

Defect-Engineered Metal Oxide-based Nanostructures for Energy Conversion and Storage Applications

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**DEPARTMENT OF CHEMISTRY
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Defect-Engineered Metal Oxide-based Nanostructures for Energy Conversion and Storage Applications

by

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Submitted

in fulfilment of the requirements of the degree of
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*Dedicated to my
Parents*

CERTIFICATE

This is to certify that the thesis entitled “**Defect-Engineered Metal Oxide-based Nanostructures for Energy Conversion and Storage Applications,**” being submitted by **Mr. Ajay** 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. He has worked under my supervision and has fulfilled the requirements, which, to my knowledge, has reached the requisite standard for submitting the thesis. The results in this thesis have not been submitted to any other university or institute, whether in part or full, for the awards of any other degree or diploma.

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ABSTRACT

The increasing global energy demand, the finite nature of fossil fuels, and growing environmental concerns have intensified the search for clean and sustainable energy alternatives. While renewable energy sources such as solar and wind are crucial components of this transition, their inherent intermittency and reliance on weather conditions underscore the need for robust energy conversion and storage systems. Among the various candidates explored, metal oxide-based semiconductors have gained considerable attention due to their earth-abundant nature, structural versatility, and tunable electronic properties. Nevertheless, practical deployment is hindered by challenges such as suboptimal light absorption, inefficient charge separation, and limited energy storage capacity, issues often rooted in intrinsic electronic structure and interfacial limitations.

This thesis addresses these bottlenecks by employing a rational defect-engineering approach to tailor the properties of transition metal oxides, thereby enhancing both photoelectrochemical (PEC) performance for solar-to-fuel conversion and electrochemical behavior for energy storage. A comprehensive investigation into the role of intrinsic defects especially oxygen vacancies and cationic non-stoichiometry, is undertaken to understand and manipulate the underlying charge transport and interfacial mechanisms.

Chapter 1 outlines the motivation for this work, presenting the dual functionality of metal oxide semiconductors in solar-driven PEC reactions and supercapacitor-based energy storage. Particular attention is given to Fe-based oxides, which offer rich redox chemistry and high defect tunability. Key phenomena such as photocurrent polarity switching, ambipolarity, and oxygen vacancy-mediated band modulation are introduced as foundational concepts for improving device efficiency and versatility.

Chapter 2 details the synthesis routes employed, including spin coating, solvothermal growth, and thermal decomposition, allowing for fine-tuning of composition and morphology. A broad suite of characterization tools X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–visible spectroscopy, Raman spectroscopy, and electrochemical measurements, is used to correlate structural and electronic features with device-relevant performance metrics.

Chapter 3 explores the phenomenon of photocurrent polarity switching in BiFeO₃ (BFO) nanoparticulate films through electrolyte engineering. By systematically varying ionic strength and dissolved oxygen concentration, the study demonstrates a reversible switching of

photocurrent direction dictated by the critical state potential. A predictive model based on the Nernst equation and semiconductor surface kinetics is proposed, linking electrolyte parameters with semiconductor energetics.

Chapter 4 advances this concept by showing that internal defect manipulation—through the deliberate tuning of Bi/Fe stoichiometry in BFO—can similarly control the photocurrent switching behavior. Variations in bismuth or iron content adjust oxygen vacancy concentrations, thereby shifting the Fermi level and altering the surface band bending. XPS and PEC results support this stoichiometry–defect–functionality correlation, highlighting material composition as a powerful lever for device modulation.

Chapter 5 extends the defect-engineering strategy to nitrogen-doped Ni-Zn ferrite (Ni-ZnFe₂O₄) systems. Nitrogen incorporation introduces electronic states within the bandgap, enabling ambipolar photocurrent responses in a typically unipolar n-type semiconductor. The demonstration of bidirectional photocurrent without reliance on volatile elements suggests the generality of the defect-based tuning framework.

Chapter 6 transitions the focus to electrochemical energy storage by exploring the role of defect chemistry in flexible NiFe₂O₄-based supercapacitors. Through control of oxygen vacancies and cationic distributions, the study demonstrates enhanced proton intercalation, higher conductivity, and superior capacitive performance in acidic electrolytes. The work establishes NiFe₂O₄ as a viable candidate for flexible energy storage devices, capable of achieving high energy and power densities.

In **Chapter 7**, selenium-doped MnFe₂O₄ is synthesized to further enhance redox activity and charge transport. Se doping modulates lattice strain, oxygen vacancy content, and multivalent cation states, resulting in a significant boost in specific capacitance, Coulombic efficiency, and cyclic durability. The synergy between defect engineering and structural distortion in this flexible solid-state configuration underscores the effectiveness of compositional tailoring in supercapacitor optimization.

Chapter 8 synthesizes the key findings, integrating the insights from both PEC and energy storage studies into a unified defect-engineering framework. The results demonstrate how systematic manipulation of oxygen vacancies, electronic states, and stoichiometry can be leveraged to develop high-efficiency, multifunctional devices. Finally, future research directions are outlined, such as extending this approach to low-dimensional materials, tandem PEC-cell architectures, and hybrid energy conversion–storage modules.

In conclusion, this thesis presents a comprehensive and scalable strategy for improving metal oxide semiconductors through defect design. By elucidating the connection between atomic-scale imperfections and macroscopic performance, it contributes valuable design principles for the realization of next-generation solar and storage technologies.

