



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled “*Reduced Graphite Oxide and MoS₂ Based Electrodes for Hydrogen Generation and Supercapacitor Applications*” by **Shanu Mishra** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of comprehensive examination, candidacy and SOTA for the award of Ph.D. Degree.

Date:

Place: Varanasi

Dr. Ashish Kumar Mishra
(Supervisor)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION BY THE CANDIDATE

I, “*Shanu Mishra*”, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of “*Dr. Ashish Kumar Mishra*” from “*July 2017*” to “*July 2022*”, at the “*School of Material Science and Technology*”, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

Date.....

Place: Varanasi

(Shanu Mishra)

CERTIFICATE BY THE SUPERVISOR

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Dr. Ashish Kumar Mishra
(Supervisor)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

(Coordinator)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: *Reduced Graphite Oxide and MoS₂ Based Electrodes for Hydrogen Generation and Supercapacitor Applications*

Name of the Student: *Shanu Mishra*

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*”.

Date:

Place: Varanasi

(Shanu Mishra)

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

Acknowledgements

*Even though the title page of this thesis only lists one name, several people were involved in its acquisition. First and foremost, I want to thank God Almighty for all the privileges and possibilities He has given me throughout my life. I would like to express my deepest gratitude to my supervisor **Dr. Ashish Kumar Mishra** for all the fruitful scientific discussions and insightful comments while thesis completion. Without his kind support, valuable time, guidance and cooperation, I would not have been able to complete my Ph.D thesis successfully.*

I express my gratitude to my RPEC members Dr. S. Kumar, Prof. R. Prakash for their significant scientific discussion and appreciation during the whole journey. I wish to express deep regards to Prof. D. Pandey, Prof. P. Maiti, Dr. (Mrs.) C. Rath (Coordinator), Dr. A. K. Singh, Dr. C. Upadhyay, Dr. S. K. Mishra, Dr. S. Singh, Dr. N. Kumar, Prof. J. Kumar and Dr. J. Harjwani for their inspiration and kind support.

I am also thankful to all the technical, non-teaching as well as office staffs of the School of Material Sciences, IIT (BHU) Varanasi for their assistance and support whenever required.

My appreciation also goes to my colleagues working in our group for their great help during my PhD journey- Dr. Bishnu Pada Majee, Mr. Prince Kumar Maurya, Mrs. Ankita Singh, Mr. Jay Deep Gupta, Ms. Priyanka Jangra, Mr. Rohit Gupta, Ms. Antima Panday and my M.Tech juniors-Mahendra, Nilesh, Vishal, Shweta, Somesh, Yogesh, Himanshu, Shiksha, Vikash and Kundan.

I share my gratefulness to those very special people who stood like a pillar of strength during this journey- Mrs. Krishna Prajapati, Ms. Pooja Soonkar, Ms. Akanksha Gupta, Dr. Shwarnima Singh, Mr. Tribhuwan Prasad Bind, Mrs. Snehalata Rai, Rajshree Saini, Ekta Sharma and other whoever helped me in this period. I could not be supposed to have a

better friendly environment for my PhD life at IIT (BHU). I also appreciate Mr. Shivam, Ms. Sweta, Ms. Priya, Mr. Manish, Mr. Abhay, Mr. Subhajt for their uncountable supports and motivations.

Furthermore, I extent my warm gratitude to all the mess and canteen staffs of my hostel who provided us good, delicious and flavorsome food. Our hostel life would not be special and memorable without all the staff of this hostel.

My solemn gratitude to the very important person of my life- my friend Ms. Debarati Pal who stood by me no matter what. I am indebted to her for the support, help, friendship, pamper and nourishments. She is a true blessing in my life.

Finally, my deepest gratitude to my family, without whom this thesis could not be possible. I am lucky to thank my elder brother Mr. Raghavendra Mishra, younger sister Purnima Mishra and my cousin Vedant Mishra for providing me love, support, happiness and direction in life whenever I needed. I can't forget to thank my uncle-Mr. Neeraj Sharma for treating me as his own child. I would also like to express my heart-felt gratitude towards grandparents- Mrs. Nayanwasi Pathak, Late Sri Vasant Pathak, Late Sri Gajanan Mishra and Late Mrs. Rajeswari Mishra for shaping me what I am today. My heartfelt gratitude is extended to the soul of my life- "my parents"- Mrs. Geeta Mishra and Mr. Sashi Bhushan Mishra, for their love, support and blessing at every step of my life that cannot be expressed in words. Most importantly they inspired me to become a honest and kind-hearted person above all. I genuinely feel that this thesis belongs to them more than to me.

