Novel earth-abundant and highly efficient electrocatalysts for hydrogen and oxygen production

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**NOVEL EARTH-ABUNDANT AND HIGHLY EFFICIENT
ELECTROCATALYSTS FOR HYDROGEN AND OXYGEN PRODUCTION**

JEAN MARIE VIANNEY NSANZIMANA

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2019

**NOVEL EARTH-ABUNDANT AND HIGHLY EFFICIENT
ELECTROCATALYSTS FOR HYDROGEN AND OXYGEN PRODUCTION**

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School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University in partial fulfilment
of the requirement for the degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

11 April 2019

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Date

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Jean Marie Vianney Nsanzimana

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

11 April 2019

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Date

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Prof. Wang Xin

Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as J. M. V. Nsanzimana, Y. Peng, Y. Y. Xu, L. Thia, C. Wang, B. Y. Xia, and X. Wang, An Efficient and Earth-Abundant Oxygen-Evolving Electrocatalyst Based on Amorphous Metal Borides. *Advanced Energy Materials* 8, 1701475 (2018). DOI: 10.1002/aenm.201701475.

The contributions of the co-authors are as follows:

- Prof Wang suggested the material's domain and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof. Xia, Xu, and Dr. Wang.
- Dr Thia assisted in the manuscript editing.
- I performed all the laboratory work at the School of Chemical and Biomedical Engineering. I analyzed the data as well.
- All sample preparation, structure, and electrochemical characterization was conducted by me.
- Peng assisted in the collection of the X-ray diffraction data.

Chapter 4 is published as J. M. V. Nsanzimana, Y. Peng, M. Miao, V. Reddu, W.

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The contributions of the co-authors are as follows:

- Prof Wang provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Miao and Prof. Xia.
- I performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- Sample preparation and electrochemical characterization was conducted by me.
- All microscopy characterization was conducted by me with the assistance of Dr Wenyu and Reddu in the Facility for Analysis, Characterization, Testing and Simulation.
- Prof H. Wang performed the density functional theory calculations.
- Peng assisted in the collection of the X-ray diffraction data.

Chapter 5 is published as J. M. V. Nsanzimana, V. Reddu, Y. Peng, Z. Huang, C. Wang and X. Wang, Ultrathin Amorphous Iron–Nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production. *Chemistry – A European*

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The contributions of the co-authors are as follows:

- Prof Wang suggested the material's area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Reddu and Prof. C. Wang.
- I performed all the materials synthesis and electrochemical characterization at the School of Chemical and Biomedical Engineering. Performed scanning electron microscopy and transmission electron microscopy and conducted data analysis.
- Peng assisted for X-ray diffraction data collection in the at the School of Chemical and Biomedical Engineering.
- Dr Huang assisted in spectroscopy data interpretation.

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The contributions of the co-authors are as follows:

- Prof Wang edited the manuscript drafts.

- I wrote the drafts of the manuscript. The manuscript was revised together with Reddu, Prof. Yan, and Prof. C. Wang.
- I designed the project and performed all the materials synthesis and electrochemical characterization. Performed scanning electron microscopy and transmission electron microscopy and conducted data evaluation.
- Dangol, Dr Duo, and Dinh assisted for EDS pattern collection and HRTEM imaging in the Facility for Analysis, Characterization, Testing and Simulation.
- Peng assisted for X-ray diffraction data collection.
- Dr Huang performed the density functional theory calculations.

11 April 2019

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Abstract

Hydrocarbon fuels are a primary source of energy worldwide, but this resource is quickly becoming depleted, and carbon dioxide emissions from burning said fuel contribute greatly to global warming. Alternative clean energy sources are thus required for the development of a sustainable environment and society. The so-called ‘hydrogen economy’ is a promising candidate to provide green and sustainable energy due to its high energy density and carbon-neutral fuel. Water electrolysis has recently gained much attention as an environmentally friendly technology for hydrogen production. However, the occurrence of oxygen evolution reaction (OER) at the anodic electrode of water electrolyzer, a thermodynamically uphill reaction exhibiting sluggish kinetics, severely limits the overall efficiency of water splitting. OER is a critical challenge to be considered, not only for water electrolysis but also for other energy storage and conversion technologies. Currently, the state-of-the-art catalysts for both hydrogen evolution reaction (HER) and OER are noble metal-based materials. However, their high cost, poor long-term durability, and scarcity hinder application at an industrial scale. Thus, the development of economically viable materials for HER and OER is crucial and relevant to their easier deployment for large-scale applications in electrochemical energy storage and conversion technologies.

In the first part of this dissertation, an earth-abundant and efficient oxygen-

evolving electrocatalyst based on metal borides is presented. Amorphous nanoparticles were prepared by chemical reduction of metal ions with sodium borohydride in aqueous solution. This method allowed homogeneous incorporation of transition metals in nickel boride nanostructure which improved the electrochemical activity of the catalyst. The as-prepared metal boride materials outperformed the existing commercial precious metal-based catalyst (Ir/C) for OER and for overall water splitting. In addition, multimetallic borides outperformed monometallic borides due to the synergistic effect from well-distributed transition metal constituents.

In the second part of this dissertation, an earth-abundant tungsten–nickel alloy electrocatalyst for superior hydrogen evolution was developed and deployed as an electrode without an organic binder. The electrode was prepared by a hydrothermal process followed by annealing in the presence of H₂ environment. The as-prepared electrode displayed bifunctional application both for HER and OER. Owing to the excellent electrocatalytic performance arising from the synergistic effect of tungsten–nickel interaction through d-orbital electron transfer, the as-prepared material was comparable to some of the best tungsten-based HER electrocatalysts. The lower adsorption energy of water molecules and a small Gibbs free energy of hydrogen adsorption on tungsten atoms, as measured from DFT calculations, revealed favorable water electrolysis kinetics.

Thirdly, in order to boost the electrochemical performance of unsupported metal borides studied in the first piece of work, a practical approach for incorporating metal boride nanosheets onto a highly conductive substrate is presented. The developed material displayed better oxygen evolution activity compared to the unsupported metal borides and advanced stability in harsh alkaline electrolytes. A synergistic effect between highly abundant catalytically active sites and the 3D porous substrate improved the electron transport arising from the presence of highly negative boron and the high conductivity of the substrate, resulting in an outstanding electrocatalytic activity. The results of this work showed an effective method to boost the electrochemical performance of metal borides by supporting them on a highly conductive substrate.

Inspired by (1) the facile preparation of metal borides by reducing metal ions in aqueous solution as presented in the first and third parts, and (2) the possibility of reducing graphene oxide by the same reducing agent used in these experiments, a fast and simple method of synthesizing amorphous ternary metal borides while simultaneously reducing the graphene oxide (GO) sheets was developed in the fourth part of this thesis. The as-prepared hybrid material exhibited outstanding OER performance and stability as compared to the pristine catalyst of the same composition under prolonged OER operation. In 1.0 M KOH, only 230 mV was required to afford a current density of 15 mA cm^{-2} with a small Tafel slope of 50 mV dec^{-1} . This electrocatalytic performance was also much better

compared to the commercial RuO₂ catalyst. DFT calculations suggested that the in situ formation of MO_xH_y during electrochemical activation acted as active sites for water oxidation. The superior OER activity of the as-prepared catalyst was attributed to (i) its unique amorphous structure to allow abundant active sites, (ii) synergistic effect of constituents, and (iii) strong coupling of active material and highly conductive rGO.

Finally, the last chapter summarizes the results of these projects and proposes an outlook for future works based on them.

Keywords: earth-abundant, metal boride, alloy, electrocatalyst, hydrogen evolution reaction, oxygen evolution reaction, synergistic effect

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List of Abbreviations

AC	Alternating Current
BET	Brunauer-Emmett-Teller
CNT	Carbon Nanotube
CO ₂	Carbon Dioxide
CV	Cyclic Voltammetry
DFT	Density Functional Theory
DI	Deionized
DIW	Deionized Water
ECSA	Electrochemical Active Surface Area
EDX	Energy-Dispersive X-Ray Spectroscopy
EIS	Electrochemical Impedance Spectrum
eV	Electron Voltage
FESEM	Field Emission Scanning Electron Microscopy
GCE	Glass Carbon Electrode
GO	Graphene Oxide
HAADF-STEM	High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy
HER	Hydrogen Evolution Reaction
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
<i>iR</i> -corrected	Ohmic Drop Compensated
LSV	Linear Sweep Voltammetry
M	Molarity
MoS ₂	Molybdenum Disulfides
OER	Oxygen Evolution Reaction

PAW	Projector Augmented Wave
PBE	Perdew–Burke–Ernzerhof
PCET	Proton-Coupled Electron Transfer
pH	Potential Hydrogen
RDE	Rotating Disk Electrode
RDS	Rate-Determining Step
rGO	Reduced Graphene Oxide
RF	Roughness Factor
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TOF	Turnover Frequency
TW	Terawatt
VASP	Vienna ab Initio Simulation Package
WO ₃	Tungsten Trioxide
WO _{3-x}	Oxygen-Deficient Tungsten Oxide
Wt%	Weight Percentage
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
ΔG	Gibbs Free Energy Change

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Chapter 1. Introduction and Scope of the Thesis

1.1. Introduction

With current energy demands surging and a resultant increase in the emission of carbon dioxide, which is a major contributor to global warming, alternative and highly efficient power sources are urgently needed. Electrochemical energy conversion and storage technologies, including rechargeable metal–air batteries, regenerative fuel cells, and water splitting, have received intense global interest for clean energy generation and efficient energy storage.¹⁻⁴ In this context, electrochemical water splitting is considered a sustainable and green technology for storing energy in the form of chemical bonds from renewable but intermittent sources, such as wind and solar energies.⁵ However, it is constrained by the thermodynamically unfavorable OER, a sluggish kinetic reaction which contributes significantly to the loss of energy efficiency for water splitting.⁶ Consequently, mass production is not economically feasible yet, due to the large energy consumption. Thus, the efficiency must be improved, while the overpotential of the overall electrolysis reaction must be reduced. Therefore, developing a highly effective and robust electrocatalyst for the OER is crucial to increase the efficiency of water electrolysis system. Figure 1-1 illustrates an ideal water electrolysis technology system.

Figure 1-1. Scheme of ideal water electrolysis technology coupled to renewable electricity sources.

Currently, precious metal-based materials, such as Platinum (Pt)-based catalysts, are the best candidates for HER,⁷ as they have near-zero overpotential requirement. However, these materials lose considerable catalytic performance during operating condition.⁸ Again, noble metal-based materials, such as Ruthenium (Ru)-, and Iridium (Ir)-, are the benchmark electrocatalysts for OER.⁹ Unfortunately, both are physically and chemically degradable within a relatively short period of time. In addition, their low natural abundance and higher cost make them impracticable for widespread applications. Hence, using these electrocatalysts to produce H₂ is not as viable and cost-effective as fossil fuels which are the current widely used energy resources. In the case of HER, highly

efficient and low-cost catalyst metal chalcogenides, nitrides, carbides, borides and phosphides, and lastly metal-free materials, have gained interest recently as candidates which can replace Pt.¹⁰ On the other hand, cost-effective and earth-abundant materials such metal-based and metal-free are promising OER catalysts. Nonetheless, there is a need for further material development to better understand the control of synthesis towards more efficient noble-metal free electrocatalysts.

Despite a recent boost in developing cost-effective electrocatalysts for half-reactions of water electrolysis, the activity is often limited due to inefficient utilization of electrochemically active sites, limited charge transfer, poor surface area, conductivity, and stability.¹¹ To promote the efficiency of electrocatalysts, developing materials with optimized structural features to overcome the as-mentioned limitation, is critical. Amorphous materials which are also known as glassy materials, are generally characterized by unique structural disorder or short-range order and metastable structure with abundant defects, and as a consequence exhibit flexible properties such as versatility in composition and structure, and superior charge transfer.¹² Furthermore, compared to crystalline materials, the amorphous ones show good elasticity, high strength, outstanding chemical stability, and a large surface area implying a larger number of active sites are available for surface reaction.¹³ For instance, some features of amorphous materials are critically important for surface reactions including half-reaction of water electrolysis. These include, (i) large number of structural defects facilitating

adsorption of intermediates and the diffusion of electrolyte allowing more available sites for reactions,¹⁴ (ii) short-range order promoting facile in-situ transformation which optimizes the active sites, especially for the catalysts which undergo transformation during water oxidation,^{15, 16} (iii) easy pathways for intercalation/deintercalation of charges which can improve charge-transfer rate and electronic conductivity during electrolysis,¹⁷ and (iv) flexible structure allowing electrochemical durability.¹⁸ Together with other features beyond crystalline materials, it is desirable to develop amorphous earth-abundant transition metals based electrocatalysts in which surface groups could undergo conversion into electrochemically active sites during OER, such as metal non-oxides and metal-metalloids materials.

1.2. Scope of the Thesis

The focus of this thesis is to develop highly efficient earth-abundant materials for potential application as electrodes in water splitting reactions, prepared by facile methods.

Chapter 1 is a brief background on the need to develop earth-abundant materials for electrochemical water splitting.

Chapter 2 focuses on the fundamentals of water splitting electrochemistry, reaction mechanisms, literature review and describes challenges in developing electrocatalytic materials.

In chapter 3, a one-step synthesis of metal borides by chemical reduction of transition metals in aqueous solution is studied. We developed an effective strategy to boost the oxygen-evolving catalytic activity of metal borides. The prepared metal boride nanoparticles were characterized by structural analysis techniques, followed by water oxidation testing in alkaline electrolytes.

Chapter 4 provides insights into the synthesis of a binary metal alloy on a highly conductive support, as a potential electrode for bifunctional activity. Besides the electrochemical performance study of this self-standing electrode for OER and HER in alkaline solution, the HER activity was also tested in acidic medium.

In chapter 5, based on the results and inferences gathered from chapter 3, a simple and one-pot chemical reduction synthesis method was adopted to design a self-supported electrode. To avoid the use of binders and aliquot preparation step, a self-supported electrode of ternary boride nanosheet was prepared and its water oxidation activity was examined in alkaline solution. The optimization of this ternary boride electrode was conducted by varying the iron to nickel ratio in the aqueous solution.

Chapter 6 presents an effective one-step, rapid reduction of graphene oxide with simultaneous hybridization with metal boride. This method was studied for both binary and ternary borides by simply varying the metal ratio in aqueous

solution. The hybrid was prepared by a facile preparation method and was tested on a glassy carbon electrode for OER in alkaline electrolyte.

The last chapter of this dissertation summarizes the findings and recommends future works based on the results presented in this thesis.

Chapter 2. Literature Review

2.1. Fundamentals on Electrochemical Water Splitting

The process of electrically splitting water into oxygen (O_2) and hydrogen (H_2) gases is known as water electrolysis. Even though water electrolysis was known as a technique to produce H_2 at the cathodic electrode (Equation 1) and O_2 at the anodic electrode (Equation 2) in the 19th century (Figure 2-1),^{19, 20} it was in the last few decades that it received tremendous attention. One of the reason is that the overall water splitting (Equation 3) is thermodynamically unfavorable ($\Delta G = 237.2 \text{ kJ/mol}$),²¹ and as consequence, energy in the form of overpotential is required to drive this process.

Figure 2-1. On the left, William Nicholson and Anthony Carlisle are observing water electrolysis. They took a small tube, which was mounted vertically and filled it with water. Then they sealed it and inserted a platinum wire which was connected

to one of the two terminals of a voltaic pile at either end. As the tips of the wires gradually advanced towards each other, they observed that a stream of bubbles was produced from each tip. One was found to be of oxygen, and the other was found to be that of hydrogen. On the right, is the scheme of a water electrolyzer where water is oxidized into oxygen on the anodic electrode (gray spheres) and hydrogen evolution takes place on the cathodic electrode (green spheres). Reprinted with permission from Ref.²⁰ (Copyright © 2018, American Chemical Society).

In alkaline solutions (pH = 14) the water electrolysis equations are:

where E°_{c} and E°_{a} are the equilibrium half-cell potentials at standard conditions of 25 °C and 1 atm at cathode and anode, respectively.

Combining this half reaction pair yields the overall decomposition of water into O₂ and H₂ and the equilibrium potential is 1.23 V vs RHE.¹⁹

The water electrolysis is regarded as a promising candidate for hydrogen production which has been agreed to be a clean fuel of the future as it is a carbon-free energy source. Although there are several concerns for hydrogen economy

such as delivery, storage, safety, and hazard risk assessment, the capital and maintenance costs of hydrogen production by water electrolyzers are at the bottleneck of this green technology. Over the last few years, there has been a tremendous interest in developing a cost-effective water electrolysis system. This is revealed by considering the number of publications on half-reactions of water electrolysis published each year (Figure 2-2).²² Despite this great interest, a small proportion (4%) of hydrogen in the market is currently being produced by water electrolysis, while the remaining percentage is produced from fossil fuel-based sources which eventually emit CO₂ to the atmosphere.²³ This is mainly due to the difference in cost of hydrogen production. For instance, the capital cost for Alkaline Electrolysis Cells (AEC), a widely used carbon-free water electrolysis technology, is estimated to be around two to three times more expensive than steam methane reformers (SMR), the carbon-based incumbent technology for hydrogen.²⁴ This manufacturing cost of water electrolysis system and its operating cost can be further reduced by using cost-effective and highly efficient electrocatalysts with a huge current density at a reduced overpotential, thereby reducing the electricity consumption during hydrogen production.

Figure 2-2. Statistical histogram of the number of scientific reports on half-reactions of water electrolysis from 2005 to 2017. Reproduced with permission from Ref.²² (Copyright © 2019, The Royal Society of Chemistry).

To commercially exploit this technology, large actual cell voltages of 1.7–2.1 V compared to ideal reversible cell potential needed to split water (1.23 V at 25 °C and 1 atm required to initiate the water electrolysis) must be reduced implying that the large power consumption caused by large overpotential should be avoided.²⁵ For instance, on an industrial scale, a higher current density of 200–400 mA cm⁻² requires even higher potential of 1.8–2.4 V for alkaline water electrolyzers designed with a highly efficient electrocatalyst.^{26, 27} This potential is proportional to the electricity consumption. For example, at current densities up to 0.3 A cm⁻² the electric energy consumption is between 4.1–4.3 kWh Nm⁻³ of H₂ due to the power losses arising from the large overpotential of both half-reactions of water electrolysis at electrodes and from the ohmic drop across the electrolyte.²⁸

Hence, the search for materials to reduce this overpotential is at the heart of the commercialization of water electrolysis. These materials must be scalable, efficient with long-term stability to overcome the challenges of state-of-the-art electrocatalysts used for water electrolysis in large scale application.

The OER is a reaction with sluggish kinetics, most likely due to the many intermediates required to accomplish the complete $4\text{H}^+/4\text{e}^-$ oxidation of water.²⁰ Thus, theoretically a higher electrode potential value (1.23 V vs H_2/H^+) required to initiate the water electrolysis is associated with the anodic reaction.^{19, 29} Hence, to make water electrolysis economically feasible, this energy consumption in the form of overpotential must be reduced by developing cost-effective and efficient. Consequently, a highly efficient catalyst is important during the electrochemical water splitting process. Two parameters, namely: (1) exchange current density (i_o) and (2) Tafel slope are very important to benchmark the electrocatalytic activity.³⁰ A low Tafel slope and a high i_o indicate an ideal and better electrocatalyst. The slope (b) in Equation 4 is known as Tafel slope which is the linear relationship between overpotential (η) and the logarithm of current density (j); where η is defined as the difference between the reversible potential and the operating potential.^{31, 32} Furthermore, Tafel slope can be used to understand a catalyst's kinetics.³³

$$\eta (E - E^0) = a + b \log j \quad (4)$$

2.1.1. Hydrogen Evolution Reaction

The production of H_2 at the cathodic electrode through water electrolysis is recognized as the hydrogen evolution reaction (HER). Theoretically, HER takes place in three possible steps: Volmer, Heyrovsky, or Tafel (Figure 2-3). It can either follow Volmer–Heyrovsky mechanism (Equations 5 and 6) or Volmer–Tafel mechanism (Equations 5 and 7).³⁴ In order to determine the rate-determining steps (RDS), Tafel equation (Equation 4) is a very useful method. If the Tafel slope is 120 mV dec^{-1} , it implies that the Volmer step is rate-determining while if the Tafel slope is 40 or 30 mV dec^{-1} , this suggests that Heyrovsky or Tafel reaction could be RDS.³⁵ For example, Pt demonstrates a high catalytic activity for HER. Its mechanism follows Volmer–Tafel mechanism with a Tafel slope of 30 mV dec^{-1} , which implies that the Tafel step is the RDS.

Figure 2-3. Schematic representation for HER mechanism.

HER in the acidic and basic electrolyte:

2.1.2. Oxygen Evolution Reaction

The thermodynamically unfavorable OER during water electrolysis involves a four-electron transfer process (Figure 2-4). Thus, its mechanism is more complex as compared to the pathways suggested for HER. In an alkaline solution, a series of elementary steps occurs according to following equations (where the asterisk indicates the surface adsorbed species):^{34, 36}

In acidic, the following reactions are applicable:

Figure 2-4. Conventional OER mechanism involving proton-electron transfers on the surface metal centers. A perovskite structure ABO₃ has been used as a

representative catalyst where the orange, green, and red spheres represent the A-site cations, B-site cations, and the oxygens, respectively. For binary oxides, only the terminating BO layer can be considered. Reproduced with permission from Ref.²⁰ (Copyright © 2019, American Chemical Society).

Primarily, water electrolysis has been used to produce H₂ rather than O₂ in technical applications. However, due to the sluggish kinetics and high η of OER at the anode which affects overall water splitting (OWS), more efforts have been devoted to the development of a more efficient electrocatalyst to improve OER.³⁷⁻⁴⁰ Hence, by using low-cost materials which can result into highly efficient electrocatalysts with outstanding stability, OER would lead to the cost reduction for the overall process. Thus, exploring and developing high-performance electrocatalysts ranging from metal-based to metal-free catalysts is a research topic which has attracted much interest in the last decades.

2.2. HER and OER Electrocatalyst

In an effort to reduce the η required to drive the water splitting, the materials which are being used can be grouped into three main categories.⁴¹ The first group consists of molecular catalysts which offer the advantage of studying the active sites.⁴² However, their stability is a major drawback for practical use. The second category is that of crystalline catalysts which are advantageous due to their structure. The constituent atoms show a well-defined long-range order on the

surface where the water splitting reactions occur. Due to their better stability in comparison to the molecular catalysts, they are promising materials for practical use.⁴³ The third class is that of the amorphous catalysts which are defined as materials whereby the active sites and atomic arrangements are not known. In some cases, they exhibit much better activity as compared to their corresponding molecular and crystalline analogs.⁴¹ One of the reasons for this is their large surface area which allows more number of exposed active sites for catalytic reactions. In the following section, major groups of materials for HER and OER have been briefly introduced.

2.2.1. HER Electrocatalyst

The HER electrocatalysts are usually identified and compared based on the volcano plot of exchange current density vs Gibbs free energy of adsorption of hydrogen (Figure 2-5).⁴⁴ The best catalyst for HER would have a Gibbs free energy close to zero (i.e., $\Delta G_H^0 \approx 0$), binding hydrogen neither too weakly nor too strongly.⁴⁵ From this plot, other materials can be benchmarked against the best HER electrocatalyst, which is the Pt metal.

Figure 2-5. A volcano plot of exchange current density vs Gibbs free energy of adsorption of hydrogen on pure metals and MoS₂ catalysts. Reproduced with permission Ref.⁴⁴ (Copyright © 2019, American Association for the Advancement Science).

Despite the superior activity of the Pt catalyst for HER, it exhibits poor stability. Thus, non-precious metal alloys and metal–nonmetals based catalysts such as chalcogenides, phosphides, carbides, borides, and nitrides have emerged as alternative materials. A variety of these materials ranging from single metal to multiple metal-based electrocatalysts have been studied and some of them show activity comparable to Pt catalyst.⁴⁶ The improved electrocatalytic activity of these active materials was found to depend on either metal or nonmetal element and/or on highly conductive support materials such as graphene, carbon cloth, and carbon nanotubes.³⁵ In the following paragraphs, competent HER materials toward the replacement of Pt catalyst are summarized.