सार

यह शोध प्रबंध बढ़ती वैश्विक ऊर्जा मांग, जीवाश्म ईंधनों की सीमितता और पर्यावरणीय चिंताओं के संदर्भ में स्थायी ऊर्जा विकल्पों की खोज को संबोधित करता है। हालांकि सौर और पवन ऊर्जा जैसे नवीकरणीय स्रोत महत्वपूर्ण हैं, लेकिन उनकी अस्थिरता के कारण उन्नत ऊर्जा रूपांतरण और भंडारण प्रणालियों की आवश्यकता होती है। इस संदर्भ में, धातु ऑक्साइड-आधारित अर्धचालक उनके समायोज्य इलेक्ट्रॉनिक गुणों, पर्यावरणीय अनुकूलता और संरचनात्मक विविधता के कारण संभावित उम्मीदवार के रूप में उभरे हैं। हालांकि, प्रकाश से विद्युत में रूपांतरण की अक्षमता और सीमित चार्ज भंडारण क्षमता जैसी चुनौतियाँ बनी हुई हैं, जो मुख्य रूप से अंतर्निहित इलेक्ट्रॉनिक संरचना और इंटरफेस सीमाओं से उत्पन्न होती हैं।

यह शोध प्रबंध संक्रमण धातु ऑक्साइड्स के गुणों को दोष इंजीनियरिंग के माध्यम से अनुकूलित करके इन चुनौतियों का समाधान करता है, जिससे फोटोइलेक्ट्रोकेमिकल (PEC) प्रदर्शन और ऊर्जा भंडारण व्यवहार में सुधार होता है। इसमें विशेष रूप से ऑक्सीजन रिक्तियों और कैटायनिक गैर-स्टॉइकियोमेट्री जैसे अंतर्निहित दोषों की भूमिका का व्यापक अध्ययन किया गया है, ताकि चार्ज परिवहन और इंटरफेस तंत्र को समझा और नियंत्रित किया जा सके।

अध्याय 1 इस कार्य की प्रेरणा को रेखांकित करता है, जिसमें धातु ऑक्साइड अर्धचालकों की सौर-चालित PEC प्रतिक्रियाओं और सुपरकैपेसिटर-आधारित ऊर्जा भंडारण में दोहरी कार्यक्षमता प्रस्तुत की गई है। विशेष ध्यान Fe-आधारित ऑक्साइड्स पर दिया गया है, जो समृद्ध रेडॉक्स रसायन और उच्च दोष अनुकूलन क्षमता प्रदान करते हैं। फोटोकरेंट ध्रुवीयता स्विचिंग, एम्बिपोलैरिटी और ऑक्सीजन रिक्ति-मध्यस्थ बैंड मॉड्यूलेशन जैसी प्रमुख घटनाओं को डिवाइस दक्षता और बहुमुखी प्रतिभा में सुधार के लिए मूलभूत अवधारणाओं के रूप में प्रस्तुत किया गया है।

अध्याय 2 उपयोग की गई संश्लेषण विधियों का विवरण देता है, जिसमें स्पिन कोटिंग, सॉल्वोथर्मल वृद्धि और थर्मल अपघटन शामिल हैं, जो संरचना और संरूपण को सूक्ष्मता से नियंत्रित करने की अनुमति देते हैं। एक व्यापक विशेषता निर्धारण उपकरणों का उपयोग किया गया है, जैसे कि एक्स-रे विवर्तन (XRD), एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS), यूवी-दृश्य स्पेक्ट्रोस्कोपी, रमन स्पेक्ट्रोस्कोपी और इलेक्ट्रोकेमिकल मापन, ताकि संरचनात्मक और इलेक्ट्रॉनिक विशेषताओं को डिवाइस-प्रासंगिक प्रदर्शन मेट्रिक्स के साथ जोड़ा जा सके।

अध्याय 3 इलेक्ट्रोलाइट इंजीनियरिंग के माध्यम से BiFeO_3 (BFO) नैनोकणीय फिल्मों में फोटोक्रेन्ट ध्रुवीयता स्विचिंग की घटना का अन्वेषण करता है। आयनिक शक्ति और घुले हुए ऑक्सीजन सांद्रता को व्यवस्थित रूप से बदलकर, अध्ययन एक रिवर्सिबल फोटोक्रेन्ट दिशा स्विचिंग को प्रदर्शित करता है, जो क्रिटिकल स्टेट पोटेन्शियल द्वारा निर्देशित होती है। एक पूर्वानुमान मॉडल, जो Nernst समीकरण और अर्धचालक सतह गतिशीलता पर आधारित है, प्रस्तावित किया गया है, जो इलेक्ट्रोलाइट पैरामीटरों को अर्धचालक ऊर्जा के साथ जोड़ता है।

अध्याय 4 इस अवधारणा को आगे बढ़ाता है, यह दिखाते हुए कि BFO में Bi/Fe स्टॉइकियोमेट्री को जानबूझकर समायोजित करके आंतरिक दोषों में हेरफेर करके फोटोक्रेन्ट स्विचिंग व्यवहार को समान रूप से नियंत्रित किया जा सकता है। बिस्मथ या आयरन सामग्री में भिन्नताएं ऑक्सीजन रिक्ति सांद्रता को समायोजित करती हैं, जिससे फर्मी स्तर और सतह बैंड झुकाव में परिवर्तन होता है। XPS और PEC परिणाम इस स्टॉइकियोमेट्री-दोष-कार्यात्मकता सहसंबंध का समर्थन करते हैं, जो डिवाइस मॉड्यूलेशन के लिए सामग्री संरचना को एक शक्तिशाली लीवर के रूप में उजागर करते हैं।

अध्याय 5 नाइट्रोजन-डोपेड Ni-Zn फेराइट ($\text{Ni-ZnFe}_2\text{O}_4$) प्रणालियों में दोष इंजीनियरिंग रणनीति का विस्तार करता है। नाइट्रोजन समावेशन बैंडगैप के भीतर इलेक्ट्रॉनिक अवस्थाओं को प्रस्तुत करता है, जिससे एक सामान्यतः एकध्रुवीय n-प्रकार अर्धचालक में एम्बिपोलर फोटोक्रेन्ट प्रतिक्रियाएं सक्षम होती हैं। वाष्पशील तत्वों पर निर्भरता के बिना द्विदिश फोटोक्रेन्ट का प्रदर्शन दोष-आधारित ट्यूनिंग ढांचे की सामान्यता का सुझाव देता है।

