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INDIAN INSTITUTE OF TECHNOLOGY BANARAS HINDU UNIVERSITY

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It is certified that the work contained in the thesis titled ***"Reduced Graphite Oxide and MoS_2 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.

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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.

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(Shanu Mishra)

Dedicated to my beloved parents

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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 (1M Na_2SO_4)

and acidic (1M H_2SO_4) electrolytes. Among the studied materials, MoS_2 nanoflowers electrode shows best capacitive performance of 382 F g^{-1} at 1 A g^{-1} in neutral (1M Na_2SO_4) 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-Na_2SO_4) and acidic (PVA-H_2SO_4) electrolytes. Among the studied SSC devices, MoS_2 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-Na_2SO_4) 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 MoS_2 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 MoS_2 nanostructures (nanoclusters, nanoflowers and nanosheets) and MoS_2-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, MoS_2 nanostructures and MoS_2-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, MoS_2 nanostructures and MoS_2-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, MoS_2-nanostructures and MoS_2-rGO heterostructure based SSC devices with neutral (PVA-Na_2SO_4) and acidic (PVA-H_2SO_4) 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.