



SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY INDIAN INSTITUTE OF TECHNOLOGY (BANARAS HINDU UNIVERSITY) VARANASI -221005, INDIA

Prof. Pralay Maiti School of Materials Science and Technology

Tel # +91- 9935141321

Email: pmaiti.mst@itbhu.ac.in

CERTIFICATE

It is certified that the work contained in the thesis titled **"Development of Functionalized Polyurethane Gel Electrolytes for Quantum Dots Sensitized Solar Cell"** by **"Ravi Prakash"** has been carried under my supervision and this work has not been submitted elsewhere for a degree. It is further certified that the student has fulfilled all the requirement of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. degree.

Date:

(Supervisor)

Place: IIT (BHU) Varanasi

Prof. Pralay Maiti

DECLARATION

I, **Mr. Ravi Prakash** certify that the work embodied in this thesis is my own bonafied work and carried out by me under the supervision of "**Prof. Pralay Maiti**" from "30/12/2016 to 12/05/2022" at "School of Materials Science and Technology", Indian Institute of Technology (BHU) Varanasi. The matter embodied in this thesis has not been submitted for award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to research worker wherever their work cited in my work in this thesis. I further declare that I have not willfully copied any others work, paragraph, text, data results etc. reported in journal books magazines, reports, dissertations thesis etc. or available at websites and have not included them in this thesis and have not cited as my own work.

Date

Ravi Prakash

Place: IIT (BHU Varanasi

Certificate by the Supervisor

It is certified that above statement made by the student is correct to the best of my knowledge.

Supervisor

Prof. Pralay Maiti School of Materials Science and Technology Indian Institute of Technology (Banaras Hindu University) Varanasi 221005, India

Date

Signature of the Coordinator/HOD

Title: Development of Functionalized Polyurethane Gel Electrolytes for Quantum Dots Sensitized Solar Cell

Date:

Place: IIT (BHU) Varanasi

Signature of the student

(Ravi Prakash)

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the "*Doctor of Philosophy*".

Signature of Student (Ravi Prakash)

Note: However, the author may reproduce or authorize others to reproduce materials extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that and Institute's copyright notice are indicated.

ACKNOWLEDGEMENTS

It's my great pleasure to acknowledge the help, support, encouragement and guidance that I have received from number of peoples in the course of completion of the thesis. I am extremely grateful to my research guide, **Prof. Pralay Maiti**, Professor, School of Materials Science and Technology, IIT (BHU), Varanasi for his valuable guidance, scholarly inputs and consistent encouragement I received throughout the research work. This work was possible only because of his scientific vision and unconditional support.

I have spent continuously 5 years in the School of Materials Science and Technology, IIT (BHU), Varanasi. During this period, I learned a lot of things along with research work which I hope will be helpful in my life. Remaining research periods was completed during service whenever I got leave from working institute. I would like to thank all the respected teachers of the school, **Prof. Rajiv Prakash**, **Dr. Chandana Rath**, **Dr. Akhilesh Kr. Singh**, **Dr. Chandan Upadhyay**, **Dr. Bhola Nath Pal**, **Dr. Ashish Kumar Mishra**, **Dr. Shrawan Mishra**, **Dr. Sanjay Singh and Dr. Nikhil Kumar** for their valuable suggestions and encouragement during research work.

I am also grateful to my Research Program Evaluation Committee (RPEC) members **Prof. Nira Misra** from School of biomedical Engineering, **Prof. K. D. Mandal** from Department of Chemistry, IIT (BHU) I would like to express gratitude to **Dr. Pankaj Srivastava**, Associate Professor, Department of Chemistry, Institute of Science, Banaras Hindu University, and Varanasi for technical and critical support during device fabrication. Thanks to my co-workers **Amita Santra**, and **I.C. Maurya (BHU)** for their constant and coherent support during experimental characterization. I also thank to my lab mates **Dr. Sunil Kumar**, **Dr.** Akhand Pratap Singh, Dr. Dinesh Kumar Patel, Dr. Arun Kumar Mahanta, Dr. Sudipta Senapati, Dr. Arpan Biswas, Dr. Anupama Gaur, Dr. Aparna Shukla and Dr. Dipti Saxena. Mr. Sunil Kumar, Dr. Om Prakash, Mr. Shivam Tiwari, Mr. Pravesh Kumar Yadav, Mr. Swapan Maity, Ms. Sudipta Bauri, Ms. Amita Santra, Ms. Swikriti Tripathi, Mr. Shubham Mandal, and Mr. Avishek Malik Chaudhary for the cooperation and pleasant company.