अध्याय 6 लचीले NiFe_2O_4 -आधारित सुपरकैपेसिटर्स में दोष रसायन की भूमिका का अन्वेषण करके इलेक्ट्रोकेमिकल ऊर्जा भंडारण पर ध्यान केंद्रित करता है। ऑक्सीजन रिक्तियों और कैटायनिक वितरणों के नियंत्रण के माध्यम से, अध्ययन अम्लीय इलेक्ट्रोलाइट्स में बेहतर प्रोटॉन इंटरकलेशन, उच्च चालकता और उत्कृष्ट कैपेसिटिव प्रदर्शन को प्रदर्शित करता है। यह कार्य NiFe_2O_4 को लचीले ऊर्जा भंडारण उपकरणों के लिए एक व्यवहार्य उम्मीदवार के रूप में स्थापित करता है, जो उच्च ऊर्जा और शक्ति घनत्व प्राप्त करने में सक्षम है।

अध्याय 7 रेडॉक्स गतिविधि और चार्ज परिवहन को और बढ़ाने के लिए सेलेनियम-डोपेड MnFe_2O_4 का संश्लेषण करता है। Se डोपिंग जाली तनाव, ऑक्सीजन रिक्ति सामग्री और बहुवैलेंट कैटायन अवस्थाओं को मॉड्यूलेट करता है, जिसके परिणामस्वरूप विशिष्ट कैपेसिटेंस, कूलॉम्बिक दक्षता और चक्रीय स्थायित्व में महत्वपूर्ण वृद्धि होती है। इस लचीले ठोस-राज्य विन्यास में दोष इंजीनियरिंग और संरचनात्मक

विकृति के बीच तालमेल सुपरकैपेसिटर अनुकूलन में संरचनात्मक अनुकूलन की प्रभावशीलता को रेखांकित करता है।

अध्याय 8 प्रमुख निष्कर्षों को संश्लेषित करता है, PEC और ऊर्जा भंडारण अध्ययनों से अंतर्दृष्टियों को एकीकृत करके एक एकीकृत दोष-इंजीनियरिंग ढांचे में। परिणाम दिखाते हैं कि ऑक्सीजन रिक्तियों, इलेक्ट्रॉनिक अवस्थाओं और स्टॉइकियोमेट्री में प्रणालीगत हेरफेर का लाभ उठाकर उच्च दक्षता, बहु-कार्यात्मक उपकरण विकसित किए जा सकते हैं। अंत में, भविष्य के अनुसंधान दिशाओं की रूपरेखा प्रस्तुत की गई है, जैसे कि इस दृष्टिकोण को निम्न-आयामी सामग्री, टैंडम PEC-सेल आर्किटेक्चर और हाइब्रिड ऊर्जा रूपांतरण-भंडारण मॉड्यूल तक विस्तारित करना।

निष्कर्षतः, यह शोध प्रबंध दोष डिजाइन के माध्यम से धातु ऑक्साइड अर्धचालकों में सुधार के लिए एक व्यापक और स्केलेबल रणनीति प्रस्तुत करता है। यह परमाणु-स्तरीय अपूर्णताओं और मैक्रोस्कोपिक प्रदर्शन के बीच संबंध को स्पष्ट करके अगली पीढ़ी की सौर और भंडारण प्रौद्योगिकियों की प्राप्ति के लिए मूल्यवान डिजाइन सिद्धांतों में योगदान देता है।

TABLE OF CONTENTS

| | |
|--|-------------|
| CERTIFICATE | iii |
| ACKNOWLEDGMENT | iv |
| ABSTRACT..... | vi |
| ABBREVIATIONS AND SYMBOLS | xii |
| TABLE OF CONTENTS..... | xiv |
| LIST OF FIGURES | xvii |
| LIST OF TABLES..... | xxiv |
| Chapter 1. Introduction | 1 |
| 1.1 Background and Motivation | 1 |
| 1.1.1 Clean Energy Transition: A Dual Pathway of Conversion and Storage..... | 2 |
| 1.1.2 Electrochemical Energy Storage Devices..... | 3 |
| 1.1.3 Photoelectrochemical (PEC) Devices and Mechanisms..... | 4 |
| 1.2 Semiconductor–Electrolyte Interface: A Unifying Framework for Energy Conversion and Storage..... | 5 |
| 1.2.1 Interface Physics and Energy Band Alignment..... | 6 |
| 1.2.2 Charge Carrier Dynamics and Surface States..... | 7 |
| 1.2.3 Electrical Double Layer and Interfacial Capacitance | 7 |
| 1.2.4 Interface Engineering for Performance Enhancement | 7 |
| 1.3 Photoelectrochemical Photocurrent Switching (PEPS) Effect: From Scientific Curiosity to Functional Smart Interfaces | 8 |
| 1.3.1 Recent Advancements..... | 9 |
| 1.3.2 Literature Gap | 9 |
| 1.4 Supercapacitors and Charge Storage Mechanisms | 10 |
| 1.4.1 Challenges and gap area | 11 |
| 1.5 Electrode Material and Rationale | 11 |
| 1.6 Objectives | 13 |
| 1.7 Structure of Thesis | 13 |
| 1.8 References | 15 |
| Chapter 2. Methodology | 19 |
| 2.1 Synthesis Methodology | 19 |

| | |
|---|-----------|
| 2.1.1 Synthesis of BiFeO ₃ Nanoparticles | 20 |
| 2.1.2 Synthesis of BiFeO ₃ thin films with varying Bi/Fe stoichiometry | 21 |
| 2.1.3 Synthesis of Nickel Ferrite, Zinc Ferrite and Nickel-Zinc Mixed Ferrites | 21 |
| 2.1.4 Synthesis of Nickel Ferrite via Glycolate Route..... | 21 |
| 2.1.5 Synthesis of Selenium doped Manganese Ferrite | 22 |
| 2.2 Material Characterizations | 22 |
| 2.2.1 Powder X-ray Diffraction | 22 |
| 2.2.2 Fourier Transform Infrared Spectroscopy | 23 |
| 2.2.3 Raman Spectroscopy | 24 |
| 2.2.4 Energy-dispersive X-ray Spectroscopy | 25 |
| 2.2.5 X-ray Photon Spectroscopy | 26 |
| 2.2.6 Electron Microscopy | 27 |
| 2.2.7 X-ray Absorption Spectroscopy | 27 |
| 2.2.8 Electronic and Band Structure | 28 |
| 2.3 Photoelectrochemical characterization | 29 |
| 2.4 Electrochemical Characterization for charge storage | 30 |
| 2.5 Parameters for evaluating Electrochemical Performance | 31 |
| 2.6 References | 32 |
| Chapter 3. Changeable critical state for switchable photocurrent direction via photoelectrochemical photocurrent polarity switching effect in BiFeO₃ nanoparticulate films | 34 |
| 3.1 Abstract | 34 |
| 3.2 Introduction | 35 |
| 3.3 Results and Discussions | 36 |
| 3.3.1 Physicochemical Characterizations | 36 |
| 3.3.2 Photoelectrochemical characterization towards PEPS effect..... | 39 |
| 3.3.3 Effect of salt on PEPS effect | 41 |
| 3.3.4 PEPS Effect and shift in switching potential | 43 |
| 3.4 Conclusion | 45 |
| 3.5 References | 45 |

