Dedicated to my beloved

"Maa"

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

Prof. Pralay Maiti **Tel # +91- 9935141321**

School of Materials Science and Technology **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

Date **Prof. Pralay Maiti**

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

Signature of the Coordinator/HOD

COPYRIGHT TRANSFER CERTIFICATE

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

Date: **Signature of the student**

Place: IIT (BHU) Varanasi **(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: **Ravi Prakash**

Place: Varanasi

CONTENTS

Chapter 1: Introduction and Literature review

Chapter 2: Experimental Section

List of Scheme

List of the Figures

LIST OF TABLES

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
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
QDSSCs	Quantum dots sensitized solar cells
E_g	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
T_g	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 polyurethane 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 polyurethane 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 TiO_2/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 "Non-toxic $CuInS_2$ 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.