In the end, my sincere gratitude to the MHRD for providing me the fellowship, training, a wonderful learning experience and a chance to collaborate with the people with great expertise in the field outside my university. My warm thanks to the CIFC, IIT (BHU) instrumental facility, and the DST-SERB, India grant.

(Shanu Mishra)

Dedicated to my beloved parents

Table of Contents

<i>Certificate</i>	<i>iii</i>
<i>Declaration by the Candidate</i>	<i>v</i>
<i>Copyright Transfer Certificate</i>	<i>vii</i>
<i>Acknowledgements</i>	<i>ix</i>
<i>Table of Contents</i>	<i>xiii</i>
<i>List of Figures</i>	<i>xvii</i>
<i>List of Tables</i>	<i>xxi</i>
<i>List of Abbreviations</i>	<i>xxiii</i>
<i>Preface</i>	<i>xxv</i>
Chapter 1 Introduction and Literature Survey	1-24
1.1 Introduction	1
1.2 Reduced Graphite Oxide	3
1.2.1 Properties of Reduced Graphite Oxide.....	7
1.3 Molybdenum Disulfide (MoS ₂).....	9
1.3.1 Properties and Application of MoS ₂ Nanostructures.....	12
1.4 Hydrogen Evolution Application	13
1.5 Supercapacitor Applications.....	17
1.6 Scope and Objective of the Present Work.....	23
Chapter 2 Synthesis and Characterization Techniques	25-45
2.1 Materials Synthesis.....	25
2.1.1 Hydrothermal Synthesis of Nanostructures.....	26
2.1.1.1 Synthesis of rGO Nanostructure	27
2.1.1.2 Synthesis of MoS ₂ Nanostructure.....	29
2.1.1.3 Synthesis of MoS ₂ -rGO Heterostructure.....	30
2.2 Characterization Techniques.....	31
2.2.1 X-ray Diffraction (XRD).....	31
2.2.2 Scanning Electron Microscope (SEM).....	32
2.2.3 Transmission Electron Microscope (TEM).....	34
2.2.4 Raman Spectroscopy.....	35
2.2.5 Fourier Transform Infrared Spectroscopy (FTIR).....	36

2.2.6	Electrochemical Characterization.....	37
2.2.7	Three-cell Electrochemical Measurements.....	42
2.2.8	Design of Hydrogen Producing Electrochemical Cell.....	43
2.2.9	Design of Solid State Supercapacitor (SSC) Device.....	44

Chapter 3 Reduced Graphite Oxide and MoS₂ Based Electrodes for Hydrogen Generation.....47-78

3.1	Introduction	47
3.2	Fundamental of HER.....	49
3.2.1	Reaction of HER.....	52
3.2.2	Volcano Plot.....	53
3.3	Results and Discussion.....	55
3.3.1.	Reduced Graphite Oxides Electrodes for HER.....	55
3.3.1.1	Characterization of rGO Samples.....	55
3.3.1.2	Electrochemical Activity of rGO Electrodes.....	57
3.3.2	MoS ₂ Nanoclusters Electrodes for HER.....	59
3.3.2.1	Characterization of MoS ₂ Nanoclusters.....	59
3.3.2.2	Electrochemical Activity of MoS ₂ Nanoclusters Electrodes.....	61
3.3.3	MoS ₂ Nanoflowers Electrodes for HER.....	63
3.3.3.1	Characterization of MoS ₂ Nanoflowers.....	63
3.3.3.2	Electrochemical Activity of MoS ₂ Nanoflowers Electrodes.....	65
3.3.4	MoS ₂ Nanosheets Electrodes for HER.....	67
3.3.4.1	Characterization of MoS ₂ Nanosheets.....	67
3.3.4.2	Electrochemical Activity of MoS ₂ Nanosheets Electrodes.....	70
3.3.5	MoS ₂ -rGO Heterostructure Electrodes for HER.....	72
3.3.5.1	Characterization of MoS ₂ -rGO Heterostructure.....	72
3.3.5.2	Electrochemical Activity of MoS ₂ -rGO Heterostructure Electrodes.....	74
3.3.6	Hydrogen Producing Electrochemical Cell using MoS ₂ Nanoflowers as Cathode Material.....	77
3.4	Conclusion.....	78

