Chapter 6

Conclusions and Future Perspectives

6.1. Conclusions

In this thesis, photovoltaic redox reactions have been realized through polyurethane ionomer in Quantum dot sensitized solar cells. Thermoplastic polyurethanes are composed of hard segments and soft segments contents. Electrolyte active pendant groups have been introduced on different chemical environment of hard segment contents. Free structured polyurethane ionomer has been realized as electrolyte matrix for photovoltaic reaction in Quantum dot sensitized solar cell. In other words, semiconducting behaviour was realized through variation of chain structure on polyurethane ionomer backbone. Electrolyte active redox groups played a crucial role in photovoltaic reactions. Functionalized redox active urethane linkages function as redox mediating center for conversion of solar energy through Quantum dot sensitized solar cells. Quantum confinement regulates energy gap and energy levels in polyurethane ionomer. Polyurethane ionomer exhibits ionic conductivity because of variation of composition and density of pendant groups between hard segments and soft segments. In this thesis, we have focused on functionalization of hard segment content within polyurethane chain. Photovoltaic redox mediation has been explored via sulfonated polyurethane with different chemical environments in Quantum dot sensitized solar cells. Functionalized polyurethanes have been attracted great attention towards development of ionomer gel electrolyte (matrix) because of corrosion resistant, efficient adhesive nature and better electrochemical stability. Semiconducting behaviour has been achieved due to presence of ionomeric unit (pendant group) on hard segment content. Thus, various polyurethane ionomers have been studied via structural variation across hard segment contents to investigate the solar characteristic performance. The major concluding remarks of the thesis are explained below chapter wise.

In **chapter 3** Polyurethane has been synthesized through reaction of (HMDI+PTMG+EDA) at hard segment contents of 30%. Polyurethane hard segments contents (urethane and urea linkages) have been functionalized with sulfonating agents (NaH+ϒ-propane sultone) to generate ionic segments contain mononegative charge**.** In practice, ionic segment contains Na^+ as counter ion. The degree of hard segment functionalization increases with increase in weight ratio of sulfonating agents. Various spectroscopic technologies have been used to investigate structural and functional features. Polyurethane ionomer (sulfonated polyurethane) showed almost spherical size and texture in TEM micrograph. Electrolyte active group embedded polyurethane showed spherical atmosphere due to possible minimization of surface energy. Thermal resistance property was enhanced because of presence of covalently linked ionic segments. The introduction of ionic pendant group causing crystalline regions in the polyurethane ionomers. The variation of functionalization has been proved through UV-visible absorption spectra. The functionalized polyurethane showed red shifted absorption band and absorption peak shifted due to variation of HOMO-LUMO energy gap. HOMO-LUMO energy gaps and energy levels were controlled through optimization of functionalizing agents. Pristine polyurethane showed electrochemical inactive features. However, ionic segment offers charged redox active center to polyurethane chain and redox active behaviour was characterized with clear signature of oxidation and reduction peaks. Hydrophilic pendant group offered electrical regions on the surface of polyurethane chain. Solution phase ionic conductivity has been studied via tuning the composition of electrolyte active pendant anion across polyurethane hard segments. Ionomer gel electrolyte was prepared in a mixture of highly polar organic solvents.

Disodium salt of ethylene diamine tetraaceticacid stabilized the surface structure of CdS QDs. Quantum confinements effect were investigated through blue shifted absorption spectra of synthesized CdS particle. Particle size was analysed through DLS and TEM measurements. The average size of 4 nm and band gap (E_g = 2.69eV) were established in CdS particle. The photovoltaic device was fabricated through layer structure design using spin coating and doctor blade technique. The fabricated device (QDSSC) showed photovoltaic characteristic curve and photovoltaic reaction was realized through measurement of photocurrent density and open circuit potential. The electrolyte features was realized in the open circuit potential range (0.45-0.65V) in QDSS cell. The optimized photovoltaic conversion efficiency was analysed 1.25% with well structural stabilization efficiency in ionomer electrolyte.

In **chapter 4** polyurethanes have been synthesized through structural variation of chain extenders (diamine and diol based) at constant HSC of 30%. Electrolyte activity was explored via creating structural, functional and size difference in polyurethane ionomers. Oxygenic rich polyurethane was also synthesized using PCL-diol in place of PTMG during polymerization reaction. The functionalization reaction was optimized with constant weight ratio of sulfonating agents. The ionomeric segments were generated on different hard segment contents of polyurethane chain. The degree of ionization level was characterized using NMR, FTIR and UV-visible absorption spectra. The constant weight ratio of sulfonating agents offered different energy gap (HMO-LUMO) which was probably due to different degree of reactivity of hard segments in polyurethane chains. Thermal resistance and glass transition temperature were characterized with TGA and DSC measurements. Hydrophilic ionic segments (pendant group) offered different degree of ionic conductivity because of different degree of segmental motion and structural movements of polyurethane ionomer chains. The lifetime of free electrons were measured on the different surface of functionalized hard segments of polyurethane ionomers. Ionomer gel electrolytes were prepared using 20% and 30% (w/v) polyurethane ionomers in mixture of highly polar solvents.

