NANOSTRUCTURED COMPOSITES OF MOLYBDENUM-BASED COMPOUNDS ($Mo_2C/Mo_2N/MoS_2/MoP$) AND GRAPHENE AS ELECTROCATALYSTS FOR HYDROGEN EVOLUTION REACTIONS

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by

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Submitted
in fulfillment of the requirements of the degree of Doctor of Philosophy

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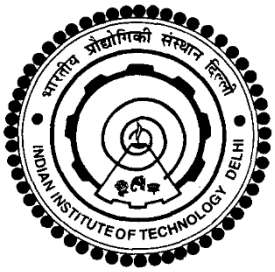

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October 2016

Dedicated to my Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled, **"Nanostructured Composites of Molybdenum-based Compounds (Mo_2C/Mo_2N/MoS_2/MoP) and Graphene as Electrocatalysts for Hydrogen Evolution Reactions"** being submitted by **Mr. Kasinath Ojha** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Kasinath Ojha has worked under our guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

Two of the outstanding challenges for society are to move towards a clean environment and availability of sufficient energy and interestingly hydrogen is the key to both these challenges. Hence tremendous interest exists on hydrogen generation from electrochemical or photoelectrochemical water splitting. Unlike carbon based fuels, hydrogen having highest energy density per unit mass, is eco-friendly as it produces only water after combustion as a direct fuel or after transformation to electricity in fuel cells. Hydrogen evolution reaction (HER) is a green and renewable process to get hydrogen from electrolysis of water. Among earth abundant non-noble metals, molybdenum-based materials are important for hydrogen evolution reaction because of its low cost, good conductivity and catalytic efficiency.

This thesis deals with composites of Mo based compounds (Mo_2C, Mo_2N, MoS_2 and MoP) with reduced graphene oxide. Electrocatalytic activity and stability of these composites for hydrogen evolution reactions were investigated.

In chapter 2, we have synthesized reduced graphene oxide based composites of Mo_2C rods using carbonization of anilinium complex of molybdenum in inert environment at 750 °C. First a complex was synthesized by reacting aniline with ammonium molybdate at 50 °C in pH of 3.5. For the synthesis of rGO based composites, we used rGO which was synthesized using graphite oxidation followed by thermal exfoliation at 1100 °C for 10 mins. Different amount of rGO was used to get different composites with Mo_2C. The composite samples were marked as MC-G50, MC-G100, MC-G350 and MC-G500 for 50 mg, 100 mg, 350 mg and 500 mg of rGO respectively. We have also used different carbon like activated carbon sheets and graphite to check HER activities of these composites. All

the composites were characterized using powder XRD, TGA and Raman. The structure and morphology of the composites were analyzed using FESEM, TEM and elemental analysis were carried out using XPS and EDAX.

In chapter 3, we have investigated the facile synthesis of different morphologies of Mo_2N using g-C_3N_4 as N-source and have investigated the effect of the g-C_3N_4 loading on the morphology of Mo_2N and their hydrogen evolution activity. We have demonstrated that thin elongated hexagonal sheets of Mo_2N nanoparticles are much better electrocatalyst for hydrogen generation from water than earlier reported on modified Mo_2N based systems. Mo_2N nanostructures were synthesized using anilinium complexation method in presence g-C_3N_4 followed by heating at 700 °C in N_2 atmosphere. Different amount of g-C_3N_4 were used to get various morphologies of Mo_2N nanostructures. These samples were named as MN60, MN100, MN300, MN600 and MN900 for having g-C_3N_4 of 60 mg, 100 mg, 300 mg, 600 mg and 900 mg respectively. Bulk Mo_2N was synthesized by heating ammonium molybdate and guanidium hydrochloride mixture at 700 °C in H_2 atm. All the materials were characterized using powder XRD, TGA, Raman, FESEM and TEM. Elemental analysis was carried out by EDAX and XPS.

