Engineering nickel based layered double hydroxides and their derivatives for water electrolysis

Dinh, Ngoc Khang

2020

Dinh, N. K. (2020). Engineering nickel based layered double hydroxides and their derivatives for water electrolysis. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/137864>

<https://doi.org/10.32657/10356/137864>

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**ENGINEERING NICKEL BASED LAYERED DOUBLE
HYDROXIDES AND THEIR DERIVATIVES FOR WATER
ELECTROLYSIS**

DINH NGOC KHANG

**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2020

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HYDROXIDES AND THEIR DERIVATIVES FOR WATER
ELECTROLYSIS**

DINH NGOC KHANG

INTERDISCIPLINARY GRADUATE SCHOOL

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

2020

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This thesis contains material from 3 papers published in a/the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 4 is published as K. N. Dinh, Y. Sun, Z. Pei, Z. Yuan, A. Suwardi, Q. Huang, X. Liao, Z. Wang, Y. Chen, Q. Yan. Electronic Modulation of Nickel Disulfide towards Efficient Water Electrolysis. *Small* (2020). DOI: 10.1002/sml.201905885.

The contributions of the co-authors are as follows:

- Prof. Qingyu Yan and Prof. Yuan Chen provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Zengxia Pei, Prof. Yuan Chen, and Prof. Qingyu Yan.
- I co-designed the study with Prof. Yuan Chen, Prof. Qingyu Yan and Dr. Zengxia Pei and performed all the laboratory work at the School Chemical and Biomolecular Engineering, The University of Sydney.
- I carried out XRD, XPS characterization. I analyzed the data.
- SEM were conducted by Mr. Ziwen Yuan.
- Ms. Qianwei Huang and Dr. Xiaozhou Liao assisted in the TEM characterization. I analyzed the data.
- Ms. Yongxiu Sun constructed the DFT model study and provided theoretical calculation results with the support from Prof. Zhiguo Wang
- Dr. Ady Suwardi assisted with electrical characterization

Chapter 5 is published as K. N. Dinh, X. Sun, Z. Dai, Y. Zheng, P. Zheng, J. Yang, J. Xu, Z. Wang, Q. Yan. O₂ plasma and cation tuned nickel phosphide nanosheets for highly efficient overall water splitting. *Nano Energy* **54**, 82-90 (2018). DOI: 10.1016/j.nanoen.2018.10.004

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- I co-designed the study with Prof. Qingyu Yan and Dr. Zhengfei Dai and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data with the assistance from Dr. Penglun Zheng.
- Dr. Yun Zheng and Dr. Jianwei Xu carried out XPS characterization. I analyzed the data.
- XRD, SEM were conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Contact Angle Measurements were conducted by me at the School of Materials Science and Engineering. I also analyzed the data
- Dr. Jun Yang assisted in BET measurements. I analyzed the data
- Dr. Yun Zheng assisted in the TEM characterization. I analyzed the data.
- Dr. Xiaoli Sun constructed the DFT model study and provided theoretical calculation results with the support from Prof. Zhiguo Wang

Chapter 6 is published as K. N. Dinh, P. Zheng, Z. Dai, Y. Zhang, R. Dangol, Y. Zheng, B. Li, Y. Zong, Q. Yan. Ultrathin porous NiFeV ternary layer hydroxide nanosheets as a highly efficient bifunctional electrocatalyst for overall water splitting. *Small* **14**, 1703257 (2018). DOI: 10.1002/sml.201703257.

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- XRD, SEM was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
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- Dr. Yu Zhang and Dr. Yun Zheng assisted in the TEM characterization. I analyzed the data.

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Abstract

The world demands a reliable and renewable energy to replace the soon-to-be-depleted fossil fuel. Solar power has arisen as the best solution so far, in which storage energy in the form of chemical bonds is the key. Among all candidates, storing energy via hydrogen produced by solar-light-coupled electrochemical water splitting is the most viable one. However, the catalysts employed to facilitate the electrolysis of water are still based on precious metals (Pt at the cathode and Ir/Ru at the anode), which hinders their large-scale implementation. Recent studies have demonstrated the promise of Ni-based layered double hydroxides (LDHs) as alternatives to noble metals towards alkaline electrolysis due to the low overpotentials and decent stability. Notwithstanding, the poor electronic conductivity and limited specific surface area are the main reasons holding them back from being applied. Therefore, this dissertation focus on the scalable facile fabrication and engineering of low-cost Ni-based LDHs and their phosphide/sulfide derivatives materials to address the aforementioned issues and further optimizing water electrolysis.

In the very first part of the research work, the electronic reconfiguration of LDH-derived sulfides NiS_2 by cation doping is proposed. The semiconductor-to-conductor transition of NiS_2 after Cu incorporation has been validated by both DFT calculations and temperature-dependent resistivity measurements. Such transition can facilitate reaction kinetics, reduce the loss of electron transport during electrocatalysis, increase the density of active sites, and give rise to intrinsic activities. Further calculations also confirm the advantages of Cu incorporation, which does not only significantly reduce Gibbs free energy of H adsorption of Ni site from 1.33 eV to 0.07 eV but also activate the inert S sites. Besides, Cu-doped NiS_2 surface offers even more favorable water dissociation than that of Pt (111), making the former perform well in alkaline conditions. Thus, the modulated Cu- NiS_2 illustrates remarkable improvement in electrocatalytic activity toward HER and OER. Specifically, it needs overpotentials of only 240 mV and 139 mV to drive OER and HER current densities of $\pm 10 \text{ mA cm}^{-2}$.

In the second part, a combined-strategy of cation tuning and surface engineering for the fabrication of highly active, earth-abundant, and robust LDHs-derived Ni₂P is reported. Density functional theory (DFT) calculations suggest the effectiveness of vanadium doping and oxygen plasma, which do not only enhance the density-of-state at Fermi level, but also make the Ni sites more susceptible to OH⁻ adsorption. The O₂ plasma treatment increase the wettability of the catalyst toward KOH solution, improving the contact angle from 44.95° to 16.8°, and also induce a higher BET surface area; hence, more active sites and lower charge transfer resistance are obtained. As a result, the catalyst requires small overpotentials of 257 mV and 108 mV to drive $\pm 10 \text{ mA cm}^{-2}$ alongside with modest Tafel slope of 43.5 mV dec⁻¹ and 72.3 mV dec⁻¹ for OER and HER in 1.0 M KOH solution, respectively. When employed for overall water splitting, the catalyst demonstrates a low voltage of 1.56 V to achieve 10 mA cm⁻² with good stability and durability, outperforming the state-of-the-art IrO₂ || Pt/C which needs 1.69 V.

Last but not least, the incorporation of vanadium into the hydrothermally growth of NiFe-LDHs nanosheets on nickel foam (NF) substrate to form NiFeV-LDHs/NF is reported as a highly efficient electrode toward overall water splitting in alkaline media. The lateral size of the nanosheets is about few hundreds of nanometers with the thickness of ~10 nanometers. Among all molar ratio investigated, the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode depicts the optimized performance. It displays an excellent catalytic activity with a modest overpotential of 231 mV for OER and 125 mV for HER in 1.0 M KOH. Its exceptional activity is further shown in its small Tafel slope of 39.4 mV dec⁻¹ and 62.0 mV dec⁻¹ for OER and HER, respectively. More importantly, remarkable durability and stability are also observed. When used for overall water splitting, the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrodes require a voltage of only 1.591 V to reach 10 mA cm⁻² in alkaline solution. These outstanding performances are mainly attributed to the synergistic effect of the ternary metal system that boosts the intrinsic catalytic activity and active surface area while lower the charge transfer resistance.

Lay Summary

The world demands a reliable and renewable energy to replace the soon-to-be-depleted fossil fuel. Solar power and wind power have arisen as the best solution so far. However, due to their intermittency, there is an increasing need to store energy for times when or where the sun goes down or the wind does not blow. Among all candidates, storing energy in the form of chemical bond *via* hydrogen produced by solar-light-coupled electrochemical water splitting is the most viable one. Hydrogen obtained from this process can be stored and oxidized to discharge energy when needed. The challenge is that the catalysts employed to facilitate the electrolysis of water are still based on precious metals (Pt at the cathode and Ir/Ru at the anode), which hinders their large-scale implementation. Previous studies have shown the potential of Ni-based layered double hydroxides (LDHs) as alternatives to noble metals towards alkaline electrolysis due to the high activity and decent stability. Nonetheless, the poor electronic conductivity and limited specific surface area are the main reasons holding them back from being applied. Therefore, this dissertation focus on the scalable facile fabrication and engineering of low-cost Ni-based LDHs and their phosphide/sulfide derivatives to address the aforementioned issues and further optimizing the water electrolysis.

In the very first part of the research work, the electronic reconfiguration of LDH-derived sulfides NiS₂ by cation doping is proposed. The semiconductor-to-conductor transition of NiS₂ after Cu incorporation has been validated by both theoretical calculations and experimental results. Such transition can facilitate reaction kinetics, reduce the loss of electron transport during electrocatalysis, increase the density of active sites, and give rise to intrinsic activities. Further calculations also confirm the advantages of Cu incorporation, which significantly activates the active sites. Besides, Cu-doped NiS₂ surface offers even better pre-reaction condition than that of Pt, making the former perform well in alkaline conditions. Thus, the modulated Cu-NiS₂ illustrates remarkable electrocatalytic activity performance, surpassing the noble metal counterparts.

In the second part, a combined-strategy of cation tuning and surface engineering for the fabrication of highly active, earth-abundant, and robust LDHs-derived Ni_2P is reported. Theoretical calculations suggest the effectiveness of vanadium doping and oxygen plasma, which do not only enhance the charge transfer processes, but also make the Ni sites more susceptible to anodic half reaction. The oxygen plasma treatment also increase the wettability of the catalyst toward KOH solution and induce a higher BET surface area; hence, more active sites and lower charge transfer resistance are obtained. As a result, when employed for overall water splitting, the optimized catalyst even outperforms the state-of-the-art noble metals.

Finally, the incorporation of vanadium into the hydrothermally growth of NiFe-LDHs nanosheets on nickel foam (NF) substrate to form NiFeV-LDHs/NF is reported as a highly efficient electrode toward overall water splitting in alkaline media. The optimized catalyst displays an excellent catalytic activity along with remarkable durability and stability. When used as both cathode and anode, a single 1.5V-battery unit is able to drive water electrolysis in alkaline solution. These outstanding performances are mainly attributed to the synergistic effect of the ternary metal system that boosts the intrinsic catalytic activity and active surface area while lower the charge transfer resistance.

Acknowledgements

First and foremost, I would like to express my heartfelt gratitude to my two brilliant supervisors, my main supervisor, Professor Qingyu (Alex) Yan and my co-supervisor, Professor Hongjin Fan. To Professor Qingyu (Alex) Yan: Thank you for accepting me into your research group and helping me to find out my interest in studies of energy conversion processes. Thank you for your outstanding guidance, your support; and most importantly, your inspiration. I really appreciate the fruitful discussions which have sharpened my thought process and shown me how to transform my mistakes into skills. Your wisdom was very much my pillar of support throughout my projects and encouraged me to achieve my goal in my research. I consider myself blessed to have you working with me and helping me through the process. To Professor Hongjin Fan: Thank you for all the instructive advices and valuable knowledge you have provided me during my research work. I am truly grateful to have such a fulfilling experience working with you.

I am also indebted to my mentor, Professor Qichun Zhang: Thank you for being a good mentor and for guiding me on the right path as well as providing me with the necessary materials and knowledge to work with my project. Moreover, your creative ideas about the projects have impressed and inspired me a lot.

I am also grateful to Prof. Yuan Chen from University of Sydney for the great opportunity of doing exchange program there. I learned a lot from that one year.

Thank you Dr. Kedar Hippalgaonkar for letting me work in your lab. Though the time is short but I did learned a lot from you and your group members, especially during fruitful group meetings.

In addition, I really appreciate Mr. Van Chinh Hoang, Prof. Yu Zhang, Dr. Yun Zheng, Dr. Edison Huixiang Ang, Dr. Zengxia Pei, and Prof. Zhengfei Dai for their patience in guiding and assisting me through my Ph.D. study.

Thank you my best buddy – Dr. Penglun Zheng. You did pick me up when I was at the peak of desperation. I will always remember the time you cried asking me to stay to work with you. Thank you for staying in lab late over and over again just to wait for me finishing experiment. I love you man (not in a gay way).

Thank you Dr. Raksha, for always treating me as the brother you never had. Congratulation on your wedding!

I would like to extend my appreciativeness to my fellow lab mates: Mr. Jose Recatala-Gomez, Dr. Ady Suwardy, Dr. Ghimire Purna Chandra Dr. Jianli Zhang, Dr. Jun Yang, Prof. Jin Zhao, Dr. Hao Ren, Dr. Weixin Li, Dr. Guilue Guo, Prof. Hong Yu, Dr. Huiteng Tan, Prof. Haosen Fan, Dr. Yufei Zhang Prof. Chengfeng Du, Dr. Qinghua Liang, Dr. Yubo Luo, Dr. Hongbo Geng, Prof. Huanwen Wang, Prof. Fei Liu, Dr. Zhou Zheng, Ms. Lan Yang, Mr. Xian Yi Tan, Mr. Ziwen Yuan, Dr. Asif Mahmood, Dr. Li Wei, Ms. Xiao Sui, Mr. Junsheng Chen, Mr. Chaojun Wang, Mr. Muhammad Adil Riaz, and Prof. Xinglong Wu who have been working with me and sharing their experience and knowledge to me. Thank you for all the joy, laughter and friendships to help me get over the stress and make my research much easier.

I also would like to thank my beloved family and friends for their unconditional love and support that enables me to concentrate on my pursuits.

Finally, I would like to thank my future beloved wife for not screwing up my Ph.D. studies. With you, this work would be nowhere near done. I love you 3000.

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Abbreviations

AFM	Atomic Force Spectroscopy
BE	Binding Energy
BEI	Backscatter Electron Images
BET	Brunauer-Emmett-Teller
BSE	Backscattered Electron
CA	Contact Angle
C_{dl}	Double Layer Capacitance
CHNS	Carbon Hydrogen Nitrogen Sulfur
Cu-NiS ₂	Cu-doped NiS ₂
Cu-NiS ₂ -DC	Cu-doped NiS ₂ derived catalyst
CVD	Chemical Vapor Deposition
DOS	Density of States
ΔG_H^*	Gibbs free energy for hydrogen adsorption
ECSA	Electrochemical active Surface Area
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
GGA	Generalized-Gradient Approximation
HAADF	High Angle Annular Dark Field
HER	Hydrogen Evolution Reaction
HRTEM	High Resolution Transmission Electron Microscopy
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LDHs	Layered Double Hydroxides
NF	Nickel Foam
OER	Oxygen Evolution Reaction
O-V-Ni ₂ P	Oxygen plasma treated V-doped Ni ₂ P
PBE	Perdew-Burke-Ernzerhof
PDOS	Partial Density of States
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction

SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
SIESTA	Spanish Initiative for Electronic Simulations with Thousands of Atoms
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
V-Ni ₂ P	V-doped Ni ₂ P
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

The world demands a clean and renewable energy to replace the depleting fossil fuel and the development of energy conversion processes (i.e. hydrogen generation, fuel cells) is answering that call. In this chapter, the research background of energy conversion processes, specifically on the current research progress of hydrogen generation by water splitting and their main barriers will be demonstrated. After that, motivation and objectives of the project will be proposed based on that background. Finally, the thesis organization will be offered.

1.1 Hypothesis/Problem Statement

Known natural oil and gas reserves are only sufficient for less than 3 decades at the current consumption rate.¹ Accounting for the current rate of world population growth which would inevitably results in even faster depletion of fossil fuel (the global energy demand will climb by up to 3 times its 2006's value by the year 2050),² the conventional oil and gas may last within 15 years. Fortunately, the recovery of unconventional oil, *i.e.* oil sands, tight oil, and oil shale, could possibly supplement another 3 decades.³ Notwithstanding, there is no doubt that the world oil reserves is not able to sustain for long at the current demand.

Moreover, the combustion of fossil fuels has resulted in the significant increment concentration of CO₂ (the most influential greenhouse gas) in the Earth's atmosphere from 280 ppm (in 19th century) to 380 ppm in 2006.¹ Consequences of this increase include more frequent and intense extreme weather events, change in evaporation/precipitation rates, oceans warming and acidifying, and sea-level rise.⁴

Because of these reasons, the world's energy system has no choice but go through a profound transformation from one heavily based on fossil fuels to an efficient and renewable zero-carbon energy system. By far, solar energy is the largest intermittent source of renewable energy ($\sim 1.2 \times 10^{11}$ MJ s⁻¹ is received at Earth's surface), followed by wind power (~ 1.7 MJ m⁻² in the Southern Hemisphere during 1979 to 2010).⁵⁻⁶ In fact, it is expected that wind and solar will be able to make up the vast majority of generation capacity and $\sim 60\%$ of all electricity generation by 2050. This being said, renewable energy's contribution of global energy needs would increase from 18% today to 65% in 2050. With the growth of our dependence on sustainable but intermittent energy, energy storage becomes more crucial for times when or where the sun goes down or the wind does not blow.⁷

Storing energy in the form chemical bonds would be the key here. Among all candidates, hydrogen (H₂) has been considered as the most viable one for years. In fact, it can be traced back to early 1970s when the term "hydrogen economy" is first coined by

Professor John Bockris.⁸⁻⁹ The hydrogen produced by solar-light-coupled/ windfarm-coupled water electrolysis ($2\text{H}_2\text{O} + E_{\text{solar/wind}} \rightarrow \text{O}_2 + 2\text{H}_2$) can be compressed and stored, then easily oxidized (either by consuming in a fuel cell or burning in air) to discharge energy and give back H_2O , offering a desired carbon-free fuel generation and utilization cycle.¹⁰

Water electrolysis is the term for a chemical reaction in which water is split into oxygen and hydrogen. This reaction is endothermic which needs $285.83 \text{ kJ mol}^{-1}$ – equivalent to 1.23 V. However, additional voltage (overpotential) must be applied to make the reactions proceed at reasonable rates. The faster the rate of the reaction, the higher the overpotential that have to applied. Electrocatalysts are needed to lower this overpotential as far as possible. However, the state-of-the-art electrocatalyst so far is still based on the expensive precious metals (platinum at the cathode and iridium/ruthenium-based oxide at the anode). That is the main obstacle slowing down further development of this technologies. In addition, there is problem with stability. Today, only 4% of H_2 are being produced by water electrolysis. Therefore, the discovery of earth-abundant, low-cost, high activity electrocatalysts to achieve efficient water electrolysis is highly desired.

A wide range of earth-abundant catalytic materials with different morphologies, structure or loaded on various substrates have been developed, including transition metal oxides/hydroxides,¹¹⁻¹⁵ borides, carbides,¹⁶⁻¹⁸ sulfides/selenides,¹⁹⁻²² and nitrides/phosphides.²³⁻²⁵ Among them, nickel-based layered hydroxides with outstanding catalytic activity and stability are demonstrated as the promising alternatives to the precious metal-containing water splitting electrocatalysts in alkaline solutions (overpotential to drive water splitting of less than 300 mV).²⁶ A representative compound in that family, NiFe layered double hydroxides (LDHs), has been reported to be one of the best performing bifunctional electrocatalyst so far.²⁶ However, the poor electronic conductivity of the Ni-based hydroxides limits its practical application as a catalytic electrode material. Coupling with conductive carbon like graphene, carbon nanotubes, or carbon quantum dots are reported.^{11, 27-28} Nonetheless, given that those conductive carbon are not active towards water splitting, their presence may block the active sites of the Ni-

based hydroxides; not to mention, their fast degradation under highly oxidative anodic water electrolysis. In addition, the way Ni-based layered hydroxides being synthesized so far results in very limited specific surface area; hence, less active sites are being exposed to the electrolyte, offsetting water splitting performance. Exfoliation of such Ni-based LDHs into monolayer or few layers by scotch tape technique or liquid phase exfoliation has been proposed to solve the issue. However, the major drawback of low-yield make this process difficult to commercialize.

1.2 Objectives and Scope

The goal of this thesis is to develop Ni-based layered double hydroxides and their sulfides, phosphides derivatives toward highly efficient and stable electrocatalysts for overall water splitting. Specifically, the objectives mainly contain the following categories:

(1) Realizing semiconductor-to-conductor transition of Ni-based LDH-derived sulfides toward water electrolysis

- Prepare NiS_2 and Cu-doped NiS_2 *via* gas sulfidation of $\text{Ni}(\text{OH})_2$ and NiCu-LDHs synthesized by facile hydrothermal method.
- Characterize the as-obtained NiS_2 and Cu-doped NiS_2 .
- Study the change in electrical property of NiS_2 and Cu-doped NiS_2
- Evaluate the electrocatalytic properties of the catalyst towards HER, OER, and water splitting

(2) Tuning Ni-based LDH-derived phosphides *via* O_2 plasma and cation tuning towards advanced water splitting devices

- Design and prepare the vanadium doped Ni_2P (V- Ni_2P) by phosphidation of NiV-layered double hydroxides synthesized by facile hydrothermal method
- Subject the optimized V- Ni_2P into oxygen plasma treatment to obtain O-V- Ni_2P
- Characterize the as-obtained O-V- Ni_2P
- Investigate the change in surface area and hydrophilicity of the as-obtained Ni_2P

and O-V-Ni₂P

- Evaluate the electrocatalytic activity of O-V-Ni₂P towards HER, OER, and water splitting.
- Understanding the active sites of the prepared catalysts *via* first principle calculation.

(3) Vanadium incorporation into NiFe-LDHs grown on nickel foam substrate by scalable one-step hydrothermal treatment towards unprecedented water electrolysis.

- Grow NiFeV-layered double hydroxide on conductive nickel foam substrate (NiFeV-LDHs/NF) by a facile hydrothermal treatment
- Characterize the synthesized NiFeV-LDHs/NF
- Investigate the electrocatalytic properties of the prepared NiFeV-LDHs/NF towards HER, OER, and water splitting

1.3 Dissertation Overview

The thesis organization is divided into seven chapters.

Chapter 1 introduces the important role of hydrogen production by electrochemical water splitting as the energy carrier in modern society due to the depletion of fossil fuel. After that, the challenges slowing down hydrogen economy are pointed out. According to that research background, the motivation and objectives were established.

Chapter 2 gives an overview of the up-to-date progress of currently available methods of preparing Ni-based LDHs and their sulfides, phosphide derivatives. Then, the research efforts on the Ni-based LDHs and their sulfides phosphides derivatives for potential applications in electrocatalytic water splitting are discussed, including the role of S and P, and the real active sites.

Chapter 3 discusses the rationale for the selection of materials and synthesis methods. In

addition, brief summaries of the principles underlying various characterization techniques and reasons why these techniques are needed are also stated in this chapter.

Chapter 4 proposes the electronic modulation of the semiconducting LDH-derived sulfides NiS_2 by cation doping. Both theoretical calculations and temperature-dependent resistivity measurements indicate the semiconductor-to-conductor transition of NiS_2 after Cu incorporation. Such transition can facilitate reaction kinetics, reduce the loss of electron transport during electrocatalysis, increase the density of active sites, and give rise to intrinsic activities. Further calculations also suggest the advantages of Cu dopant to cathodic water electrolysis by bringing Gibbs free energy of H adsorption at both Ni sites and S sites much closer to zero. Noteworthy, water dissociation on Cu-doped NiS_2 (Cu-NiS_2) surface is even more favorable than those on NiS_2 and Pt (111). Thus, the prepared Cu-NiS_2 show noticeably improved performance towards alkaline HER and OER and eventually, water electrolysis.