3-mercaptopropeonic acid functionalized the surface of CdS particles. Size confinement effects were analyzed through blue shifted absorption spectra. The optimized band gap (E_g = 2.71eV) and average size 12-15 nm were stabilized with 0.65M MPA. Solar device has been fabricated using spin coating and doctor blade techniques. The ionomer gel electrolyte was sand whiched between surface treated (PANi or SGO coated photoanode) and counter electrodes. Photovoltaic characteristic curves were obtained through J-V measurements under illumination of 100 mW/cm^2 intense White LED light. Photovoltaic effect was realized through redox reaction of ionomer gel electrolyte in QDSS cells. The QDSS cells open circuit potentials were analyzed in the range of 0.2 - 0.65V for different ionomer electrolytes. The optimized device (QDSSC) showed maximum power conversion efficiency of 1.16% with carbon black decorated polyurethane ionomer gel.

In **chapter 5** GO implanted polyurethane ionomers have been developed as gel electrolytes with content 0.2%, 0.5% and 1% GO. The optimized PUI-GO (0.5%) has been studied extensively in QDSSCs. The gel polyelectrolyte activity was realized due to presence of pendant anions (sulfonate and carboxylate ion) linked on composite polyurethane backbone. The GO implanted ionomers were characterized with ^{1}H NMR, FT-IR, TGA, DSC and UV-visible spectroscopy. Electrochemical characteristics have been studied with the help of CV and EIS measurements. The surface morphologies (size, surface texture, chemical interaction and interfacial wettability) have been investigated with SEM, AFM and TEM measurements. Structure-function characteristic features have been correlated with surface morphology. RGO has been coated on conductive surface of FTO to improve electron injection and transport properties. Quantum dots sensitized solar cell has been fabricated with MPA caped CdS Quantum dots as photosensitizer. The polyelectrolyte activity of developed structure was studied comparatively with pristine polyurethane ionomer (PUI). The optimum GO content improved the electrical regions in polyurethane ionomer. The fabricated Quantum dot sensitized solar cell consist a configuration FTO-RGO/TiO_2/MPA-CdS/PUI-GO/FTO-Pt for photovoltaic characterization. The optimized QDSS cell showed conversion efficiency of 1.63% with open circuit potential of 0.594V with efficient passivation (retards charge recombination) and redox activity between photoanode and counter electrode.

6.2. Scope for future work

The present work has explored synthesis, characterization and hole conduction or redox mediation behaviour of functionalized/sulfonated polyurethane ionomer gel in Quantum dot sensitized solar cell. Polyurethane ionomer were explored as single ion conducting polyelectrolyte. The role of functionalize hard segment content is to maintain reversible charge transport between photoanode and photocathode. Photovoltaic redox mediation has been revealed via tuning Quantum confinement, polyurethane chain structure (variation of hard segment, soft segment and chain extender), and degree and composition density of pendant group around urethane linkage. However, highly functionalized polyurethane ionomer exhibited poor photovoltaic performance with diffused saturation current density /steady curve in CdS based QDSS cells. Therefore, still needed to improve the structural stability around pendant group or hydrophilic moiety in the chain structure of polyurethane. Sustainable redox mediation requires development of composite phase matrix. Electrolyte structure is key component in Quantum dot sensitized solar cell. There are some following facts which will definitely improve the functioning of ionomeric hard segment content and redox mediation capacity.

- Synthesis of polyurethane ionomer as nanocomposites via incorporation of carbonaceous 2D nanomaterials, 2D conducting fiber, metal nanoparticles and conducting polymer to improve ionic conductivity and structural stability around ionomeric urethane linkage.
- Variation of pendant groups (aliphatic, aromatic and fused ring based structure) at hard segment content of polyurethane.
- Comparative photovoltaic studies incorporating carboxylate and phosphate group as anionic pendant group in polyurethane hard segment contents.
- Variation of polyurethane structure via Soft segments and chain extender having tagged anionic content (site).
- Incorporation of specific structural content into polyurethane ionomers which may ultimately reduce the extent of moisture absorption.
- Incorporation of electron withdrawing functional group in the chain framework of polyurethane ionomer to improve electrocatalytic reduction via counter electrode or photocathode.
- Variation of design and fabrication
- Appropriate engineering of interfacial band structure of device might favours the fabrication of efficient device.