

CONTENTS

Chapter 1: Introduction and Literature Review

| | | |
|-------|--|----|
| 1.1 | Introduction..... | 1 |
| 1.2 | Renewable energy sources and its global distribution..... | 1 |
| 1.3 | Solar cell..... | 2 |
| 1.3.1 | Components and design of solar cell..... | 3 |
| 1.3.2 | Working principle of solar cell..... | 3 |
| 1.3.3 | General classifications of solar cells..... | 4 |
| 1.3.4 | Dye materials and dye sensitized solar cells..... | 5 |
| 1.3.5 | Perovskite materials and perovskite sensitized solar cells..... | 7 |
| 1.3.6 | Quantum dots and quantum dots sensitized solar cells..... | 8 |
| 1.4 | Redox active couples/electrolyte and its various hole transporting phase..... | 13 |
| 1.4.1 | Liquid electrolyte..... | 14 |
| 1.4.2 | Polysulfide redox couple..... | 15 |
| 1.4.3 | Gel polymer electrolyte..... | 16 |
| 1.4.4 | Solid polymer electrolyte..... | 19 |
| 1.5 | Electrolyte additives..... | 20 |
| 1.5.1 | Variation of redox mediation in polysulfide with different chemical environment..... | 22 |
| 1.6 | Electrocatalytic reaction of redox active electrolyte with photocathode..... | 22 |
| 1.7 | Control of interfacial defects states and charge recombination phenomenon... | 23 |
| 1.8 | Polyelectrolyte..... | 24 |
| 1.8.1 | Polyurethane ionomers..... | 26 |
| 1.9 | Scope and objective of present work..... | 28 |
| 1.10 | Plan of the present work..... | 30 |

Chapter 2: Experimental Section

| | | |
|---------|---|----|
| 2.1 | Synthesis of thermoplastic polyurethane and its functionalization..... | 33 |
| 2.1.1 | Materials..... | 33 |
| 2.1.2 | Synthesis of aliphatic polyurethane..... | 33 |
| 2.1.3 | Functionalization of polyurethane chain..... | 34 |
| 2.1.3.1 | Preparation of Functionalized polyurethane ionomer gel electrolyte..... | 34 |
| 2.2 | Synthesis of polyurethane through variation of chain extenders (Diamine | |

| | | |
|--------|--|----|
| | and diol based chain extender)..... | 35 |
| 2.2.1 | Synthesis of polyurethane using polycaprolactone diol (PCL-diol)..... | 36 |
| 2.2.2 | Sulfonation of different hard segment content in polyurethane chain..... | 36 |
| 2.2.3 | Preparation of polyurethane ionomer gel electrolytes..... | 36 |
| 2.3 | Synthesis of graphene Oxide and its functionalization through γ - propane sultone..... | 37 |
| 2.3.1 | Synthesis of GO implanted polyurethane and its ionomer..... | 38 |
| 2.4 | Synthesis of CdS quantum dots and its surface quantization effect..... | 39 |
| 2.4.1 | Synthesis of CdS QDs using ethylenediamine (EDA)..... | 39 |
| 2.4.2 | Synthesis of CdS QDs by using ethylenediaminetetraacetic acid (EDTA).... | 39 |
| 2.4.3 | Synthesis of CdS QDs by using 3-mercaptopropeonic acid (MPA)..... | 40 |
| 2.5 | Fabrication of device..... | 41 |
| 2.5.1 | Washing and cleaning of FTO..... | 41 |
| 2.5.2 | Preparation of photoanode..... | 41 |
| 2.5.3 | Preparation of counter electrode or photocathode..... | 41 |
| 2.5.4 | Fabrication of quantum dot sensitized solar (QDSS) cells..... | 41 |
| 2.6 | Characterization techniques..... | 42 |
| 2.6.1 | ^1H NMR spectroscopy..... | 42 |
| 2.6.2 | Fourier-transform infrared (FTIR) spectroscopy..... | 43 |
| 2.6.3 | Thermogravimetric analysis (TGA)..... | 43 |
| 2.6.4 | Differential scanning calorimetry (DSC)..... | 43 |
| 2.6.5 | UV-visible spectroscopy..... | 44 |
| 2.6.6 | X-ray diffraction..... | 44 |
| 2.6.7 | Dynamic light scattering..... | 44 |
| 2.6.8 | Atomic force microscopy..... | 45 |
| 2.6.9 | Scanning electron microscopy..... | 45 |
| 2.6.10 | Transmission electron microscopy..... | 45 |
| 2.6.11 | cyclic voltammetry..... | 46 |
| 2.6.12 | Linear sweep voltammetry..... | 46 |
| 2.6.13 | Electrochemical impedance microscopy..... | 46 |
| 2.7 | Measurement and calculation..... | 47 |
| 2.7.1 | Degree of sulfonation in polyurethane hard segment content..... | 47 |
| 2.7.2 | Calculation of crystallinity..... | 47 |

