Metal-Organic Frameworks and Nanomaterials for Oxygen Evolution Reaction

Thesis Submitted for the Degree of

Doctor of Philosophy

By

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Acknowledgement

The work presented in this thesis would not have been possible without my close association with many peoples who were always there when I needed them the most. I take this opportunity to acknowledge them and extend my sincere gratitude for helping me make this thesis a possibility. At this moment of accomplishment, first of all, I would like to pay homage to the founder of Banaras Hindu University, Pandit Madan Mohan Malvia ji, who made this glorious temple to realize spiritual, technical, and scientific knowledge about this vast existing universe.

I embrace the opportunity to express my deep sense of gratitude to my supervisor ***Dr. Rajiv Prakash****, Professor, School of Materials Science & Technology, IIT (B.H.U.), Varanasi, (now Director, IIT Bhilai, Raipur, Chattisgarh) for his constant guidance, valuable suggestions, and kind encouragement during my association with his research group. His encouragement, constant support, intellectual stimulation, perceptive guidance, immensely valuable ideas, and suggestions from the initial to the final level enabled me to develop an understanding of the subject. His scholarly suggestions, prudent admonitions, immense interest, constant help, and affectionate behaviour have been a source of inspiration for me. His suggestions will remain with me as an inexhaustible source of scientific learning throughout my life.*

I would like to express my sincere and whole-hearted gratitude to ***Prof. Dhananjay Pandey, Prof. Jitendra Kumar, Prof. Pralay Maiti, Dr. S. R. Singh, Dr. Chandan Upadhyay, Dr. Chandana Rath, Dr. Akhilesh Kumar Singh, Dr. Bola Nath Pal, Dr. Ashish Kumar Mishra, Dr. Sanjay Singh, Dr. Shravan kumar Mishra and Dr. Nikhil Kumar, Dr. Ravi Panwar*** *(School of Materials Science and Technology, IIT-BHU, Varanasi) for discussion during seminars and valuable suggestions given by them and* ***Dr. Nand Kishore Prasad*** *(Metallurgiacal Engineering Department) for using his lab furnace. I am indeed obliged and sincerely thankful to my RPEC member* ***Dr. Indrajit Sinha****, Department of Chemistry, IIT- BHU, for his guidance and untiring attention right from the inception to the successful completion of assigned research work. I am thankful to the unknown reviewers who have rejected my papers several times in some of the*

international conferences and journals. The comments that they provided helped to polish our articles in better shape. But the bigger and nobler cause of thanking them is that the rejections have equipped me with a high level of patience and helped me a lot to exercise/implement my spiritual thoughts in practice.

My acknowledgement will never be complete without the special mention of my lab seniors who have taught me the lab culture and have lived by example to make me understand the hard facts of life. I would like to acknowledge ***Dr. Narsingh Raw Nirala, Dr. Uday Pratap Azad, Dr. Monika Srivastava, Dr. Ashish Kumar, Dr. Ashish Kumar Singh, Dr. Rajiv Kumar Pandey, Dr. Gopal Ji, Dr. Neeraj Giri, Dr. Madhu Tiwari, Dr. Kashish, Dr. Preeti Tiwari, Dr. Manish Kumar Singh, Dr. Richa Mishra, Dr. Vinita, Dr. Chandrajeet Verma, Dr. Annirudha Jaiswal, Vineet Kumar Mall, Dr. Ravi Prakash Ojha, Dr. Nikhil and Dr. Ajay Kumar*** *for all their support and motivation during the initial days of my PhD. I can see my thesis in the good shape because of his help in formatting the entire thesis. I express my special thanks to* ***Dr. Ashish Kumar and Dr. Uday Pratap Azad*** *for his guidance, support, motivation and valuable suggestions.*

Also, I am thankful to my lab fellows and juniors of my lab specially ***Dr. Subhajit, Dr. Priya, Shivam, Saurabh, Radhe, Rajpal, Shipra, Nupur, Preetam and Gaurav*** *for their helping behavior. It's my fortune to gratefully acknowledge to my research seniors and fellows from the Materials Science,* ***Dr. Neela Pal, Dr. Bishnu Pada Majee, Pooja, Krishna, Dr. Shanu, Manish, Dr. Shivam and Abahy.*** *Also from the Department of Chemistry,* ***Dr. Shaili Pal, Dr. Daraksha Hussain, Dr. Jyoti Kuntal*** *and from the Department of Physics,* ***Dr. Kanchan Yadav****. I am also thankful to my dear friends,* ***Dr. Aarti, Dr. Priya, Dr. Subhajit, Dr. Arshala, Dr. Jyoti, Dr. Anjali, Dr. Shubham****,* ***Dr. Ashvani****,* ***Dr. Asish, Dr. Surendra*** *and to whom I could not mention here who helped me directly or indirectly throughout the work. I am thankful to all non–teaching staff of SMST, IIT (BHU) and all CIFC (Central Instrumental Facility Centre) members for their cooperation at all levels. I express my indebtedness to my Bade Papa* ***Sri. Awadhesh Kumar Pal*** *and Badi Mammi* ***Smt. Abhilasha Pal*** *and my parents* ***Sri. Dinesh Kumar Pal and Smt. Shashi Pal. Also,***