| | |
|---|-----------|
| Chapter 4. Stoichiometric Regulation of Charge Carrier Dynamics for Photocurrent Polarity Switching in BiFeO₃ Nanoparticulate Thin Films | 48 |
| 4.1 Abstract | 48 |
| 4.2 Introduction | 49 |
| 4.3 Results and Discussions | 50 |
| 4.3.1 Physicochemical Characterizations | 50 |
| 4.3.2 Photoelectrochemical characterization towards PEPS effect | 55 |
| 4.4 Conclusion | 57 |
| 4.5 References | 58 |
| Chapter 5. Ambipolarity Can Be Induced in Metal Oxides with Non-Volatile Cations: A case study on Ni-Zn ferrite. | 60 |
| 5.1 Abstract | 60 |
| 5.2 Introduction | 61 |
| 5.3 Results and Discussions | 62 |
| 5.3.1 Physicochemical Characterizations | 62 |
| 5.3.2 Optoelectronic Properties..... | 66 |
| 5.3.3 Photoelectrochemical Characterization..... | 67 |
| 5.4 Conclusion | 70 |
| 5.5 References | 70 |
| Chapter 6. High performance flexible supercapacitor based on single precursor derived NiFe₂O₄ spinel with tailored cationic distribution and oxygen vacancies in acidic medium | 73 |
| 6.1 Abstract | 73 |
| 6.2 Introduction | 74 |
| 6.3 Results and Discussions | 75 |
| 6.3.1 Physicochemical Characterizations | 75 |
| 6.3.2 Electrochemical Characterization in Three-electrode Configuration..... | 80 |
| 6.3.3 Charge storage mechanism for NFO ₂ in acid electrolyte | 82 |
| 6.3.4 Full-Cell Configurations (symmetric and asymmetric) ... | 85 |
| 6.4 Conclusion | 89 |
| 6.5 References | 89 |

| | |
|---|------------|
| Chapter 7. Site Specific Selenium Substitution Enhances Charge Storage Performance in Solid-State Flexible MnFe₂O₄-based Supercapacitors Devices via Modulated d band center | 93 |
| 7.1 Abstract | 93 |
| 7.2 Introduction | 94 |
| 7.3 Results and Discussions | 95 |
| 7.3.1 Physicochemical Characterizations | 95 |
| 7.3.2 Electrochemical Analysis in Three-electrode Configuration... | 100 |
| 7.3.3 Electrochemical Analysis in Two-electrode Configuration... | 102 |
| 7.4 Conclusion | 105 |
| 7.5 References | 105 |
| Chapter 8. Conclusion and Future Perspectives | 108 |
| 8.1 Conclusion of Thesis | 108 |
| 8.2 Future Perspectives | 109 |
| 8.3 References | 111 |
| Appendices | 112 |
| Appendix 1 | 112 |
| Appendix 2 | 117 |
| Appendix 3 | 124 |
| Appendix 4 | 128 |
| Appendix 5 | 137 |
| Curriculum Vitae | 145 |

LIST OF FIGURES

| Figure No. | Figure Caption | Page No. |
|-------------------|---|-----------|
| 1.1 | Global Energy Consumption Trends and Projections (1980–2030). | 1 |
| 1.2 | Schematic illustration of electrochemical energy storage systems, highlighting key components i.e. batteries, supercapacitors, and fuel cells—along with energy sources and practical applications such as electric vehicles, grid storage, and portable electronics. | 2 |
| 1.3 | Schematic illustration of a photoelectrochemical (PEC) cell configuration showing an n-type semiconductor as a light absorber interfaced with an electrolyte. | 4 |
| 1.4 | Electrostatic potential distribution at the semiconductor–electrolyte interface showing space charge, Helmholtz, and Gouy layer contributions. | 6 |
| 1.5 | Schematic showing types of Supercapacitors according to their charge storage mechanism (a) EDLC (b) Pseudo capacitor and (c) Hybrid Capacitors. | 10 |
| 1.6 | Advantages and limitations of metal oxides for energy applications, highlighting key properties such as ease of synthesis, abundance, and tunability, along with challenges like poor conductivity and limited visible light activity. | 12 |
| Scheme 2.1 | Schematic illustration of the thermal decomposition process for metal oxide nanoparticles. | 19 |
| Scheme 2.2 | Schematic illustration of the spin coating process for thin film synthesis. | 20 |
| Scheme 2.3 | Schematic illustration of the solvothermal synthesis for Metal Oxide synthesis. | 20 |
| 2.1 | Bragg diffraction of X-rays from parallel atomic planes separated by distance d . Constructive interference occurs when the path difference $2d \sin \theta$ equals an integer multiple of the wavelength $n\lambda$. Diagram illustrates the case for $n = 2$, with incident and reflected angles equal. | 23 |
| 2.2 | Schematic of FTIR spectroscopy. Incident IR light interacts with a sample, leading to absorption and transmission based on molecular vibrations. The resulting spectrum shows characteristic peaks corresponding to symmetric, asymmetric, scissoring, and twisting vibrations of molecular bonds. | 24 |
| 2.3 | Raman scattering mechanism showing Rayleigh (elastic), Stokes, and anti-Stokes (inelastic) transitions via virtual states, with corresponding Raman shifts illustrated spectrally. | 25 |
| 2.4 | Schematic of XPS principle showing core-level photoelectron ejection by incident X-ray ($h\nu$), with kinetic energy defined as $E_{kin}=h\nu - BE$; spin–orbit splitting in 2p levels is indicated. | 26 |
| 2.5 | Schematic of X-ray absorption spectroscopy (XAS): (a) Transmission mode with incident and transmitted X-ray beam through sample thickness t ; (b) Absorption spectrum showing XANES, EXAFS, and pre-edge features; (c) Electronic excitation from a core level to continuum states; | 28 |