| | | |
|--------|---|----|
| 2.7.3 | Estimation of optical band gap..... | 47 |
| 2.7.4 | Calculation of HOMO-LUMO energy levels..... | 47 |
| 2.7.5 | Ionic conductivity..... | 48 |
| 2.7.6 | Electronic conductivity..... | 48 |
| 2.7.7 | Electrolyte uptake or solvent absorbent power..... | 48 |
| 2.7.8 | Free electron lifetime measurement..... | 48 |
| 2.7.9 | Calculation of peak to peak separation potential..... | 49 |
| 2.7.10 | Theoretical calculation of open circuit potential..... | 49 |
| 2.8 | J-V characteristic measurement and its photovoltaic parameters..... | 49 |
| 2.8.1 | Short circuit current density (J_{SC})..... | 49 |
| 2.8.2 | Open circuit potential or photovoltage (V_{OC})..... | 50 |
| 2.8.3 | Fill factor (FF)..... | 50 |
| 2.8.4 | Photovoltaic conversion efficiency (η)..... | 50 |

Chapter 3: Functionalized Thermoplastic Poly (urethane-urea) as Hole Conductor for Quantum Dot Sensitized Solar Cell

| | | |
|--------|--|----|
| 3.1 | Introduction..... | 52 |
| 3.2 | Results and discussion..... | 55 |
| 3.2.1. | Pendant group and its interaction with hard segment content of polyurethane chain..... | 55 |
| 3.2.2 | Electrochemical characteristic response of polyurethane ionomer..... | 61 |
| 3.3 | Quantum dots, quantum confinement effect and its optimization..... | 62 |
| 3.3.1 | Electrochemical characteristics of capped CdS particle and PANi..... | 65 |
| 3.3.2 | Extent of interaction, chemical capping and particle size response of CdS.... | 66 |
| 3.4 | Fabrication of QDSS Cell and its solar (light) energy conversion response..... | 69 |
| 3.4.1 | Energy levels, photosensitization and photovoltaic charge transfer Phenomenon..... | 69 |
| 3.5 | Photovoltaic reaction and hole conduction studies in QDSS cells..... | 71 |
| 3.6 | Conclusions..... | 77 |

Chapter 4: Redox Mediation through Integrating Various Chain Extenders in Active Ionomer Polyurethane Hard Segments in CdS Quantum Dot Sensitized Solar Cell

| | | |
|-------|---|-----|
| 4.1 | Introduction..... | 79 |
| 4.2 | Results and discussion..... | 81 |
| | Chain extension, structural variation and interaction of hydrophilic group in | |
| 4.2.1 | polyurethane chain..... | 82 |
| | Electrochemical properties of electrolyte responsive component in polyurethane | |
| 4.2.2 | ionomers..... | 91 |
| 4.3 | MPA functionalized CdS QDs and quantum confinement effect on stabilized | |
| | Structure..... | 96 |
| 4.4 | Functionalized graphene oxide and extent of functional interaction of γ - | |
| | propane sultone..... | 98 |
| 4.5 | Electron lifetime studies and control of recombination center in polyurethane | |
| | ionomers..... | 100 |
| 4.6 | Fabrication scheme and interfacial alignment of energy levels in QDSS | |
| | cells..... | 102 |
| 4.7 | Photovoltaic properties of Quantum dot sensitized solar cells..... | 104 |
| 4.7.1 | Influence of different ionomer electrolyte matrix for photovoltaic reaction in | |
| | QDSS cell..... | 104 |
| 4.7.2 | Variation of chain length and functionality in ionomer electrolyte structure..... | 106 |
| 4.8 | Conclusions..... | 110 |