Chapter 5 illustrates the effective incorporation of vanadium into LDH-derived nickel phosphide material, followed by surface engineering by oxygen plasma treatment. By experimental results and first-principle calculation, such rational design could simultaneously achieve: (1) increased BET surface area, and consequently, increased number of active sites; (2) much-improved hydrophilicity towards electrolyte; (3) enhanced density-of-state intensity which fasten charge-transfer kinetics; (4) Ni-V as co-electron deficiency centers are formed making Ni site to be more susceptible to OH^- adsorption; thus, promoting OER. Benefitting from these unique features, excellent electrochemical HER, OER, and water splitting performances are obtained.

Chapter 6 includes the growth of NiFeV-LDHs on conductive nickel foam substrate (NiFeV-LDHs/NF) via facile hydrothermal treatment. The as-prepared NiFeV-LDHs/NF was directly employed as electrodes for electrochemical HER, OER, and water electrolysis. By virtue of the integration of V into NiFe-LDHs , lower charge transfer resistance, increased electrochemical active surface area, and most importantly, higher intrinsic catalytic activity are obtained. Also, the *in-situ* growth of LDHs on conductive

Ni foam eliminates the use of additional binder, provides an efficient pathway for electron transport, partially solves the conductivity issue.

Chapter 7 gives a summary of my thesis work and several recommendations for future works.

1.4 Findings and Outcomes/Originality

This Ph.D. study has led to the following significant and novel outcomes:

- (1) The electronic configuration of LDH-derived NiS_2 is controllably regulated by simple Cu incorporation. The material transform from semiconducting nature to metallic one. Consequently, faster reaction kinetics, better electrical transport, and efficient electrical contact with the electrolyte are obtained. Moreover, Cu dopant also tunes the adsorption/desorption processes of the hydrogen-containing intermediates; hence, facilitating HER.
- (2) The incorporation of vanadium into Ni-based LDHs (particularly NiFe-LDHs) and LDH-derived Ni_2P is extremely important for highly efficient water electrolysis. By appropriate amount of V doping, lower charge transfer resistance, higher number of exposed active sites to the electrolyte, and most importantly, higher intrinsic catalytic activity are obtained.
- (3) By oxygen plasma treatment, the surface of LDH-derived V-doped Ni_2P is engraved; leading to higher specific surface area. In addition, the wettability towards electrolyte of interest (1.0 M KOH) is tuned, resulting in higher number of active sites in contact with electrolyte, lower the charge transfer resistance significantly.

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Chapter 2

Literature Review

In this chapter, introduction to electrochemistry of water splitting reaction including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is presented. After that, currently available approach to synthesize Ni-based layered double hydroxides (LDHs) and their phosphide/sulfide derivatives are outlined. Last but not least, research efforts on their potential applications in water electrolysis are overviewed.

2.1 Electrochemistry of the water splitting reaction

2.1.1 Hydrogen evolution reaction (HER)

The mechanism of hydrogen evolution reaction (HER) includes an adsorption step and desorption steps as the following:

In acidic conditions: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ($E^\circ = 0 \text{ V vs. RHE}$)

(1) Volmer adsorption step: $\text{H}_3\text{O}^+ + \text{e}^- + * \rightarrow \text{H}^* + \text{H}_2\text{O}$

(2) desorption step *via* Heyrovsky mechanism:

or recombination step *via* Tafel mechanism: $2\text{H}^* \rightarrow \text{H}_2 + 2*$

In alkaline conditions, H_2O works as both reactant and proton source,¹ thereby, HER must involve an O-H bond dissociation step of the H_2O reactant,² which is kinetically sluggish: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ ($E^\circ = -0.83 \text{ V vs. RHE}$)

(1) Volmer adsorption step: $\text{H}_2\text{O} + \text{e}^- + * \rightarrow \text{H}^* + \text{OH}^-$

(2) desorption step *via* Heyrovsky mechanism:

or recombination step *via* Tafel mechanism: $2\text{H}^* \rightarrow \text{H}_2 + 2*$

Wherein $*$ represents catalysts' active site and H^* represents the adsorbed hydrogen on the active site. Depending on the concentration of H^* (or hydrogen adsorption coverage), the HER can proceed through Volmer–Heyrovsky or Volmer–Tafel mechanism. For instance, with high hydrogen adsorption coverage, HER on a Pt (111) surface progresses *via* Volmer–Tafel mechanism in which the Tafel step is rate-determining.

The effectiveness of electrocatalysts is evaluated by various descriptors. Of most importance is the overpotential (η) that need to be applied to achieve specific current density (j). The smaller the overpotential, the less energy is wasted to overcome reaction barrier. Secondly, Tafel slope, which is the gradient of linear portion of “ η vs. $\log(j)$ ” plot, gives us an idea how fast the current density (equivalent to H_2 generation) increase with the small increment of overpotential; hence, electrocatalysts with small Tafel slope are desirable. In addition, based on the value of Tafel slope, reaction mechanism can be elucidated. Tafel slopes of $\sim 120 \text{ mV dec}^{-1}$ illustrate the rate-determining step to be

Volmer reaction. Whereas, the values of $\sim 40 \text{ mV dec}^{-1}$ and $\sim 30 \text{ mV dec}^{-1}$ are observed when electrochemical desorption Heyrovsky reaction and recombination Tafel reaction are rate determining steps, respectively.³ Last but not least, high Faradaic efficiency and long-term durability of electrocatalysts are also essential.

The HER electrocatalytic activities of various catalysts can also be determined in “volcano plot” which reflects the Sabatier principle. This principle states that desired electrocatalytic performances can be obtained on catalyst surfaces with just-right binding energies for intermediates (free energies for intermediates adsorption). In case of weak binding energy, the reaction is difficult to occur. On the other hand, too strong binding energy would poison the catalysts (products cannot dissociate to release active sites).² Particularly, for HER, Sabatier principle is disclosed based on Gibbs free energy for hydrogen adsorption (ΔG_{H^*}) which is a common descriptor of HER catalytic activity. In volcano plots, HER exchange current density (j_0) are plotted versus Gibbs free energy for hydrogen adsorption on the surface of catalyst (Figure 2.1).⁴ A HER catalyst with catalytic surfaces displaying ΔG_{H^*} approach zero is considered as an ideal catalyst. Not surprisingly, Pt resides close to the apex of this volcano with ΔG_{H^*} of zero and incredibly high j_0 .

Figure 2.1 Volcano plot of the exchange current density (j_0) as a function of the DFT calculated ΔG_{H^*} .⁴

2.1.1 Oxygen evolution reaction (OER)

The anodic half – oxygen evolution reaction (OER) is the key issue in electrocatalytic water splitting due to the kinetically sluggish anode reaction, which involves multiple electron transfer requiring O–O bond formation. Its mechanism can be described as follow:

In acidic conditions: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ($E^\circ = 1.23 \text{ V vs. RHE}$)

In basic conditions: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ($E^\circ = 0.40 \text{ V vs. RHE}$)

Wherein * represents catalysts' active sites; and *OH, O*, and *OOH represents the adsorbed OH, O, and OOH on the active sites, respectively. Similar to the case of HER, one of the strongest tool applied to analyze OER mechanism is Tafel slope. Difference in Tafel slopes typically comes with the difference in rate determining step or in mechanism. High Tafel slope value ($\sim 120 \text{ mV dec}^{-1}$) can be observed in the case of poorly active materials which bind intermediates weakly; hence, the discharge of water molecules (in acidic solutions) or OH^- (in basic solution) are the rate determining steps. For the materials which bind intermediates strongly, a surface rearrangement step or electrochemical oxidation step takes the role of rate determining (Tafel slopes of $\sim 60 \text{ mV dec}^{-1}$). While for Tafel slopes of $\sim 40 \text{ mV dec}^{-1}$, the oxygen evolution step is rate-determining. In addition, the binding energies between catalyst surface and oxygen-containing intermediates has also been demonstrated to have significant impact on the Tafel slope.⁵⁻⁶

Regarding activity descriptor of OER, they are the same as HER, namely, overpotential,

Tafel slope, Faradaic efficiency, and long-term durability. Similar to HER, one of the most profound advances in the study of electrocatalyst towards OER in general is also the volcano plot which reflects Sabatier's principle (Figure 2.2). Based on the plot, RuO_2 located near the apex of the “volcano” shows its excellent performance for OER followed by PtO_2 and IrO_2 .

Figure 2.2 Volcano plot of oxygen evolution reaction of metal oxide-based materials.⁷

2.2 Introduction to Ni-based layered double hydroxides (LDHs)

LDHs are a class of compounds with ionic lamellar consisting of positively charged metal layers with interlayers made up of charge balancing anions and water molecules. The metal cations reside in the centers of edge-sharing octahedra, whose six-vertex are hydroxide ions (OH^-) that link to establish infinite two-dimensional sheets.⁸ As the one gained most attention in the field of electrocatalysis, Ni-based LDHs have the general formula of $[\text{Ni}^{2+}_{1-x}\text{M}^{m+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n} \cdot z\text{H}_2\text{O}$, where M^{m+} usually be M^{2+} or M^{3+} as in Al^{3+} , V^{3+} , Fe^{3+} , Mn^{3+} , Cu^{2+} , Co^{2+} , Co^{3+} , *etc.* M^+ , M^{4+} , and M^{5+} cations are sometimes possible in Ni-based LDHs but restricted to specific examples like Li^+ , Ti^{4+} , and V^{5+} .⁹⁻¹⁰ A^{n-} is a negatively interlayer charge compensating anions, *e.g.* NO_3^- , CO_3^{2-} , F^- , Cl^- , Br^- , SO_4^{2-} , CH_3COO^- , OH^- , ClO_4^- .¹⁻⁸ z is the number of solvation molecules between layers.

Figure 2.3 displays the structure of representative LDHs.

Figure 2.3 Crystal structure of representative LDHs.¹¹

In LDHs, composition of metal layers can be higher than two. Metal cations can be added to form ternary or quaternary or multi-metal LDH-like compounds.¹² Density and chemical properties change accordingly. The interlayer anions between the LDH layers can be exchange by other halides anions, non-metal oxoanions, oxometallate anions, anionic biomolecules, anionic polymers, anionic complexes of transition metals, or organic anions. Due to this anion-exchange property, LDHs are also known as “anionic clays”. The ease of exchange of interlayer anions depends largely on electrostatic interaction between the host layers and exchanging anions. Besides, the radius, spatial structure and charge density properties of the exchanged ions should be taken into account.

In respect of thermal stability, LDHs are quite decent.¹³ At the heating temperature of less than ~ 250 °C, only desorption of interlayer water then dehydroxylation take place. Slightly higher than that till ~ 450 °C, volatile CO_2 and H_2O are released; carboxyl groups of the LDH laminate are desorbed. Consequently, BET surface area and total pore volume of the LDHs become larger. The layer structure does not collapse at this point.¹³ At higher than ~ 450 °C, the lamellar structure of LDH collapses to form metal oxides,

thereby reducing the micropore volume, and improving the thermal stability. The metal oxides formed by thermal decomposition of LDHs at $\sim 450\text{--}500\text{ }^{\circ}\text{C}$ can be recovered to layered structure of LDH in an aqueous solution containing intercalating anions under suitable conditions. This is attributed to so-called “structural memory effect”. However, as the calcination temperature increases, memory function deteriorates before diminishing.¹³⁻¹⁵

Due to the fruitful chemistry of LDHs, they can be directly used or precursor for catalytic materials,¹⁶ carbon dioxide adsorption materials,¹⁷ polymer/LDH nanocomposites for enhanced physicochemical properties and functionality of polymer matrix,¹⁸ and other applications.

2.3 Synthesis of Ni-based LDHs and their sulfides, phosphides derivatives

2.2.1 Synthesis of Ni-based LDHs

There are a number of methods have been adopted to synthesize Ni-based LDHs, depending on requirements for specific applications. By selecting suitable synthesis approach and rational optimization of reaction parameters, various Ni-based LDH materials have been successfully synthesized. Generally, there are three main methods, *i.e.* urea hydrolysis, sol–gel, and hydrothermal, which are summarized below. Also, their influence on physico-chemical properties by means of crystallinity, phase purity, surface area, morphology, and electronic property of the synthesized LDH are emphasized.

Urea hydrolysis. With two NH_2 groups linked to a carbonyl functional group ($\text{H}_2\text{N-CO-NH}_2$), urea is widely considered as the optimal precipitation agent to synthesize hydroxides.¹⁹⁻²⁰ Due to unique properties of weak Brønsted-Lowry base and highly-soluble in aqueous solution,²¹ the hydrolysis can develop controllably by changing reaction temperature, allowing low degree of supersaturation; hence, better precipitation and controllable particle size of synthesized LDHs. Besides, by using urea, the nucleation step and particle growth step are separated, and Oswald ageing can be avoided from the start.²²⁻²³

Introducing surfactant or complexing agent to urea hydrolysis is a good way to enhance

quality in term of purity of resulting LDHs. Liu *et al.* have introduced sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot n\text{H}_2\text{O}$) as the complexing agent to successfully prepare highly crystalline NiFe-LDHs with well-defined hexagonal shape.²⁴ In typical NiFe-LDHs synthesis, amorphous $\text{Fe}(\text{OH})_3$ is formed at first as pH increases:

Further pH increment would lead to the transformation of $\text{Fe}(\text{OH})_3$ into NiFe-LDHs:

However, the very small solubility constant of $\text{Fe}(\text{OH})_3$ ($K_{\text{sp}} = 2.5 \times 10^{-20}$) makes the transformation to NiFe-LDHs close to that of $\beta\text{-Ni}(\text{OH})_2$ formation.

In the presence of sodium citrate, $\text{Fe}(\text{OH})_3$ are better dissolved in the solution by chelating with citrate ion ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) to form $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_7)_2]^{5-}$ complex, subsequently favoring the formation of highly crystalline NiFe-LDHs with controllable size.

Sol-gel method. In a typical sol-gel process, metal precursors are hydrolyzed in aqueous or alcohol solution under room conditions to obtain a polymeric/particulate sol. A suitable amount of acid is sometimes introduced during hydrolysis to expedite precipitation.²⁵ LDHs synthesized by sol-gel method are cost-effective (low-temperature processing) and highly pure. Besides, it offers various advantages over urea hydrolysis. First, small particle size and controllable morphology are possible, which suits the synthesized LDHs to many applications. Secondly, the uniformity and structural properties of the resulting products can be regulated by changing precursor's composition, temperature, aging time, and ejection/addition of reactants. Therefore, the prepared LDHs offer homogeneous distribution of catalytic active sites. Last but not least, LDHs synthesized by sol-gel method normally possess high BET surface area of $\geq 150 \text{ m}^2 \text{ g}^{-1}$. These advantages provide LDHs with better electron transport as well as a larger number of exposed active sites for catalysis.

Valente *et al.* reported the fabrication of multi-metallic NiAl-LDHs and NiCoAl-LDHs with various morphologies *via* sol-gel method.²⁶ The synthesized LDHs shows low

crystallinity but high surface are ($290 \text{ m}^2 \text{ g}^{-1}$), and narrow pore size distributions ($\sim 3\text{--}4 \text{ nm}$), which is beneficial for catalysis applications. They attribute this encouraging success to precise control of synthesis conditions as well as the rate of complexation of the metal precursors to balance the rates of condensation and hydrolysis in order to generate transparent gels.

Hydrothermal method. This is the most common and easily scalable way to prepare multimetallic LDHs.^{19, 27} In this method, a mixed solution of metal salts in adequate proportions and alkaline solution with controlled pH are slowly added into a Teflon-lined stainless steel reactor, followed by coprecipitation of the metal salts under hydrothermal condition. The LDHs are then obtained by centrifuging, washing, and drying. The mechanism of this method is relied on the condensation of metal aquo complexes $[\text{M}(\text{H}_2\text{O})_n]^{z+}$, resulting in a built-up of brucite-like layers made of homogeneously dispersed metal cations with solvated inter-layer anions.

This method offers a number of process parameters to better control the resulting LDHs, namely, pH, ratio of cations, hydrothermal treatment temperature and duration, and concentration. Depending on process parameters, highly crystalline LDHs or quasi-amorphous ones can be obtained with controlled crystal sizes, purity, narrow size distribution, and stability.¹⁹ To obtain the desired materials, the synthesis conditions needs to be optimized for each system. Taking pH as an example, if pH is too low, it is hard to guarantee all the different metal ions would precipitate together; while too high pH would lead to uncontrollable morphology or the resulting LDHs. Practically speaking, pH of 7-10 are normally employed to synthesize LDHs.²⁸⁻²⁹

Despite those superiorities, hydrothermal method still faces the problems of not being adequate for the fabrication of LDHs with precise stoichiometry and not working well if metal salts have largely different solubilities.

Hydrothermal synthesis for LDHs are normally done at low supersaturation in which all precursor solution are added to the autoclave by a titration device while maintaining the desired pH. After precipitation at room temperature, hydrothermal treatment at optimized temperature and duration is applied to enhance LDHs' crystallinity. Anions in the autoclave normally possess high affinity for LDH materials and should effortlessly go in

the interlayer space between positively charged metal layers to expel the foreign anions. Whereas at high supersaturation, a high number of crystallization nuclei are formed at the beginning; therefore, poor crystallinity and small particle sizes LDHs are often obtained. Furthermore, the prepared LDHs may contain impurity of single metal hydroxides; also making it difficult to control the metal ratio in LDHs.

Besides those above-mentioned methods, to accelerate the growth and aging steps of LDHs synthesis, microwaves and ultrasound are also employed.³⁰⁻³¹ Generally, specific surface area and porosity of the synthesized LDHs are enhanced with increasing duration of exposure to microwave. Meanwhile, larger particle size are obtained with higher ultrasonic power.³²

2.2.2 Synthesis of Ni-based LDHs-derived sulfides, phosphides

Thanks to the versatility in synthesis method, LDHs is considered as an ideal precursor for the fabrication transition metal phosphides or sulfides. The synthesized sulfides/phosphides would inherit the morphology of the LDHs precursors which are easy to adjust. More importantly, this method of using LDH precursor enables the synthesis of various multi-metal phosphides/sulfides which have the highly uniform distribution of every metal throughout the crystal structure.

The hydrothermal/solvothermal method is the most widely used approach to achieve LDH-derived transition metal sulfides. In a typical process, LDHs and sulfur source (*e.g.*, sodium sulfide, thiourea, and thioacetamide) are dissolved in organic solvent (mostly alcohol) or water or sometimes a mixture of water and organic solvent, before being heated in a Teflon-lined stainless steel vessel at specific temperature for a period of time.³³⁻³⁴ Moreover, this process also allow the sulfidation even when the LDHs are grown on substrates. Another approach to synthesize LDH-derived transition metal sulfides is gas sulfidation which employs H₂S or S vapor as the sulfur source. The reaction is conducted in a tube furnace with H₂S gas flow; or more commonly, with argon or nitrogen carries S vapor from upstream to LDHs at the downstream.

Regarding LDH-derived phosphides, phosphidation is usually done under PH₃ environment. However, PH₃ is highly toxic and lethal (LD₅₀ = 3.03 mg kg⁻¹); therefore,

PH_3 onsite generated by hypophosphite such as sodium hypophosphite and ammonium hypophosphite at $\sim 250\text{--}300^\circ\text{C}$ are used as substitution according to their decomposition below:

The reaction is called pseudo-chemical vapor deposition (pseudo-CVD) wherein the PH_3 upstream is carried by protective gas flow (argon or nitrogen) and react with LDHs downstream at $300\text{--}350^\circ\text{C}$ to produce metal phosphides. The reaction is fast, surfactant-free, easily scalable, and the generated by-products Na_2HPO_4 (in case of NaH_2PO_2 is used) in the upstream are environmentally friendly and easily washed away.

Figure 2.4 (a) Synthetic route of LDHs-derived NiCoP nanosheet on nickel foam. (b) X-ray diffractograms of NiCo-LDHs and NiCoP (*: nickel foam). (c-d) SEM of NiCo-LDHs and NiCoP. (e) EDS elemental mappings of the NiCoP.³⁵

Recently, this pseudo-CVD process to synthesize metal phosphides was advanced to a new level by employing plasma technique. The hydrothermally synthesized NiCo-LDHs/Ni foam was placed into plasma-enhanced chemical vapor deposition (PECVD) system, followed by PH_3 plasma treatment at 250°C for 15 minutes (Figure 2.4a-e).³⁵ Compared to the common PH_3 route described above, this small modification allows a lower temperature phosphidation at a much shorter time (15 minutes compared to $\sim 1\text{--}3$ hours).

2.3 Ni-based LDHs and their sulfides, phosphides derivatives for water splitting

2.3.1 Ni-based LDHs

The Ni-based LDHs is highly attractive towards electrochemical oxygen evolution reaction due to the easy accessibility to electrolyte *via* anion exchange.³⁶ Nonetheless, the major problem holding Ni-based LDHs back is their poor electronic conductivity. Realizing that shortcoming, Dai *et al.* in their report in 2013, demonstrate for the first time the NiFe-LDHs covalently attached on multi-walled carbon nanotubes (MWCNTs) by slow hydrolysis of metal precursors, followed by solvothermal crystallization (Figure 2.5a-b).³⁷ The resulting NiFe-LDHs with the size of 5 nm coupled MWCNTs showed exceptional OER performance. To achieve a current density of 5 mA cm⁻², it needs only 0.25 V overpotential; alongside with a Tafel slope of only 31 mV dec⁻¹ (Figure 2.5c-d). Not surprisingly, without coupling with MWCNTs, the bare NiFe-LDHs revealed ~30 mV higher in overpotential at the same current density.

Figure 2.5 (a-b) SEM and TEM images of NiFe-LDH nanoplates grown over a network of MWCNTs, respectively. (c) iR-compensated polarization curves of NiFe-LDH/CNT

hybrid on carbon paper measured at 0.1 mVs^{-1} in 0.1 M KOH and 1.0 M KOH and (d) their corresponding Tafel plots.³⁷

Since then, numerous works have employed similar strategy of improving OER activity by coupling with highly conductive materials; eg. grow on conductive Ni foam/carbon cloth/carbon paper substrate,³⁸ grow on graphene.³⁹ Hybridizing with carbon quantum dots (CQDs) is also employed.⁴⁰ Kang and co-workers report the highly conductive carbon quantum dots (CQDs) with size of $\sim 5 \text{ nm}$ decorated on NiFe-LDHs nanoplates. The CQDs/NiFe-LDHs hybrid displays admirable OER electrocatalytic activity with an overvoltage of $\sim 235 \text{ mV}$ at 10 mA cm^{-2} along with high durability and stability. This value exceeds most of previously reported Ni-based compounds and surpass those of the precious metal based catalysts.