| | | |
|------------|---|-----------|
| | (d) Representation of the local electronic environment around the absorbing atom. | |
| 3.1 | a) XRD pattern, b) FTIR spectrum, and (c & d) HRTEM images with different magnifications of BFO NPs. | 37 |
| 3.2 | High-resolution CL XPS spectra for Bi 4f (a), Fe 2p (b), and O 1s (c) elements of BFO NPs. (d) UV-Vis. absorption spectrum with corresponding Tauc plot as inset, (e) valence band edge position determined using XPS, and (f) band edge alignment with fermi level diagram. | 38 |
| 3.3 | (a) Photocurrent vs voltage curves for BFO photoelectrode in Na ₂ SO ₄ , (b) enlarged portion showing the switching potential, (c) transient photocurrent at switching potential and the potential above or below the switching potential. | 40 |
| 3.4 | (a) Photocurrent vs voltage curves for BFO photoelectrode in different electrolyte compositions, (b) enlarged portion of (a) showing the switching potential and shift in onset of photocurrent. Plots of (c) Mott-Schottky, and (d) switching potential vs ionic strength. | 43 |
| 3.5 | Mechanism diagram of carrier transport between BFO working electrodes with electrolytes. | 44 |
| 4.1 | (a) Schematic of BiFeO ₃ synthesis detailing solution preparation, spin coating at 3500 rpm, and (b) calcination at 500°C for 2 hours. (c–g) FESEM images display the morphology of the films with varied composition: (c) BF1.1O, (d) BF1.05O, (e) BFO, (f) B1.05FO, and (g) B1.1FO, illustrating surface textures and microstructural differences. | 50 |
| 4.2 | (a) Rietveld refined XRD pattern of B1.1FO, confirming the R3c perovskite structure with minor impurity phases. (b) HRTEM image of B1.1FO, showing well-defined lattice fringes. (c) SAED pattern of B1.1FO, indicating the crystalline nature of the sample. (d–f) Corresponding XRD, HRTEM, and SAED patterns for B1.05FO. (g–i) Corresponding patterns for BFO. (j–l) Corresponding patterns for BF1.05O. (m–o) Corresponding patterns for BF1.1O. | 51 |
| 4.3 | CL XPS spectra of (a) Bi 4f, (b) Fe 2p, and (c) O 1s. (d) Tauc plot illustrating the optical band gap, (e) valence band XPS spectra, and (f) UPS secondary cut-off energies providing insights into electronic structure and band alignment of the samples. | 53 |
| 4.4 | Band edge alignment diagram for all the samples, showing the CBM, VBM, and E _f positions (dotted green horizontal lines) across varying Bi/Fe compositions with reference to NHE as well as Vacuum energy levels. | 55 |
| 4.5 | (a) Photocurrent vs. voltage curves for all photoelectrodes in 0.1 M Na ₂ SO ₄ , (b) Mott-Schottky plots for the samples, illustrating the photoelectrochemical performance and charge carrier properties, and (c) OCP response under chopped light. | 56 |
| 5.1 | (a) XRD patterns of NFO, ZFO, NZFO, and NZFON. (b) Raman spectra of the corresponding samples. (c) FTIR spectra illustrating the vibrational modes. (d) FTIR spectra highlighting variations in M–O bonding due to nitrogen doping. (e) EDX analysis depicting the atomic composition of NZFON. (f) FESEM image of NZFON. (g–k) EDX elemental mapping of NZFON, showing the spatial distribution of constituent elements. | 63 |

| | | |
|------------|--|-----------|
| 5.2 | (a) XPS survey spectrum of NZFO and NZFON confirming elemental composition. (b–e) Core-level XPS spectra of (b) Ni 2p, (c) Zn 2p, (d) Fe 2p, and (e) O 1s, illustrating the oxidation states and bonding environments of the respective elements. (f) N 1s spectrum of, confirming nitrogen incorporation in NZFON and its chemical state within the spinel structure. | 65 |
| 5.3 | (a) Tauc plots derived from UV-visible DRS for NZFO and NZFON, estimating the optical bandgap. (b) XPS valence band spectra showing differences in the valence band maximum (VBM) and Fermi energy. (c) UPS spectra indicating the SECO and fermi level position. (d) Energy level diagrams derived from UPS, XPS valence band and optical bandgap measurements, highlighting the shifts in CBM, VBM, and E_f . | 66 |
| 5.4 | (a) LSV curves for NZFO under chopped illumination, highlighting the photocurrent response under applied bias. (b) LSV curves for NZFON under chopped illumination. (c) (OCP) measurements under chopped light illumination. (d) Mott-Schottky plots for NZFO and NZFON, illustrating variations in N_d and V_{fb} . (e) 3D representation of W_{SC} , N_d and V_{fb} extracted from Mott-Schottky analysis, showing the impact of nitrogen doping. (f) IPCE spectra for NZFO and NZFON. | 69 |
| 6.1 | (a) XRD patterns, (b) Raman Spectra, (c) FTIR spectra and (d) enlarged portion of FTIR spectra of NFO1, NFO2, and NFO3 nanoparticles. | 76 |
| 6.2 | FESEM, TEM and HRTEM images of (a, d, g) NFO1, (b, e, h) NFO2, (c, f, i) NFO3 samples. | 78 |
| 6.3 | a) Survey spectra and high-resolution CL XPS spectra for (a) Ni 2p, (b) Fe 2p, and (c) O 1s of NFO1, NFO2 and NFO3, respectively. | 79 |
| 6.4 | Comparison of (a) CV curves at 25 mV s^{-1} , (b) GCD curves at 20 A g^{-1} , (c) EIS within frequency range of $1\text{-}10^4 \text{ Hz}$, and (d) Bode plot for NFO1, NFO2, and NFO3 electrodes. | 81 |
| 6.5 | Electrochemical analysis of NFO2: a) CV curves at 20 mV s^{-1} within varying potential windows, (b) CV (within $5 - 150 \text{ mV s}^{-1}$) and (c) GCD curves at varying potential windows, (d) GCD curves at varying current densities, (e) Ragone Plot for 3-electrode configuration (Inset: C_{sp} vs current density) and (f) Trend of C_{sp} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, Ov/OL , and Fe^{3+} (O_h/T_d) for NFO1, NFO2 and NFO3. | 82 |
| 6.6 | Comparative charge storage mechanism in acidic and basic medium via (a, b) \log (anodic current) vs $\log \nu$ at varying potentials (c, d) b -values vs potential, and (e, f) percentage of capacitance contribution for NFO2 at different scan rates. | 83 |
| 6.7 | CV of NFO2 (a) after 100 cycles at 25 mVs^{-1} in 0.1 M KOH , (b) at 25 mVs^{-1} in $0.1\text{M H}_2\text{SO}_4$. The capacitive, and diffusion-controlled contribution at scan rate of 10 mV s^{-1} in (c) 0.1 M KOH , (d) $0.1\text{M H}_2\text{SO}_4$. | 85 |
| 6.8 | NFO2//NFO2 device:(a) GCD curves at varying current densities ($2\text{-}12 \text{ A g}^{-1}$), (b) Ragone plot and C_{sp} values at varying current densities (Inset), (c) C_{sp} retention up to 3,000 cycles at 4 A g^{-1} , (d) Comparative CV curves for NFO2 and AC at 25mVs^{-1} . NFO2//AC device: (e) GCD curves with varying current densities ($2\text{-}12 \text{ A g}^{-1}$), (f) Ragone plot and C_{sp} values at different current densities (Inset). | 87 |
| 7.1 | (a) Schematic showing the solvothermal synthesis of MFO and MFO-Se at $180 \text{ }^\circ\text{C}$ for 12 hrs. (b–f) TEM images illustrating the morphological and | 96 |