Chapter 5: Multifunctional Graphene Oxide Implanted Polyurethane Ionomer Gel Electrolyte for Quantum Dots Sensitized Solar Cell

| | | |
|-------|---|-----|
| 5.1 | Introduction..... | 112 |
| 5.2 | Results and discussion..... | 114 |
| 5.2.1 | Structural and functional impact of pendant anion on GO functionalized | |
| | polyurethane chain..... | 114 |
| 5.2.2 | Thermal and structural stabilization characteristics..... | 120 |
| 5.2.3 | Morphological and structure-function characteristics..... | 121 |
| 5.2.4 | Electrochemical and structure-activity characteristics..... | 122 |
| 5.3 | MPA functionalized QDs, functional structure and size quantization | |
| | effect..... | 126 |
| 5.4 | Interfacial energy levels, band structure and electron injection phenomenon | 129 |
| 5.4.1 | QDSSCs fabrication and Interfacial gel polyelectrolyte activity..... | 131 |

| | | |
|-----|---|-----|
| 5.5 | Photovoltaic performance of QDSSCs via PUI and PUI-GO gel polyelectrolytes..... | 131 |
| 5.6 | Conclusions..... | 135 |

Chapter 6: Conclusions and Future Perspectives

| | | |
|-----|-------------------------------|-----|
| 6.1 | Conclusions..... | 138 |
| 6.2 | Scope of the future work..... | 142 |
| | References..... | 144 |

List of publications

Conference contributions

LIST OF SCHEME

| | | |
|-------------------|--|----|
| Scheme 1.1 | Schematic representation of energy levels (TiO ₂ , Dye, electrolyte) and open circuit potential in DSS cell with three electrolyte (I/I ₃ ⁻ , [Co (bpy) ₃] ^{2+/3+} and [Cu (dmp) ₂] ^{1+/2+} | 6 |
| Scheme 1.2 | Operating principle and schematic redox mediation in QDSS cell | 11 |
| Scheme 1.3 | The comprehensive energetic scheme of the density of states in TiO ₂ for different molar concentration of salt in (a) Liquid (b) solid polymer electrolyte | 15 |
| Scheme 1.4 | Schematic illustration of energy level diagram, photoexciton generation, potential barrier and hole transport across multiphases within CdSe sensitized solar device showing electron injection with simplified potential diagram | 20 |
| Scheme 1.5 | Schematic diagram of charge transport with role of additive in polysulfide electrolyte in QDSS cell | 22 |
| Scheme 1.6 | General schematic reaction pathways for polyurethane ionomer synthesis | 28 |
| Scheme 2.1 | Synthetic reaction scheme of GO and its functionalization | 38 |
| Scheme 2.2 | Schematic representation of synthesis and surface functionalization of CdS quantum dots | 40 |
| Scheme 2.3 | Schematic fabrication of basic QDSS cell | 42 |
| Scheme 3.1 | Schematic reaction mechanism of polyurethane synthesis and its chemical functionalization | 56 |
| Scheme 3.2 | HOMO-LUMO energy levels of sulfonated polyurethane and its alignment with band structure of TiO ₂ and CdS quantum dots. Photosensitization and charge transport mechanism with hole conducting sulfonated polyurethane gel matrix | 70 |
| Scheme 3.3 | Schematic mechanism of photovoltaic reaction | 71 |
| Scheme 4.1 | (A) Chemical structure of chain extenders (1) EDA (2) BD (3) HDA (4) DDA (5) PDA. (B) Schematic representation of (a) Synthesis of ether based polyurethanes through variation of chain extenders and structural modification of hard segment contents in polymer chain (b) Synthesis of ester based polyurethane by maintain chain extending unit (EDA) constant. (c) Fabrication of QDSS cell through structural | 82 |

| | | |
|-------------------|--|-----|
| | integration of components in layer design and indication of pathways for charge transport under photo illumination | |
| Scheme 4.2 | (a) Systematic representations of energy level, band diagram and its interfacial alignment. (b) Charge transport and recombination pathways at the interface photoanode/ionomer electrolyte/counter electrode. (c) Possible functional mechanism (photovoltaic reaction) of ionomer electrolyte with QDs and counter electrode | 103 |
| Scheme 5.1 | Schematic presentation of polyurethane ionomer (PUI) bearing electrolyte active groups | 115 |
| Scheme 5.2 | Schematic reaction pathway for synthesis of multifunctional graphene oxide implanted polyurethane ionomer | 116 |
| Scheme 5.3 | Fabrication of thin film quantum dots sensitized solar cell via insertion of gel polyelectrolyte (PUI-GO) between photoanode and counter electrode | 131 |

