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CERTIFICATE

It is certified that the work contained in the thesis titled **"Thermoplastic Polyurethane Ionomers as Gel Electrolyte for CdS Quantum Dots Sensitized Solar Cell"** by **Sunil Kumar** 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.

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Place: IIT (BHU) Varanasi **(Supervisor)**

DECLARATION

I, **Mr. Sunil Kumar** 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 "21/07/2015 to 17/12/2021" 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.

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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 contineousely 2.5 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. Bholanath Pal**, **Dr. Ashish Kumar Mishra**, **Dr. Shrawan Mishra**, **Dr. Sanjay Singh, 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.

I gratefully acknowledge **Dr. Shantanu Das**, Assistant Professor, and Departments of ceromic engineering for availing electrochemical instrument and measurement during initial research phase. I also thank to my labmates **Dr. Dinesh Kumar Patel**, **Dr. Sunil Kumar**, **Dr.Akhand Pratap Singh**, **Dr. Arun Kumar Mahanta**, **Dr. Sudipta Senapati**, **Dr. Arpan Biswas, Dr. Anupama Gaur, Dr. Aparna Shukla** and **Dr. Dipti Saxena**, **Mr**. **Om**

Prakash, **Mr. Ravi Prakash**, **Shivam Tiwari**, **Mr. Pravesh Kumar Yadav, Mr. Swapan Maity, Sudipta Bauri, Swikriti Tripathi, Amita santra, Shubham Mandal** for the nice 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 (**Sunaina Devi**) and father **(Jayhind Prasad)** for their unconditional love and unwavering support at every stage of my life. I owe a lot to my wife (**Rangoli Jaiswal**) for her patience and cooperation and brothers (**Kamal and Arvind**) for their endless love and support, who are always there for me. My special thanks to my son (**Rishwik Jaiswal**) for continuous love and keeping patience during manuscript and thesis design.

I am grateful to all colleagues who have helped me in my struggle to achieve my dream of becoming a Ph. D. I am thankful to Dr. Pankaj Kumar Chaurasia, Assistant Professor, L.S. College, Muzaffarpur for the technical support during the manuscript design and management. I am also grateful to Dr. Sanjay (Principal, L.N.T. College) and Dr. Mamta Rani (Principal, R.B.B.M. College), B.R.A. Bihar University Muzaffarpur for cooperation and assistance to complete Ph.D. at academic ground.

Last but not the least, I express my deep sense of gratitude to Almighty God without his divine grace and blessing, above all this task would have been virtually impossible.

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Title of the Thesis: Thermoplastic Polyurethane Ionomers as Gel Electrolyte for CdS Quantum Dots Sensitized Solar Cell

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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**
HMD	**Hexamethylene diisocyanate**
CE	**Counter electrode**
P_{MAX}	**Maximum power density**
HOMO	**Highest occupied molecular orbital**
LUMO	**Lowest unoccupied molecular orbital**
QDs	**Quantum dots**
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

Quantum dot sensitized solar cells (QDSSCs) are highly interesting because of multiexciton generation (MEG) nature that can be used in achieving stable and higher efficiency solar cells. QDSCs, having the advantages of low-cost assembling process, economically viable materials, and intrinsic optoelectronic properties of QD sensitizers, are regarded as attractive candidates for the low-cost third generation solar cells. The collaborative performance of QDSCs is dependent on the charge excitation from the QD sensitizer, injection into the metal oxide (TiO_2), and transport in the circuit, as well as the transfer of the photogenerated holes and regeneration of the redox active electrolyte. The work intensifies the development of highly-efficient electrolyte matrix in the general field of QDSCs. Redox active polymer electrolyte plays an important role to drive reversible and bidirectional charge transport within electronic device i.e., battery and photovoltaic device (solar cell). Redox active liquid electrolyte destroys the device structure due to corrosion, leakage and high penetration. Liquid electrolyte creates poor device performance and durability. Gel polymer electrolyte draws more attention towards electrolytic function because of better adhesion and interfacial contact. Research scientists have developed more number of redox active ionic couples (inorganic / organic couples and complex ions) for Quantum dot sensitized solar cell. Photovoltaic conversion efficiencies were found to be degraded due to poor performance of electrolyte. Recently, Science and technologies have ignited to develop highly efficient gel polymer electrolyte through functionalization, grafting or structural variation. Redox potential and electrical conductivity play a key role to estimate photovoltage of the device. Device efficiency can be improved by tuning the redox potential of electrolyte. Therefore, researchers are trying to develop composite gel polymer electrolyte to enhance the stability and durability of device. Gel polymer electrolytes provide an attractive choice for maintaining good ionic conductivity and reducing the cell leakage problems.

Hence the main objective of thesis is to develop efficient gel polymer electrolyte by using thermoplastic polyurethane ionomer. Thermoplastic pristine polyurethanes does not have sufficient electrical conductivity. However, electrical conductivity can be created through chemical and structural modification around hard segment content in polyurethane chain. By using chemistry, polyurethanes were converted into conductive matrix due to functionalization or grafting of redox active pendant group on urethane linkage. Short chain ionic group structurally modifies the physical properties of native polyurethanes. The ionic pendant group is preferred due to hydrophilic and stabilization efficiency in polyurethane chain. By changing the chemical environment around urethane linkage, redox properties have been tuned. The differential electrolytic (hole conduction) behaviour was observed with better interconnection in composite ionomer structure. Polyurethane ionomers having more oxygenic rich functional groups, showed efficient hole conduction because of greater interaction with nanopores of photoanode. Finally, GO implanted polyurethane ionomers have been developed for Quantum dots sensitized solar cell. The photovoltaic parameters were observed to be improved due to enhanced electrical conductivity and passivation effect of resultant gel polyelectrolyte. The complete synthesis, characterization and photovoltaic studies of the materials in QDSS cell have been discussed in the thesis. In summary, it can be concluded that polar functional groups are observed more efficient in electrolyte structure. The resultant gel polyelectrolyte functions as better substitute of traditional polysulfide electrolyte due to combined effect of redox mediation as well as interfacial passivation effect on photoanode.