It is worth noting that compared to Ni(OH)_2 , the small addition of Fe to form NiFe-LDH leads to dramatically increase in OER catalytic activity; while it is widely known that Fe-based materials are inferior towards OER. Therefore, a systematic study of $\text{Ni(OH)}_2/\text{NiOOH}$ and $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2/\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ toward OER by Trotochaud *et al.* was conducted which first revealed the 30-fold increase in conductivity after the incorporation of Fe.⁴¹ Furthermore, their study on turnover frequency (TOF) suggests an Fe-induced partial charge transfer activation mechanism on nickel, which resembles what observed at noble-metal electrode surfaces. Apart from Fe^{3+} , other earth-abundant metal elements have been tried to incorporate into nickel hydroxides for efficient water oxidation. Among all, NiCo-LDHs and NiMn-LDHs received the most attention due to promising activity;⁴²⁻⁴⁵ however, it was not comparable to NiFe-LDHs under the same testing conditions.⁴⁶ To further optimize Ni-based LDHs, first principles calculation also came into play. Diaz-Morales *et al.* examined Ni-based LDHs with optimized ratio of Mn, Cr, Co, Fe, Zn, and Cu for OER, and yet among those contenders NiFe-LDHs still shows the best activity.⁴⁷ It was until recently, Fan *et al.* reported ultrathin NiV-LDHs which shows advanced OER performance compared to NiFe-LDHs synthesized at the same condition.⁴⁸ They ascribed the better performance to the lower charge transfer resistance and the higher electrochemical active surface area. More importantly, their DFT calculations reveals that the V dopant facilitates the formation of OOH^* and its

adsorption, which is usually the rate-determining step for water oxidation.

2.3.2 Phosphide derivatives

Recently, Ni-based LDH-derived materials including transition metal phosphides and sulfides have been intensively studied as electrocatalysts for water electrolysis. They demonstrate good catalytic activities due to the combined advantages of Ni-based LDHs (easily controllable composition, morphology, and electronic structure) and their synergistic effect with sulfur and phosphorus in respective sulfides and phosphides.

It is known long before that Ni_2P is highly active for hydrosulfurization (HDS) reaction,⁴⁹⁻⁵⁰ whose mechanism also relies on the reversibility of hydrogen adsorption/desorption. Moreover, DFT calculations by Ping Liu and José A. Rodriguez indicated that the most stable surface of nickel phosphides Ni_2P (001), with exposed Ni sites and P sites, shows an ensemble effect, whereby both hydride-acceptor and proton-acceptor centers are there to expedite HER electrocatalysis.⁵¹⁻⁵² Also, with similar structural and electronic properties to the active sites of NiFe-hydrogenase, Ni_2P (001) should resemble HER catalytic activity of NiFe-hydrogenase as well. Inspired by these analyses, combined with metallic-like conductivity of metal phosphides that can promote electron transfer during electrocatalytic processes, Ni-based LDHs-derived metal phosphides have been widely investigated for HER.^{35, 53-55}

Regarding the anodic half of water splitting, the surface of metal phosphides can be easily oxidized during high oxidative OER condition to give hydroxides/oxyhydroxides surface which is proven to be highly active toward OER.^{35, 55} Actually, those oxidized surface usually show even higher OER performance than the corresponding metal hydroxides/oxyhydroxides synthesized directly.^{35, 56-57} There are several potential reasons for that phenomena which were pointed out by Jin Song in his letter.⁵⁸ First, the newly formed metal hydroxides/oxyhydroxides might have high surface area. Secondly, the conversion process from phosphides may lead to unusual amorphous hydroxides/oxyhydroxides or metastable hydroxides/oxyhydroxides that are more electrocatalytically active but otherwise difficult to gain access to by conventional synthesis. Thirdly, the conductive metal phosphides core might play the role of

conductive scaffolds for the electro-active shell metal hydroxides/oxyhydroxides. Last but not least, synergistic interactions between the different components makes the core/shell catalysts better than the direct synthesized hydroxides/oxyhydroxides. Motivated by those speculations, many research groups have spared no effort to develop various Ni-based LDHs-derived phosphides with various structures and compositions. Lots of them reveal excellent catalytic activity and great potential towards practical water electrolysis.

Generally, incorporating one or more metal elements into metal phosphides could noticeably enhance electrochemical performances by altering their electronic structure. To illustrate, a DFT study for Ni₂P and NiCoP was conducted which firstly show a much-increased density of state (DOS) intensity of NiCoP compared to Ni₂P indicating faster charge transfer kinetics (Figure 2.6a-b,d-e). In addition, d-states of NiCoP is shown to be closer to Fermi level in comparison with Ni₂P, suggesting a lower OH⁻ adsorption energy which is normally the rate-determining step (RDS) of OER.^{35, 54} Regarding HER, NiCoP (0001) surface showed the ΔG_{H^*} value significantly close to 0 than that of Ni₂P (-0.15 and -0.14 eV compared to -0.86 eV and -0.45 eV for sites 1 and sites 2, respectively, Figure 2.6c). Another point needs to be considered is that the HER reactions in neutral and basic environments require a prior step of water dissociation, and the adsorption energy of H₂O molecules on both Ni₂P (0001) and NiCoP (0001) mark the value of ~18 eV, even higher than Pt (111) at 8.97 eV suggesting NiCoP is a promising HER electrocatalyst to replace Pt in non-acidic condition (Figure 2.6f). Experimentally, Hu *et al.* reported the NiFe-derived(Fe_xNi_{1-x})₂P nanoarrays for OER in both basic and neutral conditions.⁵⁹ The shifted peaks in X-Ray diffractograms and XPS spectra indicated that the doped Fe have modulated electronic structure of Ni₂P. This would alter the local electric dipole, facilitating adsorption/desorption of OER intermediates; hence, a smaller kinetic barrier and better electrocatalytic activity were obtained. Specifically, in 1.0 M KOH solution, the resulting catalyst only needs a modest overpotential of 255 mV to achieve a current density of 0.5 A cm⁻². This decent activity is also observed in neutral condition (0.1 M phosphate buffer solution) with potential of 1.626 V at 10 mA cm⁻².

Figure 2.6 (a,d) Crystal structures in unit cell of Ni₂P and NiCoP. (b,e) Electronic band structures and PDOS of the bulk Ni₂P and NiCoP (spin-up, green curves; spin-down, red curves). (c) Free-energy diagram for H adsorption. (f) Adsorption energy for H₂O. (g-h)

HER and (i-j) OER electrocatalysis in 1.0 M KOH. (g,i) iR-corrected polarization curves and (h,j) their corresponding Tafel slopes. (e) STEM annular dark field (ADF) image of the NiCoP. (f,g) Inverse Fourier-filtered images of the squares marked areas in a showing the presence of edge dislocations.³⁵

Another study that took advantage of this multi-metal concept was presented by Seong Chan Jun's group.⁶⁰ Derived from NiCoFe-LDH, their NiCoFe_xP indicated a decent overpotential of 39 mV at -10 mA cm^{-2} toward HER alongside with a Tafel slope of 50 mV dec^{-1} ; while all other double metal phosphides show poorer performances, *i.e.* NiFeP (109 mV, 112 mV dec^{-1}); CoFeP (91 mV, 102 mV dec^{-1}); NiCoP (86 mV, 88 mV dec^{-1}). Considering the other half of water electrolysis – OER, similar performance trend was observed in which NiCoFe_xP (η_{50} of 275 mV, and Tafel slope of 56 mV dec^{-1}) outperforms other double metal phosphides and even the benchmark RuO₂ by a great margin. Another strategy to achieve high performance LDH-derived metal phosphides is to create and stabilize defects, which would tune their chemical and physical properties. Liang *et al.*, by employing PH₃ plasma to phosphorize NiCo-LDHs, the obtained NiCoP nanosheets are defect-rich nanosheets which can be observed through the uniform distributed nanopores in the TEM images and the presence of edge dislocations in the STEM inverse Fourier-filtered images (Figure 2.6k-m). This defect-rich structure would grant higher electrochemically surface active area, increase electrolyte diffusion to better utilize the active sites; consequently, boost up the electrocatalytic activity. Therefore, toward HER, the NiCoP by PECVD method showed a current density of -10 mA cm^{-2} at only 32 mV overpotential and Tafel slope of 37 mV dec^{-1} , which is much better than 86 mV and 88 mV dec^{-1} of the NiCoP synthesized *via* common PH₃ route presented by other works (Figure 2.6g-h).⁶⁰ The OER performance shows similar pattern where overpotential at specific current density and Tafel slope of the former is notably lower than the latter ($\sim 330 \text{ mV}$ and 87 mV dec^{-1} compared to 346 mV and 121 mV dec^{-1} , Figure 2.6i-j).

Though LDHs-derived phosphides have shown their huge potential towards electrochemical water splitting, there is yet a lot of unexplored space. For instance, engineering surface structure and surface hydrophilicity or creating nano/micro porous

structures to enhance the number of exposed active sites to electrolyte. In addition, integrating high valence metal species into Ni-based LDHs-derived phosphides could also be an interesting approach to enhance the sluggish OER.

2.3.3 Sulfide derivatives

Similar to the role of P in metal phosphides, surface S atoms in metal sulfides play the role as proton adsorption/desorption centers. However, due to the higher electronegativity of S, the resulting bond strength S–H during adsorption process is sometimes too strong (S–H (363 kJ mol⁻¹) > P–H (322 kJ mol⁻¹)); hence, poorer HER activity might be obtained.⁶¹ However, there are still some well-engineered Ni-based LDH-derived metal sulfides reported to be active towards water reduction process such as α -NiFeS,⁶² Fe-doped Ni₃S₂,⁶³ NiCo₂S₄@NiFe LDH.⁶⁴ In those works, multi-metal sulfides display much improved HER, OER activity than the single metal ones due to synergistic effect and the change in electronic structure. To illustrate, Yang and co-workers synthesized NiFe-LDHs derived α -iron–nickel sulfide (INS), which demonstrated decent activity as well as stability towards HER.⁶² The authors also compare the activity with β -iron–nickel sulfide (β -INS) synthesized by topotactic conversion. Compared to β -INS nanosheets, the NiFe-LDH derived α -INS shows better HER performance with potential of -105 mV at -10 mA cm⁻² along with a Tafel slope of 40 mV dec⁻¹ thanks to lower charge transfer resistance and higher density of active sites (Figure 2.7a-d). To deeply comprehend the origin of that fascinating performance, DFT calculations were conducted which show favorable hydrogen adsorption/desorption capability of α -INS compared to NiS. Specifically, on α -INS, the energy required for hydrogen adsorption was only 0.01 eV, much lower than 0.19 eV on NiS (Figure 2.7e-f). Moreover, when H₂ are desorbed from active sites, α -INS releases higher energy (2.39 eV) than that of NiS (2.19 eV). They attributed this to the change in electronic configuration of electrocatalytically active sites after Fe incorporation.

Figure 2.7 (a) HER polarization curves of Pt, α -INS, β -INS, β -NiS and (b) their corresponding Tafel slopes. (c) Electrochemical surface area (ECSA) of β -INS and α -INS. (d) Electrochemical impedance spectra (EIS) of β -INS and α -INS at HER overpotential of 100 mV. (e) HER reaction pathway on α -INS in acidic condition (The blue, red, and yellow spheres denote Ni, Fe, and S atoms, respectively). (f) HER kinetic energy barrier profiles on α -INS and α -NiS.⁶²

Regarding OER, very much similar to metal phosphides, metal sulfides were proven to be surface-oxidized after highly-oxidative OER, resulting in hydroxides/oxyhydroxides formation on their surface. Those derived metal hydroxides/oxyhydroxides are actually

the true active sites of metal sulfides towards OER.^{56, 58}

Despite having fascinating properties toward HER and OER, some sulfide phases are suffering from unsatisfied electron/charge transport during reactions due to semiconducting nature. In this regard, forming nanocarbon/sulfides hybrid to enhance the conductivity might just be the way to go, and yet have not been reported. Another difficult but highly rewarding approach is to modulate the electronic structure of Ni-based LDH-derived sulfides to transform semiconducting sulfides to metallic-like one.

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Chapter 3

Experimental Methodology

In this chapter, the rationale for the selection of materials and method are outlined. Then, a brief interpretation of the synthesis methods as well as characterization techniques and equipment are elucidated.

3.1 Rationale for Material and Method Selection

3.1.1 Selection of materials

In the first part of this dissertation, Ni-based LDHs with low cost, outstanding catalytic activity and stability has shown its huge potential to replace the precious metal-containing water splitting electrocatalysts in alkaline conditions.¹ A representative compound in that family, NiFe layered double hydroxides (LDHs), has been reported to be one of the best performing bifunctional electrocatalyst so far.¹ However, the poor electronic conductivity of the Ni-based hydroxides, which inhibits electron/charge transportation, limits its practical application as a catalytic electrode material. Coupling with conductive carbon like graphene, carbon nanotubes, or carbon quantum dots are reported.²⁻⁴ Nonetheless, given that those conductive carbon are not active towards water splitting, their presence may block the active sites of the Ni-based hydroxides; not to mention, their fast degradation under highly oxidative anodic water electrolysis.

This issue can be solved by appropriate elemental doping, which can modify electronic structure, introduce defects and crystalline dislocation; therefore, increasing the number of active sites and carrier concentration. In this respect, the choice of metal to be doped is of great importance. Besides the commonly iron, cobalt, or manganese dopants, rationally predictions combined with well-designed experiments are needed to further tune electrocatalytic activity of Ni-based LDHs towards water splitting. Vanadium, which is relatively cheap, earth-abundant, and versatile in electronic structure, is a promising candidate for several reasons. Firstly, multi-valence nature of vanadium makes it very flexible to adjust electronic structure to tune the electrocatalytic performances. Also, the five-valence configuration of V ensures high 3d electron orbits and tunable electro-accepting/donating properties, which may promote the OER electrocatalysis in alkaline condition ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$).⁵ In addition, V as the dopant can enhance DOS intensity; thus, fasten the charge-transfer kinetics, which is crucial for both HER and OER.⁶⁻⁸ Last but not least, theoretical calculation also indicated that vanadium doping could significantly lower the overpotential for the rate-determining step.⁹ Another method of interest is the post-treatment of the synthesized Ni-based LDHs by

phosphidation or sulfidation. This approach allows the transformation of insulating LDHs to low bandgap semiconducting or metallic Ni-based phosphides/sulfides while maintaining the layered structure of LDHs.¹⁰⁻¹¹ However, appropriate binding energy optimization by metal dopant should be considered since the way H₂O and hydrogen- and oxygen-containing intermediates behave at sulfides/phosphides surface are different from that on hydroxides surface.

3.1.2 Selection of synthesis and engineering methods

All Ni-based LDHs in this study were all synthesized by hydrothermal method using self-developed and conditions. This method of synthesis was chosen for the study by virtue of its versatility, scalability, and wide range of available precursors and surfactants that can be used. In addition, this method offers a number of process parameters to better control the resulting LDHs, namely, pH, ratio of cations, hydrothermal treatment temperature and duration, and concentration.

However, the big issue of not only Ni-based LDHs synthesized hydrothermally but of all Ni-based LDHs in general is the limited specific surface area; hence, less active sites are being exposed to the electrolyte, offsetting water splitting performance. Exfoliation of such Ni-based LDHs into monolayer or few layers by scotch tape technique or liquid phase exfoliation has been proposed to solve the issue. However, the major drawback of low-yield make this process difficult to commercialize. In this regard, surface engineering by plasma technologies might be an answer, which can engrave the surface to give higher active surface area while introducing vacancies, which might also be beneficial for catalysis.¹² Moreover, the architecture of electrode materials and the interfacial interaction between the catalyst and electrolytes is of great important for the high performance water electrolysis. The good wettability of electrocatalysts with electrolytes has a significant impact on providing easy access of reactant. Also, improved wettability can enhance the catalyst-electrolyte contact points, leading to higher exposed active sites to the electrolyte and better charge transfer. In contrast, hydrophobic surface of electrocatalyst is detrimental to electrolyte penetration; and thus, limits the reaction kinetics, resulting in unsatisfactory water electrolysis.¹³ Therefore, rationally designed

nanostructures with superior hydrophilicity towards electrolyte of interest could be an effective approach for enhanced electrochemical water splitting performance. By dint of these rationale, with only O₂ plasma treatment, the surface can be modified to increase the number of active sites. At the same time, the wettability toward aqueous solution can be adjusted. Moreover, when applied O₂ plasma treatment to LDH-derived phosphides, surface oxidation of phosphide materials due to oxygen plasma will create the phosphate-phosphide interface region, which was theoretically indicated to facilitate the simultaneous adsorption of both hydrogen and oxygen-containing intermediates;¹⁴ thus, expediting overall water electrolysis.

As for method of sulfidation of Ni-based LDHs, solvothermal method with thioacetamide as the sulfur precursor was chosen due to similar reasons as LDHs hydrothermal synthesis.

Differently, PH₃ generated on-site (by NaH₂PO₂, NH₄H₂PO₂) was selected for Ni-based LDHs phosphidation mostly by dint of its scalability, reliability compared to other methods that employ organic phosphine or elemental phosphorus (toxic, high temperature, energy-intensive). In addition, the reaction is facile, free of surfactant, and the generated by-products in the upstream are easily washed away.¹⁵ Importantly, while metal phosphides synthesize by organic phosphine normally result in amorphous carbon layer, which hinder the active sites towards HER and OER; gas phosphidation by PH₃ completely eliminates that problem.

3.2 Principles of synthesis methods

3.2.1 Hydrothermal and solvothermal method

By definition, hydrothermal method is a technique that involves heating an aqueous-based reaction mixture at temperature higher than 100 °C and under autogenous pressures within a completely sealed vessel (autoclave).¹⁶ In case of heterogeneous reaction (*e.g.* Ni-based LDHs sulfidation in this thesis), the high temperature and pressure promote solvent's capability to dissolve solids and accelerate the reactions. In a typical synthesis, precursors and solvent are mixed at desired ratio in a Teflon-lined stainless steel

autoclave, which is then put into a pre-set oven at appropriate temperature and duration. The products are then collected by centrifugation/filtration, washing, and drying in vacuum oven.

The concept of solvothermal method is analogous as that of hydrothermal method. The only difference is that in solvothermal reaction, organic solvent (mainly alcohols) are used instead of aqueous solution. Alternatively, the reactions are called alcohol-thermal and glycol-thermal when alcohols and glycerol/glycol are used as the reaction media, respectively.¹⁶

For solvothermal sulfidation of Ni-based LDHs in this dissertation, thioacetamide, which is highly soluble in ethanol, serves as the source of sulfide (S^{2-}) ions. Specifically, at appropriate temperature and pressure in autoclave, Ni-based LDHs are slowly dissolved into metal ions depending on their precipitation products (K_{sp}), sulfidation reaction is then proceed *via* the following:

3.2.2 Gas Phosphidation

Regarding LDH-derived phosphides, phosphidation is usually done under hydrogen phosphine (PH_3) environment. However, PH_3 is highly toxic and lethal (LC_{50} of 11 ppm in male rats);¹⁷ therefore, PH_3 onsite generated by hypophosphite such as sodium hypophosphite and ammonium hypophosphite at $\sim 250\text{--}300$ °C are used as substitution according to their decomposition below:^{15, 18}

The reaction is called pseudo-chemical vapor deposition (pseudo-CVD) wherein the PH_3 upstream is carried by protective gas flow (argon or nitrogen) and react with LDHs downstream at $300\text{--}350$ °C to produce metal phosphides. The reaction is fast, surfactant-free, easily scalable, and the generated by-products in the upstream are environmentally friendly and easily washed away.

3.3 Characterization

Along with the fast development of material synthesis and engineering, there are also lots of advancements that has been made in characterization techniques, which help to comprehensively understand the materials in regards of structure, morphology, and other properties. In this section, all of the material characterization methods employed in this dissertation are summarized in brief.

3.3.1 Scanning electron microscopy

Resolution of optical microscopes is limited by the wavelength of visible light according to the classic Rayleigh criterion:¹⁹

$$\delta = \frac{0.61\lambda}{\mu \sin\beta} \quad (3.4)$$

wherein λ , μ , and β are the wavelength of the radiation, the refractive index of the viewing media, and the semi-angle of collection of magnifying lens, respectively. With the wavelength of 550 nm (mid of visible spectrum), the best resolution an optical microscope can achieve is only 0.3 μm , which is far from sufficient for nanostructured materials. Fortunately, Broglie's ingenuity solved the problem by his famous equation showing that the wavelength of electron is closely related to its energy (E):¹⁹

$$\lambda = \frac{1.22}{E^{1/2}} \quad (3.5)$$

This fundamental invention gave rise to two powerful techniques called scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

SEM is one of the most common electron microscopies for examination of morphology, topographical features, and crystal orientation of materials by scanning the surface of a sample with a high-energy beam of electrons (raster scan).²⁰ The electron beam will hit and interact with atoms at various depths in the sample depending on the accelerating voltage and samples' density, producing various signals (secondary electrons, Auger electrons, backscattered electrons, and characteristic X-rays) that deliver surface information of the samples. Of these signals, secondary electrons, which can be detected by Everhart-Thornley detector, are emitted due to the inelastic scattering interactions of specimen atoms with the electron beam within a few nanometers from the specimen surface. Hence, high resolution imaging of as low as ~ 1 nm (JEOL JSM-7600F operating

at an accelerating voltage of 15 kV) is possible in this secondary electron imaging (SEI) mode. Due to that main reason of its ability to examine materials at nanometer scale, SEM in SEI mode was used extensively in this thesis. Besides, the ease of sample preparation and the reasonably short time needed for this characterization are also the reasons for choosing this technique.

The as-prepared samples grown on nickel foam substrate or powder samples were directly placed and pressed on carbon tape for SEM characterization. In chapter 4-5, SEM image were obtained on a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) at the accelerating voltage of 5 kV with a working distance of 8 cm and probe current of 7 μ A. While in chapter 6, ULTRA Plus SEM (Zeiss) operating at 20 kV with a working distance of 8 cm and probe current of 0.2 μ A was used

3.3.2 Transmission electron microscopy

By far, TEM is one of the most common and powerful tools to obtain detail information of nano-scaled materials. In TEM, a high energy beam of electrons with much higher acceleration voltage compared to that of SEM is passes through a very thin sample, the interaction between the electron beam and atoms in the sample can provide knowledge on crystallinity, shape, lateral size, grain boundaries, structure dislocations/defects, interlayer distance, and elemental composition.²¹

For example, the lateral size of nanosheets can be directly and precisely measured *via* low magnification TEM images. In addition, by measuring the vertically-aligned nanosheets, information on thicknesses can be obtained as well. The high-resolution TEM images (HRTEM) and selected area electron diffraction (SAED) patterns are widely used to investigate the crystal structure, structure dislocations, crystal orientation and exposed crystal facets of nanosheets. With the point resolution of as low as 0.5 Å, HRTEM allows imaging of nanomaterial at atomic scale. It can also be used to confirm the crystal structure by calculating the distance of crystal lattice fringes. Moreover, the HRTEM also enable qualitative study on the crystallinity of materials, *i.e.* crystalline materials give well-aligned lattice fringes, whereas no crystal lattices are observed in HRTEM images of amorphous ones. Furthermore, the crystallinity, *e.g.* single-crystalline, polycrystalline and

amorphous structure of a material, can also be revealed by the SAED pattern. Single-crystalline materials present clear bright-dot patterns, polycrystalline ones show ring-like patterns, and amorphous one do not show any SAED patterns.

In chapter 4-5, low-magnification TEM images, selected area electron diffraction (SAED) patterns were collected by a JEOL JEM 2010UHR instrument at an accelerating voltage of 200 kV. High resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on a JEOL 2100F at an accelerating voltage of 200 kV.