LIST OF FIGURES

| | | |
|-------------------|---|----|
| Figure 1.1 | (a) The distribution ratio of different energy resources at global scale showing 19% of the total contribution comes from renewable energy sources. Data from International Energy Agency (iea.org) (b) Elevation ratio of renewable energy during 1965-2020 | 1 |
| Figure 1.2 | Electrical energy generation by energy resources on global level in 2020. | 2 |
| Figure 1.3 | Components, configuration and design of third generation (3G) solar cell | 4 |
| Figure 1.4 | Nanoparticle size dependent absorption (color variation) enables tuning of colloidal quantum dot spectrum | 9 |
| Figure 1.5 | (a) Schematic presentation of absorption transition, interfacial charge transport and various recombination pathways occurring at the interface of TiO ₂ /QDs/electrolyte. (b) Systematic representation of surface trap, defect states and charge recombination happening on the surface of quantum dots | 10 |
| Figure 1.6 | Classifications of hole transport redox active phases (materials) | 14 |
| Figure 1.7 | Chemical structures of polyelectrolyte polymers | 25 |
| Figure 3.1 | (a) ¹ H NMR investigation for polyurethane and its functionalized matrix. The spectra were recorded after dissolving the sample in d ₆ -DMSO solvent. (b) FTIR study of polyurethane and its functionalized matrices FT-IR spectra shows that the intensity of stretching frequency increases with degree of sulfonation and interaction. (c) TEM image of SPU-3 film. (d) XRD pattern of polyurethane urea film and its functionalized structure. (e) Thermogravimetric analysis of polyurethane and sulfonated polyurethane at various level of functionalization | 59 |
| Figure 3.2 | Polyurethane and its functionalized matrix: sulfonation at hard segment content with variation of sulfonating agent. (a) UV-visible spectra of pure PU and SPUs with variable content of sulfonating agent. (b) Determination of energy gap (Tauc's plot) from absorption edge | 60 |

| | | |
|-------------------|---|----|
| | transition. (c) Solution phase cyclic voltammetry of solvent NMP, PU and SPU-1 with scan rate of 20 mV/s at room temperature. (d) Cyclic voltammetry of SPU-2, SPU-3 and SPU-4. (e) EIS measurement solution phase PU, SPU-2 and SPU-3 for the measurement of charge transfer resistance | |
| Figure 3.3 | UV-visible absorption spectra of Ethylenediamine (EDA) capped CdS QDs to investigate extent of capping around CdS particle. (b) Estimation of direct band gap (Tauc's plot) | 63 |
| Figure 3.4 | (a) UV-visible absorption spectra of various EDTA capped CdS solid thin film. (b) Tauc's plot for estimation of direct band gap. (c) UV-visible absorption spectra of thin film on layered structure. (d) Tauc's plot for estimation of direct band gap | 64 |
| Figure 3.5 | Electrochemical characteristic response: (a) Cyclic voltammetry measurement of EDA capped CdS at various concentration of capping agent. (b) Cyclic voltammetry of EDTA capped CdS through variation of concentration of Sulfide ion in EDTA capped CdS solutions with scan rate of 10 mV/s measured at room temperature. (c) Cyclic voltammetry of optimized EDTA capped CdS and PANi Solution | 66 |
| Figure 3.6 | (a) SEM image of uncapped CdS and EDTA capped CdS. SEM revealed that capping reduced the agglomeration as a result little homogeneous distribution of particle.(b) AFM image of capped CdS nanoparticle. (c) TEM image of EDTA capped CdS QDs with inset histogram of particle size distribution. Image displayed spherical particle distribution with maximum size range 4 ± 0.7 nm. (d) DLS measurement of EDTA capped CdS QDs showing solvated dynamic size as 8, 11 and 15 nm for different band gap particle.(e) FTIR spectra of uncapped CdS , EDTA and EDTA capped CdS | 69 |
| Figure 3.7 | (a) Room temperature fabrication and layered assembly of Photoanode, polyurethane ionomer gel and counter electrode. (b) J-V characteristic curve of QDSS cell through photosensitization FTO/TiO ₂ /CdS-4 using liquid ionomer electrolyte (SPU-1) in DMSO.(c) J-V characteristic measurement (In dark and light) of QDSS cell using polyurethane ionomer gel (SPU-1 and SPU-2) through photosensitization of | 74 |