| | | |
|-------------|---|------------|
| | microstructural variations of (b) pristine MFO, (c) MFO-Se 2.5%, (d) MFO-Se 5%, (e) MFO-Se 7.5%, and (f) MFO-Se 10%. | |
| 7.2 | (a) XRD patterns of MFO and MFO-Se confirming the phase purity, (b) a shift of the (311) peak to lower 2θ values due to Se doping induced lattice contraction. (c) FTIR spectra reveal characteristic vibrational modes and their changes with doping. (d) EPR spectra show Se doping incited defect generation in the lattice. (e) Raman spectra show vibrational modes of MFO, with (f) a shift of F_{1g} and E_g modes to lower wavenumbers, reflecting structural distortion. | 97 |
| 7.3 | (a) CL XPS spectra of Fe 2p, (b) Mn 2p, and (c) O 1s showing the chemical state of the constituent elements in MFO-Se. (d) Normalized XANES spectra at Se K-edge, compared with Se metal and Na_2SeO_3 standards, highlighting the oxidation state of Se in the material. (e) Fourier-transformed EXAFS spectra at the Se K-edge, with experimental data represented by scatter points and theoretical fits by coloured data points, providing insights into the local atomic environment around Se. (f) d-band center estimation from XPS VB spectra. | 98 |
| 7.4 | Electrochemical measurements of the MFO and Se-doped MFO electrodes: a) CV curves at a scan rate of 25 mV s^{-1} , (b) GCD curves at a current density of 10 A g^{-1} within a fixed potential window, showing maximum discharge time for MFO Se-7.5%. (c) Trend of C_{sp} at a constant current density of 10 A g^{-1} from GCD, with maximum C_{sp} for MFO Se-7.5%, (d) Capacitance retention up to 5000 cycles at 10 A g^{-1} , (e) EIS within the frequency range of $1-10^4\text{ Hz}$, (f) CVs (within $5 - 100\text{ mV s}^{-1}$), (g) $\log(I_{anodic})$ vs $\log v$ at varying potentials, (h) b -values vs potential, and (i) the capacitive, and diffusion-controlled contribution at scan rate of 10 mV s^{-1} for MFO Se-7.5%. | 100 |
| 7.5 | Electrochemical characterization of MFO Se-7.5% symmetric device: (a) CV curves at various scan rates ($5-100\text{ mV s}^{-1}$), (b) GCD and (c) C_{sp} values at varying current densities, (d) Ragone plot at varying power densities, (e) C_{sp} retention up to 3,000 cycles at 20 A g^{-1} (Inset: initial and final GCD cycles), (f) EIS in frequency range of 0.1 to 10^4 Hz with corresponding equivalent circuit diagram, (g) CV curves at bending angles of 360° , 90° , and 180° , (h) LED illumination using 3 symmetric devices stacked in series at different bending angles. | 104 |
| A1.1 | TGA plot of Bi-Fe Glycolate Precursor. | 112 |
| A1.2 | (a) TEM image (low magnification) of pristine BFO NPs, (b) size distribution profile (histogram), (c) FESEM image of pristine BFO NPs, (d) SAED pattern of BFO NPs. | 112 |
| A1.3 | Survey XPS spectrum of pristine BFO NPs. | 113 |
| A1.4 | UPS survey scan of BFO NPs. | 113 |
| A1.5 | Critical state at switching potential for different ionic strengths. | 114 |
| A1.6 | (a) Photocurrent vs voltage curves for BFO photoelectrode in different electrolyte compositions ($Na_2SO_4 + NaClO_4$), (b) enlarged portion of (a) showing the switching potential and shift in onset of photocurrent. | 114 |
| A1.7 | Photocurrent vs Voltage curves for BFO photoelectrode in 0.1 M Na_2SO_4 (red curve) and O_2 saturated 0.1 M Na_2SO_4 (green curve). | 115 |
| A1.8 | Mott-Schottky plots of BFO electrode in O_2 saturation and depletion conditions. | 115 |