Chapter 4 Reduced Graphite Oxide and MoS₂ Based Electrodes for Supercapacitors	79-104
4.1 Introduction.....	79
4.2 Results and Discussion.....	83
4.2.1 Reduced Graphite Oxides for Supercapacitors Application	84
4.2.1.1 Capacitance Study of rGO-HH Electrodes.....	84
4.2.1.2 Capacitance Study of rGO-Urea Electrodes.....	88
4.2.2 MoS ₂ Nanoflowers Electrodes for Supercapacitor Application.....	91
4.2.3 MoS ₂ Nanosheets Electrodes for Supercapacitor Application.....	95
4.2.4 MoS ₂ -rGO Heterostructures Electrodes for Supercapacitor Application.....	99
4.3 Conclusion.....	104
Chapter 5 Reduced Graphite Oxide and MoS₂ Nanostructures Electrodes for Solid State Supercapacitors.....	105-128
5.1 Introduction.....	105
5.2 Results and Discussion.....	108
5.2.1 Reduced Graphite Oxides Based Solid State Supercapacitors.....	109
5.2.2 MoS ₂ Nanoflowers Based Solid Supercapacitors.....	113
5.2.3 MoS ₂ Nanosheets Based Solid Supercapacitors.....	117
5.2.4 MoS ₂ -rGO Heterostructure Based Solid State Supercapacitors.....	122
5.3 Conclusion.....	127
Chapter 6 Conclusion and Future Scope of the Work.....	129-131
References.....	133
List of Patents, Publications, and Book Chapters.....	159
Schools/Workshops/Conferences Attended	161

List of Figures

- Figure 1.1** Schematic of few layer reduced graphite oxide..... (6)
- Figure 1.2** Schematic diagram of MoS₂ polytypes-1T, 2H, and 3R along with the side views.....(10)
- Figure 1.3** Schematic of hydrogen evolution reaction.....(14)
- Figure 1.4** (a) Schematic illustration of electrochemical double layer capacitor, (b) The charge storage mechanism of the electrochemical double-layer capacitor.....(20)
- Figure 2.1** Schematic diagram of synthesis process for 2D-nanostructures.....(26)
- Figure 2.2** Photograph of the used hydrothermal cell.....(27)
- Figure 2.3** Schematic diagram of experimental condition for synthesis of rGO nanostructures.....(28)
- Figure 2.4** Schematic diagram for synthesis of GO and rGO nanostructures.....(29)
- Figure 2.5** Schematic diagram of experimental condition for the synthesis of different morphologies of MoS₂ nanostructures.....(30)
- Figure 2.6** Schematic representation of X-ray diffraction process.....(32)
- Figure 2.7** Schematic representation of interaction of electron beam with sample in SEM.....(33)
- Figure 2.8** Schematic representation of electron beam interaction with sample in TEM.....(34)
- Figure 2.9** Schematic representation of a Raman spectrometer.....(35)
- Figure 2.10** Graphic representation of FTIR spectrometer.....(36)
- Figure 2.11** Graphic representation of three cell electrochemical setup.....(37)
- Figure 2.12** (a) Linear voltage sweep with respect to time, (b) LSV curve at fixed voltage sweep rate.....(38)
- Figure 2.13** Schematic illustration of typical CV curves for EDLCs and pseudocapacitors.....(39)
- Figure 2.14** Schematic illustration of typical GCD curves for EDLCs and pseudocapacitors.....(40)
- Figure 2.15** (a) Schematic illustration of typical Nyquist plots for EDLCs and pseudocapacitors, (b) Schematic illustration of Bode Plot.....(42)

