparticles and polyurethane /sulfonated polyurethane were determined by using the relation:

$$E_g = \frac{1240}{\lambda(nm)} \quad \text{and} \quad (\alpha h\nu)^2 = \beta(h\nu - E_g) \quad (2.4)$$

Where, β is a constant, E_g is the band gap of the material, α is the absorption coefficient (cm^{-1}), h is the Planck's constant and ν is the photon frequency. The Tauc's plots, i.e. variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for different samples. E_g values were obtained by extrapolating the linear portion of the curve to x-axis at a $\alpha = 0$.

2.7.4. Calculation of HOMO-LUMO energy levels

Cyclic voltamogram was used to calculate HOMO and LUMO energy levels. The oxidation and reduction potentials were recorded by extrapolating onset peak potential at X-axis $y = 0$.

$$E(\text{LUMO}) - E(\text{HOMO}) = \text{Electrochemical energy gap (eV)} = \text{optical band gap (eV)}$$

$$E(\text{HOMO}) = -eV(E_{\text{ox}} + 4.4) \quad (2.5)$$

$$E(\text{LUMO}) = -eV(E_{\text{red}} + 4.4) \quad (2.6)$$

2.7.5. Ionic conductivity

Electrical (ionic) conductivity was evaluated through interfacial charge transfer resistance obtained from Nyquist plot with NOVA 2.1 software. The Nyquist plot is spectrogram which is recorded as a function of real impedance Z' (ohm) vs. imaginary $-Z''$ (ohm). The ionic conductivity was calculated by following relation.

$$\sigma \text{ (S/cm)} = \frac{l}{R_{ct}A} \quad (2.7)$$

Where l is film thickness or distance between working electrode and counter electrode, R_{ct} (Ω) charge transfer resistance and $A(\text{cm}^2)$ is area of Pt disc (working electrode).

2.7.6. Electronic conductivity

$$\sigma_{\text{electronic}} = \frac{0.693}{\pi\delta} \frac{\delta I}{\delta V} \quad (2.8)$$

Where δ (mm) indicates thickness of the film and $\frac{\partial I}{\partial V}$ slope of the linear fit. Current –voltage characteristic measurements were performed for thin film in the potential range -10V to +10V

2.7.6. Electrolyte uptake or solvent absorbent power

Elevation in liquid electrolyte loading has an acceleration effect on photovoltaic performances.

$$\text{Electrolyte uptake or solvent loading(\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2.9)$$

2.7.7. Free electron lifetime measurement

Bode plot is recorded as a function of frequency (log f) vs. impedance Z (Ω) in EIS measurement. The lifetime of free electron or photoexcited electron was calculated through following relation:

$$\tau = \frac{1}{2\pi f_{\max}} \quad (2.10)$$

Where τ denotes lifetime of free electrons and where, f_{\max} is the peak frequency of the curve in the lower or intermediate frequency region in Bode plot.

2.7.8. Calculation of peak to peak separation potential (E_{PP})

$$E_{PP} = E_{AE} - E_{CE} \quad (2.11)$$

Where E_{PP} , E_{AE} and E_{CE} indicate peak to peak separation potential, onset anodic potential and onset cathodic potential, respectively.

2.7.9. Theoretical calculation of Open circuit potential

$$V_{OC} = |E_{CB} - E_{redox}| \quad (2.12)$$

2.8. J-V characteristic Measurement and its photovoltaic parameters

J-V characteristic measurement was performed with Metrohm Auto lab the data was recorded with NOVA 2.1 software. The device was illuminated with He lamp with white light as a neutral source at intensity of 100 mW/cm^2 . The working function of a solar cell absolutely depends on semiconducting nature and work function of active layer which in turn characteristic to the photoelectric effect and more commonly known as photovoltaic cell. A solar cell is basically a semiconductor device and characteristic is similar to p-n junction diode. The photo illumination generates photocurrent through photoexcited charge transport and reversible charge transport was maintained through interfacial redox activity of gel polymer electrolyte. The electro catalytic activity was controlled through Pt counter electrode. The photo voltage (V_{OC}) and short circuit current density (J_{SC}) were measured through photogram or photovoltaic curve.

2.8.1. Short circuit photocurrent density (J_{SC})

The photo current density (J_{sc}) is characteristic of the current under short circuit state of the linked photoanode and photocathode in photovoltaic device. The short-circuit photocurrent depends on intensity of incident light on the surface of solar cell corresponds to air mass of solar spectrum. The AM1.5 corresponds to 1000 W/m^2 . The maximum current that the solar cell can produce strongly depends on the optical properties, surface area and degree of absorption by the photoactive layer. Higher the number density of photogenerated electron, higher is the photocurrent density corresponds to external circuit.

2.8.2. Open circuit potential or photovoltage (V_{OC})

The open-circuit potential is a point on x-axis of J-V curve correspond to zero photocurrent density on y-axis. It is the maximum bias potential at which photocurrent density lowered down to zero or origin point. Open circuit potential depends on redox potential of electrolyte and temperature of the characteristic measurement. It is a measure of degree of interfacial charge recombination in the layer structured photovoltaic device.

2.8.3. Fill factor (FF)

The solar characteristic fill factor is expressed as the ratio between the maximum power point ($P_{max} = J_{mpp} \times V_{mpp}$) with power generated by device.

$$FF = \frac{J_{mpp} \times V_{mpp}}{J_{sc} \times V_{OC}} \quad \text{or} \quad \frac{P_{max}}{J_{sc} \times V_{OC}} \quad (2.13)$$

The notation **mpp** indicates the maximum power point of the photovoltaic J-V curve i.e. J_{mpp} stands for photocurrent density of maximum power point while V_{OC} depicts voltage corresponds to maximum power point.

2.8.4. Photovoltaic conversion efficiency (η)

The energy conversion efficiency is estimated via dividing maximum generated power with power of light intensity. As depicted above above, solar characteristic curve is produced

under the standard test condition, AM1.5 (air mass 1.5) spectrum has characteristic illumination intensity of $P_{in} = 100 \text{ mW/cm}^2$.

$$\eta (\%) = \frac{P_{max}}{P_{in}} \times 100 \quad \text{or} \quad \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100 \quad (2.14)$$