2.2.1.1. Metal Chalcogenides

Among metal chalcogenides, molybdenum sulfides, especially disulfide (MoS_2), have emerged as promising earth-abundant materials for making electrochemical production of hydrogen possible.⁴⁷ This is due to its hydrogen-evolving activity and superior stability during water reduction operation. However, their poor conductivity and lesser exposed HER active sites hinder their deployment for a widespread application. To address these challenges, a great effort is being made to (1) increase the catalytic activity of the active sites, such as via metal hybrids,⁴⁸ (2) increase the number of active sites of the catalyst via morphology control such as designing thin layered/nanostructured catalysts which leads to high density of exposed edges,⁴⁹ and (3) improve the electrical contact to these sites via support on highly conductive and high surface area substrates.⁵⁰ For example, very recently, an ultrathin MoS_2 nanosheet/rGO hybrid was found to overcome high electrical resistance between the layers in conventional MoS_2 , which hampers the bulk charge transfer.⁵⁰ As a result, this hybrid only required an overpotential of 66 mV to afford 10 mA cm^{-2} . Despite this progress on improving the performance of MoS_2 , an effort to achieve highly preferred single layered ultrathin MoS_2 nanosheets is still required.

Furthermore, other metal sulfides, such as tungsten sulfide (WS_x), have shown catalytic activity towards HER.⁵¹ The morphology of tungsten sulfide is also crucial for catalytic activity and to further improve its catalytic performance, it can be supported

on high conductive substrates, such as carbon-based substrates, to form hybrid materials. For example, on a carbon substrate, ultrasmall WS_x nanoclusters were found to exhibit advanced HER activity compared to WS_2 nanoplates. It was revealed that a larger density of active bridging S_2^{2-} sites of the former compared to the latter was a contributing factor.⁵² It is crucial to note that even though the synthesis of multimetallic systems boosts HER activity, these materials should be systematically designed to tailor the catalytic properties. In some cases, a multimetal–nonmetal catalyst has shown a poor performance compared to its corresponding single metal-based catalyst. For instance, in one systematic study on metal chalcogenide's (ME_2 , where M stands for Ni, Fe, and Co, E for S and Se) films grown on glassy carbon electrodes, ternary iron cobalt sulfide ($\text{Fe}_{0.43}\text{Co}_{0.57}\text{S}_2$) showed superior HER activity compared to binary iron sulfide (FeS_2) and cobalt sulfide (CoS_2). However, ternary nickel cobalt sulfide ($\text{Ni}_{0.68}\text{Co}_{0.32}\text{S}_2$) exhibited poor hydrogen-evolving activity compared to corresponding binary NiS_2 and CoS_2 catalysts (Figure 2-6a).⁵³ Furthermore, binary cobalt selenide (CoSe_2) outperformed binary iron selenide (FeSe_2), binary nickel selenide (NiSe_2), and ternary nickel cobalt selenide ($\text{Co}_{0.56}\text{Ni}_{0.44}\text{Se}_2$) (Figure 2-6b,c). This exception to the generally accepted method for metal doping to boost the catalytic activity can be explained as the reactive states near the Fermi level are most responsible for the catalytic activity,⁵⁴ and as a result, the optimum activity was obtained for ME_2 ($\text{Fe}_{0.43}\text{Co}_{0.57}\text{S}_2$ and CoSe_2) in which the e_g band is partially filled.⁵³ Hence, their robust HER performance is likely due to the unique electronic structures.

Figure 2-6. Polarization curves of transition metal (a) disulfides and (b) diselenides films. c) Tafel slopes. Reprinted with permission from Ref.⁵³ (Copyright © 2019, The Royal Society of Chemistry).

2.2.1.2. Metal Phosphides

Besides an interest in metal chalcogenides, metal phosphides have also received attention as hydrogen-evolving materials. Due to the low cost, abundance, and high efficiency of transition metals, transition metal phosphides are ideal HER catalysts.⁵⁵ The catalytic origin of advanced HER of phosphides was investigated on nickel phosphide (Ni₂P) and it was suggested that the presence of (1) a weak “ligand effect”

due to Ni-P bonds facilitates the dissociation of molecular H₂, (2) "ensemble effect" of P decreases the number of active sites on the surface which prevents poisonous effects due to high coverage, and (3) P sites provide a moderate bonding strength to the evolved hydrogen molecule.⁵⁶ Besides these factors that contribute to HER catalytic activity, the effect of morphology was also considered. For example, cobalt phosphide (CoP) nanotubes outperformed corresponding CoP nanoparticles which implied that the activity is also associated with the structure.⁵⁷ To achieve a current density of 10 mA cm⁻², the former required an overpotential of 129 mV while the latter one needed 297 mV. Additionally, it was found that metal phosphide nanosheets showed a better activity compared to films due to more accessible sites for protons and faster mass diffusion.⁵⁸

In addition to the structure of metal phosphides which acts as a key contributing factor for their HER performance, metal doping is an established technique to boost the catalytic activity. Based on theoretical and experimental models, it was found that a ternary iron-cobalt phosphide (Fe_{0.5}Co_{0.5}P) alloy had near-optimal ΔG_H at the top of transition metal phosphides' volcano plot (Figure 2-7) and the activity was better as compared to corresponding binary phosphides (FeP and CoP).⁵⁹ To further boost the electrochemical performance of metal phosphides, these two contributing factors (morphology and metal doping) can be combined to prepare a self-standing electrode. For instance, in addition to one-dimensional nanowire and two-dimensional nanosheets of CoNiP on 3D nickel foam, the highly conductive substrate was also a contributing

factor to provide a large surface area. A simple hydrothermal technique was used to prepare $\text{CoNi}(\text{OH})_x\text{F@NF}$ electrode followed by sintering in the presence of a phosphorous source. The as-prepared self-standing electrode (CoNiP@NF) required an overpotential of 60 mV to deliver 10 mA cm^{-2} in an acidic electrolyte.⁶⁰

Figure 2-7. Activity volcano plot for transition metal phosphides. Reprinted with permission from Ref.⁵⁹ (Copyright © 2019, The Royal Society of Chemistry).

2.2.1.3. Metal Carbides and Nitrides

Metal carbides have also been explored for their potential to replace Pt catalyst for HER. Some of the engineering approaches for designing and improving the hydrogen-evolving activity, including nanostructure synthesis, optimization of hydrogen binding energy, interaction with the supporting material, and exploitation of

hybrid structures, are also applicable to metal carbides.⁶¹ For example, a hybrid of bimetallic cobalt molybdenum carbide (CoMoC@C) prepared by one-step pyrolysis exhibited HER activity close and superior to that of 20% Pt/C catalyst under both low pH (0–1) and over a broad pH range (2–14) at a given overpotential.⁶² The activity was not only attributed to CoMoC core but also to the presence of an outer N-doped C shell capable of influencing the H⁺ adsorption behavior. Similar to metal phosphides, the cobalt selenide (CoSe₂) nanoparticles outperformed the film CoSe₂ at the same active material loading.⁵³

As the presence of nonmetal elements, such as N and C, in metal–nonmetal catalysts play an important role to influence the nature of the electronic structure of the materials, the combination of more than one nonmetal element was found to be a special approach to improve the HER performance. Based on theoretical calculations, the electronic structure of carbides and nitrides involves: (1) metallic bonding related to metal–metal bonds, (2) ionic bonding from charge transfer, and (3) covalent bonding between metal and nonmetal atoms.⁶³ Importantly, the direction and the amount of charge transfer are determining factors for the electronic structure.⁶⁴ As a consequence, the design of metal carbonitrides (C and N) would show a variety of electronic structures between metal carbides and nitrides. For example, the hybrid Ni–C–N nanosheets prepared by a nitrogenation/exfoliation process showed comparable catalytic activity to a Pt catalyst in an acidic electrolyte.⁶⁵ The doping of N in tungsten carbide (WC₂) was found to enhance the hydrogen-evolving activity by decreasing

hydrogen binding energy.⁶⁶ This trend of advanced activity observed on transition metal carbonitrides has also been reported for transition metal phosphosulphides (P and S), sulfoselenides (S and Se), and other binary nonmetals such as amorphous MoS_xCl_y .⁶³

2.2.1.4. Metal-free and Metal–nonmetal Hybrids

Furthermore, just as the presence of nonmetals (N, C, B, S, Se, and P) in metal–nonmetal catalysts is crucial to influence their catalytic activity, metal-free hydrogen-evolving catalysts including doped graphene and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) have also been reported. The combination of metal-free material is found to be an effective method to modify the H-adsorption energy as it is more positive (≈ 0.8 eV) for graphene while it is more negative (-0.5 eV) for $\text{g-C}_3\text{N}_4$, which implies an unfavorable adsorption/desorption process and hence, poor HER performance. For example, $\text{g-C}_3\text{N}_4$ @graphene showed promising HER activity which was comparable to metal-based electrocatalysts due to abundance of exposed edges, defects, and fast electron transport.⁶⁷ Very recently, the presence of three nonmetals in borocarbonitrides ($\text{B}_x\text{C}_y\text{N}_z$) was found to be an important factor as it allowed easy tunability of bandgap, provided delocalized π -electrons, and active sites provided by B- and N-doping could lower the hydrogen adsorption/desorption energies close to zero, resulting in improved HER activity.⁶⁸ As the activity of these carbon-materials still needs improvement, the nonmetal doped carbon nanomaterials are used in hybrids with metal-based catalysts.⁶⁹

Alternatively, mixing HER active material with carbon nanomaterials boosts the electrocatalytic activity, thereby assisting in conductivity. As metal borides are lesser investigated for HER compared to the aforementioned metal–nonmetal catalysts, the carbon nanomaterial impregnation was found to improve their electrocatalytic property. For example, amorphous cobalt boride nanoparticles were found to afford hydrogen evolving current density of 10 mA cm^{-2} at an overpotential of 328 mV compared to Pt/C. However, this overpotential was reduced to 127 mV when the nanoparticles were impregnated with nitrogen-doped graphene.⁷⁰ As metal borides have emerged recently for water electrolysis application, their HER activity, such as of those prepared by chemical reduction of metal ions in aqueous solution, is still poor when compared to Pt catalyst. On the other hand, molybdenum borides prepared by solid-state methods show better activity towards HER rather than OER.⁷¹ The previously discussed HER performance of metal–nonmetal materials arose from the structure, morphology, size, composition, and highly conductive supporting substrates. Hence, the synthesis methods are of crucial importance towards the synthesis of novel metal–nonmetal catalysts.

2.2.1.5. Metal alloys

Metal alloy-based materials such as Ni-, Co-, Fe- alloys have been studied extensively for HER, mainly due to their electrochemical and mechanical properties along with high corrosion resistance.⁷² The boosting of hydrogen-evolving catalytic activity in metal alloys is mainly due to the modulation of free

energy of adsorbed hydrogen intermediates compared to pure metals, and thus, the metal alloys exhibit better activity compared to corresponding pure metals. For example, a nickel alloy would create a variety of adsorption sites which have near-optimal hydrogen binding energy which are not available in pure nickel.⁷³ It was found that the HER performance of binary nickel–silver alloy was significantly better compared to pure metal (Figure 2-8). Based on theoretical calculations, the HER activity correlated with the nickel to silver ratio in the alloy and the activity of optimized alloy $\text{Ni}_{0.75}\text{Ag}_{0.25}$ was approximately twice that of pure nickel. This was attributed to the availability of a variety of adsorption sites which are near to Pt in the volcano plot (Figure 2-5).

Figure 2-8. Above, combined theoretical-experimental volcano plot for most-active sites for Ni–Ag alloy. Below, selected images of the calculated surface structures are shown. Reprinted with permission from Ref.⁷³ (Copyright © 2019, The Royal Society of Chemistry).

Furthermore, a binary nickel–molybdenum alloy is known for its high hydrogen evolution activity in alkaline electrolytes due to its superior microscopic porosity and advanced intrinsic catalytic activity.⁷³ The method of tuning the hydrogen evolution activity applicable for binary alloys can also be extended to ternary alloys which further reduces the hydrogen binding energy and brings it

closer to Pt (located at the top of volcano plot).⁷⁴ For instance, a nickel–molybdenum–cobalt alloy was found to exhibit outstanding HER activity compared to pure nickel catalysts (~20 fold higher than Ni).⁷⁵ Overall, in the literature, the HER activity of metal alloys has been attributed to reduction of charge transfer resistance, better mass transport through catalyst pores due to well-developed surface area, metal alloy synergism, and weakened hydrogen binding energy.^{73, 75} Even though some of these hydrogen-evolving materials have been projected to replace a Pt-based catalyst, there is still a need for the development of hydrogen-evolving materials that are practically applicable in large scale production.

2.2.2. OER Electrocatalyst

The OER which is involved in many renewable energy technologies limits the efficiency of water splitting in both photo-driven and electro-driven water electrolysis, mainly due to its sluggish kinetics arising from four sequential complex proton-coupled electron-transfer (PCET) steps (Figure 2-9),⁷⁶ which complicate the electron transfer kinetics.⁷⁷ To boost the OER kinetics, a variety of noble metal-free, supported and non-supported earth-abundant electrocatalysts such as metal oxides/hydroxides, metal–nonmetals, and finally, metal-free catalysts have been explored.⁷⁸

Figure 2-9. The free energies of the intermediates on O^{*}-covered RuO₂ at three different potentials ($U = 0$, $U = 1.23$, and $U = 1.60$ V) are depicted. At the equilibrium potential ($U = 1.23$ V) the reaction steps are uphill in free energy. Reproduced with permission from ref.⁷⁶ (Copyright © 2019, Elsevier B.V.).

2.2.2.1. Metal Oxides and Hydroxides

Fundamentally, an OER electrocatalyst should have high electric conductivity to facilitate electron transport in a complex four-step process in which the OER occurs.^{79, 80} Earth-abundant first-row transition metals have been known as promising candidates due to their higher electronic conductivity in comparison with metal oxide/hydroxide/oxyhydroxide counterparts. Among the metal oxide and (oxy)hydroxide electrocatalysts for OER, first transition metals' based catalysts such as Ni-, Fe-, and Co-derivatives have been widely explored for their oxygen-evolving activity.⁸¹⁻⁸⁴ Their catalytic activities are likely related to the OH-M^{2+ δ} bond strength ($0 < \delta < 1.5$) with the order of Ni < Co < Fe.⁸⁵ Furthermore, Trotochaude *et al.* found a similar trend where NiO_x was the best oxygen-evolving

catalyst followed by CoO_x followed by FeO_x catalyst.⁸⁶ These catalytic trends are associated with the binding energy of the reaction intermediates of metal oxides just as it is for other oxygen-evolving catalysts such as perovskites (Figure 2-10).⁸⁷ The best oxygen-evolving catalysts are at the top of the volcano plot and close to Ru- and Ir-oxides.

Figure 2-10. Activity volcano of theoretical overpotential for oxygen evolution vs the difference between the ΔG^0 of two subsequent intermediates ($\Delta G^0_{O^*} - \Delta G^0_{HO}$) for binary oxides (left) and perovskite oxide (right). Reproduced with permission from ref.⁸⁷ (Copyright © 2019, The Royal Society of Chemistry).

To boost the activity of these transition metal-based catalysts, doping with one or more metals has been found to be an effective method. Thus, binary and ternary metal oxides have been explored and they showed promising efficiency compared to single metal-based catalysts.^{79, 88} Among multimetal-based catalysts, iron-nickel based materials have been explored since iron can modulate the

electronic configuration of nickel oxide.⁸⁸⁻⁹⁰ Furthermore, due to the fact that almost all metal oxides are semiconductors with wide band gap or insulators, supporting metal oxides on highly conductive substrates or carbon nanomaterials have been studied and showed an improvement in electrocatalyst properties.

2.2.2.2. Metal-free and Molecular OER electrocatalyst

With the urgent global need for sustainable energy, carbon nanomaterials and nanotechnologies have paved a new avenue for the discovery of high-performance energy-conversion and storage devices.^{91, 92} In the field of catalysis, carbon nanotechnologies offer great promises due to their exceptional electrical, chemical, thermal and mechanical properties, tunable molecular structures, abundance, and strong tolerance to acidic/alkaline environments. As a result of this, carbon nanomaterials doped with heteroatoms such as N and P have been studied extensively as metal-free electrocatalysts.⁹³⁻⁹⁶ For example, the OER activity in N-doped graphene originated from the electron-withdrawing pyridinic N moieties as catalytically active sites in N-GRW.⁹⁷ Together with other findings, it was revealed that functionalized carbon nanomaterials are active due to the interplays of doped heteroatoms in the carbon nanomaterial structure.⁹² Furthermore, the functionalized sites and hydrophobic groups in these carbon nanomaterials enhance the interaction with water molecules and are thus more accessible to them for OER.⁹³ Additionally, carbon nanomaterials received a great role as support for molecular electrocatalysts.⁴² The molecular catalysts are studied due to their well-

known and fully exposed active sites to reactants. To name a few, manganese, ruthenium, and iridium are highly studied molecular catalysts for water oxidation.⁹⁸

2.2.2.3. Metal-nonmetals Materials

Recently, metal–nonmetals materials, which are referred to as OER pre-catalysts, such as metal chalcogenides, pnictides, and metalloids, have received an increasing interest among researchers for their application in the water oxidation process.^{99, 100} Though the catalytically active centers for metal–nonmetals catalysts are oxidized superficial metals rather than the metal–nonmetals themselves, they have been proven to evolve even more oxygen than their metal oxide/hydroxide counterparts.¹⁰¹⁻¹⁰³ These advanced electrocatalytic activities have been attributed to the following three features.¹⁰⁴ Firstly, the in situ transformation to metal oxides/hydroxides during water oxidation leads to high surface area nanostructures. Secondly, the high conductivity of some metal–nonmetals materials, such as metal chalcogens and phosphides, acts as the conductive scaffold for the active metal oxide/hydroxide species. Lastly, the synergistic electronic effects of different components formed by in situ transformations during electrochemical testing.

Besides metal chalcogenides and pnictides as metal–nonmetals catalysts for OER, metal alloys, such as a nickel-based alloy, show promising activity due to the feasibility of further tuning of their catalytic property.¹⁰⁵ In fact, Ni–Fe based

alloys are more advanced and are the most common OER catalysts employed in the industry.¹⁰⁵ Among others, the conversion of FeCoNi layered double hydroxide to the corresponding trimetallic alloy by calcination showed better activity compared to hydroxide precursors.¹⁰⁶ This reveals that the metal alloys' OER activity outperforms metal hydroxides in some cases. The metal alloys are susceptible to oxidation when exposed to air, though the severity would depend on the preparation method. Interestingly, engineering of a metal oxide layer is a well-established approach to improve the oxygen-evolving activity of metal alloy catalyst, as the metal oxyhydroxide is the active center for OER. For example, in situ etching of SiO₂ template from NiCo–SiO₂ composite film by potentiostatic electro-codeposition was found to lead to the formation of a NiCoO_x layer on NiCo alloy and this resulted in a superior OER activity whereby it delivered 100 mA cm⁻² at 326 mV.¹⁰⁷ Due to the in situ transformation to a composite of metal alloy and hydroxides/oxyhydroxides, (where the former accelerates electron transport while the latter acts as an active site) they are often unstable in alkaline solution.

From this perceptive, metal–metalloids have received a lot of interest mainly due to their expected stability in alkaline solution while keeping better electron transfer intact. Due to strong bonds and the formation of borates and phosphates on the surface, these materials show promising stability.⁷⁰ Especially, as the metal borides are very sensitive to preparation methods, the catalytic properties are results of carefully choosing a method to produce the product with

chemical properties of interest.¹⁰⁸ Among a variety of methods to prepare metal borides, chemical reduction of metal salts in aqueous media (aprotic or protic) by using a strong reducing agent, such as sodium or lithium borohydride (NaBH_4 or LiBH_4).¹⁰⁹ These metal borides are prone to undergo severe oxidation when exposed to air after the synthesis and thus, they are covered by metal oxides/hydroxides and oxidized-boron species leading to a core@shell (metal boride@metal oxide/hydroxide) structure (Figure 2-11).¹¹⁰ This surface oxidation does not have a detrimental effect on OER as the active sites for OER on metal–nonmetal catalysts are metal oxyhydroxides. The other method for metal borides preparation is solid-state synthesis, such as heat treatment of metal and boron powder,¹¹¹ metal chloride and sodium borohydride,¹¹² or boron.¹¹³ Metal–metalloid materials such as metal borides allow the synthesis of amorphous materials that undergo various phase and oxidation changes during water oxidation which facilitates the formation and breakage of chemical bonds, thereby potentially lowering kinetic barriers.⁴¹ Despite these advantageous features of metal–metalloids, it is just recently that there is a renewed interest in their electrocatalytic activity. Hence, the aim of this work was to study the facile and feasible methods to synthesize highly efficient electrocatalysts based on transition metal borides and metal alloys for water electrolysis reactions.

Figure 2-11. a) Ni 2p and b) B 1s XPS core-level spectra of Ni_xB minimally exposed to air (i) and after prolonged air exposure (ii). Reproduced with permission from ref.¹¹⁰ (Copyright © 2019, John Wiley and Sons, Inc.).

Chapter 3. An Efficient and Earth-Abundant Oxygen-Evolving Electrocatalyst Based on Amorphous Metal Borides

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3.1. Background Introduction

As discussed in chapter two, the OER is involved in many electrochemical energy technologies, including rechargeable metal–air batteries, regenerative fuel cells, and water splitting. However, this reaction is thermodynamically uphill and exhibits sluggish kinetics coupled with multiple electrons and protons; thus, it accounts for the major efficiency loss of the overall electrochemical process.²⁹ Due to the complex nature of OER, multimetal-based catalysts in most of the cases outperform single metal counterparts. Recently, various metal–nonmetal compounds materials have been reported to exhibit promising OER electrocatalytic activities.^{70, 114-116} This has been attributed to the charge transfer between different elements and the modified electronic structures, which consequently lowers the kinetic energy barriers of the electrochemical processes.^{117, 118} In this regard, to extend such applications on metal borides is reasonable, wherein metal borides

share certain properties with metal phosphides, such as bonding properties.¹⁰⁸ Recently, the application of monometallic borides such as cobalt boride, iron boride, and nickel boride as well as cobalt-borate-based graphene hybrid as the oxygen-evolving catalysts have been reported to exhibit promising electrocatalytic activity for OER in alkaline media.^{70, 110, 114, 119} However, multimetal–metalloid boron-based material, herein referred to as an amorphous quaternary metal boride, for simplicity, as oxygen-evolving electrocatalyst, reported to date is very limited. Thus, it is still of great interest to develop metal boride-based OER catalysts and further to explore their catalytic activities. The as-identified approach to enhance electrochemical OER activities in metal–metalloid material opens a new avenue in related applications for energy devices that involve OER such as water electrolysis and metal–air batteries.

Despite the complicated structure of amorphous material, well-characterized amorphous nanomaterial as oxygen-evolving material has received attention due to the unique properties such as higher catalytic selectivity and activity.¹²⁰ A great number of under-coordinated metal atoms, and hence abundant defects, in amorphous nanomaterial may provide more reactive sites at the catalyst surface, and as a result, facilitating the binding of hydroxyls and thus enhancing OER performance.¹⁵ Furthermore, these amorphous nanomaterials have attracted much attention in other electrochemical applications such as in pseudocapacitors, Li-ion batteries, sensors, and water oxidation.^{121, 122} In some studies, it was found

that amorphous multimetal–oxygen-evolving material exhibited higher electrochemical performance than the corresponding crystalline material when annealed.¹²³ Herein, we report an amorphous quaternary metal–boron-based catalyst (designated as Fe–Co–2.3Ni–B) with a higher OER electrocatalytic activity than commercial Ir/C (20 wt%) catalyst. Incorporation of more metals has been found to be an effective strategy for tuning the catalytic activity of metal–metalloid catalyst via charge transfer.¹⁰⁸ This study not only provides the effective metal boride electrocatalysts, but also elucidates the effective approach to boost the OER electrocatalytic property of the metal–boron-based materials, and thus promotes such materials to the energy applications in OER-related systems.

3.2. Experimental Section

3.2.1. Materials Synthesis

The amorphous metal–boron-based materials were prepared by reducing aqueous mixture containing metals precursor with a strong reducing agent, sodium borohydride (NaBH₄), which also acts as the boron source. The reduction of metal ions in an aqueous solution results into a precipitate of metal boride *via* the following reaction: $2\text{MCl}_2 + 4\text{NaBH}_4 + 9\text{H}_2\text{O} \rightarrow \text{M}_2\text{B} + 4\text{NaCl} + 12.5\text{H}_2 + 3\text{B(OH)}_3$ (Equation 16).^{70, 124} However, there are control parameters to ensure the occurrence of the reaction in equation 16, as the final product depends on preparation conditions.¹²⁵ Thus, controlling BH₄[−]/M ion ratio at three times, rapid

mixing, and anaerobic handling (during preparation and drying) are considered to ensure the formation of metal borides,¹⁰⁹ hence the as-prepared is referred as amorphous metal borides. The addition of reducing solution caused a lot of bubbles and the formation of black precipitate as the result of the reaction. The precipitates were washed subsequently with ultra-purified water and ethanol several times to remove excess ions and other undesired dissolved species such as Na^+ , and Cl^- ions. During washing, the precipitates were covered with liquid to avoid any direct contact with air. The as-prepared black precipitates were collected by vacuum filtration, taken in a tubular reactor and dried overnight at 45 °C in an argon (Ar) atmosphere to obtain the final stable black powders. The powders were collected for further analysis without any further treatment. All chemicals are used as received.