Acknowledgement

I express my gratitude *to my sisters* ***Dr. Archana Pal, Dr. Shaili Pal, Sonam Pal, Akanksha Pal, Janki Pal; brothers Dr. Saurabh Pal, Dr. Suryansh Chandra, Siddhatant Chandra, Sarthak Pal, Ansh Pal, Reyansh Pal, Dr. Kumar Ramesh (jija ji),*** *and sweet little boy of my family* ***'Advik Kumar****' for their love, affection and support during every moment of my life. This work would not have been possible without the grace of the "Lord Shiva and Mata Di."*

(Shweta Pal)

CERTIFICATE

It is certified that the work contained in the thesis titled "**Metal-organic framework and nanomaterials for oxygen evolution reaction**" by ***"Shweta Pal"*** has been carried out 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 requirements of Comprehensive, Candidacy, and SOTA.

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DECLARATION BY THE CANDIDATE

I, ***Shweta Pal*** certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***Prof. Rajiv Prakash*** from **July 2017 to July 2022** at the ***School of Materials Science & Technology***, Indian Institute of Technology, Banaras Hindu University, 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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Certificate by the Supervisor

It is certified that the above statement made by the student is correct to the best of my knowledge.

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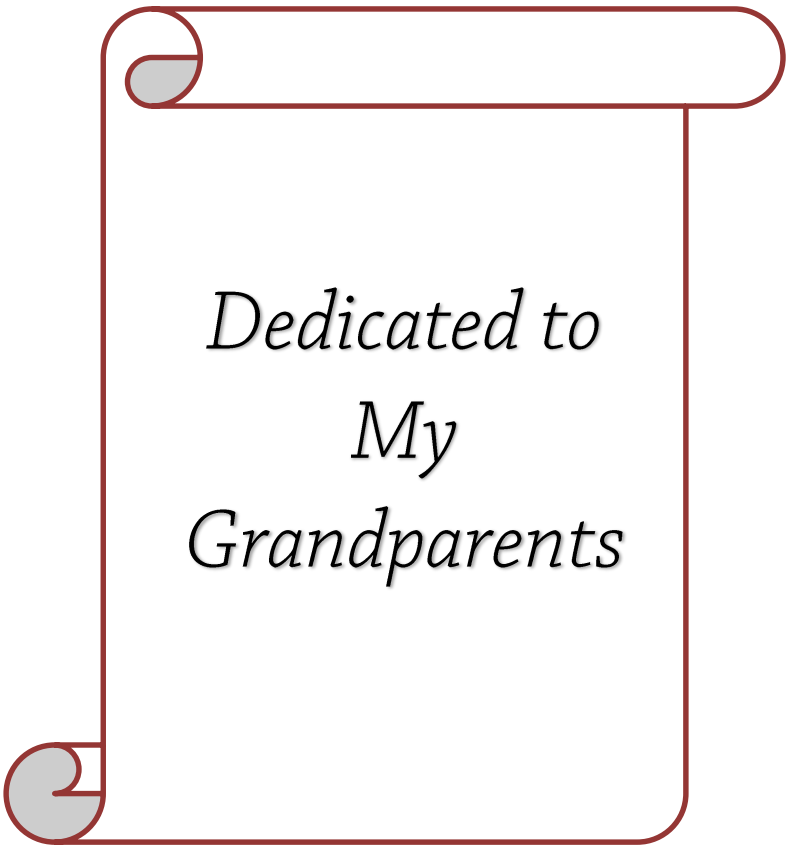

"Be Alive, Be Joyful, Be Trust on yourself.
Be passionate about your work".

List of Abbreviations

kWh	:	Kilowatt-hours
BkWh	:	Billion kilowatt hours
RES	:	Renewable energy sources
HER	:	Hydrogen evolution reaction
OER	:	Oxygen evolution reaction
ORR	:	Oxygen reduction reaction
ECS	:	Energy conversion and storage devices
LDH	:	Layered double hydroxide
TMCs	:	Transition metal-chalcogenides
MOFs	:	Metal-organic frameworks
η	:	Overpotential
b	:	Tafel slope
ECSA	:	Electroactive surface area
CA	:	Chronoampereometry
ZnDTO	:	Zincdithioxamide
Ni-Fe-PBA-NC	:	Nickel-iron-Prussian blue analogue nanocube
NSC	:	N/S/Zn-doped porous carbon
AA	:	Anthranilic Acid
DMF	:	Dimethylformamide
μL	:	Microliter
GCE	:	Glassy carbon electrode
UV-Vis	:	Ultraviolet-visible
FT-IR	:	Fourier transform infrared
XRD	:	X-ray diffraction
FE-SEM	:	Field emmision scanning electron microscopy
XPS	:	X-ray photoelectron spectroscopy