| | | |
|-------------------|---|----|
| | FTO/TiO ₂ /CdS (E _g = 2.65 eV). (d) Photovoltaic response (J-V curve) of QDSS cell using CdS (E _g = 2.69eV) and SPU-3 ionomer gel. (e) J-V characteristic measurement of QDSS cell via photosensitization of FTO/TiO ₂ /CdS-4 and FTO/TiO ₂ /CdS-4/CB (carbon black) electrode using SPU-4 ionomer gel. | |
| Figure 3.8 | (a) J-V characteristic curve of QDSS cells through variation of interface structure between FTO/TiO ₂ /CdS-4 and SPU-3 ionomer gel. (b) Solar energy conversion characteristic curves. (c) Photovoltaic J-V characteristic curve of QDSS cells using SPU-3 ionomer gel and influence of quantum confinement effect in CdS QDs. (d) solar energy conversion characteristic plots for estimation of efficiency | 75 |
| Figure 4.1 | Structural content of urethane linkage and functionalized urethane linkage in polyurethane chain (b) Solution phase ¹ H NMR spectra of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix in solvent d ₆ -DMSO with their spectral peaks resolution in the range of chemical shift (δ = 0 - 9 ppm). (c) Solid thin film based FTIR spectra of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix with spectral resolution of 4 cm ⁻¹ . (d) Thermogravimetric analysis (TGA) of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix. (e) Differential scanning calorimetry (DSC) of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix in scanning temperature range of 25-250°C | 84 |
| Figure 4.2 | (a) Thermogravimetric analysis (thermal stability) for ether based polyurethane and its ionomer matrix under different chain extending units (structural variation of HSC). (b) DSC measurements of polyurethane ionomers under different hard segment content due to integration of chain extenders | 86 |
| Figure 4.3 | (a) Solid state FTIR spectra of ester (PCL-diol) based polyurethane and its ionomer matrix. (b) Thermogravimetric analysis of ester based polyurethane, ionomer matrix and composite ionomer matrix. (c) DSC measurements of synthesized ester based polyurethane. (d) DSC measurements of ionomer matrix and composite ionomer matrix | 88 |

| | | |
|-------------------|---|----|
| Figure 4.4 | Solid state UV-visible absorption spectra of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix. (b) $(\alpha h\nu)^2$ vs. $h\nu$ plots for estimation of energy gap from absorption edge of obtained spectra. (c) UV-visible absorption spectra of polyurethanes and its ionomer matrix under different chain structure. (d) Tauc's plots of absorption spectra to estimate energy gap from absorption edge. (e) UV-visible absorption spectra of PU-PCL-EDA, SPU-PCL-EDA and S (PU+CB+EDA). (f) Tauc's plot | 90 |
| Figure 4.5 | Effect on absorption spectra of PU-DDA with variation of weight ratio of sulfonating agent (ratio of weight of NaH to weight of γ -propane sultone). (b) Tau's plot to estimate energy gap | 91 |
| Figure 4.6 | (a) Solution phase cyclic voltammetry measurements of short chain (BD) and long chain (DDA) extended polyurethanes and its ionomer matrix with a scan rate of 20 mV/s operated at room temperature. (b) Solution phase cyclic voltammetry measurement for different ionomer electrolyte (influence of chain structure on redox properties). (c) Cyclic voltammetry characterization of ionomer electrolyte in pristine and composite phase (influence of functional group on redox properties) (d) Electrochemical impedance spectroscopy measurements in solution phase of polyurethanes (PU-BD and PU-DDA) and its ionomer matrix for the estimation of electrical (ionic) conductivity at room temperature. (e) EIS measurement and influence of chain structure on ionic conductivity of polyurethane ionomers. (f) I-V characteristic measurements of ionomer gel as thin film on FTO (electronic conductivity measurements) | 93 |
| Figure 4.7 | (a) Solid state UV-visible absorption spectra of free CdS and MPA capped CdS particles under variation of concentration of MPA molecule. (b) Tauc's plot to estimate band gaps from absorption edge. (c) TEM image of MPA capped CdS nanoparticles. (d) UV-visible absorption spectra of thin film Ti – nanooxide (photocatalyst) photosensitizer, SGO and multi layered structure to characterize photo harvesting properties. (e) Solution phase CV measurements of capped CdS particles to investigate redox properties. (f) Energy levels and | 98 |