3.2.1.1. Synthesis of Binary Amorphous Metal Boride Powders

In a typical synthesis of binary metal boride (denoted as Co–B, Ni–B, and Fe–B), 10 mL of the precursor solution containing CoCl_2 (1.0 mmol, Sigma-Aldrich), NiCl_2 (1.0 mmol, Sigma-Aldrich), and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol, Sigma-Aldrich) were prepared in a three-neck flask, respectively. The reaction vessel was maintained at a lower temperature by using a water bath containing ice. The reducing solution containing NaBH_4 (Sigma-Aldrich) was also prepared in 0.1 M NaOH (Alfa Aesar), and afterwards added to the metal precursor aqueous solution by a syringe in the argon gas atmosphere. The NaBH_4 solution being a strong

reducing agent turned the aqueous solution black. The continuous vigorous mixing of this solution was maintained until the bubble stops. Then the precipitates were collected by centrifugation and washed subsequently with ultra-purified water and ethanol several times.

3.2.1.2. Synthesis of Amorphous Ternary and Quaternary Metal Boride Powders

The ternary and quaternary metal borides were prepared at the same conditions used in this study for monometallic boride catalyst. In a typical synthesis procedure of ternary metal-boron materials (denoted as Fe-2.3Ni-B and Co-2.3Ni-B, this ratio were used based on the fact that the highly quaternary metal boride was prepared in 1:1:2.3 for Fe:Co:Ni metal precursor in aqueous solution), a 10 mL precursor solution containing NiCl_2 (2.3 mmol) prepared in a three-neck flask was stirred about 30 minutes at lower temperature and in argon atmosphere. Simultaneously, the proper amount of CoCl_2 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, Sigma-Aldrich) was dissolved with respect to the desired molar ratio to the NiCl_2 precursor solution. After 30 minutes, the cobalt or iron precursor solution (10 mL) was added to the nickel precursor solution by a syringe with vigorous stirring accordingly. The reducing solution was added, and the precipitate was collected, washed and dried to obtain final ternary metal boride black powder. During washing, the precipitates were always covered with liquid to avoid direct contact with air. For amorphous quaternary metal boride optimization, the metal precursor

solution was prepared and mixed in the molar ratio: 1:1:1, 1:1:2.3, 1:1:4.6, 1:1: 9.0, 0.1:1:2.3, 1:0.1:2.3 for Fe–Co–Ni–B, Fe–Co–2.3Ni–B, Fe–Co–4.6Ni–B, Fe–Co–9.0Ni–B, 0.1Fe–Co–2.3Ni–B, and Fe–0.1Co–2.3Ni–B, respectively. These notations of the final products were designated according to the corresponding molar ratio of metals in the pre-catalyst solution. To extend the applicability of the reduced metal ions sources, Fe^{2+} was also used for highly efficient in the molar ratio of 1:1:2.3 for $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, CoCl_2 , and NiCl_2 . The conditions were maintained until the end of the stated period and the products were collected for further analysis without any further treatment.

3.2.1.3. Synthesis of Iron–Cobalt–Nickel Alloy

The iron–cobalt–nickel alloy was synthesized by using the procedure reported by Yang, Y. *et al.*¹²⁶ during synthesis of FeCo nanoplates. The hydrazine hydrate ($\text{NH}_2\text{--NH}_2 \cdot \text{H}_2\text{O}$) was used as a reducing agent to avoid any remaining boron residue that may be remained if the NaBH_4 is used for synthesizing metal alloy. Typically, 20 mL of precursor solution (solution A) was prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1 mmol, Sigma-Aldrich), CoCl_2 (1 mmol), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.3 mmol) under Ar atmosphere, a similar molar ratio for highly efficient metal boride synthesis. The reducing solution (solution B) was prepared by mixing NaOH (988 mg, Alfa Aesar) in 4 mL of $\text{NH}_2\text{--NH}_2 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich). After the addition of solution B to solution A by a syringe with continuous stirring, the reaction occurred and was witnessed by the appearance of

black colour. The mixture was maintained at 66 °C for a half-hour, and afterwards, the precipitates were collected by centrifugation. These products were washed with water and ethanol for three times, followed by drying at room temperature in the vacuum overnight.

3.2.2. Catalyst Characterization

The surface morphologies of the as-prepared metal boride powders were studied by field emission scanning electron microscopy (FESEM, JEOL JSM 6701F) equipped with energy dispersive X-ray spectrometry (EDS) which was used for elemental mapping, while JED 2300 EDS on JEOL JSM 6700F SEM is used for atomic composition. Furthermore, the transmission electron microscopy (TEM) images were taken from JEOL JEM 2100F at an accelerating voltage of 200 kV. Structural characterization was determined by recording the X-ray diffraction (XRD) patterns using the Cu K α radiation ($\lambda = 1.5414 \text{ \AA}$) in Bragg–Brentano configuration. The surface electronic states and composition of the as-prepared powders were carried out by X-ray photoelectron spectroscopy (XPS). XPS spectra were collected by a Kratos AXIS UltraDLD instrument equipped with a monochromatic Al K α (1486.71 eV) X-ray source and a hemispherical analyser.

3.2.3. Electrochemical Measurement

Electrochemical measurements of the as-prepared metal borides and commercial Ir/C catalyst (20 wt% Ir on Vulcan carbon black from Premetek Co.)

for comparison were conducted in a three-electrode cell using a rotating disk electrode (RDE, PINE Research Instrumentation) with an Autolab PGSTAT302 (Eco Chemie, Netherlands) potentiostat workstation equipped with electrochemical impedance spectroscopy (EIS) at room temperature. A platinum wire and Ag/AgCl (KCl saturated) are used as the counter and reference electrodes, respectively.¹²⁷ All the electrochemical measurements were conducted in O₂-saturated alkaline 1.0 M KOH electrolyte. The electrolyte was prepared by using potassium hydroxide pellets (semiconductor grade 99.99%, Sigma-Aldrich) and ultrapure H₂O (18.2 MΩ, Millipore).

Before loading the catalyst aliquot on GC electrodes, they were polished using aqueous alumina suspension on felt polishing pads, washed and sonicated in ethanol for a few minutes, and finally, rinsed with deionized water. The catalyst and the commercial Ir/C catalyst suspensions were prepared by dispersing 10 mg of catalyst in 1 mL of a solution containing 0.985 mL of ethanol and 15 μL of 5 wt% Nafion solution,¹²⁸ followed by sonication for a half-hour. Then appropriate aliquot was pipetted into pre-treated GC surface (0.196 cm²) to give a loading of 0.3 mg/cm² and then dried under ambient environment.

The linear polarization curves (LSV) were recorded at a sweep rate of 5 mV s⁻¹ under continuous stirring of 1600 rpm to avoid accumulation of gas bubbles over the GC electrode. Prior to linear polarization curve recording, the materials were exposed to Cyclic Voltammetry (CV) along the potential window of 0.2 V to

0.8 V vs Ag/AgCl at 100 mV s⁻¹, until a stable CV is obtained,¹²⁹ and it comes to be 10 CVs. The onset potential for trimetallic boride and Ir/C catalyst reported were determined based on the current density of 1 mA cm⁻² in the recorded LSV curves.^{130, 131} All polarization curves reported in this work were corrected for *iR* drops which were measured by the EIS technique at 0.6 V potential vs Ag/AgCl for all samples and commercial 20 wt% Ir/C catalyst, while at 1.6 V for the two-electrode system. The stability test was carried out by recording CV profiles of 1000 cycles at 100 mV s⁻¹ from 0.2 V to 0.6 V. Furthermore, the chronopotentiometric responses were measured at a fixed current density of 10 mA cm⁻².

The electrochemically active surface area (ECSA) was measured by double layer capacitance method derived from cyclic voltammetry (CV) measured in static solution.¹³² To determine the capacitance value, catalysts deposited onto glassy carbon electrode were first activated by 25 CV scans in order to observe no-faradaic region. Then 10 CV scans were performed at different scan rate in a potential window where no Faradaic process occurs, at 7 different scan rates: 16, 14, 12, 10, 8, 6, and 4 mV s⁻¹.¹³³ The capacitance was determined from the tenth CV curve of each scan rate. After data collection the following equation 17 was used for electrochemical double-layer capacitance,

$$C_{DL} = i_c/v \quad (17)$$

where C_{DL} is the double-layer capacitance (mF cm^{-2}) of the electroactive materials, i_c is charging current (mA cm^{-2}), and v is scan rate (mV s^{-1}).¹³⁴ The average specific current density, j_s ,^{132, 135} is normalized for ECSA at $\eta = 0.314$ V. It is calculated by dividing the current density per geometric area at a given overpotential, j_g , by the roughness factor of the surface as shown in equation 18:

$$j_s = j_g / \text{RF} \quad (18)$$

The average current density per geometric area at $\eta = 0.314$ V which is the overpotential required to deliver a current density of 10 mA cm^{-2} for the as-synthesized nickel boride, j_g , $\eta = 0.314$ V. The choice of $\eta = 0.314$ V is based on previously reported device models that suggest a 10% efficient solar water-splitting device should operate at 10 mA cm^{-2} .¹³² The ECSA of a catalyst sample is calculated from the double layer capacitance according to equation 19:

$$\text{ECSA} = C_{DL} / C_s \quad (19)$$

where C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions (0.040 mF cm^{-2}). The roughness factor (RF) is calculated by taking the estimated ECSA and dividing by the geometric area of the electrode, 0.196 cm^2 .¹³² All measured potentials (E) reported in this work were converted from vs Ag/AgCl to vs RHE by adding a value of $0.197 + 0.059 \times \text{pH}$. In addition, all reported current density was normalized to the geometric surface area. The

overpotential was calculated as follows:

$$\eta = E \text{ (vs RHE)} - 1.23 \quad (20)$$

considering O₂/H₂O equilibrium at 1.23 V vs RHE.

3.2.3.1. Complete Water Electrolysis

To study the functionality of this material toward water splitting, overall water electrolysis was performed in a two-electrode system where the modified carbon fiber paper (CFP) with the as-prepared material and 50% Pt carbon catalyst (50% Pt/C - GasHub Technology) used as anodic and cathodic electrode, respectively. Furthermore, a similar study was investigated by using modified carbon cloth (CC) as a sole electrode active material. The ink of amorphous quaternary Fe–Co–2.3Ni–B powder as well as 50% Pt/C prepared with similar procedure for three-electrode catalyst were loaded into the pieces of CC and/or CFP a final loading of 4.0 mg/cm² is reached, respectively. Afterwards, once the electrodes were completely dried at ambient temperature, they were mounted on both electrodes and dipped in an open cell containing 1.0 M KOH electrolyte solution. The modified electrodes were moisturized for 20 minutes, and then activated by recording 10 continuous cyclic voltammograms between 1.0 V and 2.0 V at 50 mV s⁻¹. Then polarization curve was performed across a potential window from 1.2 or 0.8 V to 2.2 V when Fe–Co–2.3Ni–B catalyst is used on both anode and cathode and when the Pt/C cathode is used, respectively, at a scan rate

of 5 mV s^{-1} . The long-term stability was also examined using a similar procedure described for OER study.

3.3. Results and Discussion

The metal boride materials are prepared by the reduction of metal precursors in the presence of sodium borohydride (NaBH_4), followed by drying at 45°C overnight under argon atmosphere. Here, NaBH_4 acts not only as a reducing agent but also as a boron precursor, and additionally, as a stabilizing element during the chemical reaction, and as a result, an amorphous product is expected.¹³⁶ Figure 3-1a shows the polydispersed nanoparticles in a typical field-emission scanning electron microscopy (FESEM) image of the as-prepared Fe–Co–2.3Ni–B product. The size of Fe–Co–2.3Ni–B nanoparticles varies in the range $\approx 30\text{--}40$ nm, as observed in transmission electron microscopy (TEM) image (Figure 3-1b). An extension of the amorphous layer, revealed in Figure 3-1b, can be observed clearly in Figure 3-1c, which is proposed as a thin metal oxide/borate layer on metal boride particles.⁷⁰ The inset of Figure 3-1c shows selected area electron diffraction (SAED) pattern with no dots or distinct rings, which indicates an amorphous structure. The absence of sharp crystalline peak and the appearance of a single broad peak at $\approx 45^\circ$ in Figure 3-1d obviously reveals that the as-synthesized trimetallic boride is amorphous, which is in agreement with the SAED result. The ternary metal–boron catalysts (designated as Fe–2.3Ni–B and Co–2.3Ni–B) also show the similar amorphous phase (Figure 3-2). The X-ray diffraction (XRD)

observation for amorphous boron-based material was used to differentiate the predominance of either metal boride, which exhibits the diffraction in the 2θ range between 40° and 50° , or 30° and 40° .¹³⁶ Obviously, the absence of a shoulder broad peak for the amorphous boron oxides in low diffraction 2θ range indicates the formation of metal borides.^{125, 137}

Figure 3-1. a) SEM, b,c) TEM images, the inset in Figure 3-1c is the SAED pattern, and d) XRD pattern of amorphous quaternary Fe–Co–2.3Ni–B powders.

Figure 3-2. a) XRD patterns of amorphous ternary Fe-2.3Ni-B, and (b) Co-2.3Ni-B powders.

The analysis of scanning electron microscopy (SEM) image and corresponding energy dispersive X-ray spectroscopy elemental mappings of the amorphous quaternary Fe-Co-2.3Ni-B nanoparticles clearly demonstrates the homogeneous distribution of Fe, Co, Ni, and B (Figure 3-3 and 4, Table 3-1). It is clear that the peak appears at ≈ 1.52 V (V vs RHE) in the first scan and maintains at ≈ 1.45 V in the following cycles (Figure 3-5). This is associated with the surface oxidation, and the formed surface oxide/hydroxide layer would serve as the catalytic sites for the O_2 evolution process.⁷⁰ This is similar to the case of metal phosphide-based oxygen-evolving catalysts where surface metal oxide/hydroxide layer is identified as the catalytic sites.^{70, 115, 131, 134, 138}

Figure 3-3. a) SEM image of the amorphous quaternary Fe–Co–2.3Ni–B powders, and (b) corresponding EDS layered image. Corresponding EDS elemental mappings; B K α 1 (c), Fe K α 1 (d), Co K α 1 (e), and Ni K α 1 (f).

Figure 3-4. a) EDS pattern for quaternary boride before, and (b) after stability test.

Notes: The peak at ~ 8.3 keV arises from (the Cu peaks arise from the Cu mesh).

Figure 3-5. Activation curves of the as-synthesized amorphous Fe–Co–2.3Ni–B catalyst at 100 mV s^{-1} scanning rate in the alkaline electrolyte at ambient temperature.

Table 3-1. EDS elemental mass percentages for amorphous quaternary metal boride catalyst.

Element	Elemental mass % ^a	Error %	Elemental mass % ^b	Error %
B	8.03	0.09	2.26	0.23
O	3.23	0.10	7.07	0.26
Fe	9.86	0.52	8.91	1.42
Co	22.62	0.79	23.93	2.15
Ni	56.26	1.02	57.8	2.77
Total	100		100	

^a Elemental mass % of Ni, Co, Fe, O, and B before the electrochemical test. ^b

Elemental mass % of Ni, Co, Fe, O, and B after the electrochemical test.

The surface chemistry and electronic structure of the as-prepared material are studied by X-ray photoelectron spectroscopy (XPS). Figure 3-6 shows XPS survey of Fe–Co–2.3Ni–B nanoparticles and the major elemental composition are B, Fe, Co, and Ni which agrees with EDS analysis (Figure 3-4). The B 1s spectrum in the amorphous Fe–Co–2.3Ni–B nanoparticles shows a peak at 188.2 eV (Figure 3-7a) corresponding to boron in metal borides, which is in agreement with previous literature.⁷⁰ A positive chemical shift of 0.8 eV for B compared to pure B is observed.¹³⁹ The formation of borides is attributed to the interactions of B with metals through the electron transfer occupying vacant d-orbitals of metal, and hybridization of B 2p states with the metal d-orbitals.¹⁴⁰ The peak around the Ni 2p_{3/2} spectrum in Figure 3-7b, with a low binding energy of 852.6 eV, corresponds to the Ni in nickel boride which is in agreement with the literature on nickel boride.¹¹⁰ Consistently, the Co 2p_{3/2} spectrum in Figure 3-7c shows a peak at 778.2 eV, which is attributed to the interaction of Co with boron in cobalt boride, while the peak at 707.1 eV is ascribed to Fe in iron boride (Figure 3-7d). The peaks of oxidized species in metal borides are inadvertently formed due to their exposure to the atmosphere.⁷⁰ Recently, the effect of exposure of nickel boride to air for a significant time was clearly explored, and the oxidized species were in predominance.¹¹⁰ The electron-transfer nature between the constituent elements,

observed by the binding energy shifts in the B 1s spectrum, makes boron electron deficient and metal enriched in electrons. This may facilitate the sluggish multistep OER process.

Figure 3-6. XPS survey spectrum for the amorphous quaternary Fe–Co–2.3Ni–B powders.

Figure 3-7. High-resolution XPS spectra of a) B 1s, b) Ni 2p, c) Co 2p, and d) Fe 2p for amorphous quaternary Fe–Co–2.3Ni–B powders exposed to air after drying in Ar atmosphere for overnight.

The OER electrocatalytic activities of the as-prepared materials are investigated in 1.0 M KOH solution. The anodic current density of quaternary Fe–Co–2.3Ni–B nanoparticle shows an onset potential of 1.46 V (at $j_{\text{geo}} = 1.0 \text{ mA cm}^{-2}$), while it is at 1.49 V for commercial Ir/C catalyst (Figure 3-8a). Furthermore, it requires an η of 274 mV to afford a j_{geo} of 10 mA cm^{-2} , while commercial Ir/C catalyst requires 317 mV. Additionally, the Tafel slope of 38 mV dec^{-1} is even smaller than that of Ir/C catalyst, 54 mV dec^{-1} (Figure 3-8b), and hence, it implies

more favorable OER kinetics for the as-prepared quaternary metal boride.⁸⁷ Figure 3-8c clearly reveals that iron-based boron material is less active than Co- and Ni-based binary metal–boron catalysts. The horizontal dashed line at a j_{geo} of 10 mA cm^{-2} in the current density vs potential plot is the current density expected for a 12.3% efficient solar water-splitting device.¹⁴¹ Interestingly, the incorporation of Fe into Ni–B catalyst to form ternary material outperforms the incorporation of Co (Figure 3-8d), whereby 294 and 317 mV overpotentials are required to derive a j_{geo} of 10 mA cm^{-2} for Fe–2.3Ni–B and Co–2.3Ni–B nanoparticles, respectively. Obviously, the presence of Fe is crucial for the high performance of OER composite catalysts.¹⁴² Furthermore, maximum improvement in OER performance is demonstrated when both Fe and Co are incorporated to form trimetallic boride (Fe–Co–2.3Ni–B) (Figure 3-8d; Table 3-2).

Figure 3-8. Electrochemical study of the as-synthesized metal borides and commercial 20% Ir/C catalyst. a) *iR*-corrected LSV curves for quaternary and ternary metal–boron catalysts, and b) the corresponding Tafel slopes. c) *iR*-corrected LSV curves for a quaternary, mixture of M–B, and binary catalysts. d) Comparison of different metal–boron material and Ir/C catalysts by using two parameters: potential required to afford a j_{geo} of 10 mA cm⁻² versus Tafel slopes.

Table 3-2. Electrochemical results of the amorphous metal–boron nanomaterial and commercial 20 wt% Ir/C catalysts in 1.0 M KOH electrolyte at room temperature.

Catalyst (Supported on GC otherwise stated)	Potential (V) ^a at J_{10} & J_{20} (mA cm ⁻²)		Tafel slope (mV dec ⁻¹)
	10	20	
Ir/C	1.547	1.578	53
Fe–Co–2.3Ni–B	1.504	1.516	38
0.1Fe–Co–2.3Ni–B	1.537	1.555	54
Fe–0.1Co–2.3Ni–B	1.536	1.554	67
Fe–Co–Ni–B	1.514	1.531	49
Fe–Co–4.6Ni–B	1.521	1.542	59
Fe–Co–9.0Ni–B	1.522	1.545	63
Fe–2.3Ni–B	1.524	1.542	53
Co–2.3Ni–B	1.547	1.561	49
Co–B	1.552	1.574	72
Ni–B	1.544	1.561	52
Fe–B	1.595	1.622	72
Mixture of M–B ^b	1.537	1.558	57

^a reversible hydrogen electrode, ^b mixture of cobalt boride, iron boride and nickel boride in the mass ratio 1:1:2.3, Fe–B:Co–B:Ni–B powders.

Electrochemical impedance spectroscopy was further used to characterize the OER kinetics.¹⁴³ The reduced semicircular diameter in Nyquist plots compared to the ternary ones and commercial Ir/C catalysts (Figure 3-9) reveals charge-transfer resistance reduction when both Co and Fe are incorporated into the nanoparticles.^{87, 144}

Figure 3-9. Nyquist plots of the amorphous quaternary Fe–Co–2.3Ni–B, Fe–2.3Ni–B, Co–2.3Ni–B, and commercial 20 wt% Ir/C catalyst. The electrochemical impedance spectroscopy (EIS) measured at 0.6 V vs Ag/AgCl at room temperature in 1.0 M KOH electrolyte. Notes: Z' is the real part and $-Z''$ is the imaginary part. The high-frequency intercept of the semicircle on the real axis is assigned to the ohmic series resistance (R_s). R_s for Fe–Co–2.3Ni–B, Fe–2.3Ni–B, Co–2.3Ni–B, and Ir/C are 6.0, 5.2, 5.6, 5.2 Ohm, respectively.

We investigated the electrochemical double-layer capacitance, which is proportional to the electrochemically active surface area (ECSA).^{132, 134, 145} As can

be seen, the measured capacitance for quaternary Fe–Co–2.3Ni–B nanoparticles is 0.17 mF cm^{-2} , which is roughly twice of monometallic Ni–B nanoparticles (Figure 3-10). Additionally, the derived ECSA from capacitance is 4.25 and 2.5 cm^2 for trimetallic and monometallic nanoparticles, respectively, and thus indicating an enhanced electrocatalytic active site density. Furthermore, the specific activity defined as the specific current density per catalyst surface area (j_s) is further calculated.¹³² The specific current density per catalyst surface area (j_s) at $\eta = 0.314 \text{ V}$ is calculated from the measured double-layer capacitance by using general specific capacitances of $C_s = 0.040 \text{ mF cm}^{-2}$ in 1.0 M NaOH based on typical reported values,^{132, 146-148} and it is 4.1 and 0.7 mA cm^{-2} for the as-prepared amorphous metal boride and monometallic nickel boride, respectively. This observation is in agreement with the reduced η required to afford a j_{geo} of 10 mA cm^{-2} by 40 mV , and the reduction of the Tafel slope Ni–B nanoparticles from 52 to 38 mV dec^{-1} for quaternary metal boride at the same loading (Figure 3-8d and Table 3-2). Hence, this supports the enhancement of specific catalytic activity through the incorporation of Co and Fe compared to monometallic nickel–boron-based nanoparticles. For multimetal-based OER electrocatalyst, it has been suggested that the thermodynamic barrier of a proton-coupled electron transfer pre-equilibrium could be reduced while facilitating O–O bond formation by adding other metal in monometallic-based catalyst, and thus, leading to an enhanced catalytic activity.¹¹⁸

Figure 3-10. a) Cyclic voltammograms in the double layer region at scan rate of 16, 14, 12, 10, 8, 6, 4 mV/s (along the arrow direction) of Ni-B nanoparticles, and (b) Fe-Co-2.3Ni-B nanoparticles. c) Current density as a function of scan rate derived from (a) and (b).