List of Abbreviations

BET	:	Brunauer–Emmett–Teller
TGA	:	Thermogravimetric analysis
CV	:	Cyclic voltammetry
LSV	:	Linear sweep voltammetry
EIS	:	Electrochemical impedance spectroscopy
R_{ct}	:	Charge-transfer resistance
R_{so}	:	Solution resistance
QPE	:	Constant phase element
RHE	:	Reversible hydrogen electrode
DTO	:	Dithioxamide
RuO_2	:	Ruthenium oxide
Co_3O_4	:	Cobalt oxide
mA	:	Milliampere
eV	:	Electron volt
C_{dl}	:	Double-layer capacitance
ICP-MS	:	Inductively coupled plasma mass spectrometry.
V	:	Volt
Z' (Z_{real})	:	Impedance at X-axis
Z" (Z_{img})	:	Impedance at Y-axis
$mVdec^{-1}$	:	Milivolt per decade
mV	:	Mili volt
AW	:	Acid wash
NSC-AW	:	N/S/Zn-doped porous carbon with acid wash
PB	:	Prussian blue
PBA	:	Prussian blue analogue
MAB		Metal-air battery

List of Abbreviations

NiFe- PBA-NG	:	Nickel iron-Prussian blue analogue nanocage
λ	:	Wavelength
Ω	:	Ohm
℃	:	Degree celsius

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Preface

Energy is the foremost factor for the growth of any country and its economic development. In developing countries like India, energy consumption increases at a fast rate due to population growth and development infrastructure. Currently, most of the energy demand is full-filled by coal-based power, which creates pressure on fossil fuels. In 2017, approximately 73.5% of the electricity was produced from the fossil-fuels and the combustion of fossil fuels generates greenhouse gases which affect the environment severely, leading to climate change. This creates a big problem for energy conservation and environmental protection for the next generation. The scientific community worldwide is continuously making efforts to find effective alternatives to these fossil-based fuels. Renewable energy sources (REs) such as solar, wind, water electrolysis (water-splitting) and geothermal energy are clean and environmentally friendly energy sources and integration of these renewable sources in power generation manages the energy requirement up to a certain level. Among the various REs, water-splitting shows great promise in producing green fuel as a hydrogen gas (H_2) and molecular oxygen (O_2) as an oxidant. It is driven by two half-reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) and fossil fuel consumption is greatly reduced by using H_2 as a fuel carrier because of its high energy density (120-142 MJ kg^{-1}), which in turn controls the climate change and display a path for sustainable green fuel.

Using H_2 as a fuel effectively is possible when water splits into H_2 and O_2 simultaneously through HER and OER, respectively. Compared to HER, OER is a more complex reaction, and it requires a high overpotential to reach the same current density, which implies that the kinetic barrier of OER is harder to overcome. Besides being requisite in water-splitting as a half-reaction, OER is also significant for generating molecular oxygen (O_2). Oxygen is a vital component for living and in the corona-pandemic, we learned about the importance of oxygen. Asides from this, it has multifaceted utilizations in

various industries. In energy conversion and storage devices such as fuel cells and metal-air batteries, OER plays a vital role in electrochemical conversion cycles between renewable electricity and chemical fuels via the generation of pure oxygen in a short period. Therefore, accelerating the development of OER is urgent for close-looped clean energy infrastructure and overcoming the shortage of oxygen due to growing pollution.

Ru and Ir-based catalysts are considered as state-of-the art OER electrocatalysts but due to the high cost and element scarcity are not sustainable choices. At the same time the electrochemical stability of the oxides of these materials (RuO_2 and IrO_2 transform into [(Ru^{8+}) O_4] and [(Ir^{6+}) O_3], respectively in the aqueous solution) hiders their applications at large-scale. Transition metal oxides, with various physical and electronic properties, are considered promising low-cost alternatives. In this, spinel-type oxides with significant performance have been extensively investigated as OER electrocatalysts. On the other hand, metal-organic frameworks have emerged as an important class of functional material due to their well-defined structural designs, high surface area, porosity, excellent thermal and mechanical stability and diverse chemical functionalities.