| | | |
|--------------------|--|-----|
| | band diagram for different CdS nanoparticles | |
| Figure 4.8 | (a) TEM image of sulfonated graphene oxide (b) Solid state FTIR spectra of GO and SGO. (c) XRD measurements of GO and SGO (d) CV measurements of GO and SGO (e) ESI measurements for GO, SGO and MPA capped CdS QDs. (F) electrocatalytic and corrosion behaviour of SGO with reference to : (a) Coated Layered structure of fabricated device. (b) J-V characteristic measurements of QDSS cells using SPU-EDA ionomer electrolyte on different interfaces of photoanode.(c) J-V curves QDSS cells with SPU-HDA ionomer electrolyte (d) J-V curve of QDSS cells using SPU-PDA ionomer electrolyte. Each ionomer gel consists of 30% (w/v) | 100 |
| Figure 4.9 | Bode plot for ionomer electrolyte in solution phase (a) influence on free electron lifetime measurement on the surface of active group of different chain extended ionomer electrolyte (b) influence on lifetime with oxygenic functionalities in pristine and composite ionomer structure. (c) Bode plots for QDs and SGO in solution phase. (d) Charge transport and recombination –activation on PANi coated CdS photoanode. (e) Charge transport and recombinations on SGO coated photoanode sensitized device | 101 |
| Figure 4.10 | (a) Coated Layered structure of fabricated device. (b) J-V characteristic measurements of QDSS cells using SPU-EDA ionomer electrolyte on different interfaces of photoanode.(c) J-V curves QDSS cells with SPU-HDA ionomer electrolyte (d) J-V curve of QDSS cells using SPU-PDA ionomer electrolyte. Each Ionomer gel electrolyte 30% (w/v) | 106 |
| Figure 4.11 | (a) Photovoltaic curves of QDSS cells using SPU-BD and SPU-DDA with direct free interface of photoanode/counter electrode. (b) Photovoltaic curves of QDSS cells using SPU-BD and SPU-DDA at the interface doped photoanode/counter electrode.(c) Influence on photovoltaic curves of QDSS cells using SPU-EDA and SPU-DDA at different interface of photoanode/counter electrode. (d) Photovoltaic curves of QDSS cells using SPU-PCL-EDA and composite S (PU+CB)-PCL-EDA at different interfaces of photoanode/counter | 108 |

| | | |
|--------------------|--|-----|
| | electrode. Each ionomer gel consists of 30% (w/v) | |
| Figure 4.12 | J-V characteristic curve of QDSS cells with variation of chain structure in ionomer electrolyte under photovoltaic reaction with ionomer gel 20% (w/v) (a) PANi coated photoanode (FTO/TiO ₂ /CdS/PANi) (b) SGO coated photoanode FTO/TiO ₂ /CdS/SGO | 109 |
| Figure 5.1 | (a) ¹ H NMR spectra of pristine poly (urethane-urea) and polyurethane ionomer (PUI). (b) FTIR spectra of poly (urethane-urea) and its ionomer | 117 |
| Figure 5.2 | (a) Solution state ¹ H NMR spectra of PU-GO and PUI-GO showing spectral peaks in downfield and upfield regions. (b) Solid state FTIR spectra of PU-GO and PUI-GO showing specific and characteristic peaks. (c) Solid state UV-visible absorption spectra of PU-GO, PUI and PUI-GO showing shifted red shifted absorption band. (d) Tauc's plot for investigation of energy gap and structural confinement effect | 118 |
| Figure 5.3 | (a) TGA curves of PU-GO (0.5%), PUI and PUI-GO (0.5%). (b) DSC thermogram of PU-GO (0.5%) and its ionomer (PUI-GO) | 121 |
| Figure 5.4 | TEM image of PUI-GO (0.5%). (b) AFM image of PU-GO (0.5%) and PUI-GO (ionomer) film spin coated on silicon wafer. (c) SEM image of PU-GO (0.5%) and PUI-GO | 124 |
| Figure 5.5 | (a) Solution phase cyclic voltammetry of PU-GO (0.5%), Pristine PUI and PUI-GO recorded at room temperature with scan rate of 20 mV/s. (b) Electrochemical impedance spectroscopy (EIS) of PU-GO (0.5%), PUI and PUI-GO (0.5%). (c) Tafel plot for the investigation of electrocatalytic activity and corrosion inhibition. (d) Bode plots for the investigation of lifetime of free electron on the surface of electrolyte active group) in PUI and PUI-GO (0.5%) | 124 |
| Figure 5.6 | (a) Solid state FTIR spectra of free CdS (uncapped) and MPA capped CdS. (b) Fe-SEM image of free CdS (c) Fe-SEM image of MPA capped CdS. (d) AFM image of MPA capped CdS coated on silicon wafer | 127 |
| Figure 5.7 | (a) Solid state UV-visible absorption spectra of of free CdS and MPA capped CdS. (b) Tauc's plot for determination of band gap through absorption edge transition. (c) Dispersed phase cyclic voltammetry | 128 |