Figure 2.16 (a) Schematic illustration of components of electrochemical cell, (b) photograph of designed electrochemical cell.....	(44)
Figure 2.17 Photographs of components of solid-state supercapacitor device.....	(44)
Figure 3.1 Schematic representation of electrolysis of water.....	(48)
Figure 3.2 Current vs. potential (I–V) graph of electrolysis of water.....	(51)
Figure 3.3 Mechanisms for hydrogen evolution on the surface of an electrode in acidic media.....	(53)
Figure 3.4 (a) Valcano plot predicting catalysts with zero hydrogen binding energy will have the highest activity, (b) Volcano plot showing probable electrocatalysts for HER [1].	(54)
Figure 3.5 SEM images of (a) rGO-HH and (b) rGO-Urea, (c) XRD patterns, (d) Raman spectra and (e) FTIR spectra for rGO-HH and rGO-Urea.....	(56)
Figure 3.6 (a) LSV curves, (b) Tafel plots, and (c) Nyquist plot for rGO-HH electrodes, (d) LSV curves, (e) Tafel plots, and (f) Nyquist plot for rGO-Urea electrodes.	(58)
Figure 3.7 (a) SEM image and (b) XRD pattern, (c) Raman spectrum and (d) FTIR spectrum for MoS ₂ nanoclusters.....	(61)
Figure 3.8 (a) LSV curves at different voltage scan rates, (b) Corresponding Tafel plots, (c) Nyquist Plot of MoS ₂ nanoclusters and (d) stability test for MoS ₂ nanoclusters electrode at 20 mV s ⁻¹	(63)
Figure 3.9 (a) SEM, (b) TEM, (c) HRTEM images, (d) XRD pattern (e) Raman spectrum, and (f) FTIR-spectrum for MoS ₂ nanoflowers.....	(65)
Figure 3.10 (a) LSV curves at different scan rates, (b) Corresponding Tafel plots, (c) Nyquist plots and, (d) stability test at 20 mV s ⁻¹ for MoS ₂ nanoflower electrodes...	(67)
Figure 3.11 (a) SEM image, (b) TEM image, (c) HRTEM image, (d) XRD pattern, (e) Raman spectrum, and (f) FTIR spectrum for MoS ₂ nanosheets.....	(69)
Figure 3.12 (a) LSV curves at different scan rates, (b) Corresponding Tafel plots, (c) Nyquist Plot, and (d) HER stability test at 20 mV s ⁻¹ for MoS ₂ nanosheet electrode..	(71)
Figure 3.13 (a) SEM image, (b) TEM image, (c) XRD pattern, (d) Raman spectrum, and (e) FTIR spectrum for MoS ₂ -rGO heterostructure.....	(73)
Figure 3.14 (a) LSV curves at a scan rate of 2 mV s ⁻¹ , (b) Corresponding Tafel plots, (c) Nyquist plot, and (d) stability test at 20 mV s ⁻¹ for MoS ₂ -rGO heterostructure electrodes.....	(75)

Figure 3.15 (a) Photograph of hydrogen production and collection unit, (b) Photograph of electrochemical cell and (c) Amount of volume produce in different cycles at 0.2 V.....(77)

Figure 4.1 Configurational outlines of conventional capacitors, supercapacitors and batteries.....(80)

Figure 4.2 Ragone plot for different energy storage and conversion devices.....(80)

Figure 4.3 Electrochemical measurements for rGO-HH electrode (a) CV curves at different scan rates and (b) GCD curves at different discharge current densities with 1M Na₂SO₄ electrolyte; (c) CV curves at different scan rates and (d) GCD curves at different discharge current densities with 1M H₂SO₄ electrolyte.(86)

Figure 4.4 Electrochemical measurements for rGO-HH electrode (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots and (c) Bode phase plots and (d) Cyclic stability test at 100 mV s⁻¹ in neutral and acidic electrolytes.....(87)

Figure 4.5 Electrochemical measurements for rGO-Urea electrode (a) CV curves at different scan rates and (b) GCD curved at different discharge current densities 1M Na₂SO₄ electrolyte; (c) CV curves at different scan rates and (d) GCD curves at different discharge current densities with 1M H₂SO₄ electrolyte..... (89)

Figure 4.6 Electrochemical measurements for rGO-Urea electrode (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots (c) Bode phase angle plots and (d) Cyclic stability test in neutral and acidic electrolytes.....(90)

Figure 4.7 Electrochemical measurements for MoS₂ nanoflowers electrode (a) CV curves at different scan rates, (b) GCD curves at different discharge current densities with 1M Na₂SO₄ electrolyte; (c) CV curves at different scan rates, and (d) GCD curve at different discharge current density with 1M H₂SO₄ electrolyte.....(92)

Figure 4.8 Electrochemical measurements for MoS₂ nanoflowers electrode (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots (c) Bode phase angle plots, and (d) Cyclic stability test 100 mV s⁻¹ scan rates in neutral and acidic electrolytes.....(94)

Figure 4.9 Electrochemical measurements for MoS₂ nanosheet electrode (a) CV curves at different scan rates, and (b) GCD curve at different discharge current densities; (c) CV curves at different scan rates, and (d) GCD curves at different discharge current density with 1M H₂SO₄ electrolyte.....(96)

Figure 4.10 Electrochemical measurements for MoS₂ nanosheet electrode (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots, (c) Bode phase plots (d) Cyclic stability test at a discharge current of 5 A g⁻¹ neutral and acidic electrolyte.....(98)