I gratefully acknowledge Central Instrumental Facility Centre, IIT (BHU), Varanasi, for providing various instrumental facilities. I have no words to thank my mother (**Urmila Devi**) and father (**Subhash Chandra**) for their unconditional love and unwavering support at every stage of my life.

Date:

Place: Varanasi

Ravi Prakash

CONTENTS

Chapter 1: Introduction and Literature review	
1.1 Introduction	3
1.2. Background and Development of Photovoltaics	3
1.2.1. Solar Radiation	3
1.2.2. Air Mass	5
1.2.3. History and Development of Photovoltaic	7
1.2.4. Shockley-Queisser limit	9
1.3. Classification of Solar cell	0
1.3.1 Conventional p-n Junction Solar Cells1	1
1.3.1.1 First Generation Solar cells1	2
1.3.1.2 Second Generation Solar Cells1	4
1.3.1.3Third Generation Solar cells1	6
1.3.1.3.1 Organic Solar Cells1	7
1.3.1.3.2 Perovskite Solar Cells2	1
1.3.1.3.3 Dye Sensitized Solar Cells2	3
1.3.1.3.4 Quantum Dots Sensitized Solar Cells2	4
1.4 Device Structure and Working Principle of QDSSCs2	6
1.4.1 Devices Components of QDSSCs2	8
1.4.1.1 Photoanode	8
1.4.1.2 Counter Electrode2	9
1.4.1.2.1 Platinum2	9
1.4.1.2.2 Graphene	1
1.4.1.3 Electrolytes	2

1.4.1.3.1 Liquid Electrolyte	
1.4.1.3.2 Solid State Electrolyte	
1.4.1.3.3 Gel Electrolyte	35
1.4.1.3.4 Polyelectrolyte	
1.4.1.3.5 Polyurethane Ionomer	37
1.5 Scope and Objectives of Present Work	
1.6 Plan of the Present Work	40
Chapter 2: Experimental Section	
2.1 Synthesis of Quantum dots	45
2.1.1 Materials	45
2.1.2 Synthesis of the CdS Quantum Dots via Solution Mixing Method	45
2.1.3 Synthesis of the CdS Quantum Dots via SILAR Method	47
2.1.4 Synthesis of the CdSe Quantum Dots via Hot Injection Method	46
2.2 Deposition of the ZnSe Passivation Layer	48
2.3 Synthesis of the Graphene Oxide	49
2.4 Functionalization of MWCNTs	50
2.5 Synthesis of Polymer	50
2.5.1 Synthesis of the Thermoplastic Polyurethane Polymer	50
2.5.2 Synthesis of the Chemically GO-tagged Polyurethane Polymer	51
2.5.3 Synthesis of the Chemically f-MWCMTs- tagged Polyurethane Polymer	52
2.6 Functionalization of the Polyurethane Polymer	52
2.7 Preparation of the Ionomer Gel	52
2.8 Fabrication of QDSSCs	53

2.8.1 Preparation of Photoanode	53
2.8.2 Preparation Counter Anode	.54
2.8.3 Solar Cell Measurement	.54
2.9 Characterization Technique	.55
2.9.1 ¹ HNMR Spectroscopy	.55
2.9.2 FTIR Spectroscopy	.55
2.9.3 UV-visible Absorption Spectroscopy	.56
2.9.4 X-ray Diffraction (XRD)	.56
2.9.5 Dynamic Light Scattering (DLS)	.56
2.9.6 Scanning Electron Microscopy (SEM)	.57
2.9.7 Transmission Electron Microscopy (TEM)	.57
2.9.8 Cyclic Voltammetry (CV)	.57
2.9.9 Linear Sweep Voltammetry	.58
2.910. Electrochemical Impedance Spectroscopy	.58
2.9.11 Thermogravimetric Analysis (TGA)	.58
2.9.12 Differential Scanning Calorimetry (DSC)	.59
2.10 Measurement and Calculation	.59
2.10.1 Degree of Sulfonation on Hard Segments Content in Polyurethane Ionomer	.59
2.10.2 Calculation of the % Crystallinity	.60
2.10.3 Calculation of Optical Band Gap and HOMO-LUMO Energy Levels	.60
2.10.4 Calculation of HOMO-LUMO Energy Levels	.61
2.10.5 Ionic Conductivity	.61
2.10.6 Electron Conductivity	.62