| | | |
|--------------------|---|-----|
| | (CV) of MPA capped CdS. (d) EIS plot for estimation of electrical conductivity of MPA capped CdS | |
| Figure 5.8 | (a) Energy levels of constituents materials including polyelectrolyte for assembly of QDSS cells. (b) The possible photoanode electrolyte interface showing increased density of photoexcited electron in FTO for efficient conversion | 130 |
| Figure 5.9 | (a) J-V solar characteristic measurements of QDSS cells using gel polyelectrolytes with various composition of graphene oxide under the illumination of 100 mW/cm ² intensity of white neutral LED light. (b) Power vs. Voltage plot to calculate photovoltaic conversion efficiency | 132 |
| Figure 5.10 | (a) Photovoltaic characteristic curves of designed QDSSCs with TiO ₂ /MPA-CdS/SGO/Gel polyelectrolyte/Pt-FTO configuration (b) Power vs. voltage plot for calculation of conversion efficiency | 134 |

LIST OF TABLES

| | | |
|------------------|---|-----|
| Table 1.1 | Properties and repeating structures of the most common polymer matrices used to prepare gel electrolytes | 17 |
| Table 1.2 | various composite polymer electrolytes with polysulfide and photovoltaic values for CdS sensitized solar cell | 19 |
| Table 1.3 | Photovoltaic parameters and photoactive materials of QDSCs based on polysulfide electrolytes with different additives | 22 |
| Table 3.1 | Calculation of HOMO-LUMO energy levels with UV-visible absorption spectra and electrochemical cyclic voltammetry measurement in window -2V to +2V | 61 |
| Table 3.2 | UV-visible and electrochemical parameters and its values for photocatalyst, EDTA capped CdS QDs and PANi | 66 |
| Table 3.3 | Influence on photovoltaic parameters via tuning HOMO-LUMO energy levels of sulfonated polyurethane under different size or band gap Quantum dots as photosensitizer | 74 |
| Table 3.4 | Structure of Quantum dot sensitized solar cell consisting of optimized sulfonated polyurethane ionomer gel (matrix). The photovoltaic physical parameter and its values are calculated accordingly under photo illumination with 100 mW/cm ² intensity of light operated at room temperature | 74 |
| Table 3.5 | Size quantization effects of CdS QDs on photovoltaic parameters and its values measured at constant hole conducting layer or hole conducting electrolyte | 76 |
| Table 4.1 | FTIR Wavenumber (cm ⁻¹) of Polyurethanes and polyurethane ionomers | 85 |
| Table 4.2 | Electrocatalytic redox reaction in ionomer segment at the interface of different ionomer electrolyte/counter electrode (Pt) | 93 |
| Table 4.3 | electronic conductivity of polyurethane ionomers developed as thin film over the surface of FTO | 95 |
| Table 4.4 | Photovoltaic characteristics of QDSS cells fabricated with PANi coated photoanode (FTO/TiO ₂ /MPA-CdS/PANi) and ionomer gel matrix with different electrolyte structure (sulfonated polyurethane ionomers) | 109 |
| Table 4.5 | Photovoltaic characteristic measurements of QDSS cells fabricated with SGO coated photoanode (FTO/TiO ₂ /MPA-CdS) and ionomer gel matrix | 109 |

| | | |
|------------------|--|-----|
| | with different electrolyte structure (sulfonated polyurethanes) | |
| Table 5.1 | Estimation of electrochemical parameters and characteristic values from electrochemistry of cyclic voltammetry for polyelectrolyte solutions | 124 |
| Table 5.2 | Photovoltaic parameters for the measured QDSS cells using gel polyelectrolytes with different composition | 132 |