In chapter 6, low-magnification TEM images was done JEOL JEM 2100F operating at 200 keV; whereas, HRTEM, SAED, HAADF-STEM and EDS elemental mapping were performed on FEI Themis-Z Double-corrected microscope at an accelerating voltage of 300 kV.

3.3.3 Atomic force microscopy

Atomic force microscopy (AFM) is one of the most powerful microscopy technology for studying nanostructured materials. It can image three-dimensional topography at sub-nanometer resolution, perform force spectroscopy to measure mechanical properties (*e.g.*, Young's modulus), and manipulate samples' properties in a controlled way (*e.g.*, atomic manipulation, scanning probe lithography and local stimulation of cells). All of these can be done with very minimal sample preparation.²²

A typical AFM employs a cantilever (made of Si or Si₃N₄) with a very sharp tip called probe to scan over a specimen surface. As the tip is brought into proximity of the surface, according to Hooke's Law, forces between the surface and the tip results in the deflection of the cantilever away from the surface. In this dissertation, AFM measurement is only employed for height imaging (getting information on thicknesses of nanosheets) at non-contact mode on NX10 Park System Corporation. In this mode, instead of touching the samples' surface, the tip of the cantilever is oscillated at either its resonant frequency (frequency-modulation mode) or just above (amplitude-modulation mode) wherein the oscillation amplitudes are normally less than 10 nm down to few nm. The van der Waals

interaction between the tip and the sample surface decrease the resonant frequency of the cantilever. Combined with the feedback loop system, a constant oscillation amplitude or frequency is maintained by changing the average distance between the tip to sample's surface. By measuring that distance at each point, the scanning software is able to construct a topographic image of the sample surface.

3.3.4 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique used for phase identification and obtain crystallographic information (unit cell dimensions) of materials. During operation, X-ray are generated by a cathode X-ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and bombarded the sample. If the atoms in the material are well-arranged (crystalline), constructive interference of the diffracted X-rays are achieved when Bragg's Law is satisfied:²⁰

$$n\lambda = 2d \sin \theta \quad (3.6)$$

wherein d , θ , and λ represent interplanar spacing, incident angle, wavelength of the incident X-ray, respectively. And n can be any positive integer.

With constant wavelength of incident X-ray, scanning sample through a range of θ angles would result in series of diffraction peaks due to random orientation nature of powder samples. The position of diffraction peaks can deduce d -spacings, which play as the “fingerprint” of the material since each compound has its own unique set of d -spacings.

In this dissertation, the crystallinity of the samples was examined using Bruker D8 diffractometer in chapter 4-5 and X'Pert PANalytical X-ray diffractometer in chapter 6. Both are equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The former operates at an acceleration voltage and an emission current of 45 kV and 40 mA; while the latter operates at 40 kV and 40 mA, respectively. XRD patterns were obtained at a scanning rate of $0.06^\circ \text{ s}^{-1}$, with a step size of 0.01° .

3.3.5 X-ray photoelectron spectroscopy

The principle underlying XPS technique is the photoelectric effect. The inner layer

electrons of atoms are emitted when the sample is bombarded by a sufficiently-high energy light beam. The light source used in XPS is normally a soft X-ray with energy of 200-2000 eV. When the sample absorbs the X-ray and generates photoelectrons, the total energy of photoelectrons is written as:²³

$$h\nu = KE + BE + \phi \quad (3.7)$$

wherein $h\nu$ is the total energy of the incident photon (where h is Plank's constant and ν is the frequency of the X-ray source), KE ($\frac{1}{2}mv^2$, m represents the mass of electron and v represents the velocity of excited photoelectron) is the kinetic energy of the excited photoelectron, BE is the binding energy of inner layer electrons, and ϕ is the work function.

In a typical XPS equipment, energy of the incident photon is known, ϕ value is fixed at ~ 4 eV, and KE can be measured by detector; thereby, BE can be easily obtained from the equation 3.7. The BE values tells us the oxidation states of elements of interest or the characteristic of a chemical bond between two atoms. XPS is suitable for the surface analysis because only surface photoelectrons ($< \sim 2$ nm in depth) can escape from samples.²⁴⁻²⁵

Due to its high sensitivity (0.05 atomic %), XPS was used extensively in this thesis to analyze the oxidation states, and electronic states of each element in synthesized materials. In addition, the atomic compositions were also obtained by computing the area of fitted XPS peaks.

In chapter 4-5, X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Axis-ULTRA XPS while ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) was employed in chapter 6. All binding energies were charge corrected to the adventitious C 1s peak at 284.5 eV for the former XPS and 284.8 eV for the latter one. Both equipment operate under pressure of 1.2×10^{-9} mbar using monochromatic Al K α X-ray beam (1486.6 eV) at 100 W at an incident angle of 45°. The X-ray spot size is 400 μ m. The voltage step size was 1 eV for survey spectra and 0.1 eV for high-resolution scans. The dwell time at every step was 50 ms and pass energy was 50 eV. The chemical states of each element were appointed based on the NIST XPS Standard Reference Database 20. The atomic composition was computed based on the area of fitted peaks.

3.3.6 Raman spectroscopy

Raman spectroscopy-a type of vibrational spectroscopy, is a fast and non-destructive spectroscopic technique that investigate the interaction of a monochromatic laser with molecular vibrations and rotation in a molecule to illustrate the molecular structure of a sample.²⁶⁻²⁷

For Raman bands to be appeared, the molecular vibration in the sample have to go through a change in polarization. That is to say, only molecular vibrations that can give rise to a polarization change are Raman-active. By analyzing the intensities, Raman shifts, and shape of the vibrational bands in Raman spectra, information on the molecular structure can be obtained. As each compound has its own unique vibrational energy levels, the Raman spectrum is a “fingerprint” for this particular compound.

Since nickel sulfides has lots of analogous phases (NiS, Ni₃S₂, and pyrite NiS₂), each with a different atomic ratio and arrangement. Not to mention, their XRD patterns have many overlapping diffraction peaks, which makes it very difficult to distinguish diffraction peaks of one phase from those of the others, especially when the minor phases normally have only some low-intensity peaks in the diffractogram. Therefore, Raman spectroscopy, which is able to explore the chemical bonding between atoms in a compound, was employed to confirm the purity of the synthesized NiS₂.

In this dissertation, Raman spectra were recorded on a Raman spectrometer (Renishaw InVia Qontor confocal spectrometer with upright microscope) in the range of 100-2000 cm⁻¹ at laser excitation wavelength of 532 nm with the 1800 lines mm⁻¹ grating at room temperature to study the phase and phase purity of the LDH-derived NiS₂ and Cu-doped NiS₂ powders. All the Raman spectra were calibrated by the Raman band of silicon wafer at 520 cm⁻¹ as the standard.

3.3.7 Contact angle measurements

Contact angle (CA) measurement is the most common technique to evaluate the wettability between a solid surface and a liquid of interest. When a drop of pure liquid is dropped on a solid surface, there is an adhesive force at solid-liquid interface. This

surface adhesion controls “how much the liquid is spread” and is expressed by the Young’s equation:²⁸

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \quad (3.8)$$

wherein γ_{SV} , γ_{SL} , γ_{LV} , and θ represent solid surface free energy liquid surface free energy, solid-liquid interfacial free energy, and contact angle. The smaller the contact angle θ , the better the wettability behavior of solid surface and the liquid of interest.

As the electrocatalytic reactions proceeds, the wetting states of the electrodes, which directly influence mass transfer, play a crucial role. And contact angle measurements offer an inexpensive and rapid platform to measure that wetting property. In this dissertation, the water contact angle was measured using an OCA15 (Data-physics, Germany) and 1.0 M KOH solution as the liquid of interest. The droplet volume was set to be 400 μl for consistency.

3.3.8 Brunauer-Emmett-Teller

The surface area of a material can be obtained by Brunauer-Emmett-Teller (BET) theory of physical adsorption with four main assumptions:²⁹

- all molecules of adsorbate have the same opportunity to adsorb on a homogeneous solid surface
- adsorption/desorption of adsorbate molecules is not influenced by other adsorbates.
- adsorbates and the solid surface do not interact with each other apart from van der Waals forces.
- multi-layer adsorption of adsorbates are possible, which means that adsorbate can sit on other adsorbed molecules.

The BET isothermal equation can be written as:³⁰⁻³²

$$\frac{p}{p_0 - p} = \frac{1}{CV_m} \left[1 + (C - 1) \frac{p}{p_0} \right] \quad (3.9)$$

wherein p , p_0 , V , V_m , and C represent adsorption equilibrium pressure, saturated vapor pressure of adsorbates at a specific temperature, volume of adsorbates at the equilibrium pressure of p , gas volume to form monolayer adsorption on the solid surface, and a constant.

A linear relationship can be acquired when the equation 3.9 is plotted as $p/[V(p_0-p)]$ vs. p/p_0 . In that plot, by determining an intercept of $1/(CV_m)$ and a slope of $(C-1)/(CV_m)$, V_m can be obtained as:

$$V_m = \frac{1}{\text{intercept} + \text{slope}} \quad (3.10)$$

Thereby, the specific surface area can be obtained by:

$$S_g = \frac{V_m}{V'} N_A A_m \quad (3.11)$$

wherein V' is considered to be $22.4 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ (at standard temperature and pressure), N_A is the Avogadro's number (6.022×10^{23}), and A_m is the cross-section area of a single adsorbate molecule.

In this dissertation, the surface area of the samples were elucidated using a Brunauer-Emmett-Teller (BET) method in the linear range of $P/P_0 = 0.1-0.3$ via N_2 (77.4 K) adsorption-desorption isotherms collected on ASAP Tri-star II 3020 model.

3.3.9 Inductively Coupled Plasma - Optical Emission Spectrometry

Inductively Coupled Plasma -Optical Emission Spectrometry (ICP-OES) is an analyzing technique in which precise elemental composition in samples can be obtained. In ICP-OES, samples are led into Ar plasma which is at 6,000-10,000 K. At that condition, the aerosol sample experiences desolvation, vaporization, atomization, and ionization. After that, due to extra thermal energy taken up, the electrons climb to excited states. When they come back to ground energy state, photons are emitted. The wavelength of emitted photon acts the “fingerprint” of the element that presents in the sample. Thus, by measuring the light intensity of the wavelength, concentration of element of interest in the samples can be obtained by virtue of calibration plot (intensity vs. concentration).³³

With the advantages of low detection limit, multiple element at one time, and most importantly, limited spectral interference, ICP-OES was employed to quantitatively confirm the presence of doped elements in NiFe-based LDHs, Ni_2P , and NiS_2 .

In this dissertation, the elemental composition in the synthesized samples were determined using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyzer (Elementar Vario Micro Cube) in combination with inductively coupled plasma-optical

emission spectrometer (ICP-OES, Dual view Optima 5300 DV).

3.3.10 Temperature-dependent resistivity measurements.

Resistivity of conductors or semiconductors vary with temperature as the equation:

$$\rho_t = \rho_0 [1 + \alpha (T - T_0)] \quad (3.11)$$

in which ρ_0 and ρ_t are the resistivity at a standard temperature and at t^0 C, respectively; T_0 is the reference temperature and α is the temperature coefficient of resistivity.

For conductor, temperature increment would result in the increase in the vibration amplitude of ions in lattice structure. Those vibrations lead to frequent collisions between free electrons in conductors and other electrons, draining out energy of the former and making them unable to move eventually. It means that the resistivity of conductor would increase with the increase of temperature (positive temperature coefficient, $\alpha > 0$).

Meanwhile, in semiconductor, as the temperature rises, the forbidden gap between conduction band and valence band becomes smaller; hence, the electrons are able to move from the former to the latter. This would consequently reduce the resistivity of the materials. That is why semiconductors are known to have negative temperature coefficient ($\alpha < 0$).

In this dissertation, in order to prove the semiconductor-to-conductor transition of NiS_2 after Cu doping, the temperature-dependent resistivity was measured by using the continuous mode in a Quantum Design Physical Property Measurement System (PPMS) with thermal transport option.

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Chapter 4

Electronic Modulation of Nickel Disulfide towards Efficient Water Electrolysis

In this chapter, we report the electronic modulation of the semiconducting NiS₂ by cation doping for advanced water electrolysis. Both theoretical calculations and temperature-dependent resistivity measurements indicate the semiconductor-to-conductor transition of NiS₂ after Cu incorporation. Further calculations also suggest the advantages of Cu dopant to cathodic water electrolysis by bringing Gibbs free energy of H adsorption at both Ni sites and S sites much closer to zero. Noteworthy, water dissociation on Cu-doped NiS₂ (Cu-NiS₂) surface is even more favorable than those on NiS₂ and Pt (111). Thus, the prepared Cu-NiS₂ show noticeably improved performance towards alkaline HER and OER and eventually, water electrolysis. This work opens up a new avenue to engineer low-cost and earth-abundant catalysts performing on par with noble metal-based one for water splitting.

*This section published/submitted substantially as *Small* (2020). DOI: 10.1002/sml.201905885.

4.1 Introduction

As the world population is increasing, so does the global energy demand. The conventional use of fossil fuels is not sustainable because of the environmental pollution produced, as well as the decreasing amount in nature. New, environmentally friendly and sustainable sources of power are being looked at in order to meet the demand. Among all the developing technologies, solar-light coupled electrochemical water splitting is widely perceived as one of the best solutions due to the generation of hydrogen - a sustainable and clean source of energy.¹⁻² It is known that noble group compounds, namely Pt and RuO₂/IrO₂, are the state-of-the-art electrocatalysts toward two critical half-reactions of water splitting - hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).³⁻⁴ However, the high-price and natural shortage impede their further application. Therefore, developing low-cost, efficient electrocatalyst is urgently desired.

Motivated by the challenge, a wide range of materials have been investigated and developed.⁵⁻⁹ Among them, nickel-based materials have attracted a great deal of attention mainly because their eight valence electrons in 3d orbitals enable the easy alteration of electronic structure through phase engineering (laser-induced, mechanical strain, weak Ar plasma treatment, e-beam irradiation, and plasmonic hot electron-induced), heterostructuring (NiS₂-MoS₂, Ni₃S₂-MoS₂, V-Ni₂P).^{7, 10-12} A representative compound in this nickel-based family, pyrite-type nickel sulfides (NiS₂) is emerging as a highly abundant electroactive and durable catalyst for water electrolysis due to its unique electronic and catalytic activity. Sulfur atoms in nickel-based sulfides with high electronegativity act as sites for proton attachment/detachment, benefiting HER.¹³ Whereas, the *in-situ* surface oxidation of NiS₂ results in an OER-active hydroxides/oxyhydroxides.¹⁴

Despite continuous progress made on phase engineering and morphology control of NiS₂, there are still several obstacles holding NiS₂ back from being further developed for practical water splitting. Firstly, the semiconducting nature of NiS₂ leads to slow electrode kinetics, poor electrical transport, and inefficient electrical contact with the electrolyte. By contrast, metallic-like materials with fascinating electronic structures can facilitate reaction kinetics, reduce the loss of electron transport during electrocatalysis, increase the density of active sites, and give rise to intrinsic activities.¹⁵ As known,

structural engineering would lead to changes in electronic structure; and, consequently, changes in conductivity properties.¹⁵ Therefore, conversion of semiconducting NiS₂ into metallic one by structural engineering to achieve enhancement in water electrolysis is of great interest. Secondly, there has been raising concern of too high electronegativity of S, causing too strong interaction between S and H (highly negative ΔG_{H^*}); and consequently, poor HER efficiency.^{13, 16} In this regard, structural engineering by doped metal with positively Gibbs free energy for proton adsorption (positive ΔG_{H^*}) to facilitate adsorption/desorption processes might be an answer. Among all the candidates with weak hydrogen binding energy, Cu has stood out to be one of the best due to its low cost and high natural abundance.¹⁷ Additionally, it has been demonstrated that Cu as dopant can give rise to number catalytic active sites in the case of CoS.¹⁸ As for OER, despite not being widely investigated, Cu(II) has the potential as a mediator to speed up the reaction noticeably.¹⁹⁻²⁰

In this work, with the goal of low-cost and easy-fabricated materials performing on par with noble metal-based catalysts for water splitting, we realize the semiconductor-to-conductor transition *via* electronic modulation of NiS₂ simply by Cu doping. As Ni and Cu are next to each other in periodic table, they have similar atomic size, chemical nature; combining with the same cubic structure of NiS₂ and CuS₂, the formation of homogeneous Cu-doped NiS₂ (Cu-NiS₂) is favorable. Thanks to the conversion to metallic nature verified by both first principle calculation and temperature-dependent resistivity measurements, the modulated Cu-NiS₂ illustrates remarkable improvement in electrocatalytic activity toward HER and OER. Specifically, it needs overpotentials of only 240 mV and 139 mV to drive OER and HER current densities of $\pm 10 \text{ mA cm}^{-2}$. Besides, nearly 100% Faradaic efficiency and outstanding performance durability are obtained. Detailed DFT calculation also demonstrates the significance of Cu dopant to HER performance by significantly lowering the Gibbs free energy for H adsorption of not only Ni site but also S sites. When employed as both cathode and anode for overall water splitting, the Cu-NiS₂ catalyst requires a voltage of only 1.64 V to drive a current density of 10 mA cm^{-2} , outperforming that of the benchmark Ir/C-Pt/C couple (1.71 V).

4.2 Experimental Section

4.2.1 Materials

Nafion perfluorinated resin solution (5%), 20 wt% Pt/C, copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\geq 99\%$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 98\%$), isopropyl alcohol (IPA, 99%), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT, $\geq 99.0\%$), thioacetamide (TAA, 99%) were purchased from Sigma-Aldrich (Australia). Iridium carbon (Ir/C, 40%) was purchased from FuelCellStore (US). All chemicals and materials were used without further purification.

4.2.2 Preparation of $\text{Cu}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, and NiCu-LDHs

In a typical synthesis, different molar ratio of Ni^{2+} to Cu^{2+} solution (1:0, 8:1, 8:2, 8:3, 0:1) were obtained by mixing $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ in 35 mL DI water while keeping the total amount of metal cations at 5 mmol. 10 mmol of HMT was then added and the solution was stirred until a clear solution is formed. Afterward, the above mixture solution was transferred to a 45-mL stainless-steel Teflon-lined autoclave and heated in an electric oven at 120 °C for 10 hours.

After cooling down to room temperature, the precipitate was collected by centrifugation and subsequently rinsed with technical grade ethanol for at least 5 times, followed by drying in a vacuum oven at 60 °C overnight.

4.2.3 Preparation of NiS_2 , CuS_2 , and Cu-doped NiS_2

50 mg of $\text{Cu}(\text{OH})_2$ or $\text{Ni}(\text{OH})_2$ or NiCu-LDHs is then dispersed into 50 mL of ethanol solution containing 80 mg of TAA. The mixture was then transferred to a 100-mL stainless-steel Teflon-lined autoclave and heated in an electric oven at 120 °C for 5 hours. After cooling down to room temperature, the precipitate was collected by centrifugation and subsequently rinsed with technical grade ethanol for at least 5 times, followed by drying in the vacuum oven at 60 °C overnight. Finally, NiS_2 or CuS_2 or Cu-doped NiS_2

was obtained by annealing the dried precipitate at 400 °C under Ar flow for 30 min to remove excessive Sulfur coming from TAA.

4.2.4 Structural characterizations

The crystallinity of the samples was examined using X'Pert PANalytical X-ray diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at an acceleration voltage and an emission current of 45 kV and 40 mA, respectively. The morphology and structure of the materials were characterized by scanning electron microscopy (SEM, ULTRA Plus, Zeiss) and transmission electron microscopy (TEM, JEOL, Model JEM-2100F) operating at 200 keV. The high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on FEI Themis-Z Double-corrected microscope. AFM measurement is only employed for height imaging at non-contact mode on NX10 Park System Corporation.

The X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) under pressure of 1.2×10^{-9} mbar using monochromatic Al K α X-ray beam (1486.6 eV) at 100 W at an incident angle of 45°. The X-ray spot size is 400 μm . The voltage step size was 1 eV for survey spectra and 0.1 eV for high-resolution scans. The dwell time at every step was 50 ms, and pass energy was 50 eV. All binding energies were charge corrected to the adventitious C 1s peak at 284.8 eV. The chemical states of each element were appointed based on the NIST XPS Standard Reference Database 20. The atomic composition was computed based on the area of fitted peaks.

Raman spectra were recorded on a Raman spectrometer (Renishaw InVia Qontor confocal spectrometer with an upright microscope) in the range of 200-600 cm^{-1} at laser excitation wavelength of 532 nm.

4.2.5 Temperature-dependent resistivity measurements

A total amount of 1 gram of NiS₂ or Cu-NiS₂ nanosheets powders were loaded into graphite dies of 12.7 mm in diameter and pressed using Spark Plasma Sintering System (SPS, Dr. Sinter 1050, Sumitomo Coal Mining, Osaka, Japan). NiS₂ was sintered at 500 °C for 10 minutes and pressure of 5.6 MPa. On the other hand, the Cu-NiS₂ powder was consolidated at 400 °C for 10 minutes and pressure of 6.7 MPa. Both processes were carried out under 0.1 Torr vacuum. The bulk disk samples were cut and polished to bars with length $\approx$ 6.5 mm, width $\approx$ 3.3 mm, and thickness $\approx$ 2 mm in the case of NiS₂ and length $\approx$ 7.3 mm, width $\approx$ 4.7 mm, and thickness $\approx$ 2 mm for Cu-NiS₂. Both bars were cut by using a razor blade and were subsequently polished using sandpapers.

The temperature dependence of the electrical conductivity (σ) was measured by using the continuous mode in a Quantum Design PPMS with thermal transport option.

4.2.6 Electrochemical Measurements

Electrode preparation: 5 mg of the catalyst powder was dispersed in 1 mL of solution containing 960 μ L of IPA and 40 μ L of 5 wt% Nafion by sonication for 30 minutes. Then, 10 μ L of the prepared suspension was pipetted onto a pre-polished Glassy carbon disk electrode (5 mm in diameter), followed by drying at room temperature for 1 hour.

Electrochemical measurements were performed in a conventional three-electrode system connected to a rotating disk electrode (RDE, PINE Research Instrumentation) at a rotation speed of 1600 rpm and an electrochemical workstation (CHI 760D CH Instrument) with the catalysts deposited on rotating disk glassy carbon electrode (RDE, 5mm in diameter) as working electrodes; graphite rod and Hg/HgO serve as the counter electrode and the reference electrode, respectively.

Before OER/HER tests, the electrolyte (1.0 M KOH) was purged by O₂ or H₂ flow, respectively, till saturation.

Before the electrochemical measurement, Hg/HgO electrode was calibrated in a three-electrode system in which Pt wires served as both the working electrode and counter electrode, and Hg/HgO served as the reference electrode. H₂-saturated 1.0 M KOH was employed as the electrolyte. Linear sweep voltammetry (LSV) was then conducted in the range of -0.8 to -1.0 V at a scan rate of 0.5 mV s⁻¹ (H₂ was still purged during

measurement). The potential at which the current crosses zero was taken as thermodynamic potential (*vs.* Hg/HgO) for the hydrogen electrode. Thereby, all the potentials reported in this manuscript were calibrated to a reversible hydrogen electrode (RHE) by using the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.918$; and overpotential $\eta = E_{\text{RHE}} - 1.23\text{V}$.

The half-cell reaction stability was evaluated by chronopotentiometry tests at a constant current density of $\pm 30\text{ mA cm}^{-2}$ for OER and HER, respectively.