62	2.10.7 Electrolyte Uptake or Solvent Absorbent Power
62	2.10.8 Free Electron Lifetime Measurement
63	2.10.10 Theoretical Calculation of Open Circuit Potential
63	2.11 J-V Characteristics Measurements and its Photovoltaic Parameter
64	2.11.1 Short Circuit Current Density (Jsc)
64	2.11.2 Open Circuit Voltage
64	2.11.3 Fill Factor
65	2.11.4 Photovoltaic Conversion Efficiency

Chapter 3: Functionalized Thermoplastic Polyurethane Gel Electrolyte for Cosensitized TiO₂/CdS/CdSe Photoanode Solar Cells with High Efficiency

3.1 Introduction
3.2 Results and Discussion
3.2.1 Attachment of Pendant Group and its Interaction with Polyurethane Chain70
3.2.2 Thermal Stability of Polyurethane Ionomer74
3.2.3 Electrochemical Analysis and Measurements of Polyurethane Ionomer76
3.3 Quantum Dots Synthesis, Quantum Confinements and its Optimization79
3.3.1 Electrochemical Response of CdS and CdSe Quantum dots79
3.3.2 Particle Size, Optical Response and its Interaction80
3.4 Fabrication of QDSSCs and its Photovoltaic Conversion Efficiency
3.4.1 Light Harvesting Efficiency (LHE), Energy Profile Diagram and Photovoltaic
Reaction
3.5 Hole Transportation, Redox Reaction and PCE of QDSSCs
3.6 Conclusion

Chapter 4: Functionalized Polyurethane Composite Gel Electrolyte with Cosensitized Photoanode for Higher Solar Cell Efficiency Using a Passivation Layer

4.1 Introduction	5
4.2 Results and Discussion9	7
4.2.1 Chemical Tagging of Graphene Oxide and its Interaction with Polymer Chains9	7
4.2.2 Molar Mass and Thermal stability of GO-Tagged Polyurethane Ionomer10	0
4.2.3 Electrochemical Response of GO-Tagged Polyurethane Ionomer10	2
4.3 Quantum Dots Synthesis, Morphology, and Optical Properties10	17
4.4 Energy Levels Through Electrochemistry11	0
4.5 Energy Diagram, Passivation Effect and Hole Transports Mechanism11	2
4.6 Light-Harvesting Efficiency and Device Structure11	7
4.7 Photovoltaic Performance of QDSSCs11	9
4.8 Conclusion12	2
Chapter 5: Non-toxic CuInS ₂ Quantum Dots Sensitized Solar Cell with Functionalize	d
Thermoplast Polyurethane Gel Electrolyte	
5.1 Introduction	7
5.2 Results and Discussion	9
5.2.1 Synthesis of MWCNTs-Tagged Polyurethane and its Functionalized Ionomer12	9
5.2.2 Electrochemical Behavior of the CNTs-tagged Polyurethane and its Ionomer13	6
5.3 Microscopic Characterization of CuInS2 QDs14	0
5.4 Optical and Electrochemical Properties of Polymer and QDs14	-2
5.5 Energy-Profile Diagram, Hole Transportation and Devices Structure	4
5.6 Photovoltaic Performance	.9

5.7 Conclusion
Chapter 6: The Effect of Chemical Tagging of Graphene Oxide in Thermoplastic
Polyurethane on Gelation Behavior
6.1 Introduction157
6.2 Results and Discussion158
6.2.1 Interaction of GO with Polymer Chain in terms of Gelation, Structural, Morphology and
Thermal properties158
6.3 Effect of Chemical Tagging on Rheological Behavior164
6.4 Viscous Flow Behavior165
6.5 Stress Relaxation Behavior167
6.6 Conclusion170
Chapter 7 Conclusion and Scope of Future Work
7.1 Conclusion171
7.2 Scope of the Future Work176