Figure 4.11 Electrochemical measurements for MoS₂-rGO heterostructure electrode (a) CV curves at different scan rates, (b) GCD curves at different discharge current density with 1M Na₂SO₄ electrolyte; (c) CV curves at different scan rate, and (d) GCD curves at different discharge current densities with 1M H₂SO₄ electrolyte..... (100)

Figure 4.12 Electrochemical measurements for MoS₂- rGO heterostructure electrode (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots, (c) Bode phase

angle plots, and (d) Cyclic stability test at a discharge current of 5 A g^{-1} in neutral and acidic electrolytes.....(102)

Figure 5.1 Schematic of different type of supercapacitor (a) coin type, (b) stack rectangular, and (c) flexible assemblies.....(106)

Figure 5.2 (a) Photograph of designed SSC device, (b) CV curves at varied voltage sweep rates, and (c) GCD curves at different discharge current densities for rGO-HH based SSC device, (d) CV curves at varied voltage sweep rate, (e) GCD curves at different discharge current density for rGO-Urea based SSC, and (f) Energy density vs power density curves for both SSC devices with acidic solid electrolyte.....(110)

Figure 5.3 (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance modulus plots, (c) Bode phase angle plots, and (d) Cyclic stability test for rGO-HH and rGO-Urea SSC device at discharge current of 2 A g^{-1} for rGO-HH and rGO-Urea SSC.....(112)

Figure 5.4 Electrochemical measurements for MoS_2 nanoflower based SSC (a) SEM Image of MoS_2 nanoflower, (b) CV curves at varied sweep rates, and (c) GCD curves at different discharge current densities with neutral electrolyte, (d) CV curves at varied sweep rates, and (e) GCD curves at different discharge current densities with acidic electrolyte, (f) Energy density vs power density plot for SSC device with both electrolytes.....(114)

Figure 5.5 (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots, (c) Bode phase angle plots, and (d) Cyclic stability test at discharge current density of 2 A g^{-1} for MoS_2 nanoflowers based SSC device with neutral and acidic solid electrolytes.(116)

Figure 5.6 Electrochemical measurements for MoS_2 nanosheet based SSC (a) SEM image of MoS_2 nanosheets with inset showing series connection of two SSC devices to light up the LED, (b) CV curves at varied sweep rates, and (c) GCD curves at different discharge current densities with neutral electrolyte, (d) CV curves at varied sweep rates, and (e) GCD curves at different discharge current densities with acidic electrolyte, (f) Energy density vs power density plot for MoS_2 nanosheet based SSC device with both electrolytes.....(119)

Figure 5.7 (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots, (c) Bode phase angle plots (d) Cyclic stability test of SSC device at discharge current of 2 A g^{-1} for MoS_2 nanosheet based SSC with both in neutral and acidic electrolyte with both electrolytes.....(121)

Figure 5.8 Electrochemical measurements for MoS_2 -rGO heterostructure (a) SEM image of MoS_2 -rGO heterostructure, (b) CV curves at varied sweep rates, and (c) GCD curves at different discharge current densities with neutral electrolyte, (d) CV curves at varied sweep, and (e) GCD curves at different discharge current densities with acidic electrolyte, (f) Energy density vs power density plots for with both neutral and acidic electrolytes....(123)

Figure 5.9 (a) Nyquist plots (inset shows the equivalent circuit), (b) Bode impedance plots, (c) Bode phase angle plots, and (d) Cyclic stability test at discharge current density of 2 A g^{-1} for heterostructure based SSC with neutral and acidic electrolytes.....(125)

List of Tables

Table 1.1 Comparison of Key Properties of Capacitor, Supercapacitor, and Battery.

Table 3.1 The HER Activity of Different MoS₂ Nanostructures.

Table 4.1 Capacitive Performance of rGO, MoS₂ and MoS₂-rGO Electrodes.

Table 5.1 Capacitive Performance of Fabricated SSC Devices.