| | | |
|--------------|--|------------|
| A1.9 | EIS plots at OCP for different electrolyte compositions. | 116 |
| A1.10 | Variation in width of charge space layer as a function of ionic strength. | 116 |
| A2.1 | XRD patterns of (a) all the BiFeO ₃ compositions, (b) impurity phases (Bi ₂₅ FeO ₄₀ and Bi ₂ Fe ₄ O ₉) formed in 25% Bi and Fe excess samples. (c) photocurrent vs voltage curves for impure phases, showing no PEPS effect and (d) FTIR patterns of all BiFeO ₃ compositions. | 117 |
| A2.2 | FESEM images and elemental mapping of all synthesised BiFeO ₃ compositions. | 118 |
| A2.3 | EDX elemental distribution of all synthesised BiFeO ₃ compositions. | 119 |
| A2.4 | Survey XPS spectrum of all synthesised BiFeO ₃ Compositions. | 120 |
| A2.5 | (a) Measured Bi/Fe atomic ratio all synthesised BiFeO ₃ Compositions via EDX, ICP and XPS and, (b) relative intensity ratio of O _V /O _L of all synthesised BiFeO ₃ Compositions. | 121 |
| A2.6 | UV-Vis. absorption spectra of all synthesised BiFeO ₃ compositions normalized at 800 nm. | 121 |
| A2.7 | Fermi-Dirac fitting of the secondary electron cutoff (SECO) spectra for all samples to determine the Fermi energy. | 122 |
| A2.8 | Photocurrent vs. Voltage (I-V) curves for all synthesised BiFeO ₃ compositions under visible light illumination, showing distinct anodic and cathodic response patterns based on stoichiometric variations. | 123 |
| A2.9 | (a) Variation of the switching potential and flatband potential across different BFO sample compositions and, (b) variation in width of charge space layer as a function of Bi/Fe ratio. | 123 |
| A3.1 | XRD patterns of NZFON synthesized at different temperatures (500–800°C) compared with the standard JCPDS reference (#86-2267). | 124 |
| A3.2 | FESEM images of NZFO (a), NZFON synthesized at 500°C (b), at 700 °C (c) and 800°C (d). | 124 |
| A3.3 | EDX elemental analysis of NZFON 500, indicating insufficient nitrogen incorporation. | 125 |
| A3.4 | XPS Survey scan and high-resolution CL XPS spectra of N1s of NZFON 500, indicating insufficient nitrogen incorporation. | 125 |
| A3.5 | EPR Spectra of NZFO and NZFON | 126 |
| A3.3 | Fitted UPS data for (a) NZFO and (b) NZFON. | 127 |
| A4.1 | The thermogravimetric analysis of the Ni-Fe glycolate. | 128 |
| A4.2 | Enlarged portion of XRD of NFO1, NFO2, and NFO3 suggesting peak shift to higher 2θ values. | 128 |
| A4.3 | EPR signal of NFO1, NFO2 and NFO3 for surface oxygen vacancies. | 129 |
| A4.4 | (a) FESEM image and (b) corresponding EDX spectrum of NFO1. EDX mapping depicting individual elements (c) O, (d) Ni, (e) Fe. | 129 |
| A4.5 | (a) FESEM image and (b) corresponding EDX spectrum of NFO2. EDX mapping depicting individual elements (c) O, (d) Ni, (e) Fe. | 130 |
| A4.6 | (a) FESEM image and (b) corresponding EDX spectrum of NFO3. EDX mapping depicting individual elements (c) O, (d) Ni, (e) Fe. | 130 |
| A4.7 | CV curves for NFO2 (a) in different electrolytes at 100 mV s ⁻¹ , (b) with bare Carbon cloth as substrate at 100 mV s ⁻¹ , (c) with or without externally added activated carbon at 100 mVs ⁻¹ , (d) different mass loading (mg/cm ²) at 25 mV s ⁻¹ . | 132 |

| | | |
|--------------|---|------------|
| A4.8 | (a,d) Inverse of capacitance ($1/C_{sp}$) versus square scan rate ($v^{0.5}$), (b,e) Capacitance (C_{sp}) Vs. inverse of square scan rate ($v^{0.5}$), (c,f) $I/v^{0.5}$ vs $v^{0.5}$ plot for NFO2 in the acidic medium and basic medium, respectively. | 133 |
| A4.9 | (a) XRD Patterns of NFO2 before and after cyclic stability test, (b) zoomed portion of XRD patterns of NFO2. (* indicates the peaks due to carbon cloth substrate) | 133 |
| A4.10 | a) Survey XPS spectra and (b) high-resolution CL XPS Spectra for Fe 2p before and after the cyclic stability test for NFO2. | 134 |
| A4.11 | (a) CV at a constant scan rate of 25 mVs^{-1} and (b) GCD curves at constant current density of 4 A g^{-1} within varying potential window for (NFO2//NFO2) device. | 134 |
| A4.12 | (a) CV curves of (a) symmetric (NFO2//NFO2), and (b) asymmetric (NFO2//AC) devices at varying scan rates of $5\text{-}200 \text{ mVs}^{-1}$. | 134 |
| A4.13 | EIS before and after stability tests for (a) NFO2// NFO2 (b) NFO2//AC devices in frequency range of 0.1 to 10^4 Hz , and 0.1 to 10^5 Hz respectively. | 135 |
| A4.14 | FESEM images of NFO2 before and after 3000 GCD cycles. | 135 |
| A4.15 | (a) CV at a constant scan rate of 100 mVs^{-1} and (b) GCD curves at constant current density of 4 A g^{-1} within varying potential window for NFO2//AC device. | 135 |
| A4.16 | Capacitance retention of asymmetric (NFO2//AC) device up to 10000 cycles at 4 A g^{-1} | 136 |
| A5.1 | (a) Bode plot Comparison for MFO and Se doped MFO electrodes, Electrochemical analysis of MFO Se-7.5% b) CV curves at 25 mV s^{-1} within varying potential windows, (c) GCD curves at varying current densities, (d) Trend of C_{sp} vs current density in 3-electrode configuration. | 139 |
| A5.2 | (a) Inverse of capacitance ($1/C_{sp}$) versus square scan rate ($v^{0.5}$), (b) Capacitance (C_{sp}) versus the inverse of square scan rate ($v^{0.5}$), (c) $I/v^{0.5}$ vs $v^{0.5}$ plot, (d) percentage of capacitance contribution for MFO Se-7.5%. | 140 |
| A5.3 | Electrochemical characterization of MFO Se-7.5% symmetric device: (a) CV curves at 50 mV s^{-1} (b) GCD curves at 20 A g^{-1} within different potential windows, (c) \log (anodic/cathodic current) vs $\log v$. | 141 |
| A5.4 | (a) Mn 2p and (b) Fe 2p XPS spectra for the MFO-Se 7.5% before and after charging-discharging cycles, demonstrating changes in oxidation states. (c) XRD patterns showing a shift to lower 2θ values, indicating potential lattice expansion or structural changes due to the electrochemical cycling process. (d, e) FESEM images of the sample pre- and post-cycling, revealing that the morphology remains largely intact, though slight agglomeration is observed. | 141 |