The optimization of the catalyst is studied by varying the ratios of Fe and Co precursors during the preparation of trimetallic boride, and it reveals that their incorporation has a significant influence on tuning the OER activity of trimetallic boride nanoparticles (Figure 3-8d; Figure 3-11). This is attributed to the general mechanism of metal-metalloid catalysts, where transition metal cations on the surface undergo oxidation to MOOH surrounding the catalyst core (where M = Fe,

Co, and Ni),^{20, 110} and may serve as the actual multimetal surface-active sites in multimetal oxide-based O₂-evolving catalysts.^{134, 149-151}

Figure 3-11. (a) *iR*-corrected LSV curves, and (b) corresponding Tafel slopes of amorphous trimetallic boride catalysts in 1.0 M KOH electrolyte at room temperature.

To extend the viability of this technique to synthesize oxygen-evolving trimetallic boride, another iron precursor in the aqueous solution that contains iron (II) is investigated, and the catalytic activity is merely similar. It requires 1.513 V to reach a j_{geo} of 10 mA cm⁻², which is only higher than the as-prepared Fe–Co–2.3Ni–B nanoparticles by 9 mV (Figure 3-12). The as-prepared trimetallic boride material is comparable and/or even more efficient than the other nickel, cobalt, and/or iron metal–metalloids, metal oxyphosphide and oxide catalysts for electrochemical OER application. Thus, as an earth-abundant-based catalyst is prepared by a simple approach, further studies can be carried out to the other multimetal–boron-based materials.

Figure 3-12. a) *iR*-corrected polarisation curves, and (b) corresponding Tafel slopes for amorphous Fe–Co–2.3Ni–B and Fe–Co–2.3Ni–B^a (^a prepared by using Fe²⁺ ion as iron source) recorded in 1.0 M KOH electrolyte at the same conditions.

Additionally, we further prepared iron–cobalt–nickel alloy with a similar metal precursor ratio in the aqueous solution, and its OER performance is lower than that of the amorphous quaternary Fe–Co–2.3Ni–B catalyst (Figure 3-13). It requires an η of 323 mV to achieve a j_{geo} of 10 mV cm⁻², which is 49 mV more compared to quaternary metal boride under the similar testing condition and loading. The poor performance of this metal alloy may prove that B in amorphous metal boride contributes to electronic structure and, hence, enhances charge density distribution in metal boride which facilitates the balance of chemisorption and desorption of reaction intermediates.^{146, 152, 153} This is the case for other metal–metalloids such as P, N, and Se, whereby it is suggested that these nonmetallics bear an intrinsic role in enhancing the activity of metal by in situ formation of metal oxyhydroxide active sites, while some authors attributed to the synergistic effects

between metal and nonmetal elements but not yet fully explained.^{134, 154} The enhanced electrocatalytic activity of the as-prepared quaternary metal borides may be attributed to the (1) improved active surface area compared to the monometallic nickel boride material and (2) enhanced electron transfer due to the unique amorphous multimetal–metalloid complex nanostructure capable of buffering the multistep OER process in harsh alkaline electrolytes.

Figure 3-13. (a) *iR*-corrected polarization curves, and (b) corresponding Tafel slopes for amorphous Fe–Co–2.3Ni–B and Fe–Co–2.3Ni recorded in 1.0 M KOH electrolyte at the same conditions.

The stability of oxygen-evolving catalyst is crucial for energy storage and conversion technologies. Hence, the galvanostatic test performed at a constant current density of 10 mA cm⁻² at room temperature in 1.0 M alkaline electrolyte shows a nearly constant η for amorphous quaternary metal–boron nanoparticles over a period of 12 h (Figure 3-14a). Furthermore, ternary metal–boron exhibits promising stability, whereby Co–2.3Ni–B catalyst shows an improved activity

after 1 h of the stability test and maintains the activity over time, while Fe–2.3Ni–B catalyst shows merely no significant potential loss over the whole test period (Figure 3-15a). To support the galvanostatic results, the cycle capability of the material is tested. The initial and the iR -corrected linear sweep voltammetry (LSV) curves recorded after 1000 cycles also show the promising stability (Figure 4-14b), while the similar trend is observed in ternary metal borides (Figure 3-15b). In addition, from the perspective of metal–metalloid interaction, the stability is predictable as there is a higher covalency of metal–boron bond, which is even higher than the metal–phosphorous bond that makes them extremely hard and chemically resistant.¹⁰⁸ Though precious metal-based electrodeposited IrO_x catalyst showed comparable OER activity for the as-prepared material, in which it affords 10 mA cm^{-2} current density at $\eta = 0.32 \pm 0.04 \text{ V}$, it was unstable during 2 h of constant current electrolysis in alkaline electrolytes.¹³² In contrast, the long-term durability indicates that this nonprecious metal catalyst derivative can survive in the harsh alkaline electrolytes but not the precious metal-based catalysts.

Figure 3-14. (a) Galvanostatic long-term durability test of the as-prepared amorphous Fe–Co–2.3Ni–B nanocatalyst. (b) The electrochemical stability test.

Figure 3-15. (a) Galvanostatic long-term durability test at a constant current density of 10 mA cm^{-2} over 10 h period of the as-prepared ternary Fe–2.3Ni–B and Co–2.3Ni–B catalyst at room temperature in 1.0 M KOH electrolyte. (b) The electrochemical stability test by CV of the as-prepared ternary Fe–2.3Ni–B and Co–2.3Ni–B catalysts at room temperature in 1.0 M KOH electrolyte: iR -corrected polarisation curves recorded before and after 1000 CVs in the potential window of 0.2 V to 0.6 vs Ag/AgCl at a scan rate of 100 mV s^{-1} .

Finally, a two-electrode electrolyzer using a modified carbon fiber paper (CFP) by Fe–Co–2.3Ni–B nanoparticles (denoted as Fe–Co–2.3Ni–B/CFP) and 50% Pt/C catalyst (denoted as 50% Pt/C/CFP) is demonstrated to drive the practical water splitting in 1.0 M KOH solution. Figure 3-16a shows that a low voltage of 1.52 V is required to afford a current density of 20 mA cm^{-2} , and the whole electrolysis is fairly stable during the 24 h operation (Figure 3-16b). Additionally,

though we herein report a highly efficient amorphous quaternary metal boride for OER, results also reveal that this material can work as both anode and cathode for overall water splitting (Figure 3-17). It requires a voltage of 1.66 V to deliver a current density of 10 mA cm^{-2} and also exhibits outstanding stability over a period of 10 h.

Figure 3-16. Two-electrode alkaline electrolyzer with carbon fiber paper modified by the as-prepared quaternary amorphous metal boride as the anodic catalyst and Pt/C as a cathodic catalyst; (a) Current–potential response of a two-electrode alkaline electrolyzer. (b) Galvanostatic electrolysis at 20 mA cm^{-2} over a period of 24 h. The loading of the active material is 4.0 mg/cm^2 .

Figure 3-17. Two-electrode alkaline electrolyzer with carbon cloth modified by the as-prepared quaternary amorphous metal boride as both the anode and cathode; (a) Current–potential response measured in 1.0 M KOH electrolyte, and (b) galvanostatic electrolysis at 10 mA cm⁻² over 10 hours.

3.4. Conclusion

In summary, an amorphous quaternary metal–boron-based material is synthesized by an economically viable approach. The as-prepared Fe–Co–2.3Ni–B nanocatalyst demonstrates an excellent electrocatalytic activity toward OER. The oxygen-evolving activity of trimetallic boride is associated with the oxide/hydroxide metal layer which serves as the catalytically active site in alkaline electrolyte, while B assists electron transfer. For application purposes, this material requires only 1.52 V to achieve 20 mA cm⁻² (j_{geo}) when it is used as anodic material during overall water splitting in 1.0 M KOH electrolyte. Overall, this study not only provides an earth-abundant and efficient oxygen-evolving electrocatalyst, but

it also opens up an avenue to explore the efficient and low-cost metal boride catalyst for energy technologies related to OER.

Chapter 4. An Earth-Abundant Tungsten–Nickel Alloy Electrocatalyst for Superior Hydrogen Evolution

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4.1. Background Introduction

As a promising carbon-neutral fuel alternative, hydrogen energy has gained great interest over the past decades, and clean and sustainable production of hydrogen is crucial for future hydrogen energy technologies.¹⁵⁵⁻¹⁵⁷ Among various approaches, electrochemical water splitting has gained a lot of interest due to its production of high purity hydrogen and high process flexibility, but large scale application of this technology needs efficient and cost-effective electrocatalysts.^{33,}
¹⁴¹ Over the past decades, tremendous efforts have been devoted to exploring highly effective and durable earth-abundant electrocatalysts to replace precious-metal-based catalysts for alkaline water electrolysis. Competitive materials such as chalcogenides,¹²⁷ phosphides,¹⁵⁸ nitrides,^{61, 159} carbides,^{160, 161} borides,^{70, 162} metal alloys,⁷² and metal-free catalysts have been reported.^{10, 33} Nickel-based alloys are among the most promising catalysts because of their low cost and tunable

electrocatalytic properties via the synergistic nearby elements.^{105, 163} Compared to their parent metals, nickel-based bimetallic system reduces the water molecular adsorption energy and hence small Gibbs free energy of hydrogen adsorption which results in advanced HER electroactivity.^{164, 165}

Here we present a novel tungsten–nickel alloy/Ni foam (NF) hybrid annealed at 450 °C (denoted as WNi/NF₄₅₀) with an extraordinary HER performance in 1.0 M KOH electrolyte. The sample electrode exhibits a low overpotential of 36 mV at 10 mA cm⁻² and a small Tafel slope of 43 mV dec⁻¹. Owing to the excellent electrocatalytic performance arising from the synergistic effect of binary tungsten–nickel interacting through the *d*-orbital electron transfer, the as-prepared material is the best among tungsten-based HER electrocatalyst. The lower adsorption energy of water molecules and a small Gibbs free energy of hydrogen adsorption (0.17 eV) on tungsten atoms of WNi (111) from DFT calculations reveal the favorable water electrolysis kinetics. This work presents a simple and facile approach to produce highly efficient and durable electrocatalyst toward HER in alkaline electrolyte.

4.2. Experimental Section

4.2.1. Materials Synthesis

All chemicals used in this study were used as received. The tungsten–nickel particles/nickel foam (NF) hybrid was prepared by a simple hydrothermal

technique. First, the NFs were treated with 3 M HCl solution for 10 min to ensure the surface of NFs were well cleaned before use. After acid cleaning, they were washed with deionized water (DI-water) several times to ensure the pH value reaches a neutral condition. Secondly, 0.25 M solution of ammonium metatungstate hydrate $((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O})$, Sigma-Aldrich, CAS: 12333-11-8) was prepared in 15 mL of ultra-purified water from a Milli-Q Plus system (Millipore, $>18.2 \text{ M}\Omega\cdot\text{cm}$) and stirred at room temperature for 30 minutes. One pretreated bare NF ($1 \times 3 \text{ cm}^2$)^{154, 166, 167} was submerged into the high-pressure polytetrafluoroethylene (PTFE)-lined vessel of 50 mL containing the precursor solution and ultrasonicated for 5 min prior to the hydrothermal procedure. Afterwards, it was placed and sealed in the Teflon lined hydrothermal synthesis reactor and then placed in an electric oven. The temperature was raised at a maximum of 170 °C and maintained for 20 h. After this period, it was cooled down to room temperature. Then the modified NF was taken out and washed subsequently with DI-water and ethanol, respectively. The NF was placed on cleaned and dried porcelain crucible and transferred in a tube reactor. Pure H₂ gas was flushed for 30 min to provide an air-free H₂ gas saturated atmosphere. The temperature was raised slowly until it reached reaction temperature (such as 450 °C) with a heating speed of 2 °C min⁻¹ and was maintained for an hour (h) in the presence of H₂ gas flow. The color of the as-fabricated electrode after annealing in H₂ gas was found to be black.

4.2.2. Structure Characterizations

The field emission scanning electron microscopy (FESEM, JEOL JSM 6700F) was used to study the surface morphology which was also equipped with energy-dispersive spectroscopy (EDS, INCA PentaFET-x3), which was used to analyse the material composition. To further examine the as-prepared material, the high-resolution transmission electron microscopy (HRTEM) image, SAED, elemental mapping, and the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed by TEM (JOEL JEM 2100, 200 kV). Powder X-ray diffraction (XRD) patterns were collected by using a Bruker diffractometer with Cu K radiation (D2-Phaser with LYNXEYE detector, Cu K α , $\lambda = 1.5414 \text{ \AA}$, 30 kV, and 10 mA) to get crystallographic information on the material. The surface electronic states and composition of the as-prepared material were carried out by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII instrument) with a Mg K α X-ray source.

4.2.3. Electrochemical Measurements

Electrochemical measurements were performed in a three-electrode configuration by using Autolab PGSTAT302 (Eco Chemie, Netherlands) potentiostat workstation equipped with electrochemical impedance spectroscopy (EIS) at room temperature (25 °C). A standard mercury/mercury oxide (Hg/HgO) reference electrode was used as the reference electrode, while a graphitic rod as a

counter electrode. The HER linear polarization curves were recorded in H₂-saturated 1.0 M KOH alkaline electrolyte at a sweep rate of 2 mV s⁻¹, while for OER it was O₂-saturated. All currents were corrected against ohmic potential drop measured between 10 kHz and 1 MHz. All current density reported in this study was calculated using exposed surface area of the electrode into the electrolyte solution.¹⁶⁸ The onset potential was determined based on the current density of 1.0 mA cm⁻² in the recorded LSV curves.¹³¹ The Tafel plots were plotted based on the polarization curves, which were replotted as overpotential vs log (current density) and the linear portion at lower overpotential is fitted to the Tafel equation (Equation 4).³³ The stability behaviour was examined by recording CV profiles of 1000 cycles in a potential window from -0.922 to -1.322 V vs Hg/HgO at 100 mV s⁻¹. Additionally, the long-term durability test was also examined by galvanostatic experiment in 1.0 M KOH at 25 °C by applying a fixed current density to the working electrode for 12 h. A two-electrode water electrolysis system was used to study the functionality of this material toward water splitting in an open cell containing 1.0 M KOH alkaline solution across a potential window of 1.2–2.2 V at a scan rate of 5 mV s⁻¹. Furthermore, galvanostatic long-term durability was also examined.

4.2.3.1. Electrode Preparation

For comparison, precious-metal-based catalyst: Pt/C (50 wt%, GasHub Technology) was measured at the same condition and approximately similar

loading. The ink of Pt/C was prepared by mixing 5 mg of catalyst into a 1 mL solution of 0.985 mL ethanol and 0.015 mL (5 wt% Nafion solution) and ultrasonicated for 30 min. Afterwards, the ink was cast dropped into pretreated NF until a loading of 2.8 mg/cm² is achieved. The Pt-modified NF was dried overnight at 80 °C prior to electrochemical measurements. The loading of tungsten–nickel binary catalyst on NF was calculated as follows:^{154, 166} the weight of NF was measured before hydrothermal treatment and after the annealing process. And the increment (z mg) was the loading of tungsten–nickel particles. $W_{Ni_{loading}} = z \text{ mg} \times (M_{NiW}/M_W) = z \text{ mg} \times ((183.8 + 58.6))/183.8 = z \text{ mg} \times 1.3$. And approximately it came out to be 2.8 mg/cm².

4.2.3.2. Electrochemically Active Surface Area (ECSA)

The ECSA was measured by double-layer capacitance method derived from cyclic voltammetry (CV) in static solution in a potential window where no Faradaic process occurred. After data collection, the equation 17 was used for electrochemical double-layer capacitance. The ECSA of a catalyst sample was calculated from the double layer capacitance according to the equation 19.¹³²

4.2.3.3. Calibration of Hg/HgO Electrode and Conversion versus RHE

The calibration of Hg/HgO electrode was performed in a 1.0 M KOH pre-purged and saturated with high purity H₂ standard three electrode system. Linear scanning voltammetry (LSV) was then run at a scan rate of 1.0 mV s⁻¹, and the

potential at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions.¹⁶⁹ The zero current point was observed at -0.922 V (Figure 4-1) and thus the following equation was used for conversion versus RHE: $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.922$ V. This value is in agreement with calculated value: $E \text{ vs RHE} = E \text{ vs Hg/HgO} + 0.095 + 0.059 \text{ pH}$ (Equation 21).^{117, 130, 170}

Figure 4-1. Potential calibration curve of the Hg/HgO reference electrode in 1.0 M KOH solution at ambient temperature.

4.2.4. DFT Calculations

First-principle calculations were carried out by using the Vienna *ab initio* simulation package (VASP) based on the all-electron projected augmented wave (PAW) Method.^{171, 172} The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parametrization was employed for the exchange-correlation functional. The three-layer Ni (111) and WNi (111) surfaces were used as the model for Ni and WNi (1:1) in present calculations. To prevent the artificial

interaction between repeated slab along the z-direction, 15 Å vacuum was introduced with correction of the dipole moment. During structural optimization, the bottom layers of the slab were fixed at the bulk truncated position, while the top two layers and the adsorbates were fully relaxed. The reaction barriers were calculated using climbing image nudged elastic band (CINEB) method.^{172, 173} And the final transition state (TS) structures were refined by using a quasi-Newton algorithm until the forces were less than 0.03 eV/Å.

For HER reaction, the free energy change for H* adsorption on Ni and WNi surfaces (ΔG_H) was calculated as follows,

$$\Delta G_H = E_{\text{total}} - E_{\text{sur}} - E_{\text{H}_2}/2 + \Delta E_{\text{ZPE}} - T\Delta S \quad (22)$$

where E_{total} was the total energy for the adsorption state, E_{sur} was the energy of pure surface, E_{H_2} was the energy of H₂ in the gas phase, ΔE_{ZPE} was the zero-point energy change and ΔS was the entropy change.

4.3. Results and Discussion

The three-dimensional (3D) tungsten–nickel alloy is formed by the hydrothermal treatment of Ni foam (NF) with ammonium metatungstate hydrate, followed annealing at 450 °C in the hydrogen environment (see the Experimental Section 4.2.1 for details, the obtained sample is denoted WNi/NF₄₅₀). The formation of WNi alloy follows the Ni–W phase diagram.¹⁷⁴ Herein, ammonium-

based tungsten is used as a tungsten source, while the NF acts as not only the nickel source but also the substrate for growing WNi alloys. The fabrication of WNi alloy electrode based on the present method is depicted in Figure 4-2.

Figure 4-2. Scheme of the synthesis route of WNi₄₅₀ electrode.

The NF appears overt green after hydrothermal treatment and turns black after annealing in the presence of pure H₂ gas (Figure 4-3). The as-obtained alloy hybrid is examined by field emission scanning electron microscopy (FESEM). With addition of too much tungsten precursors during hydrothermal treatment, enormous flakes and particles appear on the NF substrate (Figure 4-4). Thus, the concentration of tungsten source should be controlled to ensure the successful formation of alloys firmly anchored on the NF substrate.

Figure 4-3. Preparation process overview of tungsten–nickel/nickel foam electrode. Left: bare Ni foam after treated in 3 M HCl; middle: Ni foam after hydrothermal treatment at 170 °C for 20 hours and dried at 80 °C for 24 hours; right: the as-prepared binary tungsten–nickel/Ni foam hybrid catalyst annealed in H_2 at 450 °C for 1 hour.

Figure 4-4. SEM images of tungsten–nickel/Ni foam hybrid material prepared by different ammonium tungstate amount (a) 0.15 M, (b) 0.25 M and (c) 0.5 M in solution.

After hydrothermal treatment, many microparticles in rhombic dodecahedron shape with the size of $\sim 2\ \mu\text{m}$ are uniformly distributed on the surface of NF (Figure 4-5). Figure 4-5 shows morphological modification of substrate and reveals that the substrate acts as the support and the nickel source to form these microparticles. This is the case for some other self-supported nickel-based material grown on the highly conductive substrate in specific hydrothermal conditions.¹⁷⁵

Figure 4-5. Low and corresponding High-resolution SEM images of the as-prepared electrodes at different stages in the fabrication process. (a) and (b) bare Ni foam after treated in 3 M HCl; (c) and (d) Ni foam after hydrothermal treatment; (e) and (f) electrode annealed in H₂ at 450 °C for 1 hour.

With a closer observation by FESEM (Figure 4-6a), these microparticles are almost tightly bound to the NF (inset Figure 4-6a). After annealing at 450 °C in the presence of H₂, some microcracks appear around these microparticles (Figure 4-6b and inset). The annealing process also serves the purpose of removing residual oxyhydrogen species generated in the previous hydrothermal process. The tungsten precursor plays an important role in the consequent formation of WNi alloy. More information is obtained by high-resolution TEM (HRTEM). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a portion of WNi particle after annealing at 450 °C reveals the homogeneous distribution of both Ni and W elements (Figure 4-6c). The lattice fringes in Figure 4-6d with a spacing of ~0.20 nm correspond to predominant (111) crystal plane and indicate the formation of WNi alloy. The distinct diffraction spots in the inset of Figure 4-6d confirm the single crystallinity nature of WNi alloy particles in the as-prepared WNi/NF₄₅₀ hybrid.

Figure 4-6. (a) Low-magnification SEM images of products after hydrothermal treatment and dried at 80 °C. Inset of (a) is the corresponding high-resolution SEM image. (b) FESEM image of tungsten–nickel/NF hybrid after annealing at 450 °C (WNI/NF₄₅₀). Inset is a single WNI particle. (c) TEM image of WNI particle (i) and (ii) HAADF-STEM image of a portion of WNI particle after annealing at 450 °C. (iii, iv) Corresponding mapping for Ni and W, respectively. (d) HRTEM image of a single WNI particle. The inset is the corresponding SAED pattern of WNI particle (c (i)).

X-ray powder diffraction (XRD) analysis in Figure 4-7a also verifies the crystalline nature of as-synthesized materials. For the hydrothermal products dried at 80 °C, besides the prominent Ni peaks (PDF No. 04-0850), small shoulder peaks at 23.3°, 28.4°, and 37.3° are indexed to (020), (112), and (202) of WO₃ species (JCPDS card no. 71-0131), respectively, which are from metal (hydro)oxides formed during the hydrothermal process (Figure 4-7b). When the material was annealed at 300 °C (Figure 4-7a), only a slight change occurred where the peak at 23.3° disappeared and was replaced by a new peak at 23.8° ascribed to (010) of WO_{2.83}.¹⁷⁶

Figure 4-7. (a) XRD patterns of WNi/NF₆₀₀, WNi/NF₄₅₀, and WNi/NF₈₀ composite

before annealing. (b) XRD pattern of the WNi/NF₈₀, and WNi/NF₃₀₀ electrode. (c) Enlarged XRD pattern of the WNi/NF₆₀₀ electrode. In Figure 4-7c, metallic tungsten is ascribed with respect to metallic tungsten PDF No. 04-0806.

After annealing at 450 °C in hydrogen environment, the sample (WNi/NF₄₅₀) peeled off from the NF substrate exhibits peaks at 36°, 39°, 43°, 48°, and 54°, which are indexed to (040), (140), (042), (213), and (322) of WNi alloy (JCPDS card no. 00-047-1172), respectively, while the peak assigned to oxygen deficient tungsten oxide (WO_{3-x}) at 23.8° is still observed. With a higher annealing temperature of 600 °C, new emerged peaks at ~40.3°, 58.3°, and 73° are ascribed to (110), (200), and (211) of the metallic tungsten phase (PDF No. 04-0806), respectively (Figure 4-7c).

The atomic elemental composition is analyzed by energy dispersive spectroscopy (EDS), and the results show an atomic W:Ni ratio of approximately 1:1 in the WNi alloy supported on NF (Figure 4-8 and Table 4-1). Furthermore, this agrees with the homogeneous distribution of both Ni and W elements observed in HAADF-STEM image (Figure 4-6c). The surface state of the as-prepared WNi alloys is further examined by X-ray photoelectron spectroscopy (XPS). The XPS results reveal the absence of tungsten in the pretreated bare NFs (Figure 4-9a) and the presence of both nickel and tungsten (Figure 4-9b) with an atomic ratio close to EDS analysis (Table 4-1).¹⁵⁴

Figure 4-8. EDS pattern of the freshly annealed electrode.

Table 4-1. EDX Elemental atomic percentages and XPS atomic percentage for tungsten–nickel/Ni foam electrode.

Elements	EDX		XPS
	Elemental Weight %	Elemental Atomic %	Atomic %
Ni	19.5	20.6	9.0
W	67.1	22.6	11.8
O	9.7	37.6	45.5
C	3.7	19.2	33.7
Total	100.0	100.0	100.0

Figure 4-9. (a) XPS survey spectrum of pretreated bare NF. (b) XPS survey spectrum of WNi/NF₄₅₀ catalyst.