forman	177
terences	.//

List of Scheme

Scheme 1: Schematic reaction synthesis of the polyurethane ionomer
Scheme 2.1: Schematic synthesis of the CdS quantum dots via solution mixing method46
Scheme 2.2: Schematic diagram of the growth of the CdS quantum dots via SILAR method47
Scheme 2.3: Schematic diagram of the synthesis of CdSe quantum dots
Scheme 2.4: Schematic diagram for the deposition of ZnSe passivation layer
Scheme 2.5: Schematic preparation for the ionomer gel
Scheme 3.1: The synthesis of the pure polyurethane and its subsequent
Scheme 4.1: Reaction scheme for the synthesis of GO tagged polyurethane (PU-GO) in three
stages and its subsequent functionalization (SPU-GO)
Scheme 5.1: Functionalization of MWCNTs and synthesis of f-MWCNT tagged polyurethane
polymer (PU-CNT) and its subsequent functionalized polymer (SPU-CNT)130
Scheme 6.1: Schematic diagram of the synthesis of PU-GO polymer hybrid (PU-GO-C)159

List of the Figures

Figure 1.1 Solar radiation spectrum on the Earth's surface4
Figure 1.2 Air mass calculated from the zenith point
Figure 1.3 World's photovoltaic market growth
Figure 1.4 Growth per region of the world's photovoltaic market 2016-2022
Figure 1.5 Variation of the Shockley-Queisser Limit with band gap of various semiconductor materials
Figure 1.6 Band energy diagram of p-n junction solar cell under irradiation of light12
Figure 1.7 Cross-section of monocrystalline silicon solar cell
Figure 1.8 Energy band diagram of p-i-n junction under the irradiation of light15
Figure 1.9 Schematic diagram of a thin film solar cell
Figure 1.10 Differences between a bi layer junction (a) and a bulk heterojunction (b)18
Figure 1.11 Structure and energy level for a standard BHJ solar cell. The active blend is composed by the intermixed phase of the donor and acceptor materials
Figure 1.12 Perovskite structure of ABX ₃ where A= CH ₃ NH ₃ , B= Pb, and X= Cl, Br or I21
Figure 1.13 Two different types of perovskite solar cells diagram 22
Figure 1.14 Structure diagram of dye sensitized solar cells
Figure 1.15 Typical device structure of QDSSCs
Figure 3.1: (a) ¹ HNMR spectra of pure and various functionalized PUs (b) degree of sulfonation
as a function of the sulfonating agents72

Figure 3.2: (a) FTIR measurements of pure and various degree of functionalized PUs (b) UV-vi
spectroscopy measurements of pure and functionalized PUs

Figure 3.3: (a) TGA thermograms of pure and functionalized PUs (b) DTA of pure and
functionalized PUs (c) DSC measurements of pure and functionalized PUs75
Figure 3.4: (a) Potentiodynamic polarization (I-V) measurements of mild steel with and without
the inhibitor in 0.5 M H ₂ SO ₄ ; (b) variation of percentage inhibition efficiency with inhibitor
concentration77
Figure 3.5: (a) CV measurements of indicated PU and functionalized PUs; (b) optical band gap
of various functionalized PUs78
Figure 3.6: (a) CV measurements of CdS QDs; (b) CV measurements of CdSe QDs (c) optical
band of CdS and CdSe QDs79
Figure 3.7: (a) FTIR spectra of synthesized CdS and CdSe (b) UV-visible spectra of CdS and
CdSe QDs81
Figure 3.5: (a) TEM bright-field image and particle size distribution of CdS in the inset (b) TEM
image and particle size distribution of CdSe QDs82
Figure 3.9: (a) UV-visible absorbance spectra of FTO/TiO ₂ , FTO/TiO ₂ /CdS, and
FTO/TiO ₂ /CdS/CdSe; (b) light harvesting efficiency of photoanode (FTO/TiO ₂ , FTO/TiO ₂ /CdS,
and FTO/TiO ₂ /CdS/CdSe)
Figure 3.10: (a) comparative band energy diagram of functionalized SPU-1 and CdSe quantum
dots; (b) comparative band energy diagram of functionalized SPU-2 and CdSe quantum dots; (c)
comparative band energy diagram of functionalized SPU-3 and CdSe quantum dots
Figure 3.11: (a) Energy profile diagram of TiO ₂ , CdS, and CdSe QDs with SPU-3 gel electrolytes
with energy levels as calculated from Eg, EHOMO, and ELUMO. The arrow indicates the flow of