The electrochemical impedance spectroscopy (EIS) measurements were performed at a frequency range of 100 Hz to 1 MHz at an amplitude of 10 mV. All results were corrected for all ohmic (IR) losses throughout the system based on the solution resistance obtained from the EIS.

The Faradaic efficiency was done in an H₂- or O₂-purged close H-shape cell. The headspace of the chamber containing the working electrode is 20.0 mL. A constant current of -10 mA (or 10 mA in case of OER) was applied for 60 minutes. The H₂ (or O₂) gas generated was determined by taking 500 μL of the gas sample in the chamber containing working electrode to gas chromatography. The Faradaic efficiency was then calculated as the ratio of the measured amount of H₂ (or O₂) and the theoretical amount of H₂ (or O₂) (based on Faraday's law).

The electrochemical surface area (ESCA) was estimated from the double-layer capacitance (C_{dl}) of the films. The C_{dl} was determined by simple cyclic voltammetry (CV) method. The CV was conducted in a potential window (0.1-0.2 V *vs.* Hg/HgO) at which no faradaic processes occur at various scan rates of 20, 40, 60, 80, 100, and 120 mV s^{-1} . Then capacitive current ($j_{\text{anodic}} - j_{\text{cathodic}}$) at 0.15 V *vs.* Hg/HgO was plotted against various scan rates, while the slope obtained was divided by two to acquire the C_{dl} . The specific capacitance can be converted into an electrochemical active surface area (ECSA) using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. The specific capacitance for a flat surface is normally found to be 20-60 $\mu\text{F cm}^{-2}$. In our calculations of electrochemical active surface area we took the average value of 40 $\mu\text{F cm}^{-2}$.

Calculated electrochemical active surface area:

$$A_{ECSA} = \frac{C_{dl} \mu F cm^{-2}}{40 \mu F cm^{-2} per cm_{ECSA}^2}$$

The water splitting performance was evaluated on a home-made electrochemical cell, in which catalyst-loaded carbon papers were used as both cathode and anode. The reference catalysts are Pt/C at the cathode and Ir/C at the anode. The mass loadings of the catalysts was 1 mg cm⁻².

4.2.7 Simulation Methodology

The DFT calculations were done on Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA). The standard generalized-gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) exchange model was employed. Every possible configuration was considered, and the structure with the lowest energy was selected for later electronic structure calculation. Ionic relaxations were carried out till force components are lower than 0.02 eV Å⁻¹. As for DOS of bulk structures, the Brillouin zone is represented by the set of 15 × 15 × 15 k-grid. The 2×2 supercells were cleaved into surface structures for ΔG_{H*} calculation. For the supercell of NiS₂, a vacuum layer with a thickness of 30 Å along the z-direction was used to avoid periodic image interactions.

The electrocatalytic activity of NiS₂ and Cu-NiS₂ was evaluated by calculating the Gibbs free energy (ΔG_{H*}) of hydrogen adsorption. ΔG_{H*} was calculated by the following equation:

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \quad (6.1)$$

where ΔE_{ZPE} is the difference of zero-point energy between the adsorption state and gas phase. ΔS_H is the difference of entropy between the adsorption state of the hydrogen and gas phase. At the standard temperature of 300 K and standard atmospheric pressure of 1 bar, the value of – TΔS_H is calculated to be 0.20 eV. To sum up, the value of ΔE_{ZPE} – TΔS_H is equal to 0.24 eV. ΔE_H was calculated by:

$$\Delta E_H = E_{*H} - E^* - \frac{1}{2} E_{H_2} - E_{BSSE} \quad (6.2)$$

where E_{*H} and E* are the total energies adatom adsorbed silicene with and without

hydrogen adsorption, respectively. E_{H_2} is the total energy of the hydrogen molecule in the gas phase. E_{BSSE} is basis set superposition error (BSSE) caused by the artificial shortening of distances and enhancing of the interactions, which corrected by applying the counterpoise corrections using 'ghost' atoms. E_{BSSE} was calculated by:

$$E_{BSSE} = (E_{ghost-H} + E_{ghost-sub}) - (E_{noghost-H} + E_{noghost-sub}) \quad (6.3)$$

where $E_{ghost-H}$ and $E_{ghost-sub}$ are the energies of H and Cu-NiS₂ monolayer with replacement by ghost atoms; while $E_{noghost-H}$ and $E_{noghost-sub}$ are the energies of the system with only H and M atoms.

4.3 Results and Discussions

Figure 6.1a-b shows the schematic structure of NiS₂ and Cu-NiS₂, both indicating the same cubic crystal structure. The calculated electronic density of states (DOS) in Figure 1c shows the semiconducting nature of NiS₂ with a bandgap of ~2.4 eV, which is in good agreement with previously reported values.²¹⁻²³ After replacing a Ni atom by a Cu atom, the DOS of Cu-NiS₂ demonstrates the metallic-like behavior, which is beneficial for electron transfer during electrocatalysis (Figure 6.1c). This transition is attributed to the contribution from d orbitals of Cu atoms. Moreover, partial DOS (PDOS) of Cu-NiS₂ in Figure 6.1d reveals a strong hybridization among Cu 3d, Cu 4s, Ni 3d, and S 3p, suggesting even better conductivity. Experimentally, the temperature-dependent electrical conductivities of NiS₂ and Cu-NiS₂ were conducted on physical properties measurement system (PPMS). The samples were pressed into pellets by spark plasma sintering (SPS). Figure 6.1e shows about 4-fold lower in resistivity of Cu-NiS₂ compared to that of NiS₂ at 300 K. Importantly, temperature increasing results in the decrease in resistivity in the case of NiS₂, highlighting its semiconductor characteristic. By contrast, Cu-NiS₂ experiences resistivity increment with the increase of temperature; hence, further confirming the metallic nature of the material. These results are in good consistency with the DOS calculations earlier.

Figure 4.1 (a,b) Crystal structures of NiS₂ and Cu-NiS₂. (c) The density of states (DOS) curves of NiS₂ and Cu-NiS₂. (d) Partial density of states (PDOS) curves of Cu-NiS₂. (e) Electrical conductivity versus temperature curves of NiS₂ and Cu-NiS₂. (f) Gibbs free energy diagram for hydrogen adsorption (ΔG_{H^*}) at Ni sites and S sites on the (100) surface of NiS₂ and Cu-NiS₂. (g) Adsorption energy for H₂O.

We performed further DFT calculations to investigate the influence of Cu incorporation on HER activity. It is known that Gibbs free energy for hydrogen adsorption (ΔG_{H^*}) is the most common descriptor to predict HER activities of given catalysts. Figure 6.1f illustrates the three-state diagram of HER process showing the ΔG_{H^*} on NiS₂ (100) surface to be -1.89 eV and -1.33 eV at S site and Ni site, respectively, which suggest that the hydrogen-containing intermediates adsorb onto NiS₂ surfaces too strongly. On the other hand, Cu doping does not only lower the ΔG_{H^*} of Ni sites but also that of S sites on the surfaces significantly. Specifically, it offers close-to-ideal ΔG_{H^*} at 0.06 eV for Ni site and -0.07 eV for S site. Furthermore, it is worth noting that hydrogen evolution in basic media involves an additional step of water dissociation at the beginning.²⁴ Therefore, the adsorption energy of water molecules on (111) surface of Pt and (100) surface of NiS₂, Cu-NiS₂ were calculated. As indicated in Figure 6.1g, on Cu-NiS₂ surfaces, the adsorption energies are highly negative (-7.77 eV), which demonstrates a stronger water dissociation ability than those on NiS₂ and Pt (-7.03 eV and -5.26 eV, respectively). All

of these calculations suggest that Cu-NiS₂ is superior compared to NiS₂ and is a promising catalyst for cathodic water electrolysis.

Motivated by these theoretical predictions, NiS₂ and Cu-NiS₂ were synthesized. Ni(OH)₂ and NiCu-layered double hydroxides (LDHs) were hydrothermally prepared, followed by a solvothermal sulfurization with thioacetamide as a sulfur source.

Figure 4.2 (a) XRD patterns of NiS₂ and Cu-NiS₂. (b-e) XPS spectra of Cu-NiS₂ in (b) Ni 2p region, (c) Cu 2p region, (d) Cu LMM region, and (e) S 2p region. (f) Raman spectra of NiS₂ and Cu-NiS₂.

X-ray diffraction (XRD) was first employed to investigate the crystal structure. As shown in Figure 6.2a, the diffractogram of Cu-NiS₂ is consistent with that of NiS₂, implying that both of them are isomorphs. All diffraction peaks can be well indexed to cubic pyrite NiS₂ (space group: Pa-3, JCPDS Card No. 065-3325). However, a closer look at those diffraction peaks suggests the slight shift to smaller angles of Cu-NiS₂ as compared to NiS₂ (Figure 6.2a, inset). This kind of peak shift infers the increase in lattice parameters after Cu was doped into NiS₂ lattice. To specify, Rietveld refinement was implemented to study the change in lattice parameter (*a*); and, consequently, unit cell volume (*V*) with respect to the amount of metal dopant. Firstly, it should be noted that the refined reliability factors (*R_w*) for NiS₂, 12.5% Cu-NiS₂, 25.0% Cu-NiS₂, and 37.5% Cu-NiS₂ are 6.21%, 4.19%, 5.35%, 6.24%, respectively (Figure 6.3a-d). Such small values validate that the incorporation of Cu²⁺ has no significant impact on the crystal structure of NiS₂. Figure 6.3e-f shows that *a* and *V* are increased gradually with the increment of Cu content, confirming that bigger Cu atoms have successfully randomly substituted Ni atoms in the crystal structure.

Figure 4.3 XRD patterns and the Rietveld refinements of (a) NiS₂; (b) 12.5% Cu-NiS₂; (c) 25% Cu-NiS₂; and (d) 37.5% Cu-NiS₂. (e-f) The plots of (e) lattice parameter and (f) unit cell volume of NiS₂ versus Cu (at%) doping content.

X-ray photoelectron spectroscopy (XPS) was then employed to investigate the composition and valence state of the Cu-NiS₂. Quantitative XPS analyses show the Cu content is at 24.03 at%, which is close to that of the amount of Cu²⁺ using in the precursor (Table 6.1). Due to spin-orbit coupling, the fine-scan Ni 2p in Figure 6.2b spectrum displays 2p_{3/2} and 2p_{1/2} doublets along with 2 shake-up satellites, in which Ni-S bond is clearly observed at 853.4 eV and 870.6 eV.²⁵ The other deconvoluted peaks at 854.7 eV

and 872.5 eV belong to NiO_x due to superficial oxidation of sulfide material while storing in air. In Cu 2p XPS spectrum, two peaks located at 932.6 and 952.3 eV of Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, are ascribed to Cu-S bonds (Figure 6.2c).²⁶ Moreover, there are weak shake-up satellite peaks at 945.0 eV and 963.2 eV, suggesting the presence of the paramagnetic chemical state of Cu²⁺. The Cu²⁺ in Cu-S bonds can be further certified by the Auger Cu (LMM) spectrum in Figure 6.2d. The Cu(LMM) spectrum is centered at 568.8 eV, which is 0.4 eV lower than that of Cu₂S.²⁶⁻²⁷ Importantly, the Ni 2p XPS spectrum of Cu-NiS₂ shows unnoticeable shift compared to that of NiS₂, further confirming the even distribution of Ni, Cu atoms in the crystal structure and revealing the marginal electron transfer between Ni and Cu due to similar oxidation state. The Cu-NiS₂ formation was also supported by S 2p XPS spectrum wherein 2p_{1/2} and S 2p_{3/2} peaks are located at 163.9 and 162.6 eV, respectively, corresponding to (S₂)²⁻ in metal-sulfide bonds (Figure 6.2e).^{6, 28} The presence of the SO₄²⁻ components at 168 eV manifests inevitable surface oxidation sulfide materials.⁵

Table 4.1 Composition analysis of the synthesized Cu-doped NiS₂ by XPS

Samples	Element	Percentage by atoms (%)
12.5% Cu-NiS ₂	Cu	12.20%
	Ni	87.80
25.0% Cu-NiS ₂	Cu	24.03%
	Ni	75.97%
37.5% Cu-NiS ₂	Cu	36.16%
	Ni	63.84%

Raman spectroscopy further confirms the formation of single-phase Cu-NiS₂. Figure 6.2f indicated that the pristine NiS₂ shows two distinct peaks at 479.4 cm⁻¹ and 275.6 cm⁻¹ attributed to out-of-plane A_g vibrational mode and in-plane E_g vibrational mode of the cubic structure, respectively.²⁹⁻³⁰ As for Cu-NiS₂, those A_g and E_g peaks are still observed but slightly shifted to smaller wavenumbers of 472.7 cm⁻¹ and 269.2 cm⁻¹, revealing its atomic vibration as a unified whole; this agrees well with the XRD result. All these

results validate the successful incorporation of Cu²⁺ into the NiS₂ while keeping its crystal structure.

The morphology of Cu-NiS₂ was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). At first glance, Figure 6.4a-b show that Cu-NiS₂ inherits the nanosheets morphology of NiCu-LDHs. This is achieved by the well-controlled solvothermal sulfurization. However, higher magnification SEM images and low-magnification TEM images show that while NiCu-LDHs possesses a smooth surface, Cu-NiS₂ is composed of many nanoparticles with the lateral size of few μm (Figure 6.4c-d). Atomic force microscopy (AFM) measurement shown in Figure 6.4d (inset) indicates the thickness of few tens of nm of the nanosheets. High-resolution TEM (HRTEM) image in Figure 6.4e shows lattice fringes with an inter-planar distance of 2.84 Å corresponding to the (200) lattice planes, further confirming the NiS₂ cubic crystal structure shown by XRD measurement. The selected area electron diffraction (SAED) pattern in the inset of Figure 6.4e indicates the polycrystalline nature of the synthesized Cu-NiS₂. The high-angle annular dark-field (HAADF) image and the corresponding scanning transmission electron microscopy energy dispersive X-ray (STEM-EDS) mapping of Cu-NiS₂ show the even distribution of Cu, Ni, and S throughout the nanosheets (Figure 6.4f). Furthermore, it is worth noting that the quantitative EDS analysis also in good agreement with the above-analyzed XPS results.

Figure 4.4 (a-c) SEM images of (a) NiCu-LDHs and (b-c) Cu-NiS₂. (d) Low magnification TEM (inset: AFM image and height profile) and (e) HRTEM images of Cu-NiS₂ (inset: SAED pattern). (f) HAADF image of Cu-NiS₂ and the corresponding STEM-EDS elemental mappings of Ni, Cu, and S.

To study the electrocatalytic activities of the prepared catalyst, the HER performances in 1 M KOH electrolyte was first evaluated in the standard three-electrode system, in which graphite rod and Hg/HgO serve as counter electrode and a reference electrode, respectively.

Figure 4.5 Electrochemical performance for hydrogen evolution reaction. (a) HER polarization curves of CuS₂, NiS₂, 12.5% Cu-NiS₂, 25% Cu-NiS₂, 37.5% Cu-NiS₂, and 20% Pt/C in 1.0 M KOH solution at scan rate of 5.0 mV s⁻¹ and (b) their corresponding Tafel slopes. (c) Chronopotentiometry measurement of 25% Cu-NiS₂ at the current density of -30 mA cm⁻² in H₂-saturated 1 M KOH solution. (d) Specific activities of different catalysts at 0.2 V HER overpotential after ECSA normalization.

Linear sweep voltammograms in Figure 6.5a shows that, apart from Pt/C benchmark, 25% Cu-NiS₂ demonstrates the lowest HER onset overpotential (defined at overpotential at which $j = 1$ mA cm⁻²) of 68 mV, surpass those of CuS₂ (146 mV), NiS₂ (150 mV), 12.5% Cu-NiS₂ (106 mV), and 37.5% Cu-NiS₂ (121 mV). Overpotential at 10 mA cm⁻² (η_{10}) is another essential activity descriptor since the solar cell coupled water-splitting devices usually work at that current density under standard condition (1 Sun, AM 1.5).¹ In this manner, the optimal 25% Cu-NiS₂ with η_{10} of 139 mV is only beaten by Pt/C, while being better than CuS₂ (302 mV), NiS₂ (285 mV), 12.5% Cu-NiS₂ (199 mV), and 37.5% Cu-NiS₂ (218 mV) by a considerable margin. Remarkably, the Tafel slope of 25% Cu-NiS₂ is close to that of Pt/C, *i.e.* 77 mV dec⁻¹ compared to 60 mV dec⁻¹ (Figure 6.5b),

demonstrating both catalysts follow Volmer-Heyrovsky mechanism wherein the Volmer reaction is the rate-determining step.⁶ To assess the performance durability of the catalyst, chronopotentiometry measurement was conducted (Figure 6.5c), which shows almost no loss in current for 60 hours.

Figure 4.6 (a) XRD spectrum, (b) SEM image and (c-f) XPS spectra of 25% Cu-NiS₂ after 60 hours of HER testing in (c) Ni 2p region; (d) Cu 2p region; (e) Cu LMM region; and (f) S 2p region.

Figure 4.7 Faradaic efficiency of (a) H₂ generation and (b) O₂ generation over 25% Cu-NiS₂ catalyst.

Moreover, post-mortem XRD and SEM in Figure 6.6a-b show no noticeable changes in morphology and phases. Differences are seen by XPS spectra in Figure 6.6c-f wherein Ni-S, and Cu-S peaks are decreased intensity due to unavoidable surface oxidation by ambient air. Also, SO₄²⁻ peak in S 2p XPS spectrum is significantly higher after HER testing; however, metal-sulfur bonds are still detected. These results suggest the remarkable HER durability as well as stability of the Cu-NiS₂ nanosheets in alkaline medium. In addition, ~98% current-to-hydrogen capability is achieved when subjected to Faradaic efficiency test (Figure 6.7a).

Figure 4.8 Cyclic voltammograms (CV) of (a) NiS₂; (b) 12.5% Cu-NiS₂; (c) 25% Cu-NiS₂; (d) 37.5% Cu-NiS₂; and (e) CuS₂ taken at a potential window of 0.1-0.2 V (vs. Hg/HgO) at various scan rates of 20, 40, 60, 80, 100, and 120 mV s⁻¹ in 0.1 M KOH solution. (f) The capacitive current ($j_{\text{anodic}} - j_{\text{cathodic}}$) at 0.15 V (vs. Hg/HgO) as a function of various scan rates of those samples. (g-h) EIS spectrum measured at (g) 250 mV HER

overpotential and (h) 300 mV OER overpotential of NiS₂; 12.5% Cu-NiS₂; 25% Cu-NiS₂; 37.5% Cu-NiS₂; and CuS₂.

To better understand the excellent electrocatalytic activity of the Cu-NiS₂ nanosheets, we estimate the electrochemical surface active area (ECSA) of the catalyst *via* electrochemical double-layer capacitance (C_{dl}). The potential range of 0.1–0.2 V (*vs.* Hg/HgO), in which there is no current contribution from Faradaic reaction, was chosen (Figure 6.8a-e). Figure 6.8f shows the linear fit of the current density difference versus scan rates, which indicates ECSA of NiS₂, 12.5% Cu-NiS₂, 25% Cu-NiS₂, 37.5% Cu-NiS₂, and CuS₂ to be 0.22 mF cm⁻², 0.30 mF cm⁻², 0.53 mF cm⁻², 0.47 mF cm⁻², and 0.44 mF cm⁻², respectively. Though 25% Cu-NiS₂ only exhibits slightly higher ECSA compared to other electrocatalysts, Figure 6.5d shows that after ECSA normalization, its current density at 0.2 V HER overpotential is several-fold higher than those of others control catalysts, indicating the highest intrinsic catalytic activity. Electrochemical impedance spectroscopy (EIS) measurements in Figure 6.8e in Supporting Information reveal that the 25% Cu-NiS₂ electrode possesses a modest charge transfer resistance (R_{ct}) of 29 Ω ; thus, promoting faster electrocatalytic processes. This much smaller R_{ct} of Cu-NiS₂ compared to that of NiS₂ (up to ~4.5 times smaller) is expected due to the change in electronic structure from semiconducting to metallic explained above.

In regards to OER, it is well-known that under highly oxidizing OER condition, sulfide-based materials undergo *in-situ* surface oxidation to form a sulfide-oxyhydroxide core-shell structure.^{5, 14} Therefore, before catalytic activity measurements, the prepared catalyst electrodes were activated by a chronoamperometry at 1.6 V till reaching a stable state in order to form the OER-active oxyhydroxide on the surface of the conductive Cu-NiS₂, namely Cu-NiS₂ derived catalyst (Cu-NiS₂-DC).

Figure 4.9 (a-d) XPS spectra of Cu-NiS₂ before and after OER activation in (a) Ni 2p region; (b) Cu 2p region; (c) Cu LMM region and (d) S 2p region. (e) XRD spectra and (f) SEM image of Cu-NiS₂ after OER activation.

XPS analyses of Cu-NiS₂-DC in Figure 6.9a-c shows no signal for Ni-S (853.4 eV) or Cu-S (932.6 eV) bonding; instead, NiO_x and CuO_x peaks are clearly seen. Also, S 2p XPS spectrum only indicates sulfate signal (Figure 6.9d). Meanwhile, Figure 6.9e in Supporting Information shows the XRD pattern of Cu-NiS₂-DC, which indicates a significant phase of NiS₂ along with the presence of NiOOH peaks. SEM image of Cu-NiS₂-DC in Figure 6.9f illustrates no changes after activation process. These results

indicate that after the activation process, the surface of Cu-NiS₂ nanosheets was partially oxidized to OER-active oxyhydroxides and reached the steady-state, resulting in the desired protective and active-shell @ conductive core structure.

As shown in Figure 6.10a, the 25% Cu-NiS₂-DC shows far better activity with low overpotential at 10 mA cm⁻² (η_{10}) of 232 mV compared to 321 mV, 270 mV, 302 mV, 425 mV, and 264 mV of NiS₂-DC, 12.5% Cu-NiS₂-DC, 37.5% Cu-NiS₂-DC, CuS₂-DC, and the benchmark Ir/C, respectively. The excellent OER property is further highlighted in by the modest Tafel slope of 46 mV dec⁻¹ (Figure 6.10b), indicating fast reaction kinetics and the rate-determining step to be the dissociation of OH⁻ (*OH → *O + H⁺ + e⁻).⁷ Whereas, the Tafel slopes for NiS₂-DC, 12.5% Cu-NiS₂-DC, 37.5% Cu-NiS₂-DC, CuS₂-DC, and the benchmark Ir/C are much higher at 77 mV dec⁻¹, 119 mV dec⁻¹, 88 mV dec⁻¹, 184 mV dec⁻¹, and 91 mV dec⁻¹, respectively. It is also worth to point out that after ECSA normalization, the 25% Cu-NiS₂-DC still displays the best intrinsic catalytic activity, surpass NiS₂-DC and CuS₂-DC by a great margin, as shown in Figure 10d.

Figure 4.10 Electrochemical performance for oxygen evolution reaction. (a) OER polarization curves of CuS₂-DC, NiS₂-DC, 12.5% Cu-NiS₂-DC, 25% Cu-NiS₂-DC, 37.5%

Cu-NiS₂-DC, and 20% Pt/C in 1.0 M KOH solution at a scan rate of 5.0 mV s⁻¹ and (b) their corresponding Tafel slopes. (c) Chronopotentiometry measurement of 25% Cu-NiS₂-DC at the current density of 30 mA cm⁻² in O₂-saturated 1 M KOH solution. (d). Specific activities of different catalysts at 0.3 V OER overpotential after ECSA normalization.