LIST OF TABLES

| Table No. | Table Caption | Page No. |
|-------------|---|------------|
| 6.1 | <i>Comparison of electrochemical performance parameters for NiFe₂O₄-based electrodes reported in the literature. *E_d and P_d are mentioned for 2-electrode system.</i> | 88 |
| A2.1 | <i>Summary of the compositional variations and nomenclature for all the compositions.</i> | 117 |
| A2.2 | <i>Relative atomic percentages as determined by EDX, ICP-OES, and XPS survey spectra of B1.1FO, B1.05FO, BFO, BF1.05O and BF1.1O.</i> | 120 |
| A3.1 | <i>Summary of the compositional variations and nomenclature for all the compositions.</i> | 125 |
| A3.2 | <i>Relative atomic percentages as determined by EDX, ICP-OES, and XPS survey spectra of NFO, ZFO, NZFO and NZFON nanoparticles.</i> | 126 |
| A4.1 | <i>Relative atomic percentages as determined by EDX, ICP-OES, and XPS survey spectra of NFO1, NFO2, and NFO3 nanoparticles.</i> | 131 |
| A4.2 | <i>Details of the relative percentage of Fe²⁺/Fe³⁺, Fe³⁺(O_h/T_d), oxygen vacancies, and Ni²⁺(O_h/T_d) as determined by the integral peak area of XPS spectra for NFO1, NFO2, and NFO3 nanoparticles.</i> | 131 |
| A4.3 | <i>Details of the electrochemical performance of NFO2 in three-electrode configuration</i> | 136 |
| A4.4 | <i>Details of the EIS fitting parameters in Figure 6.4 (c)</i> | 136 |
| A5.1 | <i>Summary of the compositional variations and nomenclature for all the compositions. Relative atomic percentages as determined by ICP-OES, of pristine MFO and MFO-Se nanoparticles.</i> | 137 |
| A5.2 | <i>Details of the relative percentage of Fe²⁺/Fe³⁺, Mn²⁺/Mn³⁺ oxygen vacancies as determined by the integral peak area of XPS spectra for pristine MFO and Se doped MFO Samples.</i> | 137 |
| A5.3 | <i>Bond length, coordination number and disorder factor obtain through EXAFS fitting at Se K-edge. The x parameter defines the substitutional site percentage.</i> | 138 |
| A5.4 | <i>Comparison of electrochemical performance parameters for MnFe₂O₄-based electrodes reported in the literature. *E_d and P_d are mentioned for 2-electrode system.</i> | 142 |

ABBREVIATIONS AND SYMBOLS

| | |
|------------------|--|
| PEC | Photoelectrochemical |
| PEPS | Photoelectrochemical Photocurrent Switching |
| PV | Photovoltaics |
| STH | Solar to Hydrogen |
| OER | Oxygen Evolution Reaction |
| HER | Oxygen Evolution Reaction |
| VBM | Valence Band Maxima |
| CBM | Conduction Band Maxima |
| LSV | Linear Sweep Voltammetry |
| ASC | Asymmetric Supercapacitor |
| B.E. | Binding Energy |
| CL | Core Level |
| CV | Cyclic voltammetry |
| DTA | Differential Thermal Analysis |
| EDLC | Electrochemical double-layer capacitance |
| EESS | Electrochemical energy storage systems |
| EIS | Electrochemical impedance spectroscopy |
| FESEM | Field Emission Scanning Electron Microscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GCD | Galvanostatic Charge Discharge |
| MO | Metal oxide |
| NS | Nanostructures |
| O _{vac} | Oxygen Vacancy |
| OCP | Open circuit potential |
| SAED | Selected Area Electron Diffraction |
| STEM | Scanning Tunneling Microscopy |
| SEM | Scanning Electron Microscopy |
| EIS | Electrochemical Impedance Spectra |
| MS | Mott-Schttky |
| IPCE | Incident Photon to current conversion efficiency |
| BFO | Bismuth Ferrite |
| NFO | Nickel Ferrite |
| ZFO | Zinc Ferrite |
| MFO | Manganese Ferrite |
| Ar | Argon |
| SC | Supercapacitor |
| SSA | Specific Surface Area |
| TEM | Transmission Electron Microscopy |
| XRD | X-ray Diffraction |
| XPS | X-ray Photon Electron Microscopy |

| | |
|--------------|--|
| C_a | Areal Capacitance |
| E_d | Energy Density |
| P_d | Power Density |
| C_{sp} | Specific Capacitance |
| h | hour |
| min | minute |
| s | second |
| g | gram |
| eV | Electron volt |
| °C | degree centigrade |
| M | molar |
| R_{ct} | charge transfer resistance |
| R_s | solution resistance |
| σ | Warburg coefficient |
| t | time |
| V | voltage |
| V_{drop} | voltage drop/IR drop |
| ϵ_0 | permittivity of vacuum |
| ϵ_r | relative dielectric constant |
| WSC | Width of Space Charge |
| E_f | Fermi Level |
| RHE | Reversible Hydrogen Electrode |
| SHE | Standard Hydrogen Electrode |
| UPS | Ultraviolet Photoelectron Spectroscopy |