The Ni $2p_{3/2}$ peak at 855.3 eV is present both in WNi alloys supported on NF and bare NF (Figure 4-10a). Moreover, a new peak ascribed to metallic Ni ($\text{Ni}^{(0)}$) at 851.8 eV is observed only in WNi/NF₄₅₀ in agreement with Ni₅₉W₄₁ alloy in the literature,¹⁷⁷ showing that it is from WNi alloy instead of nickel foam, as this state is not present in the pretreated bare NF.^{139, 178} Figure 4-10b shows two major peaks about 2.3 eV away from each other with a ratio of around 4:3 at 35.5 and 37.8 eV corresponding to $4f_{7/2}$ and $5p_{5/2}$ states of W with a higher oxidation state (W^{6+}) in the WNi/NF₄₅₀, respectively. A minor peak for W $5p_{3/2}$ appears about 5.5 eV from W $4f_{7/2}$ which indicates the presence of tungsten in metallic state.^{139, 179, 180} The annealing treatment of tungsten oxide in the presence of H₂ at moderate temperature undergoes partial reduction by creating oxygen vacancies.¹⁸¹ Moreover, a peak at 33.4 eV for the W $4f_{7/2}$ state can be attributed to the formation of metallic tungsten ($\text{W}^{(0)}$) in the as-prepared material, and it experiences a

chemical shift due to the electron transfer with nickel.^{179, 182} Furthermore, the O 1s spectrum of the pretreated bare NF and WNi/NF₄₅₀ electrode shows that the predominant amount in the latter is surface lattice oxygen at 530.4 eV.¹⁸³ This further agrees with the XRD and EDS results about the oxygen presence, showing the partial reduction of the as-prepared electrode at these conditions.¹⁸⁴

Figure 4-10. (a) High-resolution XPS spectra of Ni 2p of bare Ni foam and WNi/NF₄₅₀ catalyst. (b) High-resolution XPS spectra of W 4f of WNi/NF₄₅₀ catalyst, and (c) O 1s of bare Ni foam and WNi/NF₄₅₀ catalyst.

The electrocatalytic hydrogen evolution properties of the as-prepared WNi/NF hybrid are studied in H₂-saturated 1.0 M KOH solution at room temperature. The pretreated bare NF and commercial Pt/C catalysts (50%, GasHub Technology) with the same mass loading are also prepared and studied for comparison.¹⁸⁵ The polarization curve of annealed WNi/NF₄₅₀ shows an outstanding HER electrochemical activity with a small onset overpotential of 2 mV, and then the current density rises rapidly at larger overpotentials (Figure 4-11a).¹³¹ The WNi/NF₄₅₀ catalyst affords a geometric current density (j_{geo}) of 10 mA cm⁻² at an overpotential of 36 mV, which is similar to Pt-based catalyst. In comparison, the bare NF shows insignificant HER activity and depicts a high overpotential of up to 314 mV to deliver 10 mA cm⁻². Thus, the electrocatalytic activity of this hybrid material is attributed not only to the catalyst but also to the substrate which is one of the advantages for most self-supported electroactive materials. The lower overpotential for the as-prepared hybrid electrode arises from the catalyst, assisted by a highly conductive substrate.

Figure 4-11. (a) *iR*-corrected polarization curves and (b) Tafel plots of WNi/NF₄₅₀,

bare Ni foam and Pt/C loaded on Ni foam at a scan rate of 2 mV s⁻¹.

Moreover, at higher overpotentials, WNi/NF₄₅₀ catalyst outperforms Pt/C catalyst in the cathodic current density. For example, to achieve a current density of 30 and 50 mA cm⁻², the overpotentials are only 64 and 78 mV for WNi/NF₄₅₀ but 94 mV and 150 mV for commercial Pt/C catalysts, respectively. This could be attributed not only to the synergistic effect in binary metal catalyst but also to the improved contact between the catalyst and the substrate while in Pt/C this effect is limited by binder usage and poor contact between the catalyst and the substrate. WNi/NF₄₅₀ also displays a superior activity compared to some other nickel-based HER catalysts. To name a few, based on the overpotentials required to deliver a current density of 10 mA cm⁻²,³³ this material requires less overpotential ($\eta = 36$ mV) than other excellent HER catalysts prepared on NF such as NiSe (96 mV),¹⁵⁴ Ni₂P/Ni/NF (98 mV),¹⁸⁶ HP-NiSe₂ (57 mV, in acidic medium),¹⁸⁷ V/NF (176 mV),¹⁸⁵ WS_{2(1-x)}Se_{2x}/NiSe₂ (88 mV, in acidic medium),¹⁸⁸ Mo₆Ni₆C grown on nickel foam (51 mV, in acidic medium).¹⁸⁸ Additionally, it is even better than the amorphous tungsten-doped nickel phosphide (a-WNP)/NF which exhibited an onset potential of 50 mV, overpotential of 110 mV at 20 mA cm⁻², and small Tafel slope of 39 mV dec⁻¹ in acidic medium and at 160 mV in alkaline solution.¹⁸⁰

Figure 4-11b shows a lower Tafel slope of 43 mV dec⁻¹ for WNi/NF₄₅₀ catalyst, which is similar to Pt/C (41 mV dec⁻¹) and much smaller than NF (136 mV dec⁻¹).¹⁵⁴ This reveals a favorable HER kinetics of WNi/NF₄₅₀ electrode.^{189, 190}

Fundamentally, the HER process in alkaline electrolyte proceeds with the following two or three steps: Volmer reaction (electrochemical hydrogen adsorption: $\text{H}_2\text{O} + \text{M} + \text{e} \rightarrow \text{MH}_{\text{ads}} + \text{OH}^-$, 120 mV dec⁻¹), followed by Heyrovsky reaction (electrochemical desorption: $\text{MH}_{\text{ads}} + \text{H}_2\text{O} + \text{e} \rightarrow \text{M} + \text{OH}^- + \text{H}_2$, 40 mV dec⁻¹) and/or Tafel reaction (chemical desorption: $2\text{MH}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2$, 30 mV dec⁻¹).¹⁹¹ The Tafel slope of the as-prepared WNi/NF₄₅₀ catalyst (43 mV dec⁻¹) is very close to 41 mV dec⁻¹ for Pt/C at the same condition (Figure 4-11b). This implies a similar mechanism following the Volmer–Heyrovsky mechanism while the Heyrovsky step acts as the rate-limiting step for both Pt/C and WNi/NF₄₅₀ hybrid catalysts in alkaline solution.¹⁹²

The optimization of the as-prepared catalyst is also studied by tuning the annealing temperatures in the presence of pure H₂ gas. The as-prepared electrode dried at 80 °C prior to the annealing process (denoted as WNi/NF₈₀) exhibits a poor performance compared to the samples annealed at 300, 450, and 600 °C (denoted as WNi/NF₃₀₀, WNi/NF₄₅₀, and WNi/NF₆₀₀, respectively) (Figure 4-12a). By annealing at 300 °C, a slightly enhanced catalytic performance is observed for WNi/NF₃₀₀, which may be mainly due to the insufficient removal of metal (hydro)oxides and hence insufficient alloying of tungsten and nickel. The WNi/NF₄₅₀ catalyst outperforms the rest (Figure 4-12b,c). Therefore, a high annealing temperature is needed to ensure sufficient reduction of metal oxide and formation of alloy. However, if the annealing temperature is too high, the separated

metallic tungsten domain would be formed and the surface morphology could be destroyed and thus result in a reduced electrocatalytic performance.^{185, 193} Though the optimized electrode contains partially reduced tungsten oxides, partially reduced tungsten oxide had been reported to activate molecular H₂ and exhibits high conductivity compared to inert tungsten oxide, and hence, with highly conductive substrate its presence does not severely limit the electrode activity.^{181, 194} Furthermore, it had been reported that the presence of native oxidized species including tungsten oxide in nickel tungsten alloy-based material protects the catalyst against corrosion.¹⁸⁴

Figure 4-12. (a) *iR*-corrected polarization curves of WNi/NF₈₀, WNi/NF₃₀₀,

WNi/NF₄₅₀, and WNi/NF₆₀₀ materials, and (b) Tafel plot. (c) Overpotentials required to deliver 10 mA cm⁻² current density and Tafel slopes for catalyst annealed at different temperatures.

With advanced HER activity for the as-prepared tungsten–nickel alloy, the OER activity was also studied in 1.0 M KOH at room temperature. The polarisation curve in Figure 4-13a shows the activity of the as-prepared electrode in 1.0 M KOH electrolyte. It requires an overpotential of 277 mV to deliver a geometric current density of 10 mA cm⁻². A clear observation reveals a positive shift in redox potential of approximately 60 mV for N²⁺ to Ni³⁺ for WNi/NF₄₅₀ catalyst compared to NF. Furthermore, the WNi/NF₈₀ displays the worst activity as it is even poor compared to bare NF. And thus, the importance of annealing in H₂ gas is clear. The improved OER activity is also further supported by the Tafel slope analysis (Figure 4-13b), whereby WNi/NF₄₅₀ exhibits a smaller Tafel slope and thus more OER favorable material compared to nickel. Figure 4-13c shows no significant decreases in overpotential required to deliver 20 mA cm⁻² which reveals the stability of this electrode. As this material shows HER and OER performance in the same solution, it could be used as a bifunctional electrocatalyst in the overall water splitting technology (Figure 4-13d).

Figure 4-13. (a) iR -corrected polarization curves and (b) Tafel plots of tungsten–nickel/nickel foam hybrid dried at 80 °C and sintered at 300 °C, 450 °C, 600 °C, and Pt/C on NF for OER at scan rate of 5 mV s⁻¹ in 1.0 M KOH electrolyte at room temperature. (c) Chronopotentiometric curve of WNi/NF₄₅₀ without iR correction in a three-electrode configuration. (d) iR -corrected LSV curves of water electrolysis for WNi/NF₄₅₀ and NF in a two-electrode configuration at a scan rate of 5 mV s⁻¹. The inset in Figure 4-13d is the chronopotentiometric curve of water electrolysis for WNi/NF₄₅₀ without iR correction in a two-electrode configuration.

Additionally, the optimized electrode was also electroactive in an acidic electrolyte. The silver/silver chloride electrode was used as a reference electrode and hence the measured potentials vs Ag/AgCl were converted to a reversible

hydrogen electrode (RHE) scale according to the Nernst equation (equation 23, $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.20$).¹⁰⁵ In 0.5 M H₂SO₄, an overpotential of 100 mV is required to afford a current density of 10 mA cm⁻² (Figure 4-14). The stability was first investigated by 1000 continuous cycles and the linear polarization collected before and after 1000 continuous cycles overlap and the corresponding Tafel slopes are almost similar (Figure 4-14a,b). Furthermore, a chronopotentiometric curve was collected (Figure 4-14c). Overall, it shows promising stability in the tested time period, which agrees with the literature that the presence of tungsten oxide would enhance the corrosion resistance.¹⁸⁰

Figure 4-14. (a) *iR*-corrected polarization curves and (b) Tafel plots of optimized

WNi/NF₄₅₀ electrode for HER at a scan rate of 2 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte at room temperature. (c) Chronopotentiometric curve of WNi/NF₄₅₀ without *iR*-correction at 10 mA cm⁻² in 0.5 M H₂SO₄ electrolyte.

Electrochemical stability is another crucial criterion for earth abundant catalyst to compete with the scarce and precious Pt-based catalysts. Figure 4-15a shows no significant potential loss to afford a constant high current density of 20 mA cm⁻² for 12 h. Furthermore, the polarization curves before and after continuous 1000 cycles are compared and almost overlap (Figure 4-15b). Both observations from the durability tests indicate that the as-prepared catalyst can stably survive in the harsh electrolyte solution. Additionally, electrochemical impedance spectroscopy (Figure 4-15c,d) reveals no significant changes in the series resistance (R_s), constant phase element (CPE), and charge transfer resistance (R_{ct}) after the stability test. The R_s barely changed (2.23 vs 2.24 Ω), while the R_{ct} reduced from 19.09 to 16.85 Ω . The high stability can be attributed to the thermodynamics associated with Lewis acid–base interaction of intermetallic phases, where the stabilities of the alloy are enhanced by hypo–hyper-d-intermetallic bonding.¹⁹⁵ SEM and XPS analyses of WNi/NF₄₅₀ after HER testing also indicate the similar surface structure, valence state, and the consistent constituents (Figure 4-16).

Figure 4-15. (a, b) Electrochemical stability tests: (a) Chronopotentiometric curve of WNi/NF₄₅₀ in a three-electrode configuration with a constant current density of 20 mA cm^{-2} without iR correction, and (b) iR -corrected polarization curves of WNi/NF₄₅₀ initially and after 1000 cycles. The inset of (b) shows the corresponding Tafel plots before (in solid line) and after 1000 cycles (in dotted line). (c) Electrochemical impedance spectra (EIS) Nyquist plot of WNi/NF₄₅₀ (at -1.02 vs Hg/HgO), and (d) pretreated Ni foam in 1.0 M KOH electrolyte.

Figure 4-16. (a) SEM images and (b) XPS of WNi/NF₄₅₀ after electrochemical treatment in 1.0 M KOH alkaline solution. (c) High-resolution XPS spectra of Ni 2p and (d) W 4f for post-HER long-term durability test in 1.0 M KOH solution at room temperature. (e) High-resolution O 1s spectra of WNi/NF₄₅₀ before and after

electrochemical exposure.

The excellent electrocatalytic activity can be attributed to the synergistic properties of homogeneously reduced tungsten–nickel alloy and high electrochemically active surface area (ECSA) upon annealing.^{132, 134} Firstly, an electrochemical double-layer capacitance (C_{DL}) is found at 0.13 mF cm^{-2} at 1.15 V, which is almost 3 times that of tungsten–nickel supported on NF without annealing (0.04 mF cm^{-2} , Figure 4-17). This C_{DL} which correlates with ECSA was derived from CV curves collected in a potential window where no Faradaic process occurred. The larger C_{DL} indicates more surface reactive sites of annealed samples are exposed to reaction media. These results are consistent with the rough surface observed on the tungsten–nickel particles after annealing (Figure 4-6b). Furthermore, the WNi/NF₄₅₀ catalyst shows a smaller charge transfer resistance compared to NF substrate (Figure 4-15d), which can be attributed to the binary metal system. Though the NF substrate is agreed upon as a highly conductive substrate, the reduced charge transfer resistance for the hybrid electrode shows that the catalyst alloyed onto the substrate is crucial for the outstanding performance. In this case, alloying W with Ni results in d-electron density modification and hence advanced intrinsic electrocatalytic activity.¹⁹⁵ Furthermore, a best catalyst for HER should have a Gibbs free energy for hydrogen adsorption close to zero.^{45,}¹⁹⁶ The favorable kinetics and enhanced HER electrocatalytic activity of the as-prepared WNi/NF hybrid electrocatalysts can be explained by the modification of

electron density in d-orbitals to tune the H-binding energies and optimize Gibbs free energy upon nickel–tungsten alloying.¹⁹⁶

Figure 4-17. (a) Cyclic voltammograms in the double layer region at scan rates of 25, 50, 100, 200 and 400 mV s⁻¹ (along the arrow direction) of WNi/NF₈₀ and (b) WNi/NF₄₅₀ catalyst in 1.0 M KOH at ambient temperature. (c) Current density at 1.15 V vs RHE as a function of scan rate derived from Figure 3-17a and 3-17b.

DFT calculations are carried out to better understand the water electrolysis mechanism for HER process. It has been reported that the hydrogen chemisorption energies reflects the kinetics for hydrogen-evolving catalyst.⁴⁵ Figure 4-18a shows the reaction pathways for O–H bond cleavage of water molecule at W and Ni sites

on the WNi (111) surfaces. The adsorption energy of H₂O at W sites is larger than that at Ni sites, which means that H₂O is more favorably adsorbed at W sites. The energy barriers for water dissociation are found to be 0.56 and 0.75 eV for W sites and Ni sites on (111) surfaces of WNi alloys. It suggests that W sites on WNi (111) surfaces are more reactive for O–H bond cleavage in comparison to Ni sites, which makes W sites more suitable for water splitting reaction. In Figure 4-18b, it is found that the free energy of hydrogen evolution on WNi (111) is much lower than that of Ni (111), indicating that WNi alloy is much more active than Ni catalyst, which is in well agreement with our experimental results. Moreover, W centers demonstrate a lower ΔG (0.17 eV) than Ni centers (0.32 eV) on the WNi (111) surface. This reveals W centers hold a higher catalyzing activity than Ni centers and are the main active sites in WNi catalysts.

Figure 4-18. (a, b) DFT calculation: (a) Reaction pathways for O-H bond breaking of H₂O molecule, activated H₂O adsorption, OH adsorption and H adsorption at W (black line) and Ni (red line) site on WNi (111) surfaces. (b) The calculated free energy diagram for hydrogen evolution on WNi (111) and Ni (111) surfaces.

4.4. Conclusion

In summary, 3D tungsten–nickel/nickel foam hybrid is successfully prepared by a facile hydrothermal approach followed by annealing treatment in the presence of hydrogen. The as-prepared WNi/NF₄₅₀ exhibits an extraordinary hydrogen evolution activity toward alkaline water splitting. It only requires an overpotential of 36 mV to afford the current density of 10 mA cm⁻² with a small onset potential of 2 mV and Tafel slope of 43 mV dec⁻¹, which is comparable to commercial precious Pt catalyst. The excellent electrocatalytic performance arises from the synergistic effect of binary tungsten–nickel interacting through the electron transfer of d-orbital electrons and the assistance of NF substrate. The DFT calculation results reveal that the lower hydrogen chemisorption energies and reduced Gibbs free energy on the surface of the tungsten–nickel/NF hybrid electrode promote water electrolysis process.

Chapter 5. Ultrathin Amorphous Iron–Nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production

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5.1. Background Introduction

Although transition metals, especially Ni, Co, and Fe hydroxides/oxides and/or their combinations with nonmetal elements (S, Se, P, N, and B) are very promising oxygen-evolving catalysts in high-pH electrolytes,^{81, 197-200} their industrial applications with satisfactory yields is still a hot topic in global science. Owing to the presence of boron, which diminishes the thermodynamic and kinetic barrier of the hydroxylation reaction, interest into the application of metal borides as catalysts has emerged, and the efficiency of these catalysts can be improved by tailoring their electrochemical properties. Metal borides exhibit special features, such as different shapes ranging from spherical to nanosheets, amorphous in nature, and the variation of the metal-to-boron ratio may affect the electrochemical properties.^{70, 110, 162, 201} The nanostructure of a metal boride, produced from a metal ion reduction in aqueous media, is amorphous in nature. However, metal borides

exhibit severe agglomeration, and this is an issue to be addressed. Despite a complicated structural analysis of amorphous materials compared to crystalline ones, they exhibit certain advantageous properties, such as a higher homogeneity, a controllable composition, more unsaturated atoms as active sites, and thus, an enhanced catalytic activity.^{120, 202-206} Though it is still a challenge to incorporate cations into catalytically OER-active amorphous materials,¹⁴⁷ the very amorphous nature of metal borides offers a great advantage for the incorporation of cations, thereby forming a multimetal metalloid nanostructure in a one-step process and modulating the surface electronic structure, which results in tuning of the electrocatalytic properties.^{162, 207}

Several strategies have been reported to enhance the electroactivity, such as nanostructure synthesis, metal or nonmetal doping, and hybrid catalyst synthesis with active material on highly conductive substrates, such as nickel foam, which can be applied to metal boride-based catalysts as well.²⁰⁸ In this regard, the in situ growth of nanostructure catalysts on 3D Ni foam (NF) has been rarely studied for metal boride catalysts. It may result in robust oxygen-evolving catalysts due to the synergistic effect between an electrocatalyst and a highly conductive substrate, which allows for a uniform growth of nanostructures with large surface areas, a greater surface roughness leading to an increase in the number of active sites, hence a greater wettability, and eliminates the agglomeration of nanoparticles, which causes aggregation of active sites in the metal boride nanoparticles.²⁰⁹

Low-cost nickel-based materials have been recognized for decades as the most active and stable earth-abundant materials against corrosion during the OER in alkaline media.^{34, 46} To boost their catalytic activity, iron is used as a compatible cation to tune the electronics and structures of Ni-based materials. From these perspectives, iron–nickel bimetallic catalysts are the most explored oxygen-evolving electrocatalytic materials due to the advanced catalytic properties and stability.^{105, 210} Though their application on an industrial scale is still highly attractive, iron–nickel oxides suffer from iron leaching over time at higher industrial-scale current density,²¹¹ and hence, iron–nickel bimetallic metalloids are also being explored. In this regard, a bimetallic catalyst combined with non-metallic elements to form selenides,⁹⁷ sulfides,^{212, 213} nitrides,²¹⁴ and phosphides²¹⁵ paves the way to synthesize numerous materials with different morphologies and structures, and facilitates synergistic effects between iron and nickel due to efficient electron-transfer properties within these nanostructures. To the best of our knowledge, a self-supported iron–nickel bimetallic boride catalyst onto a nickel foam substrate is not yet explored. In this regard, we present a novel bimetallic boride material on a continuous porous 3D network of NF, which is free from an organic binder and extra processes for the electrode preparation.

In the present work, we investigate the electrocatalytic properties of an ultrathin amorphous iron–nickel boride nanosheet-like material, which is fabricated through a one-step electroless deposition process onto commercial NF.

The ultrathin nanosheet was uniformly and firmly attached onto the 3D framework of a NF substrate from a reduction environment of cationic salts in a mixture of ammonium chloride and ammonium hydroxide. The structure and surface morphology of the optimized electrode was characterized by X-ray diffraction (XRD) and scanning/transmission electron microscopy (SEM/TEM). The catalyst composition was acquired by inductively coupled plasma optical emission spectroscopy (ICP-OES), whereas the chemical states before and after the OER test were analyzed by X-ray photoelectron spectroscopy (XPS). The electroactivity of the as-prepared electrode was investigated by measuring and comparing the potential required to deliver a current density of 10 mA cm^{-2} (i.e., the current density expected for a 12.3 % efficient solar water-splitting device),¹⁴¹ which is a primary criterion for the benchmarking of catalysts for the OER.¹³² Furthermore, the kinetics and electrical conductivity were determined from Tafel slopes analysis and electrochemical impedance spectroscopy (EIS) techniques, respectively, and finally, the stability in 1.0 M KOH alkaline solution was investigated. At an active mass loading of 1.0 mg cm^{-2} , this electrode shows an overpotential of 237 mV, affording a current density of 10 mA cm^{-2} . This activity is among the best both in metal borides and even comparable to other metal–metalloid catalysts. The advanced catalytic activity, facile electrode fabrication, and low costs make it a potential oxygen-evolving material, which may be extended to other energy conversion and storage technologies.

5.2. Experimental Section

5.2.1. Synthesis of the Amorphous Monometallic and Bimetallic Boride Electrodes

Two pieces of nickel foam (NF, 1 cm×0.5 cm) with similar weight were sequentially washed with acetone and ultra-purified water. Afterwards, they were ultrasonicated in a 3 M HCl solution for 45 min, followed by washing with water and ethanol several times to ensure the surface was well cleaned before use. Prior to the preparation of the metal ion source solution, the ultra-purified water was pre-purged with Nitrogen (N₂) gas to remove the dissolved oxygen (O₂). The pretreated NF pieces were then transferred into N₂-purged water (15 mL) containing 800 mg of ammonium chloride (NH₄Cl, Merck) and a given metal cation source (molar ratio: 1:1, 1:2, 1:3, 1:6, 1:9, 1:0, 0:1) from iron chloride hexahydrate (FeCl₃·6 H₂O, Sigma-Aldrich) and/or nickel chloride hexahydrate (NiCl₂·6 H₂O, Sigma-Aldrich) (3 mmol in total cation concentration) in an Ar environment. After keeping the solution undisturbed for 2 h at 50 °C to enhance the impregnation of cations onto the microporous NF surface, a solution of ammonium hydroxide (NH₃·H₂O, 25 wt %, Alfa Aesar) (0.65 mL) was added. Afterwards, one of the NFs was removed and washed to be used as a blank for the mass loading measurements. An equal volume of reducing solution containing NaBH₄ (Sigma-Aldrich) (9 mmol) in 0.1 M N₂-purged NaOH solution, was added with rapid mixing using a syringe. The mixture was kept undisturbed until the bubble formation stopped, and the NF

was removed, washed with water and pure ethanol to remove excess ions and other undesired dissolved species, such as Na^+ and Cl^- ions. It was then transferred into a tube reactor in an Ar environment and dried overnight at 50 °C. The reactor was cooled down and the fabricated electrode was then used for structural and electrochemical characterization. The catalyst loading was estimated by a well-established method for self-supported catalysts on NF.^{154, 216} The weight difference between the modified NF and the blank NF was divided by the surface area, and the catalyst loading was found to be approximately 1.0 mg/cm².