Also, approximately 96% Faradaic efficiency was also secured by 25% Cu-NiS₂-DC electrode when subjected to a constant current of 10 mA for 1 hour (Figure 6.7b). Moreover, the change in electronic structure also benefits OER by lowering R_{ct} from 146 Ω of NiS₂-DC to only 30 Ω of 25% Cu-NiS₂-DC (Figure 6.8h). Equally importance to high electrocatalytic activity, performance durability was also probed by chronopotentiometry test. In this respect, Figure 6.10c shows that inconsiderable current loss is obtained for 60 hours of anodic polarization at 30 mA cm⁻². Furthermore, no noteworthy changes can be seen by post-mortem XPS, XRD, and SEM which suggest the excellent stability in terms of chemical states, phases, and morphology of the Cu-NiS₂-DC even after 60 hours of continuous oxygen evolution (Figure 6.11).

Figure 4.11 (a-d) XPS spectra in (a) Ni 2p region, (b) Cu 2p region, (c) Cu LMM region, (d) S 2p region; (e) XRD spectrum, and (f) SEM image of 25% Cu-NiS₂ after 60 hours of OER testing.

Inspired by the outstanding electrocatalytic activity of the Cu-NiS₂ nanosheets and its derived catalyst towards HER and OER, and alkaline electrolyzer was constructed to investigate its feasibility towards practical overall water splitting. 25% Cu-NiS₂ nanosheets were loaded on carbon paper substrate and employed as both anode and cathode. State-of-the-art Ir/C-Pt/C couple was also tested for comparison. Figure 6.12a shows that the Cu-NiS₂ based electrolytic cell is able to reach 10 mA cm⁻² at a modest

voltage of 1.64 V, which is even smaller than that of Ir/C-Pt/C couple (1.71 V). Theoretically, the overpotential at 10 mA cm⁻² for water electrolysis should be equal to the sum of $\eta_{10\text{-HER}}$ and $\eta_{10\text{-OER}}$ (*i.e.* $\eta_{10} = \eta_{10\text{-HER}} + \eta_{10\text{-OER}}$).³¹ Here, the marginally smaller to ($\eta_{10\text{-HER}} + \eta_{10\text{-OER}}$) of η_{10} is expected because of the difference between 2-electrode and 3-electrode testing system. Moreover, in chronopotentiometry test in Figure 6.12b, the Cu-NiS₂ || Cu-NiS₂ cell shows an insignificant increase in voltage at various current densities for 30 hours. Such efficient and durable water electrolysis is of great importance to bring us closer to a sustainable hydrogen economy.

Figure 4.12 Electrochemical performance for overall water splitting (a) Polarization curves of the water electrolysis using Cu-NiS₂ as bifunctional electrocatalyst compared to Ir/C || Pt/C in a two-electrode system at the scan rate of 2.0 mV s⁻¹ (b) Durability performance for water splitting at 10, 30, 50 mA cm⁻².

4.4 Conclusion

In summary, we realize the semiconductor-to-conductor transition *via* electronic modulation of NiS₂ by cation doping, which has been validated by both DFT calculations and temperature-dependent resistivity measurements. Cu-NiS₂ demonstrates superior performance as HER and OER electrocatalysts compared to NiS₂. Merely 240 mV OER overpotential is required to drive 10 mA cm⁻², which is ~80 mV lower than that of NiS₂. As for HER, the improvement is even more noticeable with ~146 mV reduction in overpotential after Cu doping. Further calculations also confirm the advantages of Cu incorporation, which does not only significantly reduce $|\Delta G_{H^*}|$ of Ni site from 1.33 eV to 0.07 eV but also activate the inert S sites. Besides, Cu-NiS₂ surface offers even better water dissociation than that of Pt (111), making the former perform well in alkaline

conditions. As a proof-of-concept, an electrolyzer composed of Cu-NiS₂ as both cathode and anode needs only 1.64 V at 10 mA cm⁻², outperforming that of the benchmark Ir/C-Pt/C couple (1.71 V).

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Chapter 5

O₂ plasma and cation tuned nickel phosphide nanosheets for highly efficient overall water splitting

In this chapter, we present a novel combined-strategy of cation tuning and surface engineering for the fabrication of highly active, earth-abundant, and robust two-dimensional Ni₂P electrocatalyst. Our theoretical calculations suggest the effectiveness of vanadium doping and oxygen plasma, which do not only enhance the density-of-state at Fermi level, but also make the Ni sites more susceptible to OH⁻ adsorption. The oxygen plasma treatment can increase the wettability of the catalyst toward KOH solution, improving the contact angle from 44.95° to 16.8°, and also induce a higher BET surface area; hence, more active sites and lower charge transfer resistance are obtained.

*This section published/submitted substantially as *Nano Energy* **54**, 82-90 (2018). DOI: 10.1016/j.nanoen.2018.10.004.

5.1 Introduction

Hydrogen with high energy density and world abundance has attracted much attention as an ideal and environment-friendly alternative to fossil fuels.¹ Among the advanced energy technologies, electrochemical water splitting plays a crucial role as a promising and sustainable method to produce clean hydrogen from aqueous solutions. To achieve high electricity-to-hydrogen conversion efficiency, an electrocatalyst with a low overpotential and fast kinetic is highly desirable. Currently, noble group compounds such as Pt and RuO₂/IrO₂ are known as benchmark electrocatalysts for cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), respectively.¹⁻² However, the high cost and low natural abundance significantly hamper their industrial-scale applications. Thus, studies on next-generation bifunctional electrocatalysts with high catalytic activity, long-term stability, and high natural abundance toward the practical implementation of water splitting are extremely important.

A broad range of catalytic materials has been developed for OER and HER, such as transition metal phosphides,³⁻⁵ sulfides/selenides,⁶⁻⁹ oxides/hydroxides,¹⁰⁻¹⁴ and carbides.¹⁵⁻¹⁷ Among them, metal phosphides, especially nickel phosphides, has attracted a lot of attention as HER electrocatalysts in alkaline condition due to the existence of both proton-acceptor and hydride-acceptor centers.⁵ Also, whereas nickel shows highly negative Gibbs free energy for hydrogen-containing intermediates adsorption (ΔG_{H^*}), resulting in the blockage of active sites; the lone electron pair of P in Ni₂P plays a role of proton acceptor in facilitating hydrogen intermediates desorption.¹⁸ However, the ΔG_{H^*} of Ni₂P is slightly positive making hydrogen intermediates difficult to bind to the catalyst simultaneously.¹⁸ Regarding OER, despite lots of efforts, the onset potential to drive OER process is still relatively high for Ni₂P electrocatalysts.¹⁹ One of the reason is that the d-states of Ni₂P are relatively far to the Fermi level leading to greatly positive adsorption free energy for OH⁻. Also, its low density of state (DOS) suggests that there would be less charge carrier for the reaction. In addition, the low DOS intensity at Fermi level of Ni₂P results in poor charge-transfer kinetic.²⁰ To rationally tune the phosphides catalytic properties, two possible approaches can be considered: (1) integrating one or more metal species and (2) surface engineering.^{4, 14, 20-22} The former strategy could be an

effective way to balance the adsorption/desorption of oxygen- and hydrogen-containing intermediates. Especially, vanadium, which is relatively cheap, earth-abundant, and versatile in electronic structure, is a promising candidate for several reasons. Firstly, multi-valence nature of vanadium makes it very flexible to adjust electronic structure to tune the electrocatalytic performances. Also, the five-valence configuration of V ensures high 3d electron orbits and tunable electro-accepting/donating properties, which may promote the OER electrocatalysis in alkaline condition ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$).²³⁻²⁴ In addition, V as the dopant can enhance DOS intensity; thus, fasten the charge-transfer kinetics, which is crucial for both HER and OER.²⁵⁻²⁷ Last but not least, V substitution may possibly introduce defects and crystalline dislocation; therefore, increasing the number of active sites and carrier concentration. Surface engineering by plasma treatment is another possible way to reduce the reaction overpotential of phosphides toward HER and OER. Recently, by Ar plasma, Co^{3+} in Co_3O_4 is partially reduced to Co^{2+} alongside with oxygen vacancies formation, which enhances the catalytic activity toward OER.²¹ After that, with the same approach of creating oxygen vacancies, Na_2HPO_2 was subjected to Ar plasma process to fill in the vacancies with phosphorus; thereby, obtaining higher activity toward HER.¹⁴ Motivated by these analyses, it is expected that with only O_2 plasma treatment, we can modify the surface to increase the number of active sites; and at the same time, the wettability toward aqueous solution may be adjusted, which is not achievable through Ar plasma treatment. Moreover, surface oxidation of phosphide material due to oxygen plasma will create the phosphate-phosphide interface region, which was theoretically indicated to facilitate the simultaneous adsorption of both hydrogen and oxygen-containing intermediates; thus, expediting overall water electrolysis.²⁸

In this report, we present the O_2 plasma-treated V-doped Ni_2P nanosheets (O-V- Ni_2P) as a bifunctional electrocatalyst for overall water splitting. The Ni_2P and V-doped Ni_2P (V- Ni_2P) nanosheets were successfully prepared *via* phosphidation of $\text{Ni}(\text{OH})_2$ and NiV-layered double hydroxides (NiV-LDHs), respectively; after that, the O-V- Ni_2P was obtained by oxygen plasma treatment of V- Ni_2P . The nanosheets show lateral sizes of a few hundred nm with thicknesses of ~ 6 nm. To optimize the catalytic activity, cation doping percentage was tuned by controlling the amount of vanadium source; then, the as-

synthesized V-Ni₂P was subjected to the O₂ plasma treatment for different durations. The O-V-Ni₂P shows much-improved BET surface area (168.2 m² g⁻¹) and wettability in aqueous solution (contact angle of 16.8°) as compared to 136.2 m² g⁻¹ and 44.95°, respectively, of Ni₂P nanosheets. As a result, higher electroactive surface area and lower charge transfer resistance were obtained. Our density functional theory (DFT) calculations further confirm the strength of vanadium doping and oxygen incorporation with the noticeable enhancement in charge transfer kinetics. In addition, the charge density contour plot reveals the Ni-V co-electron deficiency centers causing the Ni sites to be more active to OH⁻ adsorption. When used as electrocatalysts for OER and HER, the optimized 3 minutes plasma treated 10% V-doped Ni₂P (O3-V10-Ni₂P) exhibits superior performance with overpotentials of 257 mV and 108 mV at ±10 mA cm⁻² alongside with modest Tafel slopes of 43.5 mV dec⁻¹ and 72.3 mV dec⁻¹, respectively. In addition, the catalyst also exhibits superior durability and decent stability when operating at 30 mA cm⁻² for up to 20 hours. Due to the remarkable bifunctional catalytic activity, O3-V10-Ni₂P was employed to water electrolyzer; and it required a voltage of only 1.56 V to drive a current density of 10 mA cm⁻², which is much lower than that of IrO₂ || Pt/C system (1.69 V). Our study demonstrates a new combined-approach of cation tuning and surface engineering to develop highly efficient electrocatalyst for overall water splitting.

5.2 Experimental Section

5.2.1 Materials

Nafion perfluorinated resin solution (5%), nickel chloride (NiCl₂), vanadium (III) chloride (VCl₃, 99.9%), urea (NH₂CONH₂, 99.98%), ammonium fluoride (NH₄F, 99.98%), commercial Pt on Vulcan XC-72 (Pt/C, 20 wt%, Premetek), potassium hydroxide (KOH, 99.99%), iridium oxide (IrO₂, 99.9%), isopropyl alcohol (IPA, 99%), and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich (Singapore). Sodium hypophosphite (NaH₂PO₂, 99%) were purchased from Aladdin (Shanghai, China). All chemicals and materials were used without further purification.

5.2.2 Preparation of Ni(OH)₂ and NiV-LDHs nanosheets

In a typical experiment, different mole ratios of Ni/V solution (1:0, 95:5, 90:10, 85:15 for the synthesis of Ni(OH)₂ and 5%, 10 %, 15% NiV-LDHs, respectively) were obtained by mixing NiCl₂ and VCl₃ in 20 mL H₂O, while the total amount of metal cations (Ni²⁺ and V³⁺) were kept at 1.2 mmol. Afterward, urea (500 mg) and NH₄F (120 mg) were added, and the solution was stirred until a clear solution is formed. Then, the above mixture solution was then transferred to a 45-mL stainless-steel Teflon-lined autoclave and heated in an electric oven at 120 °C for 16 hours. After cooling to room temperature, the as-synthesized hydroxides were collected by centrifugation and subsequently rinsed with distilled water, ethanol, and dried in vacuum oven at 60 °C overnight.

5.2.3 Preparation of Ni₂P and V-doped Ni₂P (V-Ni₂P)

The as-prepared Ni(OH)₂ or LDHs were further annealed with NaH₂PO₂ at 350 °C for 1 hour at a heating rate of 5 °C min⁻¹ under 100 sccm Ar gas flow.

5.2.4 Preparation of O₂ plasma treated Ni₂P nanosheets (O-V-Ni₂P)

10 mg of the synthesized V-Ni₂P nanosheets was then dispersed on glass slide and treated by O₂ plasma. The power of oxygen plasma and the flow rate of O₂ are fixed at 80 W and 80 sccm, respectively, with different durations (0 min, 1 min, 2 min, 3 min, 4 min). The 3 minutes plasma treated 10% V-Ni₂P nanosheets (O3-V10-Ni₂P) was used for detailed studies.

5.2.5 Structural characterizations

X-ray diffraction was performed to characterize the samples on the Shimadzu XRD-6000 X-ray diffractometer with Cu-K α irradiation ($\lambda = 1.5406 \text{ \AA}$) at an acceleration voltage and an emission current of 45 kV and 30 mA, respectively. XRD patterns were collected at a scanning rate of 0.06° s⁻¹, with a step size of 0.01°.

The morphology and structure of the materials were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL, Model JEM-2100F) operating at 200 keV. The high resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on JEOL-2100F at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Theta Probe electron spectrometer (VG ESCALAB200i-XL, Thermo Scientific) under pressure of 1.2×10^{-9} mbar using monochromatic Al K α X-ray beam (1486.6 eV). The X-ray spot size is 400 μ m. The voltage step size was 1 eV for survey spectra and 0.1 eV for high-resolution scans. The dwell time at every step was 50 ms and pass energy was 50 eV. The binding energies were charge corrected to the adventitious C 1s peak at 284.5 eV. The chemical states of each element were appointed based on the NIST XPS Standard Reference Database 20.

The elemental compositions were determined using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyzer (Elementar Vario Micro Cube) combined with inductively coupled plasma-optical emission spectrometer (ICP-OES, Dual view Optima 5300 DV). The contact angle measurement was recorded using DataPhysics Instrument (OCA 30) using 1.0 M KOH solution as the liquid of interest. Prior to measurement, the catalyst powder was pressed into pellet. The droplet volume was set to be 400 μ l for consistency. The surface area the samples were derived from N₂ (77.4 K) adsorption–desorption isotherms collected on ASAP Tri-star II 3020 model. The surface area was elucidated using a Brunauer-Emmett-Teller (BET) method in the linear range of $P/P_0 = 0.1-0.3$.

5.2.6 Electrochemical measurements

Electrode preparation: 5 mg of the catalyst powder was dispersed in 1 mL of solution containing 960 μ L of IPA and 40 μ L of 5 wt% Nafion by sonication for 30 minutes. Then, 10 μ L of the prepared suspension was pipetted onto a pre-polished Glassy carbon disk electrode (5 mm in diameter), followed by drying at room temperature for 1 hour.

Electrochemical measurements were performed in a three-electrode system connected to a rotating disk electrode (RDE, PINE Research Instrumentation) at a rotation speed of 1600 rpm and an Autolab PGSTAT302 (Eco Chemie, Netherlands) potentiostat with the catalysts deposited on GC as working electrodes; Graphite rod and Hg/HgO serve as the counter electrode and the reference electrode, respectively. All measurements were carried out in 1.0 M KOH electrolyte.

First, Hg/HgO electrode calibration was carried out in a three-electrode system in which Pt wires served as both working electrode and counter electrode, and Hg/HgO served as the reference electrode. H₂-saturated 1.0 M KOH was employed as electrolyte. Linear sweep voltammetry (LSV) was then conducted in the range of -0.8 to -1.0 V at a scan rate of 0.5 mV s⁻¹ (H₂ was still purged during measurement). The potential at which the current crosses zero was taken as thermodynamic potential (*vs.* Hg/HgO) for the hydrogen electrode (Figure 5.1).

Figure 5.1 Hg/HgO reference electrode calibration curve.

Thereby, all the potentials reported in our manuscript were calibrated to a reversible hydrogen electrode (RHE) by using the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.917$; and overpotential $\eta_{\text{OER}} = E_{\text{RHE}} - 1.23\text{V}$; $\eta_{\text{HER}} = 0 - E_{\text{RHE}}$

Before HER/OER measurements, the electrolyte (1.0 M KOH) was purged by H₂ or O₂ flow till saturation. Linear sweep voltammetry (LSV) was then performed at scan rate of

2 mV s⁻¹. By plotting overpotential η vs. logarithm of current density from polarization curves, Tafel slopes are obtained. To evaluate the durability and stability of LDHs during HER and OER testing, galvanostatic measurements at fixed current densities of -30 mA cm⁻² or 30 mA cm⁻², respectively, were conducted.

The Faradaic efficiencies of the electrode were done in an Ar-purged close H-shape cell (counter electrode was put in different chamber). The headspace of the chamber containing working electrode is 20.0 mL. A constant current of -10 mA (or 10 mA in case of OER) was applied for 60 minutes. The H₂ (or O₂) gas generated was determined by taking 500 ul of the gas sample in the chamber containing working electrode to gas chromatography. The Faradaic efficiency was then calculated as the ratio of measured amount of H₂ (or O₂) and theoretical amount of H₂ (or O₂) (based on Faraday's law).

The electrochemical surface area (ESCA) was estimated from the double-layer capacitance (C_{dl}) of the films. The C_{dl} was determined by simple cyclic voltammetry (CV) method. The CV was conducted in a potential window (0.3-0.4 V vs. Hg/HgO) at which no faradaic processes occur at various scan rates of 10, 20, 30, 40, 50, and 60 mV s⁻¹. Then capacitive current ($j_{anodic} - j_{cathodic}$) at 0.35 V vs. Hg/HgO was plotted against various scan rates, while the slope obtained was divided by two to acquire the C_{dl} . The specific capacitance can be converted into an electrochemical active surface area (ECSA) using the specific capacitance value for a flat standard with 1 cm² of real surface area. The specific capacitance for a flat surface is normally found to be 20-60 μF cm⁻². In our calculations of electrochemical active surface area we took the average value of 40 μF cm⁻².

Calculated electrochemical active surface area:

$$A_{ECSA} = \frac{C_{dl} \mu F \text{ cm}^{-2}}{40 \mu F \text{ cm}^{-2} \text{ per cm}_{ECSA}^2}$$

Overall water splitting tests were performed in a homemade two-electrode system with the O3-V10-Ni₂P loaded on Ni foam (NF) as both the cathode and anode. The mass loading was 1.63 mg cm⁻². For the benchmark noble metal-based catalysts, IrO₂/NF || Pt/C/NF was adopted with the same mass loading. The long-term durability was also evaluated by constant current electrolysis. The LSV curves were performed in 1.0 M

KOH at a scan rate of 1 mV s⁻¹ in the potential range of 1.0–2.0 V. The long-term durability was evaluated by constant currents electrolysis.

The electrochemical impedance spectroscopy (EIS) measurements were performed at potentials of 0.61 V and –1.07 V (vs. Hg/HgO) for OER and HER, respectively, with frequency range from 0.1 Hz to 100 kHz at an amplitude of 10 mV. All results were corrected for all ohmic (iR) losses throughout the system based on the solution resistance obtained from the EIS.

5.2.7 Simulation Methodology

The structure optimization and electronic structure were investigated using first principles plane-wave simulations based on DFT as implemented in the Vienna ab initio simulation package (VASP).²⁹ Electron-ion interaction and electron exchange-correlation were described using the projector augmented wave (PAW) method,³⁰ and the generalized gradient approximation was described using the Perdew-Burke-Ernzerhof (PBE) function, respectively. An energy cutoff of 520 eV was used for the plane wave basis sets. Spin-polarization was considered for all the simulations. The Brillouin zone was integrated using the Monkhorst-Pack scheme with 11×11×9 k-grid for unit cell and 2×2×1 k-grid for surface.³¹ The Ni₂P (001) surface with and without V doping were built. There are 128 atoms (84 Ni and 44 P) and the vacuum was set at 30 Å for the surface model. For O-V-Ni₂P sample, the O doped V-doped Ni₂P (001) surface was built. Every possible configuration was considered, and the structure with the lowest energy was selected for later electronic structure calculation. All the atomic positions and cell parameters were relaxed until the force on each atom is less than 0.02 eV Å⁻¹.

5.3 Results and Discussions

We prepared the two-dimensional (2D) structures of V-doped Ni₂P (V-Ni₂P) by annealing in PH₃ atmosphere NiV-LDHs nanosheets, which was synthesized by a simple hydrothermal process. By changing the Ni/V ratio in the precursors, V-Ni₂P with different doping content from 0-15% (Ni₂P, V5-Ni₂P, V10-Ni₂P, V15-Ni₂P) was also synthesized, which was measured by inductively coupled plasma-optical emission

spectrometry (ICP-OES; Table 5.1). Finally, to obtain O₂ plasma treated V-doped Ni₂P, the selected V10-Ni₂P was subjected to O₂ plasma treatment for 1–4 minutes (O1-V10-Ni₂P, O2-V10-Ni₂P, O3-V10-Ni₂P, and O4-V10-Ni₂P). Due to the similarity in phase, structures, and morphologies, V10-Ni₂P and O3-V10-Ni₂P are chosen as representative samples for V-Ni₂P and O-V-Ni₂P for detail characterizations, respectively.

Table 5.1 Composition analysis of the synthesized V-doped Ni₂P by ICP-OES

Samples	Element	Percentage by atoms (%)
Ni ₂ P	Ni	100
	V	0
V5-Ni ₂ P	Ni	94.19
	V	5.81
V10-Ni ₂ P	Ni	82.77
	V	11.23
V15-Ni ₂ P	Ni	83.47
	V	16.53

Without vanadium doping, X-ray diffraction (XRD) pattern (Figure 3.2a) confirms the formation of pure hexagonal Ni₂P (space group: P321 (150), JCPDS card No. 065–3544, $a=5.862$, $c=3.372$ Å). The diffractogram of the as-synthesized V10-Ni₂P shows the similar pattern to Ni₂P; however, the peaks slightly shift to higher angles (Figure 3.2a, inset), indicating the decrease in lattice parameters. Through finely tuned O₂ plasma treatment (*i.e.* <4 min at power of 80 W), the XRD pattern of the sample is similar, there is no detectable new peak (Figure 3.2a), which indicates the main crystalline phase of V10-Ni₂P remains unchanged.

Figure 5.2 (a) XRD spectra of O3-V10-Ni₂P, V10-Ni₂P, and Ni₂P. (b-d) XPS spectra of V10-Ni₂P and O3-V10-Ni₂P in (b) Ni 2p region, (c) V 2p region, and (d) P 2p region.