List of Abbreviation

rGO	Reduced Graphite Oxide
MoS ₂	Molybdenum Disulfide
TMDCs	Transition metal dichalcogenide
HER	Hydrogen Evolution Reaction
RHE	Reversible Hydrogen Electrode
SCs	Supercapacitors
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
FTIR	Fourier-transform infrared spectroscopy
LSV	Linear Sweep Voltammetry
CV	Cyclic voltammetry
GCD	Galvanostatic Charge-discharge
EIS	Electrochemical Impedance Spectroscopy
CPE	Constant Phase Element

Preface

The reduced graphite oxide (rGO) and Molybdenum disulfide (MoS_2) are layered structures, which possess some attractive properties such as, high conductivity, high-surface area, flexibility, and good stability in acidic/basic medium. These characteristics allow rGO and MoS_2 nanostructures to be used in next generation energy devices. This thesis entitled **“Reduced Graphite Oxide and MoS_2 based Electrodes for Hydrogen Generation and Supercapacitor Applications”** is focused on the synthesis of rGO, different morphologies for 2H MoS_2 nanostructures and MoS_2 -rGO heterostructure via hydrothermal technique for hydrogen evolution reaction (HER) and supercapacitor applications. We have synthesized two rGO samples using different reducing agents (hydrazine hydrate and urea) and three different morphologies of MoS_2 nanostructures (nanoclusters, nanoflowers and nanosheets) and MoS_2 -rGO heterostructure. We have characterized as synthesized samples by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to confirm the morphology and structure of the samples. To confirm the phase and purity of prepared samples, we have performed X-ray diffraction (XRD) and Raman spectroscopy techniques. We have also investigated the Fourier transform infrared (FTIR) study to examine the functional groups, present in the prepared samples. We have further studied electrochemical activity of prepared samples for HER and supercapacitor applications.

In the present work, MoS_2 nanoflowers electrode shows the best HER activity with Tafel slope of 69 mV dec^{-1} at voltage sweep rate of 5 mV s^{-1} among studied materials, which can be associated with 3D architecture and higher accessibility of active sites due to arranged petal formation. Further, we have utilized MoS_2 nanoflowers as cathode material and investigated real time hydrogen generation using a prototype electrochemical cell. Further, we also observe capacitive behaviour of prepared samples in neutral ($1\text{M Na}_2\text{SO}_4$)

and acidic (1M H₂SO₄) electrolytes. Among the studied materials, MoS₂ nanoflowers electrode shows best capacitive performance of 382 F g⁻¹ at 1 A g⁻¹ in neutral (1M Na₂SO₄) electrolyte. The higher value of specific capacitance can be attributed to the accessible surface area between well separated petals of flower structure and functional groups which may increase the wettability of electrode for easy transport of electrolyte. Further, solid-state supercapacitor devices with synthesized samples as electrodes have been investigated with neutral (PVA-Na₂SO₄) and acidic (PVA-H₂SO₄) electrolytes. Among the studied SSC devices, MoS₂ nanosheets based SSC device shows maximum specific capacitance of 101 F g⁻¹ at 0.2 A g⁻¹ and high energy density 36.1 Wh kg⁻¹ with neutral (PVA-Na₂SO₄) electrolyte. This high performance can be due to the enhanced wettability, accessible surface area and better interface formation between nanosheet structure and solid electrolyte membrane.

The present thesis has been organized into six chapters. The consecutive chapters are organized as follows-

Chapter 1 gives a brief introduction of rGO and MoS₂ nanostructure along with an overview of the current literature on HER and supercapacitor applications.

Chapter 2 describes the synthesis process of rGO using different reducing agents (hydrazine hydrate and urea), three different morphologies of MoS₂ nanostructures (nanoclusters, nanoflowers and nanosheets) and MoS₂-rGO heterostructure. A concise overview of the characterization instruments like XRD, SEM, TEM, Raman, FTIR is provided for structural, morphological and functional group studies of samples. This chapter also describes different electrochemical characterization methods for HER and supercapacitor applications.

Chapter 3 discusses the characterisation and HER activity of prepared rGO, MoS₂ nanostructures and MoS₂-rGO heterostructure in acidic medium. Different HER parameters have been obtained and fundamentals related to HER have been discussed in this chapter.

Chapter 4 discusses the capacitive behaviour of prepared rGO, MoS₂ nanostructures and MoS₂-rGO heterostructure in neutral and acidic electrolytes. Specific capacitance obtained via different electrochemical technique has been discussed in this chapter.

Chapter 5 describes the performance of prepared different rGO, MoS₂-nanostructures and MoS₂-rGO heterostructure based SSC devices with neutral (PVA-Na₂SO₄) and acidic (PVA-H₂SO₄) electrolytes. Different device parameters like capacitance, energy density and power density have been discussed in this chapter.

Chapter 6 summarises the thesis work and highlights the scope for the future work related to this field.