5.2.2. Catalyst Characterization

The surface morphologies of the as-prepared metal boride electrodes were studied by field emission scanning electron microscopy (FESEM, JEOL JSM 6340F), whereas energy dispersive X-ray spectrometry (EDS, JED 2300 EDS on JEOL JSM 6700F SEM) was used for elemental mapping. Additionally, the microscopic observation of the electrode was analyzed by transmission electron microscopy (TEM) on a JEM 2100F instrument at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns by using Cu K α radiation ($\lambda=1.5414$ Å) in the Bragg–Brentano configuration were used to characterize the structure of the electrodes. The elemental composition (Ni, Fe, and B) of the catalysts was conducted by using a Prodigy inductively coupled plasma (ICP-OES) spectrometer. The sample for the ICP-OES measurements was prepared by dissolving the catalyst powder obtained from the same pot in 2% w/v nitric acid.

The surface electronic states were studied from the X-ray photoelectron spectroscopy (XPS) data collected by using a PHI-5400 instrument equipment with an Al_{Kα} beam source (250 W) and a position-sensitive detector (PSD).

5.2.3. Electrochemical Measurement

The electrochemical activities of the as-fabricated self-standing electrode were investigated in a three-electrode cell by using the same Autolab potentiostat workstation described in section 3.2.3 at room temperature. The bare NF and the RuO₂ loaded onto NF at an approximately similar loading to the as-prepared electrode were also measured for comparison. A graphite rod and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. The measurements were performed in O₂-saturated 1.0 M KOH alkaline solution. The amorphous Fe-6Ni-B powder from the same pot and commercial RuO₂ catalyst suspensions were prepared by dispersing the catalyst (2 mg) in a mixture of ethanol (0.985 mL) and Nafion solution (15 μL, 5 wt%), followed by sonication for 30 min. Then an appropriate aliquot (0.250 mL onto 1 cm×0.5 cm, giving 1 mg/cm²) was transferred onto pretreated NF by using a pipette and dried under an ambient environment.

Prior to the measurement of the LSV polarization curves, which were recorded at a sweep rate of 5 mV s⁻¹ from 0.0 to 0.8 V versus Hg/HgO, the electrodes were processed by CV along the potential window 0.2 to 0.8 V versus

Hg/HgO at a rate of 50 mV s⁻¹ to ensure they reach a steady state. All potentials reported in this work, unless stated, were corrected for uncompensated iR drops, which were measured by the EIS technique at 0.6 V versus Hg/HgO. The stability test was carried out by recording CV profiles for 1000 cycles at 100 mV s⁻¹ from 0.26 to 0.66 V versus Hg/HgO. Additionally, the current–time curve of the catalyst at a constant E was studied. Furthermore, the chronopotentiometric responses were measured at a fixed j_{geo} of 20 mA cm⁻². All measured E reported in this study were converted from vs Hg/HgO to vs RHE by using equation 21. In addition, all the reported j were obtained by normalizing the current value with the area of the electrode. The η was calculated according to equation 20.

Turnover frequency (TOF) was calculated following the method applied for self-supported catalyst on the nickel foam (equation 24):

$$\text{TOF} = j \times S_{\text{electrode}} / (4F \times n), \quad (24)$$

Where j is the current density (A cm⁻²) at 1.536 V vs RHE, F is the Faraday constant (96 485 C mol⁻¹) and n is the number of active sites. In 1.0 M KOH electrolyte (pH = 14), the number of active sites was determined from the cyclic voltammograms carried out with a scan rate of 50 mV s⁻¹.

5.3. Results and Discussion

The application of a material for the OER on a large scale not only requires high catalyst efficiency but also cost-effective and facile preparation methods. Hence, a self-standing electrode was prepared by electroless plating of metal ions from an aqueous solution by using sodium borohydride (NaBH_4), which induced the reduction reaction under an argon atmosphere. As a result, an amorphous metal-metalloid nanostructure grew onto the 3D microporous skeleton of Ni foam. A schematic representation for the material preparation is depicted in Figure 5-1.

Figure 5-1. Schematic representation of the preparation of the as-prepared ultrathin amorphous nanosheet-like electrode.

The low-resolution field-emission scanning electron microscopy (FE-SEM) image in Figure 5-2a shows a uniformly covered NF in contrast to a smooth

surface of bare NF (Figure 5-2b). It is observable in Figure 5-3 that the reaction conditions affected the formation of nanosheet-like nanostructures. When the reaction was carried out in an ice water bath, nanoparticles with a spherical shape were deposited. In contrast, in the Figure 5-2a and in the inset of Figure 5-2a, the nanosheet and discrete particles appear to be firmly attached to the porous substrate.

Figure 5-2. a) SEM image of the fresh Fe-6Ni-B@NF hybrid electrode (the inset shows a high-resolution SEM image). High-resolution SEM images of bare NF.

Figure 5-3. Comparison of electrode prepared in ice and at room temperature. (a) and (b) SEM images of the amorphous iron-nickel boride prepared in an ice water bath. (c) and (d) SEM images of the as-prepared amorphous Fe-6Ni-B@NF electrode prepared at room temperature.

The high-resolution SEM image in Figure 5-4a shows ultrathin nanosheet-like nanostructures, which are about 100 nm in length and a few nanometers in width. Benefiting from the unique network-like nanostructure and the special integrated architecture onto a highly conductive substrate, the as-prepared metal boride would be useful for electrocatalyst applications. Additionally, this unique nanostructure of the nanosheets is retained even after the activation by cyclic

voltammetry (CV) test (Figure 5-4b,c) and it is observable that it has become thicker and rougher implying the growth of the metal oxide species, which is the active center for the oxygen-evolving reaction.

Figure 5-4. Microscopic measurements of the Fe-6Ni-B@NF electrode. a) High-resolution SEM image of freshly prepared electrode. b,c) High-resolution SEM image of the electrode after activation by a cyclic voltammetry test in 1.0 M KOH electrolyte solution. d) TEM image of ultrathin nanosheet-like Fe-6Ni-B scratched off from the Fe-6Ni-B@NF electrode (the insets show i) a TEM image and ii) the corresponding SAED pattern).

A close look at the transmission electron microscopy (TEM) image of the Fe-6Ni-B nanostructure scratched off from the Fe-6Ni-B@NF electrode through vigorous bath sonication in ethanol (Figure 5-4d) clearly shows a thin nanosheet-like morphology. The bottom-left inset (Figure 5-4d i) shows that this thin nanosheet-like structure is almost transparent due to its ultrathin nature, and the absence of any typical lattice fringes suggests that it is amorphous. The nature of this ultrathin nanosheet-like structure (Figure 5-4d i) was investigated by selected area electron diffraction (SAED). The top-left inset (Figure 5-4d ii) shows a SAED pattern with a broad and diffused halo ring, further confirming the amorphous nature of the as-prepared bimetallic boride nanosheets.

The material structure was studied by X-ray diffraction spectroscopy (XRD). The XRD pattern in Figure 5-5a only shows three peaks at 44° , 51° , and 75° ascribed to the (111), (200), and (220) planes, respectively, which arise from Ni foam (JCPDS No. 04-0850) and thus, implies the amorphous nature of the product. Additionally, an XRD pattern of the powder from the same pot shows amorphous nature with a roughly broad peak at around 45° (Figure 5-5b). These results agree with the SAED data and the literature, which proposed that metal borides prepared by the reduction of metal ions in aqueous solution by sodium borohydride are amorphous.^{70, 108, 110, 162}

Figure 5-5. (a) XRD pattern of (i) the as-prepared bimetallic boride electrode and (ii) of the corresponding powder from the same pot. (b) XRD pattern of bare Ni foam.

To better understand the chemical states and the elemental composition of the amorphous bimetallic iron–nickel boride electrode, X-ray photoelectron spectroscopy (XPS) measurements were performed. The XPS survey spectrum in Figure 5-6 shows that the main elemental composition includes Ni, Fe, and B, whereas the O signal originates from surface oxidation due to air contact and C is adventitious carbon from contamination during the preparation. Furthermore, energy dispersive spectroscopic (EDS) mapping of the material reveals the homogeneous distribution of these constituent elements (Figure 5-7). The elemental atomic composition of the catalyst was investigated by inductively coupled plasma spectroscopy. The metal constituent of freshly binary metal boride was found to be around twice that of B (Table 5-1) showing a metal-rich metal boride material. The composition follows the general formula M_2B , where M is the

total amount of nickel and iron. The ratio of the metals and their percentages were maintained even after activation by a CV test in alkaline solution. On the other hand, the metalloid content slightly reduced showing that the activation process leads to a predominant formation of metal hydroxides on the surface as active centers for the OER under alkaline condition, simply a Fe-Ni-B (core)/Fe(Ni)OxHy (shell) (OxHy=oxyhydroxide) nanostructure. The metal boride core is crucial for an enhanced conductivity in metal borides, metal alloys, and metal core-shell structure materials whereby, the predominant metal oxide species in the catalyst shell is responsible for the OER,^{107, 110, 162, 217} which is similar to the behavior of nickel and/or iron-nonmetal based catalysts in alkaline media such as phosphides,^{131, 138} nitrides,²¹⁸ and sulfides.³⁸ This is in agreement with the SEM image (Figure 5-4b,c) taken after the activation by a CV test, whereby the thickness of the nanosheets had increased, and hence, showed that the surface had more coverage of oxidized species compared to the freshly prepared electrode.²⁰⁷ These unusual structural properties benefit the water oxidation reaction and enhance the stability of the catalysts during the electrochemical testing as under oxidation potential these materials also get covered by metal (oxo-boro)hydroxides.¹¹⁰

Figure 5-6. XPS spectrum of Fe-6Ni-B@NF hybrid electrode.

Figure 5-7. EDX elemental mapping for constituent elements: Fe, B, O, and Ni.

Table 5-1. Atomic composition obtained by ICP-OES for the freshly prepared amorphous Fe-2Ni-B, Fe-3Ni-B, and Fe-6Ni-B catalysts and after activation by CV test in 1.0 M KOH solution.

Atomic Composition (%)						
Samples	Fe-2Ni-B		Fe-3Ni-B		Fe-6Ni-B	
Elements	Fresh	After activation	Fresh	After activation	Fresh	After activation
B	33.61	31.99	35.48	29.9	33.77	32.06
Fe	20.46	20.25	15.71	17.33	7.48	7.47
Ni	45.93	47.75	48.81	52.69	58.75	60.47
Total	100	100	100	100	100	100
Ni:Fe	2.2:1.0	2.3:1.0	3.1:1.0	3.0:1.0	7.8:1.0	8.0:1.0
M:B	2.0:1.0	2.1:1.0	1.8:1.0	2.3:1.0	2.0:1.0	2.1:1.0

As shown in Figure 5-8a, the XPS B 1s emission can be fitted with two spin–orbit doublets at 187.4 and 192.1 eV. The former can be assigned to a low-valence of boron resulting from metal–boron interaction, whereas the latter belongs to oxidized B, which might form by the aerial oxidation of the surface.^{219, 220} It is reported that due to the sensitivity of metal borides to air contact, the oxidized

species are unavoidable and predominantly form a layer of oxo-hydroxides on metal boride nanoparticles.^{146, 221} Similarly, as shown in Figure 5-8b, the XPS Ni 2p spectrum indicates the presence of metallic Ni combined with B at 852.6 eV for Ni 2p_{3/2} and at 869.3 eV for Ni 2p_{1/2}, whereas higher-oxidation state species appeared at 855.6 and 873.0 eV for Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, followed by two shake-up satellites (identified as “Sat.”), which is in agreement with the literature on nickel borides.^{110, 162} It is the same case for the Fe 2p spectrum shown in Figure 5-8c, where the peak at 706.5 eV is ascribed to the Fe 2p_{3/2} core level in iron boride, whereas the other peak at 711.2 eV is ascribed to oxidized iron species.¹⁶² Compared to bonding energy for pure B (187.1 eV),¹³⁹ boron here experienced a positive shift, which reveals electron deficiency due to electron transfer between the constituents. Though after the OER test the catalyst showed the same composition, the high-resolution XPS B 1s spectrum shows that boron is in a higher oxidation state only, which agrees with the available literature on XPS B 1s spectrum data of metal borides after the OER.^[16,24] From the high-resolution XPS of the O 1s core level (Figure 5-8d), it is clear that a large amount of oxygen is present as metal-(oxo-boro) hydroxide, which matches with the spectra of metal borides, which got exposed to air after preparation.^{110, 207} The nanostructure of transition-metal borides has been agreed upon in previous studies that it is composed of a core metal boride covered by a metal borate-rich layer. The presence of naturally occurring of a metal oxide-rich layer, as indicated by the predominance of the oxidized species, acts as a stabilizer of the core of the nanostructure as it

protects the core from further oxidation during the electrochemical test. Along with this, covalent bonds in the metal borides also contribute to the outstanding stability in alkaline solution.^{110, 162, 207}

Figure 5-8. High-resolution XPS spectra of the a) B 1s, b) Ni 2p, and c) Fe 2p core level of the amorphous iron-nickel boride electrode freshly prepared and after the OER test. d) O 1s spectrum before (i) and after (ii) OER test.

The electrocatalytic performance of the as-prepared amorphous three-dimensional metal boride electrodes towards the OER was studied in O₂-saturated 1.0 M KOH alkaline solution and the saturation was maintained over the entire electrochemical test to ensure the O₂/H₂O equilibrium at 1.23 V versus the reversible hydrogen electrode (RHE). All measurements were performed in a standard three-electrode electrochemical cell by using the as-prepared electrode as the working electrode, a Hg/HgO (1.0 M KOH) pair as the reference electrode, and a graphite rod as the counter electrode. Potentials obtained in this study were all calibrated to the reversible hydrogen electrode as a reference for comparison purpose.

Prior to the electrochemical measurements, each electrode was treated by continuous CV until reproducible voltammograms were obtained (Figure 5-9a). The increase in the anodic and cathodic intensities was remarkable in a potential window where the redox phenomenon occurred. It was associated with the growth of oxidized species (i.e., NiOOH) during the OER in alkaline media.⁷⁰ As shown in Figure 5-9a, the peak current increased and reproducible curves were obtained after forty cycles. Such an increase in the peak current is associated with an increase in the amount of electrocatalytically active sites in the nickel-based OER catalyst in alkaline media.¹¹⁰ Recently, the mechanism of the OER on nickel boride (Ni₃B) nanosheets was investigated and the anodic process was attributed to the oxidation of Ni²⁺ to Ni³⁺, whereas the reverse process is the reduction of Ni³⁺ back

to Ni^{2+} ($\text{Ni}(\text{OH})_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^-$).¹¹⁰ Simultaneously, the presence of Fe^{3+} does not hinder this redox process for Ni as it remains in its 3+ state and thus, acts as a promoter for the process.²²² Moreover, the change from the first scan to the second scan is distinct (Figure 5-9b) and this may demonstrate the permanent activation of the catalyst.

Figure 5-9. (a) Activation of Fe-6Ni-B@NF electrode by continuous potential cycling between 0.2 and 0.8 V vs Hg/HgO at 50 mV s^{-1} in 1.0 M KOH (without iR compensation), the arrows indicate the direction in which the current densities increase. (b) First and second scan for amorphous Fe-6Ni-B@NF electrode activation by continuous potential cycling between 0.2 and 0.8 V vs Hg/HgO at 50 mV s^{-1} in 1.0 M KOH (without iR compensation).

As shown by the linear sweep voltammetry (LSV) curves given in Figure 5-10a, after activation by the CV test the Fe-6Ni-B electrode showed an overpotential of 237 mV to deliver a current density of 10 mA cm^{-2} (η_{10}). On the contrary, bare Ni foam showed insignificant activity in the OER. This enhancement

in the performance can be attributed to the hybrid nature of the Fe-6Ni-B catalyst assisted by the highly conductive NF. Additionally, the as-prepared Fe-6Ni-B@NF outperforms precious metal-based catalyst supported on NF by a casting method (RuO₂/NF) as can be observed in Figure 5-10a, where the RuO₂/NF catalyst requires an overpotential of 292 mV to achieve a similar current density. Furthermore, the activity of the catalyst is comparable to other nickel- or iron-doped nickel-based catalysts supported on a high-conductivity material, such as Fe-Ni₃S₂/FeNi alloy (282 mV),²¹³ NiFeO_x/Ni foam (260 mV),²²³ Ni-B/NF (360 mV at 100 mA cm⁻², compared to 275 mV for Fe-6Ni-B@NF at the same current density),²²⁴ NiFeS/NF (231 mV),²²⁵ W_{0.5}Co_{0.4}Fe_{0.1}/NF (250 mV and 310 mV at 10 mA cm⁻² and 100 mA cm⁻², respectively),¹⁴³ NiFe LDH/NF (278 mV) and Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF (231 mV),²¹⁶ Ni-Bi NA/TM (430 mV at 10 mA cm⁻² in 0.1 M potassium borate (pH 9.2)),²²⁶ r-NiMoO₄/NF (249.5 mV),²²⁷ WNi/NF₄₅₀ (328 mV at 50 mA cm⁻²),¹⁷⁰ and NiFe-OH-PO₄/NF (249 mV at 20 mA cm⁻²).²²⁸

Figure 5-10. a) Linear sweep voltammograms (LSVs) corrected for the resistance of the electrolyte of amorphous Fe-6Ni-B@NF, RuO₂ supported on Ni foam (RuO₂/NF), and bare Ni foam at 5 mV s⁻¹ in 1.0 M KOH at room temperature. b,c) The corresponding Tafel and Nyquist plots, respectively.

The robust water oxidation activity of the amorphous Fe-6Ni-B@NF electrode was confirmed by taking insights from the OER kinetics through Tafel plots, which describe the influence of the η on the steady-state current density. The Tafel slope was acquired by replotting the polarization curve as a plot of $\log j$ versus the η and fitting it to the Tafel equation (Equation 4). The obtained Tafel slopes given in Figure 5-10b reveal favorable kinetics of the Fe-6Ni-B@NF

electrode at 38 mV dec^{-1} compared to bare nickel foam and RuO_2/NF .²²⁹ The reduced Tafel slope indicates the advancement in the OER rate due to a reduced charge-transfer resistance, which results in a remarkable increase in the current density at a higher overpotential.⁹⁹ As a consequence, this electrode achieves a current density of 100 mA cm^{-2} at 275 mV .

The electrochemical performance of the as-prepared electrode was further examined by electrochemical impedance spectroscopy tests. The high-frequency intersection with the x -axis on the Nyquist plot represents the Ohmic resistance (R_s), which is a result of all interfacial contacts and the resistance of the electrolyte. Another parameter from the EIS test is the charge-transfer resistance (R_{ct}), which can be obtained from the semicircle in the low-frequency zone and is known to relate to the electrocatalytic kinetics where its lower value corresponds to a faster reaction rate. The as-prepared electrode shows a smaller charge-transfer resistance compared to a RuO_2 catalyst loaded on NF (Figure 5-10c).

Apart from an advanced electrocatalytic OER performance of the optimized iron–nickel boride electrode (Fe-6Ni-B@NF), the corresponding monometallic boride electrodes, namely Fe-B@NF and Ni-B@NF , also display OER catalytic properties (Figure 5-11a,b). However, their performances are not as good as that of the bimetallic boride catalyst. The Ni-B@NF electrode requires an overpotential of 282 mV to deliver 10 mA cm^{-2} , which is 45 mV higher compared to that of the Fe-6Ni-B@NF electrode (Figure 5-11a). Moreover, the Tafel slope

was increased from 38 to 41 mV dec⁻¹ (Figure 5-11c). The onset potential is another important factor for the analysis of OER catalysts. The Fe-6Ni-B@NF electrode exhibits a smaller onset potential, obtained from the intersection point of the Tafel slope at the overpotential axis, of approximately 228 mV, whereas it is estimated to be 245 mV for both the Ni-B@NF and Fe-B@NF electrodes. This gives insights into the advanced kinetics in terms of a Tafel slope and a charge transfer of the bimetallic boride electrode compared to a monometallic boride electrode. Though the difference in the onset potential is only 17 mV, the bimetallic boride exhibits a dramatic increase in the current density with the potential. For example, to achieve a current density of 100 mA cm⁻², the required overpotential is only 275 mV for the Fe-6Ni-B@NF electrode but 326 mV for the Ni-B@NF electrode.

Figure 5-11. a) *iR*-corrected polarization curves for amorphous Fe-6Ni-B@NF, Fe-B@NF, and Ni-B@NF at a scanning rate of 5 mV s⁻¹. b,c) Nyquist plot and Tafel plot, respectively.

The crucial role of iron was examined by investigating the cycling voltammetry curves for the amorphous Fe-6Ni-B@NF and Ni-B@NF electrodes (Figure 5-12). The amorphous bimetallic boride catalyst shows a greater area under the curve related to the redox peak of the Ni-active center for the Ni²⁺ to Ni³⁺ oxidation.²³⁰ It is observed that, due to the presence of iron in the bimetallic catalyst, the current continuously rose after reaching the oxidative potential,

whereas in the monometallic nickel boride electrode it went down a little and rose again at higher potential.

To further examine the advanced electroactivity of the bimetallic Fe-6Ni-B@NF electrode compared to the monometallic Ni-B@NF electrode, the turnover frequency (TOF), which is defined as the amount of gas molecules generated per unit time, was also calculated. Assuming that the whole Ni content was active at 306 mV, the TOF was calculated to be 0.035 and 0.006 s⁻¹ for the bimetallic and monometallic catalysts, respectively. This can be explained by the most accepted mechanism for the synergistic effect of iron in nickel-based catalysts, in which an Fe-induced partial-charge-transfer mechanism activates the Ni centers in the catalyst.⁹⁰ Hence, iron doping is the key to overcome the major challenge of poor activity in Ni-based catalyst.^{90, 231}

Figure 5-12. The first and tenth scan curves of amorphous bimetallic Fe-6Ni-B@NF and monometallic Ni-B@NF electrodes during activation process by

continuous potential cycling between 0.2 and 0.8 V vs Hg/HgO at 50 mV s⁻¹ in 1.0 M KOH (without *iR* compensation).

The effect of iron incorporation in the amorphous Fe-6Ni-B@NF electrode was studied by tuning the Fe/Ni ratio in the precursor solution. Figure 5-13 displays the overpotential required to deliver 10 mA cm⁻² versus the Tafel slope where both are potential parameters for the analysis of oxygen-evolving catalysts.^{232, 233} It can be clearly observed that the Tafel slope varied from 38 to 43 mV dec⁻¹ for the various bimetallic borides (Figure 5-14a,b). Among the electrodes studied in this work, the smallest Tafel slope and the lowest overpotential at 10 mA cm⁻² is obtained with the amorphous Fe-6Ni-B@NF electrode.

Figure 5-13. Comparison of different metal–boron@NF electrode by using two parameters: Tafel slopes versus overpotential required to afford a current density of 10 mA cm⁻².

Figure 5-14. (a) *iR*-corrected LSV curves for amorphous monometallic and bimetallic boride electrodes with different iron to nickel ratios in the precursor solution. (b) Corresponding Tafel plots.

The importance of growing the metal boride nanostructure directly on NF and without any organic binder usage is verified by comparing the electrochemical performance of the control sample, which was prepared by drop-casting the ink containing Fe-6Ni-B particles from the same pot onto NF (Fe-6Ni-B/NF). The drop-casted electrode (Fe-6Ni-B/NF) shows a much high Tafel slope (68 vs 38 mV dec⁻¹) and a larger charge-transfer resistance (2.5 vs 0.7 Ω) (Figure 5-15). This

reveals the benefit of the direct growth of the active catalyst onto a highly conductive substrate due to better interfacial contact and elimination of the usage of chemical binders (such as Nafion in this case), which may interfere with the charge transport during the catalytic reactions and cover active sites.^{234, 235} This can be interpreted as a complex synergistic effect between the substrate and the conductive catalyst core, which provides an effective electron transport within the amorphous metal boride nanostructure to facilitate the OER active centers in the shell of the catalyst.^{207, 236, 237}

Figure 5-15. (a) *iR*-corrected LSV curves for amorphous Fe-6Ni-B@NF electrodes, amorphous Fe-6Ni-B powder from the same pot loaded into NF at

similar loading and bare NF. Their corresponding Tafel plot (b) and Nyquist plot (c).