In chapter 4, we have investigated in-situ synthesis of Mo_2C-Mo_2N composite nanowires. We have investigated the efficiency and durability for electrochemical hydrogen evolution in acidic medium. We explored the role of carbide and nitride for enhancing the stability and efficiency. In details study of electrochemical hydrogen evolution, it was found that synergistic effect of carbon and nitrogen from Mo_2C and Mo_2N nanostructures in the production of hydrogen from water was responsible for such HER activity. We have shown Mo2N rich composites having higher N-doped surfaces and interfaces exhibit much higher

electrocatalysis which is supported by the DFT calculations of HBE on N-doped Mo_2C surfaces.

In chapter 5, we have investigated the role of interfaces or heterojunctions in HER activity of composite materials like Mo_2N-MoS_2, and Mo_2N-Mo_2C-MoS_2. The synergistic effect and the role of the interfaces were demonstrated in detail. These composites were synthesized using hydrothermal method followed by annealing at 500 °C in inert atmosphere. Composites were characterized using PXRD, Raman and electron microscopy.

In chapter 6, we have synthesized rGO-MoP composites for hydrogen evolution from water in acidic medium. The synthetic mechanism were well characterized and revealed the role of complexation method to stabilize the precursor and to get well interconnected MoP nanocrystals where interparticle interactions play significant role in catalysis as reflected in HER studies. The mechanism of the HER process was investigated in detail using impedance spectroscopy and Tafel slope.

In conclusion, we have observed that MoP is the most efficient and durable electrocatalyst for hydrogen evolution reactions compared to other Mo-based compounds e.g. Mo_2N, Mo_2C and MoS_2. Our finding reveals that the electrocatalytic efficiency was observed in order of MoP > Mo_2C > MoS_2 > Mo_2N. It was found that the anions played very crucial role in the electrocatalytic activity for HER as the electronegativity of the anions changes in the order of P (2.19) < C (2.55) < S (2.58) < N (3.04). New composites and doped systems containing hetero anions like MP|S, MS|N and MP|C (M= Mo, Ni, Co, Fe, Cu etc.) can be investigated for various electrochemical reactions and conversions. Transition metal doped systems can also be explored.

TABLE OF CONTENTS

CHAPTER-2: Graphene Based Mo2C Composites: Synthesis and Performance in Electrochemical Water Splitting

CHAPTER-3: Mo2N Nanostructures: Morphology Dependent Electrocatalytic Activity in Water Splitting

CHAPTER-4: Mo2C-Mo2N Composite Nanowires: In-Situ Synthesis and Catalytic Activity in Electrochemical Water Splitting

CHAPTER-5: Heterojunctions of Mo2N, MoS2 and Mo2C Nanostructures: Effect in Electrochemical Water Splitting

CHAPTER-6: Graphene Based Mop Composites: Synthesis and Performance in Electrochemical Water Splitting

LIST OF FIGURES

LIST OF TABLES

NOTATIONS/ABBREVIATIONS

Å	Angstrom
^{o}C	Centigrade
μm	Micrometer
cm	centimeter
h	Hours
PXRD	Powder X-ray diffraction
TEM	Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Analysis
TGA	Thermogravimetric analysis
FTIR	Furrier transformed Infra-red spectroscopy
CV	Cyclic Voltammetry
LSV	Linear Sweep Voltammetry
ECSA	Electrochemically Active Surface Area
EIS	Electrochemical Impedance Spectroscopy
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
RHE	Reversible Hydrogen Electrode
j_o	Exchange Current Density
GCE	Glassy Carbon Electrode
CPE	Constant Phase Element
C_{dl}	Double layer Capacitance
EDLC	Electrochemical Double Layer Capacitor
R_{ct}	Charge Transfer Resistance
R_s	Solution Resistance
Φ	Bode Phase angle
Θ	Surface coverage by hydrogen
HBE	Hydrogen binding energy
DFT	Density Functional Theory

XPS	X-ray Photoelectron spectroscopy
BET	Brunauer-Emmett-Teller
eV	Electron – Volt
K	Kelvin
°	Degree (angle)
λ	Wavelength
Ω	Ohm