To investigate the surface chemical states and compositions of V10-Ni₂P before and after O₂ plasma treatment, X-ray photoelectron spectroscopy (XPS) measurements were conducted. The fine-scanned Ni 2p XPS spectra in both samples present two main peaks of Ni 2p_{3/2} and 2p_{1/2} at 856.8 eV and 874.5 eV, alongside with shakeup satellites (“Sat.”) at 863.1 eV and 881.5 eV, respectively (Figure 5.2b), revealing the existence of NiO_x due to unavoidable surface oxidation in ambient air. Importantly, the small peak at ~853 eV is attributed to the Ni-P bond.^{4, 20} Figure 5.2c represents the V 2p core-level XPS spectra of the two samples. Owing to the p orbital j-j coupling (peak area ratio is 1:2), there are two main structures related to V 2p_{3/2} (516.6 eV) and V 2p_{1/2} (524.0 eV).¹² By Gaussian curve fitting, the V 2p_{3/2} region can be deconvoluted into three distinguished contributors at ~515.4 eV, ~516.4 eV, and ~517.6 eV ascribing to V³⁺, V⁴⁺, and V⁵⁺, respectively. This result suggests the partial oxidation of V³⁺ into higher oxidation states during the LDHs synthesis.^{12, 24} Considering oxidative OER process (giving up 4

electrons), the high oxidation number of V is very advantageous due to its higher electron accepting property and more 3d electron orbits.²³

Whereas Ni and V chemical states show almost no change after plasma treatment, differences are observed in P 2p XPS spectra (Figure 5.2d). Both samples present two main characteristics: the doublet at 129.5 (P 2p_{1/2}) and 130.2 eV (P 2p_{3/2}) is attributed to the metal-phosphorus bond; while the other peak at 133.9 eV features the P-O bonds in the form of phosphate.^{20, 23} After plasma treatment, the intensity of phosphide peak dramatically decreases while the phosphate peak intensity increases sharply, which indicates the partial surface oxidation of Ni-P and V-P. It is noteworthy that the P 2p_{1/2} peak locates at slightly lower binding energy as compared to that of elemental P (130.0 eV), implying the strong interaction between above-described partially positive charged metals and partially negative charged P^{δ-}.²⁰ Moreover, the P^{δ-} may act as a Brønsted base to trap protons, facilitating HER electrocatalysis.

Figure 5.3 SEM image of NiV-LDHs

The scanning electron microscopy (SEM) image indicates the nanosheets morphology of NiV-LDHs with the lateral size of a few hundred nanometers (Figure 5.3). As expected, the mild phosphidation at 350 °C did not noticeably change the morphology (Figure 5.4a). Differences are only observed after O₂ plasma treatment. Whereas the pristine V10-Ni₂P shows a continuous surface, the O3-V10-Ni₂P sheets are partially broken and

discontinuous, which could effectively boost the surface area, and consequently, number of exposed active sites (Figure 5.4a-b).

Figure 5.4 The structural characterizations for (a, c, e, g) V10-Ni₂P and (b, d, f, h) O3-V10-Ni₂P nanosheets, respectively. (a-b) FESEM images, (c-d) TEM images (inset: vertically aligned nanosheet showing a thickness of ~6 nm), (e-f) HRTEM images (inset: SAED patterns), (g-h) STEM-EDS elemental mappings of Ni, V, and P.

Transmission electron microscopy (TEM) was then used to further characterize the materials. Similar to the SEM observation, the as-synthesized V10-Ni₂P in Figure 5.2c displays solid and continuous nanosheets; whereas, rough and damaged nanosheets are observed in the case of O3-V10-Ni₂P (Figure 5.2d). In addition, high magnification TEM investigation (Figure 5.5a) reveals numerous of nanopores in the plasma treated nanosheet. This porous structure may offer a higher surface area for electrochemical reaction.

Figure 5.5 TEM images of O3-V10-Ni₂P showing (a) nanopores structures and (b) amorphous phosphate layer

Figure 5.4d, inset, displays the TEM images of vertically-aligned V10-Ni₂P and O3-V10-Ni₂P nanosheets with the thicknesses of ~6 nm. High-resolution TEM (HRTEM) images of V10-Ni₂P and O3-V10-Ni₂P show the same lattice fringe spacing of 0.210 nm corresponding to the (111) plane of the hexagonal Ni₂P (JCPDS No. 065-3544) (Figure 5.4e-f). The selected area electron diffraction (SAED) patterns indicate the polycrystalline nature of the O3-V10-Ni₂P as well as V10-Ni₂P (Figure 5.4e-f, inset). Interestingly, through oxygen plasma treatment, we induce the formation of a thin amorphous phosphate layer (Figure 5.5b), which can protect the phosphide core from being continuously etched during the electrocatalysis, and more importantly, may promote the proton transfer and assist the adsorption of hydrogen and oxygen-containing species. This was discussed in previous reports on transition metal phosphide materials.²⁸ The High-Angle Annular Dark Field (HAADF) images and Scanning Transmission Electron Microscopes-Energy Dispersive X-ray spectroscopy (STEM-EDS) elemental mapping images shows that nickel, vanadium, and phosphorus are homogeneously distributed throughout the nanosheet (Figure 5.4g-h).

Figure 5.6 N₂ adsorption-desorption isotherms of Ni₂P and O3-V10-Ni₂P

The Brunauer–Emmett–Teller (BET) surface areas of the as-synthesized Ni₂P and O3-V10-Ni₂P were obtained from N₂ adsorption-desorption isotherms (Figure 5.6), which shows a higher value for O3-V10-Ni₂P (168.2 m² g⁻¹) as compared to that of Ni₂P (136.2 m² g⁻¹). In addition, it is worth noting that unlike Ar plasma treatment, the O₂ plasma can also tune the wettability behavior. The contact angle measurements were conducted to verify the improved wettability of O3-V10-Ni₂P compared to Ni₂P toward aqueous solution. As can be seen in Figure 5.7a-b, the contact angles for Ni₂P and O3-V10-Ni₂P are 44.95° and 18.1°, respectively, indicating a significant enhancement in hydrophilicity. This improved wettability can enhance the catalyst-electrolyte interaction, resulting in higher exposed active sites to the electrolyte and better charge transfer.

Figure 5.7 Contact angle measurements of (a) Ni₂P and (b) O3-V10-Ni₂P

To gain insight into OER electrocatalytic activity, a typical three-electrode cell was employed in which Graphite rod and calibrated Hg/HgO served as the counter electrode and reference electrode, respectively. All measurements were conducted at room temperature in 1.0 M KOH solution at a slow scan rate of 2 mV s⁻¹ to minimize the capacitive current. We first optimized the vanadium doping percentage toward OER performance. Figure 5.8a illustrates the polarization curves after iR correction of Ni₂P, V5-Ni₂P, V10-Ni₂P, and V15-Ni₂P. The Ni₂P exhibits a mediocre overpotential at 10 mA cm⁻² (η_{10}) of 333 mV. This value could be reduced to 326 mV by 5% V doping and to as low as 308 mV by 10% doping (Figure 5.8a). Further increasing V content to 15% would slightly increase η_{10} . In addition, the V10-Ni₂P also demonstrates a respectable Tafel slope of 75.1 mV dec⁻¹, much lower than that of Ni₂P (131 mV dec⁻¹) (Figure 5.8b).

Figure 5.8 (a, c) OER and HER polarization curves of V-Ni₂P, respectively, with varied doping percentages and their corresponding (b, d) Tafel slopes

Due to the best performance toward OER of V10-Ni₂P among all prepared V-doped Ni₂P samples, we then optimized the catalytic activity with varied oxygen plasma treatment

duration. As can be seen in Figure 5.9a, the O3-V10-Ni₂P can deliver an extremely low η_{10} of 257 mV, which is much lower than those of O1-V10-Ni₂P (288 mV), O2-V10-Ni₂P (277 mV), O4-V10-Ni₂P (298 mV), Ni₂P (333 mV), and V10-Ni₂P (308 mV). The superior activity of O3-V10-Ni₂P is further shown in its modest Tafel slope of 43.5 mV dec⁻¹; while the values for V10-Ni₂P, O1-V10-Ni₂P, O2-V10-Ni₂P, O4-V10-Ni₂P are 75.1 mV dec⁻¹, 76.9 mV dec⁻¹, 71.5 mV dec⁻¹, and 81.1 mV dec⁻¹, respectively (Figure 5.9b). This small Tafel slope of O3-V10-Ni₂P also indicates favorable OER kinetics and the rate-determining characteristic of the second step ($*\text{OH} \rightarrow *O + \text{H}^+ + e^-$).³² This excellent activity of O3-V10-Ni₂P is far better than commercially available IrO₂ (Figure 5.10), which makes it very promising as an electrocatalyst for sluggish anodic water splitting. In addition, the catalyst also shows almost 100% current to oxygen capability when subjected to Faradaic efficiency test (Figure 5.11a).

Figure 5.9 (a, c) OER and HER polarization curves O-V-Ni₂P, respectively, with varied plasma treatment duration and their corresponding (b, d) Tafel slopes. All samples are doped with 10% V.

Figure 5.10 (a) OER polarization curves of O3-V10-Ni₂P, and IrO₂ in 1.0 M KOH solution at scan rate of 2 mV s⁻¹ and their corresponding (b) Tafel slopes.

Figure 5.11 Faradaic efficiency of (a) O₂ generation and (b) H₂ generation over O3-V10-Ni₂P catalyst at a current of 10 mA for 60 minutes.

The catalytic durability of the catalyst was also tested by chronopotentiometry measurement at a fixed current density of 30 mA cm⁻². It can be seen from Figure 5.12a that a nearly constant potential was obtained for 20 hours of anodic polarization, revealing good durability of the catalyst.

Figure 5.12 Chronopotentiometry measurement of O3-V10-Ni₂P at the current density of (a) 30 mA cm⁻² and (b) -30 mA cm⁻² in 1.0 M KOH solution.

It has been widely reported that the active sites of phosphide materials for oxygen evolution reaction is indeed the metal oxides (or hydroxides/oxyhydroxides) that formed during testing.^{4, 33} Therefore, to evaluate the changes in structure and surface in terms of morphology, phase, composition and valence states of the O3-V10-Ni₂P after OER, *ex-situ* SEM, XPS and XRD were employed after OER process at 10 mA cm⁻² for 1 hour and 20 hours. After only one hour, the Ni-P peak (~853 eV) and low valent V (515.4 eV) fades away; whereas, the peaks for Ni-O and high valent V (at 516.4 eV and ~517.6 eV) are dominant (Figure 5.13a-b.). In addition, the P 2p spectrum shows only phosphate signal at 133.9 eV while the O 1s peak increased noticeably in intensity (Figure 5.13c-d). As the reaction continues (*i.e.* >1 hour), no further noticeable changes can be observed in XPS results even up to 20 hours. This indicates that the surface-bound phosphates resulted from oxygen plasma treatment was partially oxidized to oxides (or hydroxides/oxyhydroxides) before reaching the steady state, which may protect the phosphide core from being etched further as normally seen for phosphide materials after OER.³³

Figure 5.13 XPS spectra of O3-V10-Ni₂P after 1 hour and 20 hours of OER testing in (a) Ni 2p region, (b) V 2p region, (c) P 2p region, and (d) O 1s region

Ex-situ XRD further confirms that statement by the presence of oxyhydroxides peak after OER testing while maintaining a major phase of Ni₂P after prolonging OER for even 20 hours (Figure 5.14a). In addition, SEM image of O3-V10-Ni₂P after 20 hours of OER testing reveal no noticeable change in morphology (Figure 5.14b).

Figure 5.14 (a) XRD spectra of O3-V10-Ni₂P after 1 hour and 20 hours of OER testing. (b) SEM image of O3-V10-Ni₂P after 20 hours of OER testing

In light of the outstanding performance toward OER of the O3-V10-Ni₂P, electrochemically active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) measurements have been carried out. We determined the ECSA *via* electrical double layer capacitance (C_{dl}) which is estimated by half of the slope of the linear relationship between capacitive current ($j_{anodic} - j_{cathodic}$) at 0.35 V (*vs.* Hg/HgO reference electrode) and scan rates (Figure 5.15a-c). From the linear fit in Figure 5.15d, the $2C_{dl}$ of O3-V10-Ni₂P is 10.02 mF cm⁻², which is much higher than those of Ni₂P (5.31 mF cm⁻²) and V10-Ni₂P (6.77 mF cm⁻²). This is expected due to the higher BET surface area of the O3-V10-Ni₂P mentioned above and its lower contact angle guarantees more active site exposed to the solution.

Figure 5.15 Cyclic voltammograms (CV) of (a) Ni₂P, (b) V10-Ni₂P, and (c) O3-V10-Ni₂P taken at a potential window of (0.3-0.4 V vs. Hg/HgO) at scan rates of 10, 20, 30, 40, 50, and 60 mV s⁻¹ in 1.0 M KOH solution. (d) The capacitive current ($j_{\text{anodic}} - j_{\text{cathodic}}$) at 0.35 V vs. Hg/HgO as a function of various scan rates for Ni₂P, V10-Ni₂P and O3-V10-Ni₂P. (e-f) EIS spectra measured at (e) 300 mV OER overpotential and (f) 150 mV HER overpotential of O3-V10-Ni₂P, V10-Ni₂P and Ni₂P.

Nonetheless, the improved activity of O3-V10-Ni₂P is not only ascribed to the enhanced active surface area but also higher intrinsic activity. This is proven by OER performances (O3-V10-Ni₂P > V10-Ni₂P > Ni₂P) after ECSA normalization (Figure 5.16).

Figure 5.16 OER polarization curves of O3-V10-Ni₂P, V10-Ni₂P, Ni₂P after electrochemical active area (ECSA) normalization

EIS result conducted at 300 mV overpotential (Figure 5.15e) shows the noticeable lower charge transfer resistance (R_{ct}) after V substitution (from 89.7 Ω to 56.8 Ω). Interestingly, it is further reduced by O₂ plasma treatment to 35.3 Ω . This could be explained by much better wettability behavior of O3-V10-Ni₂P; hence, the better catalyst-electrolyte interaction is obtained, leading to better charge transfer.

The electrocatalytic activity of the synthesized catalysts toward HER in 1.0 M KOH solution was also investigated. Similar to OER, by linear sweep voltammetry technique we firstly probed the ideal doping percentage of the sample toward HER. Interestingly, V10-Ni₂P still performs the best with the smallest η_{10} and Tafel slope of 147 mV and 90.0 mV dec⁻¹, respectively; lower than those of Ni₂P (181 mV, 142 mV dec⁻¹), V5-Ni₂P (166 mV, 101 mV dec⁻¹), and V15-Ni₂P (167 mV, 109 mV dec⁻¹) (Figure 5.8c-d). With the superior catalytic activity of V10-Ni₂P, we used O₂ plasma treatment at an appropriate level to further tune its HER performance. Figure 5.9c present the polarization curves after iR correction of Ni₂P, V10-Ni₂P and O1-V10-Ni₂P, O2-V10-Ni₂P, O3-V10-Ni₂P, and O4-V10-Ni₂P. It is shown that the O3-V10-Ni₂P exhibit the optimal HER performance with η_{10} of 108 mV, smaller than 181 mV, 147 mV, 121 mV, 129 mV, and 135 mV of Ni₂P, V10-Ni₂P, O1-V10-Ni₂P, O2-V10-Ni₂P, and O4-V10-Ni₂P, respectively.

Moreover, the electrode composed of O3-V10-Ni₂P catalyst shows a lowest Tafel slope of 72.3 mV dec⁻¹ (Figure 5.9d) among all catalyst examined.

Figure 5.17 (a) HER polarization curves of O3-V10-Ni₂P, and commercial Pt/C in 1.0 M KOH solution at scan rate of 2.0 mV s⁻¹ and their corresponding (b) Tafel slopes.

This Tafel slope value, which is close to the benchmark Pt/C (58.3 mV dec⁻¹, Figure 5.17), suggests a Volmer-Heyrovsky mechanism of the HER, in which the Volmer reaction is rate-determine.³⁴ In addition, it is worth noting that after ECSA normalization, the O3-V10-Ni₂P still shows the best intrinsic catalytic activity, far much better than Ni₂P (Figure 5.18).

Figure 5.18 HER performance of O3-V10-Ni₂P, V10-Ni₂P, Ni₂P after electrochemical active area (ECSA) normalization

Equally importance to catalytic activity, we also probed the long-term durability and stability of O3-V10-Ni₂P toward HER. The chronopotentiometry test (Figure 5.12b) reveals an inconsiderable voltage difference (well below 1% change). In addition, post-SEM and XRD analyses show no obvious changes in morphology, structure, or phase (Figure 5.19-20). The only minor change can be observed in Ni 2p XPS spectrum (Figure 5.19b), in which Ni-P peak at ~853 eV disappear due to unavoidable superficial oxidation while exposing in ambient air. The results confirm the outstanding durability and stability of O3-V10-Ni₂P toward HER in strong alkaline condition (pH=14).

Figure 5.19 (a) XRD spectrum and (b-d) XPS spectra of O3-V10-Ni₂P after 20 hours of HER testing.

Figure 5.20 SEM image of O3-V10-Ni₂P after 20 hours of HER testing

Almost 100% Faradaic efficiency was also achieved by O3-V10-Ni₂P when testing at a constant current of -10 mA for 1 hour (Figure 5.11b). EIS was also tested at -0.15 V (vs. RHE) and the fitted Nyquist plots are shown in Figure 5.15f. Similar to OER, O3-V10-Ni₂P depicts the lowest R_{ct} of 43.5Ω , followed by V10-Ni₂P (72.8Ω); whereas, the highest belongs to Ni₂P (86.6Ω).

To better understand the mechanism of vanadium incorporation on superior HER, OER performance of the O-V-Ni₂P, perfect crystal structure of Ni₂P, V-Ni₂P, and O-V-Ni₂P were constructed, followed by density functional theory (DFT) calculations to study the changes in electronic configuration (Figure 5.21a-i). As can be seen in Figure 5.21e and h, the d-states of V in V-Ni₂P and O-V-Ni₂P show strong peaks at Fermi level; the peak is even stronger after oxygen incorporation. These observations indicate that vanadium and oxygen lead to enhancement in charge transfer kinetics, which is in a good agreement with the EIS results discussed above (Figure 5.21e-f). Furthermore, the charge density distributions of (001) surface of Ni₂P, V-Ni₂P, and O-V-Ni₂P indicate the non-uniformity of charge distribution in the case of V-Ni₂P and O-V-Ni₂P (Figure 5.21c,f, and i). Also, Ni-V as co-electron deficiency centers may cause Ni site to be more susceptible to OH⁻ adsorption; thus, benefiting the oxygen evolution reaction.

Figure 5.21 DFT calculations for (a-c) Ni₂P (001) surface, (d-f) V-Ni₂P (001) surface, and (g-i) O-V-Ni₂P (001) surface, respectively. (a, d, g) Structure representations; (b, e, h) their corresponding calculated density of states (DOS); and (c, f, i) their corresponding charge density distribution plots of (001) surface.

In light of the remarkable activities toward both HER and OER of the O3-V10-Ni₂P in alkaline solution (pH=14), two-electrode setup, in which O3-V10-Ni₂P coated on Ni foam served as both anode and cathode, was employed to evaluate the catalytic activity toward electrochemical water splitting in 1.0 M KOH solution. Remarkably, η_{10} of the O3-V10-Ni₂P || O3-V10-Ni₂P cell was as low as 333 mV, surpassing the state-of-the-art IrO₂ || Pt/C cell, which needs 457 mV (Figure 5.22a). Theoretically, the overpotential at certain current for overall water splitting should be equal to OER overpotential combined with HER overpotential ($\eta_{10} = \eta_{10\text{-HER}} + \eta_{10\text{-OER}}$). In this case, the slightly lower but close to ($\eta_{10\text{-HER}} + \eta_{10\text{-OER}}$) of η_{10} might be due to the difference in the testing system. Finally, in chronopotentiometry test for 20 hours, the O3-V10-Ni₂P || O3-V10-Ni₂P cell exhibits unnoticeable deterioration at various current densities (Figure 5.22b). These results establish a very promising step toward practical overall water splitting.

Figure 5.22 (a) Polarization curves of the water electrolysis using O3-V10-Ni₂P as bifunctional electrocatalyst compared to IrO₂ || Pt/C in a two-electrode system at the scan rate of 2.0 mV s⁻¹ (b) Durability performance for water splitting at 10 mA cm⁻², 30 mA cm⁻², and 50 mA cm⁻².

5.4 Conclusion

In conclusion, we have demonstrated O-V-Ni₂P nanosheets as a highly active bifunctional electrocatalyst for water splitting in alkaline condition (pH=14). Among various doping percentage and different plasma treatment time, the 3 minutes O₂ plasma treated 10% V-doped Ni₂P nanosheets perform the best. In 1.0 M KOH solution, its $\eta_{10\text{-HER}}$ and $\eta_{10\text{-OER}}$ are 108 mV and 257 mV, respectively. In addition, small Tafel slopes for HER (72.3 mV dec⁻¹) and OER (43.5 mV dec⁻¹) are also obtained. As an integrated bifunctional catalyst for water electrolysis, the O3-V10-Ni₂P || O3-V10-Ni₂P cell requires η_{10} of only 1.563 V, outperforming the state-of-the-art IrO₂ || Pt/C (1.687 V). The catalyst also presents remarkable durability and decent stability for 20 hours of operation. These outstanding properties are firstly attributed to the high-valence vanadium dopant, which is a good electro-acceptor assisting OER process. Vanadium doping also helps to reduce the charge transfer resistance and enhance the electroactive surface area as indicated by EIS and ECSA measurements. Our DFT calculations further confirm these advantages of vanadium and oxygen incorporation *via* density of states and charge density distribution analyses. In addition, due to O₂ plasma treatment, the phosphide surface was partially oxidized generating the phosphate-phosphide region, which balances the adsorption/desorption of the hydrogen and oxygen-containing intermediates.

Besides, after plasma, BET surface area and wettability toward aqueous solution significantly increases; thus, further tune ECSA and R_{ct} . This work explores a new combined-approach to engineer inexpensive monometallic phosphides for highly efficient water electrolysis.

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Chapter 6

Ultrathin porous NiFeV layered double hydroxide for highly efficient overall water splitting

In this chapter, ultrathin porous ternary NiFeV layered double hydroxides (LDHs) nanosheets grown on nickel foam (NF) substrate (NiFeV-LDHs/NF) has been synthesized by one-step hydrothermal process. By virtue of synergistically combination of Fe and V in Ni-based layered hydroxide and the in-situ growth of the hydroxide onto conductive Ni foam substrate, the as-prepared NiFeV-LDHs/NF electrode shows extraordinary catalytic activity towards hydrogen evolution reaction (HER), oxygen evolution reaction (OER); and hence, water splitting with low operating overpotentials, small Tafel slopes, and remarkable stability.

*This section published/submitted substantially as *Small* **14**, 1703257 (2018). DOI: 10.1002/sml.201703257.