The stability towards the OER is another important factor that should be considered for this earth-abundant metal-based electrocatalyst. To investigate the stability of the amorphous Fe-6Ni-B@NF electrode, continuous cyclic voltammetry (CV) was first conducted from 0.26 to 0.66 V versus Hg/HgO at 100 mV s⁻¹ for 1000 cycles. In Figure 5-16a, a negligible loss of the current density and a constant Tafel slope were observed after 1000 cycles of CV, demonstrating its high stability. The durability of the electrode was further verified by using chronoamperometry and chronopotentiometry methods (Figure 5-16b,c). These stability tests show that the ultrathin amorphous nanosheets onto macroporous Ni foam can maintain the catalytic activity over a long-term period. The operating stability of the electrode can be explained by the covalent character in the metal boride and the presence of B, which acts as a stabilizer.¹²⁵ The use of SEM images of an electrode before and after the electrochemical test is the most visual method to examine the morphology change of an electrode.²³⁸ As can be seen from Figure 5-4c, the electrochemical activation by a CV test leads to morphological changes as noticed by an increase in the nanosheet thickness and roughness, which implies more water retention and accessible active sites for hydroxyl species. Additionally, the predominance of borates and oxyhydroxides, as observed in the post-OER XPS spectra, can boost the OER kinetics and can even improve the stability by providing

protection to the metal boride core, which is crucial for the electrical conductivity.²³⁹ The advanced stability of this material is therefore attributed to the amorphous nature and the induced morphological changes of these catalysts during the activation.^{214, 240} Hence, this ultrathin amorphous nanosheet-like morphology is crucial for both the oxygen-evolution properties and the stability of the as-prepared bimetallic iron–nickel–boron catalyst onto 3D Ni foam. Furthermore, by controlling the preparation conditions, this method can be extended to other transition metals.

Figure 5-16. a-c) Electrochemical stability tests. a) iR -corrected polarization curves of Fe-6Ni-B@NF electrode initial and after continuous 1000 cycles (The

inset shows the corresponding Tafel plots). b) Chronoamperometric curve, and c) Chronopotentiometric curve at a potential required to afford 20 mA cm^{-2} in 1.0 M KOH solution at room temperature.

5.5. Conclusion

In conclusion, we have synthesized a self-standing electrode based on ultrathin amorphous bimetallic iron–nickel boride nanosheets onto nickel foam. The as-prepared electrode exhibits an outstanding OER performance with an overpotential of 237 mV to reach a current density of 10 mA cm^{-2} , a small Tafel slope of 38 mV dec^{-1} , and an outstanding electrochemical stability in 1.0 M KOH solution. This can be attributed to the iron incorporation at an optimal iron-to-nickel ratio and the synergistic effect due to multimetal–metalloid interplays and good contact between the catalyst and substrate. This opens the opportunity to synthesize other multimetal boride materials onto 3D Ni foam and it can be extended to other related electrochemical applications.

Chapter 6. Facile Synthesis of Amorphous Ternary Metal Borides–Reduced Graphene Oxide Hybrid with Superior Oxygen Evolution Activity

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6.1. Background Introduction

In search of alternative electrocatalyst to replace precious metal-based catalyst, earth-abundant 3d transition metal-based materials have been proposed as an alternative to precious metal-based catalyst for OER because of its electrocatalytic activity, low cost, and stability.^{79, 241} These include but not limited to the monometal catalyst such as nickel, cobalt, and iron-based oxides and (oxo)hydroxides.²⁴²⁻²⁴⁴ It was further found that doping of other metals to form a multimetal catalyst offers a great advantage for modulating the electronic structure, which results into the synergistic effect of the active centers and hence advanced OER activity.^{162, 245-247} Especially, the Ni-based catalyst has been explored due to its stability against corrosion during the OER in alkaline medium and the doping of other metals had found to tailor the electrocatalytic activities.^{170, 248, 249} Though

the OER active center in transition metal-based catalyst is an oxidized metal, other metal compound materials, such as phosphides, nitrides, sulphides, selenides, and borides, show promising activity compared to metal alloy and metal oxides.^{170, 247} This has been attributed to the unusual effect of this metal–metalloid, which acts as a precursor and thus undergoes both morphological and chemical changes in highly oxidative potentials.^{250, 251} As a result, the in situ formation of oxo-/hydroxometal species on the surface is noticed during the electrochemical oxidation process, which functions as catalytic sites for OER with superior performance.^{170, 252}

Recently, metal borides have received a new interest as efficient material which even outperforms precious metal-based catalyst in some cases.^{70, 162} It is agreed that the presence of guest element such as boron/phosphorous in metal boride contributes to advanced activity.²⁵³ Various shapes from spherical particles to ultrathin nanosheets and different structures, such as crystalline and amorphous structure, had been reported.^{108, 254} The amorphous nature of metal borides produced in an aqueous medium is important as it allows the tunable incorporation of other metals by controlling the metal ratio in metal salt solution, and this does not affect the nature of the final product. It also shows advanced activity mostly due to abundant defect sites.²⁵⁵ Hence, from an OER catalyst perspective, nanosized, amorphous metal boride material, which allows exposure of more active sites, is preferred. One of the techniques to boost the electrocatalytic activity is to

prepare catalyst hybrid on highly conductive materials, such as Ni foam and reduced graphene oxide (rGO).^{209, 256, 257} Thus, it is of great interest to develop a facile method to synthesize nanosized, amorphous metal borides on a conductive material with high activity.

Herein, we synthesized an amorphous iron-doped nickel boride coupled to co-reduced GO sheets via one-step reduction reaction at room temperature for OER. The choice of rGO as a substrate is due to its high electric conductivity, good electrochemical stability, and ultra large specific surface area.²⁵⁸ By incorporation of iron in nickel boride and controlling the ratio of GO to active material, the as-prepared electrocatalyst showed excellent OER catalytic performance and stability in an alkaline medium. A very low overpotential of 230 mV is required for achieving a current density of 15 mA cm⁻² with a small Tafel slope of 50 mV dec⁻¹, which was better than Ni-B/G and commercial RuO₂ catalyst at the same mass loading. To our knowledge, the as-prepared material exhibits outstanding activities compared to metal boride catalyst reported to date. This simple, facile, and one-step hybridization of ternary metal boride on highly conductive co-reduced GO in a short period of time can be extended to other metal borides as well.

6.2. Experimental Section

6.2.1. Materials Synthesis

GO was synthesized by mixing 2 g of graphite powder with 100 mL of

H₂SO₄ in an ice bath at 4 °C for 30 min. Afterwards, 12 g of KMnO₄ was added slowly and maintained at 4 °C for 1 h. Before adding 200 mL of DI-water, the solution was removed from the ice bath and transferred to a water bath. After 2 h at 40 °C, the DI-water was added slowly, and when the temperature was below 60 °C, hydrogen peroxide (H₂O₂) was added dropwise. The product was filtered and rinsed with 400 mL of 10% HCl three times. Before using, GO was dispersed in water, and the suspension was dialyzed for two weeks. The amorphous metal boride–GO hybrids were prepared by reducing an aqueous mixture containing metal precursors [iron (II) sulfate heptahydrate (FeSO₄·7H₂O) and nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O)] and GO with a strong reducing agent (NaBH₄), which also acts as the boron source. Typically, the total moles of the metal salt source were 1.25 mmol in 45 mL, and the reducing solution was 5 mL. The reduction reaction of metal ions in an aqueous solution results into a precipitate of metal boride via equation 16.^{70, 124}

Herein an adaptation had been used, instead of drop by drop addition of reducing solution to metal sources, rapid addition was used in the presence of saturated Ar environment. The BH₄⁻/M²⁺ ion ratio was maintained at three times to ensure the formation of metal borides.¹⁰⁹ To optimize the as-prepared material, we investigated the effect of (1) the iron-to-nickel ratio, (2) the different GO amounts, and (3) the reduction rate. The addition of reducing solution caused rapid transformation of the solution to a black precipitate well dispersed in the solution.

The black precipitates were collected and washed subsequently with ultrapurified water and with ethanol. Afterwards, the samples were dried for 12 h in an Ar saturated environment at 50 °C. The products were collected for structure and electrochemical characterizations. To analyze the behavior of GO in a reducing environment of metal ions in aqueous solution, the same amount of GO suspension used for optimized catalyst (30%) was treated with NaBH₄. The obtained black product was also cleaned with DI-water and ethanol and dried in the same environment as metal boride-rGO hybrid catalyst.

6.2.2. Catalyst Characterization

The surface morphologies of the as-prepared powders were studied by field emission scanning electron microscopy (FESEM, JEOL JSM 6701F) coupled with energy dispersive X-ray spectroscopy (EDX). Furthermore, the transmission electron microscopy (TEM) images and selected area diffraction (SAED) pattern were taken from JEOL 2010 HR while the TEM mapping and TEM-EDX were from JEOL 2100F at an accelerating voltage of 200 kV. Structural characterization was determined by recording the X-ray diffraction (XRD) patterns using the Cu K α radiation ($\lambda = 1.5414 \text{ \AA}$) in Bragg–Brentano configuration. The N₂ adsorption and desorption isotherms were acquired by using the Brunauer–Emmett–Teller (BET) method on Quantachrome Autosorb-6 to investigate the specific surface areas and pore size distribution. The surface electronic states and composition of the as-prepared catalyst and after OER test (activation by CV test till a reproducible

voltammogram were obtained and treated by chronopotentiometry at a fixed current density of 20 mA cm^{-2} for 1 h) were carried out by X-ray photoelectron spectroscopy (XPS). XPS spectra were collected by a Kratos AXIS Ultra^{DLD} instrument equipped with a monochromatic Al K α (1486.71 eV) X-ray source and a hemispherical analyser.

6.2.3. Electrochemical Measurement

Electrochemical measurements of the as-prepared material and commercial RuO₂ catalyst for comparison were conducted in a three-electrode cell using a rotating disk electrode (RDE, PINE Research Instrumentation) at the same Autolab potentiostat workstation described in section 3.2.3. The graphite rod and Hg/HgO (1.0 M KOH) were used as the counter and reference electrodes, respectively. All the electrochemical measurements were conducted in O₂-saturated alkaline 1.0 M KOH electrolyte at room temperature.

The catalyst and the commercial Ruthenium (IV) oxide (RuO₂, 99.9% metals basis, Aladdin) catalyst suspensions were prepared by dispersing 5 mg of catalyst in 1.0 mL of solution containing 725 μL of ethanol, 235 μL of water and 40 μL of 5 wt% Nafion solution, followed by sonication for 20 minutes. Then appropriate aliquot was pipetted into pre-treated GC surface (0.196 cm^2) to give a loading of 0.3 mg/cm^2 . The physical mixture of the unsupported metal boride and GO treated by NaBH₄ to mimic the co-reduced GO during the reduction process

was prepared using 30% of treated-GO.

The LSV polarization curves were recorded at a sweep rate of 5 mV s^{-1} under continuous stirring of 1600 rpm to avoid accumulation of gas bubbles over the GC electrode. Prior to LSV polarization curve recording, the materials were exposed to CV polarization curve along the potential window of 0.2 V to 0.8 V vs Hg/HgO at 100 mV s^{-1} . After recording polarization curves, the iR drop was compensated at 97% which was measured by the EIS technique at 0.6 V vs Hg/HgO. The stability test was carried out by recording CV profiles of 1000 cycles at 100 mV s^{-1} from 0.2 V to 0.6 V vs Hg/HgO. Furthermore, the chronopotentiometric responses were measured at a fixed j of 10 mA cm^{-2} . All measured E reported in this work were converted from vs Hg/HgO to vs RHE by using equation 21. The η was calculated according to equation 20.

6.2.4. Turnover of Frequency (TOF)

The TOF was calculated by using equation 24, where J is the OER current density calculated from LSV collected at 5 mV s^{-1} , F is the Faraday constant, A is the geometrical surface area of the electrode ($GC = 0.196 \text{ cm}^2$), and m is the amount of electroactive Ni, Fe, and/or Ni-Fe sites, which was obtained from integrating the charge amount of metal redox peaks area.

6.2.5. Electrochemically Active Surface Area (ECSA)

The ECSA was measured by electrochemical double layer capacitance method. The CV used for electrochemical double layer capacitance (C_{DL}) calculation was acquired in a potential window where no Faradaic process occurred. To derive the C_{DL} , equation 17 was used. The ECSA of a catalyst sample was calculated from the double layer capacitance according to equation 19.

6.2.6. Computational Methods

The electronic structures and adsorption free energy were computed by the Vienna *ab initio* Simulation Package (VASP) using spin-polarized density functional with the Hubbard model (DFT+U).^{259, 260} The projector augmented wave (PAW) model with Perdew–Burke–Ernzerhof (PBE) function was employed to describe the interactions between core and electrons.^{261, 262} An energy cutoff of 500 eV was used for the plane-wave expansion of the electronic wave function. The Brillouin zones of all systems were sampled with gamma-point centered Monkhorst–Pack grids. A $3 \times 3 \times 3$ and $3 \times 3 \times 1$ Monkhorst Pack k-point setup were used for bulk and slab geometry optimization. The force and energy convergence criterion were set to $0.02 \text{ eV } \text{\AA}^{-1}$ and 10^{-5} eV , respectively.

6. 3. Results and Discussion

Due to the presence of a large amount of hydroxyl and carboxyl groups on

GO, metal ions were adsorbed on the surface of GO, and NaBH_4 was used as both a reducing reagent and a boron source. The chemical reduction process was carried out by rapid addition of reducing solution under Ar at room temperature. It has been reported that, regardless of the other parameters, rapid mixing in the presence of Ar results in metal borides.¹⁰⁹ The obtained metal boride was strongly coupled to simultaneously co-reduced GO sheets in a short duration compared to the conventional method, whereby the reducing agent is added dropwise and considerable time is required for the complete reaction. Figure 6-1 shows a schematic representation of the catalyst synthesis (denoted as $\text{Fe}_x\text{Ni}_y\text{-B/G}$).

Figure 6-1. Schematic representation for the transition metal borides-rGO ($\text{M}_2\text{B/G}$)

The morphology of a typical catalyst ($\text{FeNi}_3\text{-B/G}$) was first studied by

electron microscopy. In the HRTEM image (Figure 6-2a) and at higher magnification FESEM (Figure 6-2b), the rGO sheets were found to have been covered by nanostructures. The amorphous nature and highly porous morphologies of the ultrathin nanostructure are supported by the absence of lattice fringe in the HRTEM image (Figure 6-2c). The EDX spectrum (Figure 6-3) contains Fe, Ni, B, C, and O elements and gives 2:1 (the inset table in Figure 6-3) metal-to-boron ratio, which indicates the formation of metal borides with a general formula of M_2B (M_2B/G) and agrees with the literature on transition metal borides produced by chemical reduction in an aqueous medium.^{70, 124} The absence of dots and appearance of halo rings from the substrate in the SAED pattern (the inset of Figure 6-2c) suggest the amorphous nature. On the contrary, GO is reported to show the presence of dots in the SAED pattern; hence, this shows that GO was simultaneously reduced to rGO, which got covered by metal boride.²⁶³ This is also observable from the HRTEM image in Figure 6-4, whereby the bare GO shows a smooth surface and the surface of Fe_xNi_y-B/G is rougher and covered by nanostructures.

Figure 6-2. (a) HRTEM image of the freshly prepared FeNi₃-B/G hybrid catalyst. (b) High magnification FESEM image. (c,d) HRTEM images. The inset in c is the SAED pattern.

Figure 6-3. EDX pattern and the inset is the EDX Table.

Figure 6-4. (a) HRTEM image of the bare GO. (b) HRTEM image of FeNi3-B/G (30% GO) catalyst.

Figure 6-5 and Figure 6-6 show HAADF-STEM images for the freshly prepared material and after OER test, as well as the corresponding TEM elemental mapping of Ni, Fe, C, B, and O, which reveal the homogeneous distribution of the constituents on the rGO. From the TEM-EDX result, the iron-to-nickel ratio was 0.27:0.73, which is close to 1:3 in the metal precursor solution for FeNi3-B/G.

Figure 6-5. HAADF-STEM image and elemental mapping images of the as-prepared FeNi₃-B/G catalyst (30% GO).

Figure 6-6. (a) HRTEM image of the FeNi₃-B/G (30% GO) catalyst after CV activation followed by chronopotentiometry at a fixed current density of 20 mA cm⁻² for one hour showing ternary metal borides still coupled on G. (b) HAADF-STEM image and Ni, Fe, C, B, and O elemental mapping results after OER test.

The structure of the as-prepared hybrid catalyst was investigated by XRD (Figure 6-7a). The FeNi₃-B/G catalyst showed two weak peaks at $2\theta = 10^\circ$ and 25° . The former matched with the strong peak of (001) plane observed in the XRD pattern of GO (Figure 6-7b), whereas the latter matched with the (002) plane from

rGO, which implies partial reduction of GO, hence denoted G.^{264, 265} The absence of any other strong peak (Figure 6-7a), which is also observed for unsupported ternary metal boride (FeNi₃-B), shows the amorphous nanostructure of the product, which agrees with the reported metal borides produced by the chemical reduction of metal salt in an aqueous solution.¹⁰⁸ The shoulder peaks at $2\theta = 35^\circ$ and at $2\theta = 61^\circ$ may arise from the metal and/or boron oxides formed inevitably in the procedure of storage and measurements under atmospheric exposure.²⁶⁶

Figure 6-7. (a) XRD pattern of GO, unsupported catalyst (FeNi₃-B), and FeNi₃-B/G catalyst. The inset is the magnified picture of the boxed area in (a). (b) XRD pattern for bare GO. (c) XRD pattern for GO and GO treated by NaBH₄

without metal ions sources (G). (d) XRD pattern for as-prepared FeNi₃-B/G catalyst by fast reduction, and FeNi₃-B/G prepared by slow rate of reduction (drop by drop over 5 minutes).

The XRD pattern of NaBH₄-treated GO (Figure 6-7c) shows a peak at 25° for the (002) plane, and a very weak peak for the (001) plane reveals partial co-reduction of GO in the presence of reducing agent and agrees with the partial reduction of GO observed for the as-prepared FeNi₃-B/G catalyst. The addition of a reducing solution to GO suspension showed a color change, validating the co-reduction of GO (Figure 6-8a-c). The weak peaks in FeNi₃-B/G suggest that the metal boride nanostructure covered the co-reduced GO as observed in TEM mapping (Figure 6-5). The exothermic reaction of metal ions in an aqueous medium of the latter in contact with NaBH₄ may have contributed to the co-reduction of GO compared to the strong peaks for the dropwise sample (Figure 6-7d), leading to strong hybridization of metal boride nanoparticles to GO.²⁶⁷

Figure 6-8. Digital photographs: (a) 45 mL of 20 mg graphene oxide (GO) suspension, (b) solution after reaction of GO with NaBH_4 , (c) black product of treated-GO (G) in ethanol after washing with DIW to achieve nearly neutral pH and centrifuged for solid collection (denoted as G).

The special surface areas of unsupported FeNi₃-B and FeNi₃-B/G hybrid were analyzed by the BET method. The N_2 adsorption and desorption isotherms show a typical H3 hysteresis loop of IV-type curve (Figure 6-9), indicating the presence of mesoporous structures.²⁶⁸ The pore size distribution curves in the inset of Figure 6-9 show a single well-defined peak at ca. 3.8 nm, further suggesting mesoporous material. The BET specific surface areas and pore volumes of FeNi₃-B/G hybrid were calculated to be $56 \text{ m}^2 \text{ g}^{-1}$ and $0.44 \text{ cm}^3 \text{ g}^{-1}$, respectively. On the other hand, the unsupported FeNi₃-B showed smaller values ($38 \text{ m}^2 \text{ g}^{-1}$ and $0.17 \text{ cm}^3 \text{ g}^{-1}$) which reveals much higher surface areas of the FeNi₃-B/G hybrid.

Figure 6-9. N₂ adsorption–desorption isotherm curves and pore size distribution curves (inset) of the unsupported FeNi₃–B and FeNi₃–B/G.

The elemental composition and the chemical states were studied by XPS. As shown in the XPS survey of FeNi₃–B/G (30% GO) (Figure 6-10), the presence of Ni, Fe, B, C, and O was found with 5.12, 1.63, 3.46, 69.36, and 20.44% atomic percentages, respectively. The metal-to-boron ratio was found to be around 2, which shows that metal boride material with the general formula of transition metal borides (M₂B) was produced.^{70, 124} The ratio of iron to nickel (0.24:0.76) followed the metal ions' ratio in metal salt solution (FeNi₃–B/G), showing a fast, easy, and efficient method for doping iron.

Figure 6-10. XPS survey spectrum of the as-prepared FeNi₃-B/G (30% GO) catalyst.

As revealed by the B 1s XPS spectrum (Figure 6-11a), B in a prolonged stored catalyst showed a peak at 188.3 eV for boron bonded to metallic elements.^{220, 269, 270} The positive shift in binding energy (BE) compared to pure B (187.1 eV),¹³⁹ and to nickel boride (187.9 eV) shows enhanced electron transfer from B to the vacant d-orbital of the metallic elements.²²⁰ Additionally, peaks of oxidized B species, such as borates, were present at 192.4 and 193.4 eV. Both nickel and iron XPS 2p spectra reveal the existence of both elemental and oxidized states (Figure 6-11b,c), which was consistent with the literature that metal borides exposed and stored for a long time in air are covered by a thin layer of hydroxides or oxides, hence identified as metal boride/metal boron-oxide complex nanostructure.^{70, 110, 271, 272} Clearly, there was no obvious change during OER test in the Fe 2p XPS spectrum (Figure 6-11b) for iron bonded to boron at 706.2 eV,

emphasizing the presence of core@oxide layer nanostructure.^{269, 271} Both metals experience severe oxidation during water oxidation because of the formation of MO_xH_y , which acts as active surface species. The O 1s and C 1s spectra in Figure 6-11d,e show not only the peak for carbonaceous bonds at 284.6 eV in pristine GO and graphite,^{273, 274} but also other peaks from GO and oxidized species because of exposure to air. After OER test, the boron content showed a significant decrease (Figure 6-11a), while there was an increase in metal-oxidized species and oxygen (Figure 6-11e and Table 6-1), showing the formation of stable metal (hydroxy)oxide, which acts as the catalytic center for OER. It is a common behavior of oxygen-evolving catalysts to undergo structural transformation and progressive oxidation during the process.^{269, 275}

Figure 6-11. High-resolution XPS spectra of the B 1s (a), (b) Fe 2p, (c) Ni 2p, (d) C 1s, and (e) O 1s core level of FeNi₃-B/G catalyst and after CV activation followed by chronopotentiometry at a fixed current density of 20 mA cm⁻² for one hour.

Table 6-1. Atomic composition for the as-prepared FeNi₃-B/G (30% GO) and

after CV activation followed by chronopotentiometry at a fixed current density of 20 mA cm⁻² for one hour (post-OER) in 1.0 M KOH.

Elements	Atomic Composition (%)	
	Before OER	Post-OER
C	69.35	54.87
O	20.44	30.91 ^a
B	3.46	2.72
Fe	1.63	3.39
Ni	5.12	8.11
M:B	2:1	4:1 ^b

^a Oxygen atomic percentage increased in expenses of Boron etched during post-OER. ^b As a results metal to boron (M:B) is increased.

We investigated the electrocatalytic activity of the as-obtained metal boride material in an O₂-saturated 1.0 M KOH aqueous electrolyte. A typical three-electrode electrochemical cell was used, where the rotating disk (GC), mercury/mercury oxide (Hg/HgO) electrode, and graphite rod were the working, reference, and counter electrodes, respectively. For comparison, the OER performance of GO and RuO₂ catalyst was measured under the same conditions. The currents measured in this study were normalized to the surface area of GC

(0.196 cm²), while the potentials were all calibrated to the RHE reference for comparison.

In the cyclic CV plot (Figure 6-12), there was a negative shift to lower potential with respect to the initial cycles of CV testing. As can be seen, steady state was attained in about 30 cycles, and the cycles became reproducible as the 30th and 50th cycles overlapped. The oxidative and reductive redox peaks in Figure 6-12 also showed an increase and become reproducible, which shows permanent morphological transformation during the electrochemical activation. Most of the metal–metalloid oxygen-evolving electrocatalysts, especially metal borides, undergo in situ activation due to continuous growth of a metal hydroxide/oxyhydroxide layer, which acts as the active site for water oxidation.^{70, 110, 269} This is in agreement with the increased content of oxidized species, and O content increased while B content decreased as observed in Table 6-1 from the XPS analysis after OER test. This is similar to the phenomenon observed in metal phosphides, whereby they transform to oxo(hydroxy-) metal species and act as the catalytic center for water oxidation.²⁷⁶

Figure 6-12. Activation of amorphous FeNi₃-B/G by continuous cyclic voltammetry between 0.2 and 0.8 V vs Hg/HgO at a scanning rate of 100 mV s⁻¹ in 1.0 M KOH at room temperature, the arrows indicate the direction of current increases.