The thesis entitled “Metal-organic framework and nanomaterials for oxygen evolution reaction” encompasses the synthesis of spinel materials; nickel ferrite (NFO), Co-doped nickel ferrite (CFO and CNFO) and metal-organic frameworks (MOFs), e.g. Co-MOF (cobalt metal-organic framework), ZnDTO (zincdithiooxamide) MOF and Ni-Fe PBA-NC (nickel-iron Prussian blue analogue nanocube) for OER. Further, MOFs are used as a precursor to derive heteroatom-doped porous carbon, nanocomposite and various nanostructures to enhance the OER activity of MOFs. Based on the findings the thesis has been divided into seven chapters.

Chapter 1 is the introductory part which describe about the water splitting, its thermodynamic feasibility at different pH, OER in water splitting, mechanism of OER in different pH and its mechanistic approach, importance of OER in other fields like metal-air batteries and fuel cells, besides the water splitting, emerging electrocatalysts for OER such as spinels, pervoskites, metal oxides, LDH (layered double hydroxide) and MOFs. This chapter also deals with the evaluating kinetic parameters for OER activity of the catalysts viz. selection of electrolyte, onset/ overpotential, Tafel slope, exchange current density, ECSA (electroactive surface area) and stability.

Chapter 2 is the experimental and instrumentation part. It covers the details of the chemicals, synthesis of the electrocatalysts, nickel ferrite (NFO), Co-doped nickel ferrite (CFO and CNFO), Co-MOF, ZnDTO MOF, N/S/Zn doped porous carbon (NSC), nanocomposite of Co_3O_4 and NSC, Ni-Fe PBA nanocube, Ni-Fe PBA nanocage and Ni-Fe mixed oxide which are used in the further chapters and their characterizations with different characterization techniques such as UV-Vis. (ultraviolet-visible), XRD (X-Ray Diffraction technique), FT-IR (Fourier transfer infrared), SEM (Scanning Electron Microscopy) etc. Further, electrode preparation and electrochemical measurement methods viz. CV (cyclic voltammetry), LSV (linear sweep voltammetry), EIS (Electrochemical impedance spectroscopy) and CA (chronoamperometry) are described to analyse the OER performance of the catalyst materials. Then the OER performance of the catalysts is compared with commercially available RuO_2.

Chapter 3 In this chapter spinel materials; nickel ferrite (NFO) and Co-doped nickel ferrite (CFO and CNFO) are used for OER analysis. Sol-gel method is used for the synthesis of nickel ferrite and for the first time Co-doped nickel ferrite. OER performance of NFO, CFO and CNFO are checked by LSV and EIS. For the stability of the best

catalyst, 200 CV cycles are recorded and then LSV is performed and compared with before 200 CV cycles.

Chapter 4 In this work, we reported a beautiful rose-like structured Co-MOF, comprising petal-like sheets, as an active material to modify the commercial glassy carbon electrode (GCE) for enhanced OER performance. The Co-MOF is synthesised by a facile precipitation method using cobalt salt (Co^{2+}) and Anthranilic acid (AA). Detailed characterization techniques thoroughly explained the complexation of Co^{2+} with AA and the flower morphology of Co-MOF. Along with that, the optimised structure of Co-MOF and HOMO-LUMO is analysed by DFT. Further, the OER activity of the Co-MOF is investigated by LSV, Tafel slope, and compared with commercially available RuO_2 and for stability measurement, CA is employed for 10800 seconds at a static overpotential of 500 mV.

Chapter 5 In this chapter, Co_3O_4 nanoparticles embedded in N/S/Zn- doped porous carbon matrices is utilized as active materials to modify the commercial glassy carbon electrode (GCE) for enhanced and highly stable oxygen evolution reaction (OER). Firstly, a metal-organic framework (spherical ZnDTO, synthesized by the complexation of Zn-salts and dithiooxamide (DTO) ligand) is used. Then, N/S doped porous carbons (NSC) are derived from ZnDTO MOF by carbonizing them at different temperatures and to investigate the role of Zn on the catalytic performance of the materials, the thermally optimized carbon matrix is treated with a suitable acid. Further to enhance the OER activity, nanocomposite is formed with Co_3O_4 nanoparticles and these carbon matrixes. All the as-synthesized materials have been well-characterized by various tools for their structural and morphological associations.

Chapter 6 explores another class of MOF, Prussian blue analogue (PBA) compounds as an OER electrocatalyst. Ni-Fe PBA nanocubes are synthesised by a precipitation method and then via a facile chemical etching process (with ammonia solution), nanocubes are transformed into nanocages. A control etching process is developed in which etching occurs preferentially on the corners constructing the hollow cubes. Further, on annealing in air, the nanocubes are converted into NiFe-oxides, porous cubes. Both the nanostructures generated from nanocubes reveals different chemical composition retaining cubic morphology. XRD refinement, FT-IR, XPS and FE-SEM well-confirmed the conversion of the nanocubes to nanocage and oxide. Then, these materials are employed for OER analysis in which NiFe oxide shows enhanced performance.

Chapter 7 includes the conclusive remarks and future prospects of the thesis.

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