excitons under a suitable energy level; (b) comparison of the energy level of the SPU polymer with
CdSe QDs showing difficulty n transport of the holes
Figure 3.12: (a) Array of the photoanode and solar excitation mechanism for the constructed solar
cells; (b) layer by layer deposition of TiO2, CdS, and CdSe to fabricate the photoanode; (c) J-V
characteristics measurements to calculate the photocurrent density and open circuit voltage under
1-sun illumination (100 mw/cm2); (d) power voltage curve to calculate the PCE of the indicated
QDSSCs
Figure 3.13: (a) represent the photocurrent density-potential curve using the SPU-1 gel electrolyte
with TiO ₂ /CdS/CdSe photoanode; (b) represent the power-voltage (J-V) curve using the SPU-1
gel electrolyte with TiO ₂ /CdS/CdSe photoanode; (c) represent the photocurrent density-potential
curve using the SPU-2 gel electrolyte with $TiO_2/CdS/CdSe$ photoanode; (d) represent the power-
voltage (J-V) curve using the SPU-2 gel electrolyte with TiO ₂ /CdS/CdSe photoanode89
Figure 4.1: (a) ¹ H NMR spectra of pure PU, PU-GO and functionalized polymer (SPU-GO), inset
figure shows the magnified spectrum in the indicated zone; (b) FTIR spectra of PP, PP-GO, PU-
GO and SPU-GO showing appearance of new peak and shifting of peak position; (c) UV-vis
absorption spectra of PP, PP-GO, PU-GO and functionalized polymer (SPU-GO) showing shifting
of peak position
Figure 4.2: (a) DSC thermograms of PP, PP-GO, PU-GO and SPU-GO showing the melting
temperatures; and (b) TGA thermograms of PP, PP-GO, PU-GO and SPU-GO showing relative
thermal stability; (c) DSC thermograms of PP, PP–GO, PU–GO and SPU–GO showing the melting
temperatures

Figure 4.3: (a) Nyquist plots for the indicated pure and functionalized PUs; **(b)** Arrhenius plots of the pure and indicated functionalized polymers......103

Figure 4.4: (a) Potentiodynamic polarization measurement of mild steel with and without the
indicated inhibitors in 0.5 M H_2SO_4 solution; and (b) percentage inhibition efficiency as a function
of inhibitor (SPU-GO-CC) concentration104
Figure 4.5: (a) UV-vis absorption spectra of CdS and CdSe showing the absorption peak; (b)
FTIR spectra of synthesized CdS and CdSe QDs107
Figure 4.6: The UV-Vis absorption spectroscopy of EDTA capped and Uncapped of CdS QDs.108
Figure 4.7: (a) TEM bright field image and particle distribution of CdS QDs; and (b) TEM bright
field image and particle size distribution of CdSe QDs109
Figure 4.8: (a) CV voltammograms of PU–GO, SPU–GO and SPU–GO–CC polymer/composite;
(b) optical band gap measurement of SPU-GO and SPU-GO-CC polymer/composite; (c) CV
voltammograms of CdS and CdSe QDs; and (d) optical band gap measurements of CdS and CdSe
QDs110
Figure 4.9: The CV measurement of functionalized polymer with varying content of conducting
carbon additives112
Figure 4.10 (a): The HOMO and LUMO energy levels of various functionalized polymers are
used to draw the energy profile diagrams of functionalized polymers113
Figure 4.10 (b): The comparative band energy diagrams of functionalized polymer with and
without passivation layer
Figure 4.10 (c): The energy levels diagrams of SPU-GO polymers and QDs115
Figure 4.10 (d): The energy levels diagrams of SPU-GO-CC polymers and QDs115
Figure 4.10 (e): The energy levels diagrams of SPU-GO-CC polymer and QDs with passivation
layer116

excitation mechanism and layered structure of fabricated QDSSCs......118

 Figure 5.7: (a) CV measurements of PU-CNT and SPU-CNT polymers, (b) optical band gap measurements of PU-CNT and SPU-CNT polymers, (c) CV measurements of CuInS₂ QDs, (d) relative light harvesting efficiency of FTO/TiO₂ and FTO/TiO₂/CuInS₂ QDs......143