The water oxidation activity of FeNi₃-B/G catalyst was compared with those of binary metal borides (Ni-B/G and Fe-B/G), commercial RuO₂ catalyst, and bare GO in 1.0 M KOH. LSV polarization curves were collected at a sweep rate of 5 mV s⁻¹ and compensated for the *iR* drop as shown in Figure 6-13a. A positive shift in the oxidation peak appeared from 1.39 to 1.43 V versus RHE for Ni-B/G and FeNi₃-B/G, respectively. The former is assigned to the Ni²⁺/Ni^{3+/4+} redox process, while the latter one is associated with both Fe and Ni redox processes, which reveals synergistic effect for water oxidation. Clearly, the anodic current increased tremendously for FeNi₃-B/G in comparison to other samples, including RuO₂ catalyst. As a consequence, it required an overpotential of only 230 mV to reach a current density of 15 mA cm⁻², which is comparable to or even

outperforms many recently developed nickel-based borides, oxides, hydroxides, borates, phosphides, and chalcogenides, such as Ni_xB ($\eta_{10} = 380$ mV),¹¹⁰ Ni-Bi/G ($\eta_{10} = 338$ mV),²⁷⁷ Ni_2B ($\eta_{10} = 350$ mV),²⁵³ Ni_2P ($\eta_{10} = 360$ mV),²⁵³ $\text{CoFe}_2\text{O}_4/\text{PANI-MWCNT}$ ($\eta_{10} = 314$ mV),²⁷⁸ Fe-Ni-B ($\eta_{10} = 294$),¹⁶² NiFeB ($\eta_{10} = 251$ mV),²⁷¹ Fe-doped NiO_x ($\eta_{10} = 310$ mV),²⁷⁹ borate-doped $\alpha\text{-Ni(OH)}_2$ ($\eta_{10} = 340$ mV),²³⁹ and CoFe-N-CN/CNTs ($\eta_{10} = 285$ mV).²⁸⁰

Figure 6-13. (a) *iR*-corrected LSV polarization curves of FeNi3-B/G, Ni-B/G, Fe-B/G, RuO_2 , and bare GO at 5 mV s^{-1} . (b) Tafel plots. (c) Overpotential at $j = 15 \text{ mA cm}^{-2}$ and Tafel slope. (d) Nyquist plots, the inset is enlarged Figure 6-13d.

Tafel slope is another crucial parameter to characterize OER catalyst

kinetics.²⁸¹ The Tafel slope, which reveals the correlation between overpotential and steady-state current density, was evaluated by analyzing the Tafel plots (Figure 6-13b). The linear portions at low overpotentials, derived from anodic polarization curve, were fitted to the Tafel equation (Equation 4).^{31, 32} The Tafel slope of FeNi3-B/G is 50 mV dec⁻¹, much smaller than the rest of the control samples, demonstrating the favorable OER reaction kinetics. It is clear in Figure 6-13c that the as-prepared ternary metal boride hybrid outperforms the binary metal boride hybrid because of the synergistic effect from material constituents.²⁷⁰ Consistent results are obtained from electrochemical impedance spectroscopic measurement (Figure 6-13d). The advanced OER performance of the as-presented material has first been attributed to the amorphous nature of the metal boride nanostructure. Second, the strong coupling of metal boride with rGO enhanced the electrical conductivity and allowed for better charge transfer. Third, once the catalyst is activated under OER process, it undergoes in situ transformation on the surface, and the presence of conducting metal-metalloid at the core ensures high conductivity of the catalyst. Last, the synergistic effect of iron and nickel in the active material is crucial for the high efficiency of the catalyst.

The optimization of the catalytic activity was performed by first controlling the percentage of GO in metal salt solution. First, all the supported ternary metal boride hybrid catalysts outperformed the unsupported ternary metal boride [FeNi3-B (0% G)] (Figure 6-14a), showing the crucial importance of highly

conductive 2D rGO to boost OER performance.^{282, 283} Thirty percent of rGO was then identified to be optimal. For example, the overpotential required to afford 15 mA cm⁻² was higher for FeNi₃-B, FeNi₃-B/G with 15% G, and 45% G when compared to FeNi₃-B/G with 30% G by 58, 45, and 36 mV, respectively (Figure 6-14b). Additionally, these catalysts have a similar Tafel slope and differ only by 5 mA dec⁻¹ (Figure 6-14c). This may imply that these catalyst hybrids and unsupported ternary metal boride with similar composition share a similar OER catalytic mechanism, while the rGO support assists in electric conductivity (Figure 6-14d).

Figure 6-14. (a,b) *iR*-corrected LSV polarization curves and overpotential required

to deliver 15 mA cm^{-2} for FeNi₃-B/G (0%, 15%, 30%, and 45% G). (c) Tafel plot. (d) Nyquist plot.

To understand, the high performance of FeNi₃-B/G, ECSA was calculated from the electrochemical double-layer capacitance (C_{DL}) derived from cyclic voltammograms (Figures 6-15 and 6-16). The C_{DL} of FeNi₃-B/G in Figure 6-15e is determined to be 0.25 mF cm^{-2} , which is much higher than 0.17, 0.04, and 0.017 mF cm^{-1} for FeNi₃-B, Ni-B/G, and Fe-B/G, respectively. The higher ECSA value for FeNi₃-B/G than for binary and ternary catalysts studied in this work represents a larger ECSA, suggesting larger exposure of active sites.

Figure 6-15. CVs at different scan rates of 20, 40, 60, 80 and 100 mV s⁻¹ in a potential window range from 0.23 to 0.33 V versus Hg/HgO for the (a) Fe-B/G, (b) Ni-B/G, (c) FeNi3-B, and (d) FeNi3-B/G. (e) Charging current density differences at 0.28 V versus Hg/HgO ($DJ = J_a - J_c$) plotted against scan rate.

Figure 6-16. CVs at different scan rates of 20, 40, 60, 80 and 100 mV s^{-1} in a potential window range from 0.23 to 0.33 V versus Hg/HgO for the (a) FeNi-B/G and (b) FeNi9-B/G. CVs in a potential window range from 0.0 to 0.1 V and 0.1 to 0.2 V versus Hg/HgO for the (c) FeNi6-B/G and (d) FeNi2-B/G, respectively. (e) Charging current density differences plotted against scan rate.

To investigate if this hybrid material exhibits a strong and direct contact with co-reduced GO, FeNi3–B catalyst mixed with NaBH₄-treated GO was tested (Figure 6-17). The results showed inferior performance ($\eta_{15} = 270$ mV compared to 230 mV for hybrid material, Figure 6-17a), similar kinetics (Figure 6-17b), and poor charge transfer (Figure 6-17c) because of poor contact between the unsupported catalyst and the highly conductive substrate.

Figure 6-17. (a) *iR*-corrected LSV polarization curves of amorphous FeNi3–B/G and physical mixture of FeNi3–B and NaBH₄-treated GO. (b) Tafel plot. (c) Nyquist plot.

Additionally, the optimized catalyst prepared by rapid mixing rate shows better performance than the catalyst prepared by slow rate (dropwise addition) (Figure 6-18). The latter required 298 mV to deliver 15 mA cm^{-2} compared to 230 mV for the former (Figure 6-18a). It also outperforms the catalyst prepared by a slower reduction rate of 1.0 mL dropwise followed by rapid reduction, whereby 266 mV and 15 mA cm^{-2} was required. Additionally, the larger Tafel slope for the samples prepared by slow rate in Figure 6-18b reveals poor OER kinetics. This correlates with larger semicircles observed in Figure 6-18c that are even larger than those of unsupported FeNi₃-B (Figure 6-18b), which indicates slow charge transfer due to poor conductivity. This may be associated with poor reduction of GO as shown above in the XRD pattern analysis (Figure 6-7d). The first semicircle represents the charge transfer resistance, and the second represents the resistance from the mass transfer during electrocatalytic reactions.²⁸⁴ Hence, the appearance of the second semicircle (Figure 6-18c) may suggest higher mass transfer resistance.

Figure 6-18. (a) *iR*-corrected LSV polarization curves of amorphous FeNi₃-B/G prepared at a fast rate of reduction, the slowest rate (drop by drop for 5 minutes) and for one-minute drop by drop followed by a fast rate of reduction. (b) Tafel plot. (c) Nyquist plot.

To get insight into the mechanism of metal borides toward water oxidation, the electronic structures, and adsorption free energy were investigated by DFT calculations. The best catalyst (at the top of activity volcano curve) can be found at the O* binding energy around 3.0 eV.³⁰ The pristine MB phase is not active and suitable for OER (Figure 6-19a–c). On the other hand, if O adsorption is too strong, the material would be spontaneously oxidized, leading to the formation of MO_xH_y

active species. This agrees with the treatment of the catalyst by CV technique (until a reproducible curve) before every OER measurement (Figure 6-12). In Figure 6-19d–f, the O adsorption energies are -3.02 , -1.97 , and -1.85 eV for Fe–B/G, Ni–B, and FeNi₃–B/G, respectively, which follows the order of electrochemical performance, Fe–B/G < Ni–B/G < FeNi₃–B/G. On the basis of many literature reports, it has been observed that the in situ changes of metal phosphides to their corresponding oxide/oxyhydroxide are very OER active and this is similar to metal borides composed of MOOH, while the core is M₂B.^{252, 253}

Figure 6-19. DFT calculations: (a-c) are the models of M₂B (Fe₂B, Ni₂B and Fe_{0.5}Ni_{1.5}B). (d-f) are the models of O-adsorbed Fe₂B, Ni₂B and Fe_{0.5}Ni_{1.5}B.

As shown in Figure 6-13a, nickel boride hybrid (Ni–B/G) is more active

than iron boride (Fe-B/G). By incorporation of iron to nickel boride, much improved activity is observed (Figure 6-13). This iron doping caused the electronic modulation of nickel boride and hence provided advanced electrochemical performance.²⁸⁵ The effect of iron doping is then further investigated by varying the iron-to-nickel ratio (Figure 6-20a,b). The LSV polarization curves in Figure 6-20a shows that 1:3 (FeNi3-B/G) offers the best activity. Similar Tafel slopes observed could suggest similar OER kinetics despite the iron-to-nickel ratio variation (Figure 6-20b). The difference in oxygen-evolving activity due to varying iron-to-nickel ratios shows the synergy between iron and nickel for optimum performance.^{269, 286} The intrinsic activity of the catalyst was calculated by the TOF. The TOF values calculated at 300 mV versus RHE (Table 6-2) shows that the as-prepared FeNi3-B/G hybrid showed eightfold TOF value compared to FeNi3-B (0.14 s^{-1}), which further suggests advanced catalytic activity of hybrid material. Doping of iron boosted the intrinsic activity, whereby the TOF of FeNi3-B/G hybrid (1.3 s^{-1}) is around 14 times compared to Ni-B/G.

Figure 6-20. (a) *iR*-corrected polarization curves for Fe_xNi_y-B/G (1:1, 1:2, 1:3, 1:6, and 1:9). (b) corresponding Tafel plot.

Table 6-2. Calculated turnover of frequency for iron-doping in nickel boride at an overpotential of 300 mV vs RHE.

Catalyst	Turnover of frequency (TOF) at 300 mV
FeNi3-B/G	1.3 s ⁻¹
FeNi3-B	0.16 s ⁻¹
Ni-B/G	0.09 s ⁻¹
FeNi-B/G	0.27 s ⁻¹
FeNi2-B/G	0.61 s ⁻¹
FeNi6-B/G	0.48 s ⁻¹
FeNi9-B/G	0.55 s ⁻¹

Another critical criterion to evaluate a competent catalyst for practical electrochemical application is its stability.¹³² For this reason, the stability was probed by continuous CV sweeps for 1000 cycles in an alkaline solution at 100 mV s⁻¹ (Figure 6-21a). The initial *iR*-corrected LSV polarization curves overlapped with the one measured after 1000 continuous cycles. The catalyst stability was

further probed by chronopotentiometry technique at a fixed current density (10 mA cm^{-2}) for 12 h (Figure 6-21b). It shows a promising stability with negligible decay over time. The stability of the as-prepared material has been attributed to the strong coupling between the active catalyst and co-reduced GO. Furthermore, the presence of oxidized metal, boron–metal covalent bond, and in situ transformation of metal boride catalyst that occurs in OER activation process have also contributed to the stability.^{70, 110, 269}

Figure 6-21. (a,b) Electrochemical stability tests. (a) *iR*-corrected LSV polarization curves of FeNi₃-B/G, initial and after continuous 1000 cycles. (b) Chronopotentiometric curve at a potential required to afford 10 mA cm^{-2} in 1.0 M KOH at room temperature.

6.4. Conclusions

Amorphous metal boride-rGO hybrid was successfully synthesized by a simple and one-step fast reduction process. The iron incorporation in nickel boride

and the ratio of active material to GO were found to be the determining factors for boosting the water oxidation performance. The optimized and ternary metal boride hybrid possesses remarkable stability and catalytic activity in alkaline electrolyte compared to the binary metal boride hybrid and commercial RuO₂ catalyst. It only needs an overpotential of 15 mA cm⁻² at 230 mV with a small Tafel slope of 50 mV dec⁻¹, which shows advanced kinetics. This highly efficient OER performance is attributed to the strong coupling of ternary iron nickel boride nanostructure with co-reduced GO, iron doping that boosted the synergistic effect, which resulted into robust metal (hydroxy)oxides as catalytic centers, and finally the unique amorphous structure. This work provides a facile approach for preparing amorphous transition metal borides coupled to co-reduced GO with outstanding activity, and hence, it could be extended to other energy storage and conversion technologies.

Chapter 7. Conclusions and Recommendations for Future Work

7. 1. Conclusions

Although water splitting viability was discovered many decades ago, it has re-emerged as a promising candidate for efficient and clean energy technology. It provides a suitable process through which renewable energy from intermittent sources is stored in the form of chemical fuels, namely hydrogen. However, the overall water splitting process is limited by the thermodynamically unfavorable anodic reaction. Therefore, the development of materials to boost the kinetics of this reaction, and thus, to increase the overall efficiency has gained increasing attention. Hence, numerous materials for both HER and OER have been developed including precious-metal based catalysts, metal-free catalysts, metal oxides, and metal–nonmetals catalysts. Although metal oxides are regarded as the most promising catalysts, recently, other materials such as metal alloys and metal–nonmetals which eventually get oxidized to metal oxyhydroxides during water oxidation, are being regarded as potential replacements for precious metal-based catalysts. Due to the in situ transformation during water oxidation, these materials are often referred to as ‘pre-catalyst’, as their catalytically active centers are metal oxyhydroxides.

A facile preparation method for earth-abundant materials is of paramount importance as it allows large scale applications. We developed a facile systematic method for metal borides preparation, which showed superior water oxidation catalytic performance. In chapter three, a one-pot chemical reduction of transition metals ions in aqueous media was used to prepare metal-rich borides. The sodium borohydride used in excess acted as both reducing agent and boron source. This simple chemical reduction allowed the doping of metals to form ternary and quaternary metal borides and the homogenous distribution of material composition in amorphous nanoparticles. Our study showed that metal doping is an efficient method to boost the electrocatalytic water oxidation in transition metal borides. This is a result of the synergistic effects of multimetal oxyhydroxides in catalytic active centers. The oxygen-evolving activity of bimetallic and trimetallic borides outperformed the commercial IrO_2 catalyst in alkaline media. This activity could be attributed to the advanced charge transfer due to catalyst composition and the modified electronic configuration, which can lower the kinetic barriers of the electrochemical reactions. For application purposes, this material showed better activity compared to precious metal-based catalysts when used as anodic material during water splitting. Overall, this work gave insights into designing highly efficient materials, for energy technologies related to OER.

Nickel alloy-based catalysts are promising materials for water splitting at an industrial scale. In chapter four, the self-standing electrode of nickel–tungsten alloy was successfully prepared by a two-step process. The hydrothermal technique

was used, followed by annealing in a hydrogen environment. As-prepared material showed bifunctional activity for both HER and OER in alkaline solution. Additionally, the prepared electrode was active for HER in acidic electrolytes. The advanced catalytic activity was attributed to the bimetallic synergistic effect and the oxygen-deficient tungsten oxide, assisted by a highly conductive substrate.

In the aforementioned study, the advanced activity of metal boride nanoparticles was observed. Based on this, we developed a self-standing metal boride nanosheet in chapter three. Due to the incorporation of bimetallic boride in a 3D architecture which is a highly conductive substrate with a large surface area, the water oxidation catalytic activity was improved. The ultrathin amorphous nanosheets were transformed in situ, induced by electrochemical activation, to become rougher and thicker. This also exposed more oxyhydroxides catalytic active centers for water oxidation. As a result, the as-prepared self-standing electrode showed superior activity compared to the precious metal-based catalyst and pristine metal borides nanoparticles for water oxidation in alkaline electrolytes.

The successful preparation of self-standing metal boride nanosheet electrode inspired the subsequent synthesis of metal boride nanosheet hybrid using highly conductive carbon nanomaterials. In comparison to the traditional time-consuming reduction of graphene oxide, this study presented a facile and fast method of metal boride preparation with simultaneous reduction of graphene oxide, thereby, forming the hybrid material. The presence of a strong reducing

agent, sodium borohydride, reduced both metal ions and graphene oxide. This process resulted in a hybrid of metal boride and reduced graphene oxide within a short period of time. The obtained amorphous ternary iron-nickel boride hybrid outperformed RuO₂ catalyst for water oxidation in alkaline solution. Furthermore, it showed superior oxygen-evolving activity compared to the pristine catalyst. Hence, the concept of improving the catalytic activity of metal boride by preparing a nanosheet hybrid with carbon nanomaterial was successfully demonstrated. As a result of this observation, we showed in this work that using a facile and fast preparation method could result in a highly active earth-abundant material with advanced stability during water oxidation. This approach could be extended to other energy conversion and storage technologies.

7.2. Recommendations for Future Work

The world's energy consumption is predicted to increase, and as a result, depleting fossil fuels and rising CO₂ emissions are of more significant concern. Hence, an alternative clean energy source is urgent, and undoubtedly, hydrogen energy is a promising candidate. The search for materials to boost the efficiency and durability of water electrolyzers are at the crux of this clean technology. As the OER reaction suffers from sluggish kinetics which reduces the efficiency of the water electrolyzers, the oxygen-evolving materials are of paramount importance. To be applicable on the industrial scale, the search for cheaper and use of earth-abundant materials with better stability, are still highly needed for research in this

field of clean energy technology. In the following sections, I propose critical points for further research, with respect to my findings in this thesis.

Fundamentally, the preparation method is one of the determining factors for the morphological, shape, size, structure and electronic properties of a catalyst. Among metal–nonmetal catalysts, it has been reported that the presence of the guest atoms seems to be the dominant factors responsible for the enhanced activity in metal phosphides and borides for OER. The preparation of metal borides using chemical reduction transition metals salts in aqueous solution leads to the production of metal-rich borides (M_2B). In M_2B , the presence of a higher electronegativity atom (B) bonding to transition metal allows the charge transfer to occur. This higher electronegative atom draws electrons from the metals, and as a consequence, positively charged local sites on the metal atoms favor hydroxyl ion capture, which boosts water oxidation. This intuitively implies that if the higher electronegative elements (N, B, S, and P) are increased or reduced, it may have a significant consequence on the electrocatalytic activity of metal–nonmetal catalysts. Thus, an alternative method which would allow the synthesis of metal borides with higher or lesser boron should be developed and investigated with regards to its catalytic properties. To achieve this suggestion, high-pressure and high-temperature solid-state method could result in the synthesis of metal borides with different compositions. Furthermore, the chemical reduction in organic or aprotic media might give the metal boride varying boron content as well. Thus, the

development and investigation of other methods to prepare metal borides need to be carried out.

It would be interesting to explore further the behavior of metal–nonmetals materials by operando characterizations since they require an in situ transformation induced by the electrochemical activation during OER. Currently, a full understanding of the morphological, structural and compositional changes which occur during electrochemical testing is limited especially on metal borides. Thus, both experimental and theoretical efforts should be carried out to understand the mechanisms and pathways which would contribute to the development of highly efficient materials for energy storage and conversion technologies. Additionally, due to the chemical reduction of metal borides which occurs quickly, it is of great importance to develop a method which allows the control of metal borides synthesis. This would become a new avenue to tune the electrocatalytic properties, by preparation of metal–multiple electronegative metalloid materials such as MPB (where M, P, and B stand for metal, phosphorous, and boron, respectively).

Furthermore, binary nickel alloy such as nickel–tungsten and nickel–molybdenum have shown superior advanced HER performance, however, their performance toward water oxidation is still limited. Thus, we recommend searching for a synthesis method which can maintain the HER properties of nickel-alloy, while boosting OER performance so that, the overpotential for overall water splitting would be reduced. Basically, the nickel HER property could be tuned by

combining with an element from higher element groups such as Mo and W through d-orbital electron transfer. On the other hand, the doping of transition metal in a nickel-based catalyst would enhance the water oxidation activity. Hence, by synthesizing multimetals nickel-based material containing elements from groups below group 4, and from transition metals such as Fe, Co, Cr, the overall water splitting would be enhanced.

Last but not least, I recommend studying the application of metal-rich boride into other energy conversion and storage technologies. For example, to investigate their effect on oxygen reduction reaction, and/or photoelectrochemical performance. To achieve this, I suggest the preparation of hybrid materials such as metal borides–plasmonic active nanostructure hybrid. The plasmonic active nanoparticles have shown to be able to boost the activity by promoting the charge transfer in the electrocatalyst hybrid through hot carriers and near-field enhancement induced by localized surface plasmon resonance (LSPR) excitation.²⁸⁷ Also in this thesis, it was observed that by choosing a preparation method carefully, the metal boride nanosheets were anchored onto highly conductive carbon nanomaterials. Thus, the plasmonic active nanoparticles which are often prepared by reduction of Au-, Ag-metal salts by reducing reagent in aqueous media such sodium borohydride, might be easily incorporated onto or decorated by metal borides nanosheets. For instance, metal borides nanoparticles and nanosheets could be easily produced at room temperature and dried at a

moderate temperature. Thus, the preparation condition would not have a detrimental effect on the plasmonic active nanostructure. As a result, I recommend preparing these hybrid materials by chemical reduction of transition metal ions in aqueous media, containing plasmonic active nanoparticles. This approach has not been investigated so far and could be vital to study the advanced activity beyond water oxidation, and into other energy conversion and storage technologies.

Publications Related to This Thesis

Journal Paper

(1) **Nsanzimana J. M. V.**, Dangol R., Reddu V., Duo S., Peng Y., Dinh K. N., Huang Z., Yan Q., Wang X., Facile Synthesis of Amorphous Ternary Metal Borides–Reduced Graphene Oxide Hybrid with Superior Oxygen Evolution Activity. *ACS Applied Materials & Interfaces* **2019**, *11*, 846-855.

(2) **Nsanzimana J. M. V.**, Reddu V., Peng Y., Huang Z., Wang X., Wang C., Ultrathin Amorphous Iron-nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production. *Chemistry – A European Journal* **2018**, *24*, 18502-18511.

(3) **Nsanzimana J. M. V.**, Peng Y., Miao M., Reddu V., Zhang W., Wang H., Xia B. Y., Wang X., An Earth-Abundant Tungsten–Nickel Alloy Electrocatalyst for Superior Hydrogen Evolution. *ACS Applied Nano Materials* **2018**, *1*, 1228-1235.

(4) **Nsanzimana J. M. V.**, Peng Y., Xu Y. Y., Thia L., Wang C., Xia B. Y., Wang X., An Efficient and Earth-Abundant Oxygen-Evolving Electrocatalyst Based on Amorphous Metal Borides. *Advanced Energy Materials*, **2018**, *8*, 1701475.

Conferences

- (1) **Nsanzimana, J. M. V.**, Wang X., Amorphous Iron–Nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production, AM30 Symposium on Advanced Emerging Sot Materials, *Poster*, Agency for Science, Technology and Research (A*STAR), Singapore, December 4th, 2018.
- (2) **Nsanzimana, J. M. V.**, Vikas Reddu, Wang X., NFL: 2992299, Earth-Abundant Tungsten–Nickel Alloy Electrocatalyst for Superior Hydrogen Evolution, Oral Only & Consider for Sci-Mix, ACS National Meeting & Expo, Boston-MA, USA, August 19-20, 2018.
- (3) **Nsanzimana, J. M. V.**, Wang X., EN11.02.02, A Novel Earth-Abundant and Highly Oxygen-Evolving Electrocatalyst Based on Amorphous Metal Boride, oral presentation, Phoenix-Arizona, MRS spring 2018, April 4th, 2018.

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