Figure 5.8: (a) Energy profile diagram of TiO₂, CuInS₂ with SPU-CNTs gel electrolyte using the

Figure 5.8: (b) Energy profile diagram of TiO₂, CuInS₂ with SPU-CNTs gel electrolyte using the

Figure 5.8: (c) Energy profile diagram	of TiO ₂ , CuInS ₂ with	h SPU-CNTs gel	electrolyte using the
Au (gold) as counter electrode			147

Figure 6.7: Stress relaxation behavior of pure PU, PU-GO-P, and PU-GO-C gels at 25 °C.....168

LIST OF TABLES

Table 1.1: The distance between the various planet and Sun and the solar irradiance on the
respected surfaces
Table 1.2: Comparison between QDSSCs and DSSCs
Table 3.1: Corrosion Current Density, Potential, and Percentage Inhibition Efficiency of
Functionalized PUs (SPUs) at Different Concentrations
Table 3.2: Short-circuit Current Density (Jsc), Open-circuit Voltage (Voc), FF, and PCE (η) of
Various Cells Using the Indicated Photoanode and SPU-3 Polymer Gel Electrolytes
Table 4.1: The resistance and conductivities of various pure and functionalized polymer / composite.
Table 4.2: The corrosion current density, potential, corrosion rate density and percentage inhibition efficiency of functionalized polymer at different concentration
Table 4.3: Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor and power
conversion efficiency, PCE (η) of various Cells using the cosensitized photoanode and polymer
gel electrolytes with and without ZnSe passivation layer
Table 5.1: The resistance and conductivities of pure, CNT-tagged and functionalized polymer137
Table 5.2: Corrosion current density, potential, corrosion rate density and percentage inhibition
efficiency of functionalized polymer (SPU-CNT) at different concentration140
Table 5.3: Photocurrent density, open circuit voltage, fill factor, and power conversion efficiency
of various cells using the SPU-CNT polymer gel electrolytes, TiO2/CuInS2 photoanode and
prepared various counter electrode152
Table 6.1: Various parameters as obtained from the fitting of the curve as per the Chasset and
Thrion equation

LIST OF ABBREBIATIONS

UV	Ultraviolet
FTIR	Fourier transforms infrared spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
DLS	Dynamic Light Scattering
CV	Cyclic Voltammetry
J_{SC}	Short circuit current density
V _{OC}	Open Circuit Voltage
FF	Fill Factor
PCE	Photovoltaic conversion efficiency
η	Efficiency
CE	Counter electrode
PTMG	Polytetramethyleneglycol
HMDI	Hexamethylene diisocyanate
CE	Counter electrode
P _{MAX}	Maximum power density
НОМО	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
QDSSCs	Quantum dots sensitized solar cells
Eg	Energy gap
R _{edox}	Redox potential
σ	Ionic conductivity

HSC	Hard segment content
PU	Polyurethane
PUI	Polyurethane ionomer
PE	Polyelectrolyte
SPU	Sulfonated polyurethane
SPUIG	Sulfonated polyurethane ionomer gel
LE	Liquid electrolyte
GPE	Gel polymer electrolyte
R _{CT}	Charge transfer resistance
GO	Graphene Oxide
SGO	Sulfonated grapheme Oxide
ESI	Electrochemical impedance spectroscopy
LSV	Linear seep Voltammetry
TGA	Thermogravimetric analysis
DTA	Differential temperature analysis
DSC	Differential scanning Calorimetry
T _{Gel}	Gel transition temperature
Tg	Glass transition temperature
T _m	Melting Temperature
PS	Photosensitizer
ETL	Electron transport layer
HTL	Hole transport layer
CEM	Counter electrode material

PREFACE

Recently, the renewable energy sources such as Solar Energy, Biomass Energy, Wind Energy, Geothermal Energy and Hydropower Energy have great attention for the world energy society. Solar energy is more attracted as compared to other resources due to endless availability of the solar energy radiation which can be used for solar cell application. The third-generation solar cell technology is the hot topic for the research and development, and the QDSSC is more promising candidate because of multiple exciton generation, hot electron transfer, low cost, easy fabrication process and its theoretical efficiency is higher than Shockley- Queisser limit. The QDSSCs are consist with photoanode, counter electrode and an electrolyte i.e., hole transport materials. Electrolytes play an important role in the QDSSCs, it behaves as redox active couple / hole transport materials i.e., the holes are transported from the photoanode to counter electrode via electrolytes in photovoltaic devices, resulting in generation of electricity. The liquid electrolytes such as polysulfide and iodide / triiodide are more common for the QDSSCs. The shortcomings of liquid electrolytes are easy vaporization, leakage, performance instability and corrosive in nature. Hence, to remove these shortcomings, some research groups have introduced the solid-state electrolyte as hole transport material in QDSSCs and but due to low ionic conductivity and poor preperformance of such kind of the devices, it required some modification to enhance the photovoltaic performance. The gel state electrolytes are good candidate for the QDSSCs because it has high ionic conductivity and good adhesive characteristics behavior due to which it becomes more suitable as a hole transport material for the fabrication QDSSCs. Some researchers have used the additive in gel electrolytes to enhance the photovoltaic performance of the fabricated solar cell. The main objective of this thesis work is to develop the thermoplastic plastic polyure polymer ionomer as a hole transport material for the quantum dots sensitized solar cell. The thermoplastic

polyurethane polymer was used due to active urethane linkage present in the polymer moiety that have flexible behavior and for synthesis purpose a variety of monomers are available. The polyurethane properties were tunned by using various type of monomers and chain extenders for the synthesis of polyurethane polymers. The polyurethane polymers are composed of diisocyanate and polyol moieties using suitable chain extenders. The sulfonate group was attached as a pendent group at polymeric chain and thermoplast polyurethane gel electrolytes was developed as a hole transport material for QDSSCs with CdS/CdSe photoanode. Further graphene oxide was tagged with polyurethane chain and enhanced the polymeric properties, and GO-tagged polyurethane polymer converts in to polyure than e ionomer and prepared a gel electrolyte. The passivation layer was also used for enhanced photovoltaic performance of the fabricated photovoltaic devices, using the suitable passivation layer which prohibits the back electron transfer and facilitate the transportation of the hole in the photovoltaic devices. Further, Carbon nanotube-tagged functionalized polyurethane ionomer was developed as a hole transport material for QDSSCs. The cadmium free zero toxic quantum dots such as copper indium sulfide quantum dots were used to fabricate the green photovoltaic devices. The rheological properties of the prepared gels give information about the gel behavior and viscosity flow behavior of the gel. The stress relaxation measurement and gelation kinetics was also evaluated through the rheological analysis. The relaxation time another important parameter was used the analyzed the gel properties.

This thesis has been divided in seven chapters. The first chapter is introduction and literature review which gives the understanding about solar cells devices, fabrication techniques, solar cells components, electrolytes (liquid, solid and gel), power conversion efficiency and detailed literature survey. The second chapter presents the different experimental techniques used for the characterization. The third chapter "Functionalized Thermoplastic Polyurethane Gel Electrolyte for Cosensitized TiO₂/CdS/CdSe Photoanode Solar Cells with High Efficiency" (work published in *Energy & Fuels.* (2020);34: 16847-16857) present the hole transport behavior of the developed gel electrolyte and devices performance of the fabricated QDSSCs. The fourth chapter "Functionalized Polyurethane Composite Gel Electrolyte with Cosensitized Photoanode for Higher Solar Cell Efficiency Using a Passivation Layer" (work published in *Nanoscale Advances.* (2022); 4: 1199-1212) discusses the effect of chemical tagging of Graphene oxide with polymer chains and use of passivation layer to improve the devices performance. The fifth chapter "Nontoxic CuInS₂ Quantum Dots Sensitized Solar Cell with Functionalized Polyurethane Gel Electrolyte" discusses the green quantum dots sensitized solar cell and multiwalled carbon nanotubes was tagged with polyurethane chain to developed as a hole transport material for cadmium free quantum dots sensitized solar cells (*Communicated*). The sixth chapter "The Effect of Chemical Tagging of Graphene Oxide in Thermoplastic Polyurethane on Gelation Behavior" (*Communicated*). The last chapter present the major conclusions drawn from this work and suggestion for the future work in this field. The reference work is given at the end.