6.1 Introduction

Hydrogen is considered as an environmentally friendly fuel, which can be produced by water electrolysis.¹⁻² However, one of the key issue in electrocatalytic water splitting is the kinetic losses while driving oxygen evolution reaction (OER) at the anode and hydrogen evolution reaction (HER) at the cathode.² By now, the state-of-the-art HER and OER electrocatalysts are based on precious metals which are reported to display the lowest overpotentials at practical current densities. For example, RuO₂ exhibit an onset overpotential of about 140 mV to drive OER in alkaline solution while Pt displays nearly zero onset potential for HER under acidic condition.² Nevertheless, because of their high cost and scarcity, the practical applications of these materials in water electrolysis is limited.¹ Also, in order to realize overall water splitting, the coupling of HER and OER electrocatalysts in the same electrolyte is a great challenge since the most of the current approaches show the contradictory integration of HER and OER electrocatalysts; thus, leading to low efficiency. Hence, the discovery of earth-abundant, low-cost, high activity bifunctional electrocatalysts to achieve low energy-intensive water electrolysis is still highly desired.

A wide range of earth abundant catalytic materials with different morphologies, structure or loaded on various substrates have been developed for OER and HER, including transition metal oxides/hydroxides,³⁻⁷ borides, carbides,⁸⁻¹⁰ sulfides/selenides,¹¹⁻¹⁴ and nitrides/phosphides.¹⁵⁻¹⁷ Among them, nickel based layered hydroxides with exceptional HER, OER activity and stability are demonstrated as the promising alternatives to the conventional precious metal-containing water splitting catalysts in basic solutions.^{5, 18-19} A representative compound in that family, NiFe-layered double hydroxides (LDHs), has been reported to be one of the best performing bifunctional electrocatalyst so far,¹⁸ in which the integration of Fe is essential for high catalytic activity.^{6, 20} However, the limited specific surface area and poor electronic conductivity of the Ni based hydroxides hinders its practical application as an electrode material.²⁰ To overcome this issue, elemental doping could be an effective approach to tune the catalytic activity of the electrocatalyst. For instance, NiV-LDHs was reported to show enhanced intrinsic catalytic property toward OER due to better conductivity and richer active sites;

theoretical calculation also indicated that vanadium doping could significantly lower the overpotential for the rate-determining step.⁵ Another work recently highlights that the Aluminum doping is found to be very advantageous since it would help to increase the number of active sites when Al atoms are partially etched under strong alkaline media.¹⁹ Also, to the extent of our knowledge, not many studies have reported HER and overall water electrolysis catalytic activity of layer hydroxide material in alkaline condition. Inspired by these analyses, it is reasonable to expect that triple metal Ni-based LDHs may synergistically combine the advantages of each component and show superior water splitting catalytic activity, which has not been well explored.

In this study, we reported the preparation of NiFeV-LDHs nanosheets grown on nickel foam (NiFeV-LDHs/NF). The nanosheets are porous with the lateral size of few hundreds of nanometers and the thickness of ~10 nm. These porous nanosheets stack together to form a flower-like structure. As a result, sufficient space for electrolyte penetration and diffusion is provided, which helps to expose more active sites. When used as an electrocatalytic electrode for OER and HER in alkaline solution (pH=14), the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF shows the optimized catalytic activity among all compositions investigated. It depicted extremely low operating overpotential (231 mV at 10 mA cm⁻²) combined with a modest Tafel slope (39.4 mV dec⁻¹) for OER. An exceptional HER activity is also acquired with an overpotential of only 125 mV at 10 mA cm⁻² and a small Tafel slope of 62.0 mV dec⁻¹. As an integrated electrocatalyst for water electrolysis, the cell exhibits a voltage of merely 1.591 V at 10 mA cm⁻². In addition, the catalyst displays superb long-term stability when continuously operating at 30 mA cm⁻² for 15 hours. This work opens up a new route to further optimizing the Ni-based hydroxides materials for better electrochemical overall water splitting to replace precious transition metal catalysts.

6.2 Experimental Section

6.2.1 Materials

Nafion perfluorinated resin solution (5%), nickel Chloride (NiCl_2 , 99.9%), Iron (III) Chloride (FeCl_3 , 97%), vanadium (III) Chloride (VCl_3 , 99.9%), urea (NH_2CONH_2 , 99.98%), ammonium fluoride (NH_4F , 99.98%), commercial Pt on Vulcan XC-72 (Pt/C, 20 wt%, Premetek), potassium hydroxide (KOH, 99.99%), Iridium oxide (IrO_2 , 99.9%), isopropyl alcohol (IPA, 99%), and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich (Singapore). Ethanol was purchased from Merck. The deionized water was purified using Milli-Q System (Millipore, Billerica, MA, USA). All the materials were used as received without any further purification.

6.2.2 Preparation of NiFeV-LDHs/NF, NiFe- and NiV-LDHs/NF, and $\text{Ni}(\text{OH})_2/\text{NF}$ electrodes

Nickel foam ($2\text{ cm} \times 0.5\text{ cm}$) was cleaned with 6 M HCl solution in an ultrasonic bath for 10 minutes to clear away the surface oxide layer. After that, the Ni foam was rinsed with distilled water, acetone, and ethanol; followed by drying under Ar atmosphere.

The LDHs nanosheets grown on Ni foam were synthesized by hydrothermal method. In a typical synthesis, different mole ratios of Ni:Fe:V solution (2:1:1, 4:1:1, 6:1:1, 8:1:1, 3:1:0, 3:0:1, 1:0:0 for the synthesis of $\text{Ni}_{0.5}\text{Fe}_{0.25}\text{V}_{0.25}$ -LDHs/NF, $\text{Ni}_{0.67}\text{Fe}_{0.165}\text{V}_{0.165}$ -LDHs/NF, $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF, $\text{Ni}_{0.8}\text{Fe}_{0.1}\text{V}_{0.1}$ -LDHs/NF, $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -LDHs/NF, $\text{Ni}_{0.75}\text{V}_{0.25}$ -LDHs/NF, and $\text{Ni}(\text{OH})_2/\text{NF}$, respectively) were achieved by mixing NiCl_2 , FeCl_3 , and VCl_3 in 20 ml H_2O , while the total amount of metal cations (Ni^{2+} , Fe^{3+} , and V^{3+}) were kept at 1.2 mmol. Afterward, urea (500 mg) and NH_4F (120 mg) were added, and the solution was stirred until a clear solution is formed.

Then, the above mixed solution and the Ni foam were transferred to a 45-mL stainless-steel Teflon-lined autoclave and heated in an electric oven at $120\text{ }^\circ\text{C}$ for 16 h. After cooling to room temperature, the as-synthesized hydroxides on Ni foam substrate was collected and subsequently rinsed with distilled water, ethanol, and dried in vacuum oven at $60\text{ }^\circ\text{C}$ for 6 hours.

6.2.3 Structural characterizations

X-ray diffraction was performed to characterize the samples on the Shimadzu XRD-6000 X-ray diffractometer with Cu-K α irradiation ($\lambda = 1.5406 \text{ \AA}$) at an acceleration voltage and an emission current of 45 kV and 30 mA, respectively. XRD patterns were collected at a scanning rate of $0.06^\circ \text{ s}^{-1}$, with a step size of 0.01° .

The morphology and structure of the materials were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL, Model JEM-2100F) operating at 200 keV. The high resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on JEOL-2100F at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Theta Probe electron spectrometer (VG ESCALAB200i-XL, Thermo Scientific) under pressure of 1.2×10^{-9} mbar using monochromatic Al K α X-ray beam (1486.6 eV). The X-ray spot size is 400 μm . The voltage step size was 1 eV for survey spectra and 0.1 eV for high-resolution scans. The dwell time at every step was 50 ms and pass energy was 50 eV. The binding energies were charge corrected to the adventitious C 1s peak at 284.5 eV. The chemical states of each element were appointed based on the NIST XPS Standard Reference Database 20.

The elemental ratio of Ni: Fe: V in the synthesized LDHs were determined using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyzer (Elementar Vario Micro Cube) combined with inductively coupled plasma-optical emission spectrometer (ICP-OES, Dual view Optima 5300 DV).

6.2.4 Electrochemical measurements

Electrochemical measurements were performed in a conventional three-electrode system connected to Solartron electrochemical work station with the as-prepared LDHs/NF as working electrodes, and Hg/HgO as the reference electrode. For HER testing, graphite rod was employed as the counter electrode while platinum plate is used in case of OER testing. All measurements were carried out in 1.0 M KOH electrolyte.

First, Hg/HgO electrode calibration was carried out in a three-electrode system in which Pt wires served as both working electrode and counter electrode, and Hg/HgO served as the reference electrode. H₂-saturated 1.0 M KOH was employed as electrolyte. Linear sweep voltammetry (LSV) was then conducted in the range of -0.8 to -1.0 V at a scan rate of 0.5 mV s⁻¹ (H₂ was still purged during measurement). The potential at which the current crosses zero was taken as thermodynamic potential (vs. Hg/HgO) for the hydrogen electrode (Figure 4.1).

Figure 6.1 Hg/HgO reference electrode calibration curve.

Thereby, all the potentials reported in our manuscript were calibrated to a reversible hydrogen electrode (RHE) by using the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.917$; and overpotential $\eta_{\text{OER}} = E_{\text{RHE}} - 1.23\text{V}$; $\eta_{\text{HER}} = 0 - E_{\text{RHE}}$

Before HER/OER measurements, the electrolyte (1.0 M KOH) was purged by H₂ or O₂ flow till saturation. LSVs was then performed at scan rate of 1 mV s⁻¹. By plotting overpotential η vs. logarithm of current density from polarization curves, Tafel slopes are obtained. To evaluate the durability and stability of LDHs during HER and OER testing, galvanostatic measurements at fixed current densities of -30 mA cm⁻² or 30 mA cm⁻², respectively, were conducted.

The Faradaic efficiency of the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode was done in an Ar-purged close H-shape cell (counter electrode was put in different chamber). The headspace of the chamber containing working electrode is 20.0 mL. A constant current of

−10 mA (or 10 mA in case of OER) was applied for 60 minutes. The H₂ (or O₂) gas generated was determined by taking 500 µl of the gas sample in the chamber containing working electrode to gas chromatography. The Faradaic efficiency was then calculated as the ratio of measured amount of H₂ (or O₂) and theoretical amount of H₂ (or O₂) (based on Faraday's law).

The electrochemical surface area (ESCA) was estimated from the double-layer capacitance (C_{dl}) of the films. The C_{dl} was determined by cyclic voltammetry (CV) method. The CV was conducted in a potential window (0.3–0.4 V *vs.* Hg/HgO) at various scan rates of 2, 4, 6, 8, 10, and 12 mV s^{−1}. Then capacitive current ($j_{anodic} - j_{cathodic}$) at 0.35 V *vs.* Hg/HgO was plotted against various scan rates, while the slope obtained was divided by two to acquire the C_{dl} value, which represents ECSA.

Overall water splitting tests were performed in a homemade two-electrode system with the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF as both the cathode and anode. The mass loading was calculated to be 1.42 mg cm^{−2}. For the benchmark noble metal-based catalysts, IrO₂/NF || Pt/C/NF was adopted with the same mass loading as above sample. To specify, for the cathode, 10.143 mg of 10% Pt/C was dispersed in 960 µl isopropanol and 40 µl 5% Nafion; then, 35 µl of the suspension was drop-casted on Ni foam (0.5 x 0.5 cm). The procedure to make the anode is similar except for the use of IrO₂ instead of Pt/C. The LSV curves were performed in 1.0 M KOH at a scan rate of 1 mV s^{−1} in the potential range of 1.0–2.0 V. The long-term durability was evaluated by constant current electrolysis.

The electrochemical impedance spectroscopy (EIS) measurements were performed at frequency range of 0.1 Hz to 100 kHz at an amplitude of 10 mV. All results were corrected for all ohmic (iR) losses throughout the system based on the solution resistance obtained from the EIS.

6.3 Results and Discussions

A simplified hydrothermal treatment was utilized to synthesize the NiFeV-LDHs/NF. Without the addition of Fe and V, the diffraction peaks at 11.4°, 22.7°, 34.0°, 38.8°, 46.0°, 60.1°, 61.3° in Figure 4.2a confirm the formation of hexagonal α -Ni(OH)₂ · 0.75H₂O

(JCPDS card No. 038-0715, $a=3.080$, $c=23.410$; the peaks mark “*” at 44.5° , 51.9° , and 76.4° belong to the Ni foam substrate). The XRD pattern of the sample with the presence of Fe and V unveils that NiFeV-LDHs and $\alpha\text{-Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$ are isomorphous, which is consistent with previous reports on Ni-based hydroxides materials.^{3, 5}

Figure 6.2 (a) XRD spectra of NiFeV-LDHs/NF and Ni(OH)₂/NF. (b-e) XPS spectra of NiFeV-LDHs/NF (b) survey spectrum, (c) Ni 2p region, (d) Fe 2p region, and (e) V 2p region.

X-ray photoelectron spectroscopy (XPS) were also conducted to confirm the presence of Ni, Fe, V in the catalyst and study their oxidation states in the materials (Figure 4.2b-f). As shown in the Fe 2p XPS spectrum (Figure 4.1c) reveals two peaks at binding energy

of 710.9 eV and 724.1 eV, which correspond to Fe $2p_{3/2}$ and $2p_{1/2}$ and are the characteristic peaks of Fe³⁺.²¹⁻²³ In the Ni 2p spectrum (Figure 4.2d), the main peaks of Ni $2p_{3/2}$ and $2p_{1/2}$ are clearly observed at 854.6 eV and 872.1 eV, respectively; along with a satellite peak at 860.0 eV. The spin energy separation is roughly 17.5 eV indicating the presence of the Ni²⁺ as reported in the literature.²⁴⁻²⁵ Regarding V 2p (Figure 4.2e), there is a pair of peak separated by approximately 7.6 eV at 515.0 eV and 522.6 eV, which is ascribed to V $2p_{3/2}$ and V $2p_{1/2}$ due to p orbital j-j coupling. The deconvolution of V $2p_{3/2}$ region in V 2p spectrum indicates three well-resolved contributions at ~513.9 eV, ~515.0 eV and ~515.9 eV, which belong to V³⁺, V⁴⁺, and V⁵⁺, respectively.²⁶⁻²⁸ This result is also consistent with the finding of earlier study that indicated the partial oxidation of V³⁺ to V⁴⁺ and V⁵⁺ during the LDHs synthesis.⁵ O 1s XPS spectrum in Figure 4.2f also confirm the formation of layered hydroxide.

Scanning electron microscopy (SEM) images of the as-prepared NiFeV-LDHs/NF is illustrated in Figure 4.3a, which shows that the NiFeV double hydroxide nanosheets were uniformly grown on the surfaces of NF substrate. In addition, the nanosheets stack together to form a porous flower-like structure. This kind of porous structure may be beneficial for electrolyte penetration and diffusion.

Figure 6.3 (a) FESEM image, (b,c) TEM images (inset: vertically aligned NiFeV-LDHs nanosheets), (d) HRTEM image, (e) SAED pattern. (f) HAADF-STEM image and (h-j) its corresponding STEM-EDS elemental mappings of (g) Ni, (h) Fe, and (i) V of NiFeV-LDHs nanosheets.

For transmission electron microscopy (TEM) analysis, the as-prepared NiFeV-LDHs/NF was vigorously sonicated in ethanol to disperse the NiFeV-LDHs nanosheets into solution, which was then dropped onto TEM grids. The low magnification TEM images of NiFeV-LDHs nanosheets are shown in Figure 4.3b-c, which are almost transparent due to ultrathin nature. The TEM image of vertically aligned NiFeV-LDHs nanosheets shows the thickness of ~ 10 nm (Figure 4.3b, inset). High resolution TEM (HRTEM) image taken from the nanosheet (Figure 4.3d) displays well-resolved lattice fringes with an interplanar spacing of 0.232 nm and 0.260 nm indexed to the (015) and (012) plane; respectively, of the hexagonal phase (JCPDS card No. 038-0715). The selected area electron diffraction (SAED) pattern (Figure 4.3e) exhibits the 6-fold point pattern. This result further confirms the hexagonal phase of the NiFeV-LDHs as seen earlier in the diffractogram. The High-Angle Annular Dark Field (HAADF) images and Scanning Transmission Electron Microscopes-Energy Dispersive X-ray spectroscopy (STEM-EDS)

elemental mapping images shows that nickel, iron, and vanadium are uniformly distributed and overlapped all over the nanosheets (Figure 4.3f-i). A closer look on the nanosheets (Figure 4.3f) clearly indicates the nanoporous structure of the material, which is beneficial to expose more active sites.

To gain insight into the electrochemical activities of NiFeV-LDHs, we firstly examined the NiFeV-LDHs/NF for OER in O₂ saturated 1.0 M KOH solution at a slow scan rate of 1 mV s⁻¹ to minimize the capacitive current using a typical three-electrode setup using Pt plate and the calibrated Hg/HgO as the counter electrode and reference electrode, respectively. All the electrocatalytic measurements were performed at room temperature and potentials reported in this work are *versus* Reversible Hydrogen Electrode (RHE). For comparison purposes, the OER activities of NiFe-LDHs/NF (Ni:Fe = 3:1, molar ratio), NiV-LDHs/NF (Ni:V = 3:1), Ni(OH)₂/NF, and bare Ni foam were investigated. We also examined the OER activities of NiFeV-LDHs/NF electrodes with different elemental ratio to optimize the composition. The elemental ratio of Ni, Fe, and V in all synthesized LDHs has been quantified by ICP-OES (Table S1), revealing the atomic ratios of Ni: Fe: V are close to what were used in the corresponding syntheses.

Table 6.1 Composition analysis of the synthesized LDHs by ICP-OES

Precursor ratio (Ni : Fe : V)	Synthesized LDHs ratio (Ni : Fe : V) (determined by ICP-OES)
2 : 1 : 1 (Ni _{0.5} Fe _{0.25} V _{0.25} -LDHs)	1.972 : 0.983 : 1
4 : 1 : 1 (Ni _{0.67} Fe _{0.165} V _{0.165} -LDHs)	3.986 : 1.100 : 1
6 : 1 : 1 (Ni _{0.75} Fe _{0.125} V _{0.125} -LDHs)	5.963 : 0.989 : 1
8 : 1 : 1 (Ni _{0.8} Fe _{0.1} V _{0.1} -LDHs)	8.102 : 1.104 : 1
3 : 1 : 0 (Ni _{0.75} Fe _{0.25} -LDHs)	3.134 : 1 : 0
3 : 0 : 1 (Ni _{0.75} V _{0.25} -LDHs)	3.121 : 0 : 1

It is shown that the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode displays an optimal OER catalytic activity an overpotential of 231 mV at 10 mV cm⁻² and Tafel slope of 39.4 mV dec⁻¹ (Figure 4.4a-b).

Figure 6.4 (a) OER polarization curves of NiFeV-LDHs/NF with different composition of Ni:Fe:V in 1.0 M KOH at 1.0 mV s⁻¹ and their corresponding (b) Tafel slopes.

Figure 4.5a displays the polarization curves with iR compensation. It is notable that the bare Ni foam gives insignificant OER activity in the tested potential range. In contrast, the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF electrodes exhibit an onset overpotential of 228 mV, which is much lower than those of NiFe-LDHs/NF (274 mV), NiV-LDHs/NF (252 mV), and $\text{Ni}(\text{OH})_2$ /NF (340 mV). In addition, it can be seen that the anodic current density rises abruptly at higher positive potentials. The superior activity of the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF electrode is further shown in its small Tafel slope of 39.4 mV dec⁻¹ (Figure 4.5b), which is lower than those of NiFe-LDHs/NF (65.7 mV dec⁻¹), NiV-LDHs/NF (54.1 mV dec⁻¹), and $\text{Ni}(\text{OH})_2$ /NF (95.9 mV dec⁻¹). It is worth noting that the flat Tafel slope of $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF electrode is in the range of 30–40 mV dec⁻¹, which indicates the rate-determining characteristic for the second step ($*\text{OH} \rightarrow * \text{O} + \text{H}^+ + \text{e}^-$).²⁹ Practically, the overpotential to drive a current density of 10 mA cm⁻² is another important parameter since solar-light-coupled water splitting system normally run at 10 mA cm⁻² under standard conditions (1 sun, AM 1.5).² At 10 mA cm⁻², the optimized layered double hydroxides of $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF shows a low overpotential of only 231 mV, which is much less than NiFe-LDHs/NF (278 mV), NiV-LDHs/NF (257 mV), and $\text{Ni}(\text{OH})_2$ /NF (347 mV) (Figure 4.5c).

Figure 6.5 (a) OER polarization curves of NiFeV-LDHs/NF, Ni(OH)₂/NF, NiFe-LDHs/NF, and NiV-LDHs/NF in 1.0 M KOH at scan rate of 1.0 mV s⁻¹ and their corresponding (b) Tafel slopes. (c) The overpotentials of above samples at the current density of 10 mA cm⁻². (d) Chronopotentiometry measurements of NiFeV-LDHs/NF electrode at the current density of 30 mA cm⁻² in 1.0 M KOH solution.

The long-term stability of the as-prepared Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode was also examined in 1.0 M KOH solution by chronopotentiometry method at fixed current density of 30 mA cm⁻² (Figure 4.5d). It can be seen that a stable operating potential is obtained for 15 hours of polarization (well below 1% change), suggesting the remarkable durability of the electrode. The crystallinity and morphology are well preserved after 15 hours of stability test, indicating the structural robustness of the electrode (Figure 4.6a-b).

Figure 6.6 (a) XRD spectrum and (b) SEM image of NiFeV-LDHs/NF after 15 hours of OER testing

In addition, to prove that all the current is due to water oxidation, the theoretical and experimental O₂ evolved by Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode at a constant current of 10 mA were carried out (Figure 4.7a). The experimental O₂ was measured by gas chromatography, showing ~100% Faradaic efficiency for 60 minutes of electrolysis.

Figure 6.7 Faradaic efficiency of (a) O₂ generation and (b) H₂ generation over Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode.

We also probed HER electrocatalytic activity of NiFeV-LDHs catalyst in 1.0 M KOH electrolyte using a typical three-electrode setup using Graphite rod as the counter electrode. To explore the optimized composition of NiFeV-LDHs for HER, LSV measurements at 1 mV s⁻¹ of samples with different metal ratio were conducted (Figure 4.8a-b), once again confirming the best HER catalytic activity of Ni_{0.75}Fe_{0.125}V_{0.125}-

LDHs/NF electrode, which shows an overpotential of 125 mV at 10 mA cm^{-2} and a small Tafel slope of 62.0 mV dec^{-1} .

Figure 6.8 (a) HER polarization curves of NiFeV-LDHs/NF with different composition of Ni:Fe:V in 1.0 M KOH at 1.0 mV s^{-1} and their corresponding (b) Tafel slopes.

Figure 4.9a illustrates the LSV curves of NiFeV-LDHs/NF, NiV-LDHs/NF, NiFe-LDHs/NF, and Ni(OH)₂/NF catalytic electrodes as well as Ni foam at a scan rate of 1 mV s^{-1} . Firstly, it should be noted that Ni foam gives a minor current density in the tested potential range. Compared to other control catalysts, the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode shows noticeably improved HER performance with an onset overpotential of 86 mV and a modest Tafel slope of 62.0 mV dec^{-1} (Figure 4.9b) indicating that the HER proceeds through Volmer-Heyrovsky mechanism, in which the Volmer reaction is the rate-determining step.³⁰ Moreover, an overpotential to drive a current density of 10 mA cm^{-2} of 125 mV is achieved (Figure 4.9c), revealing a superior cathode for hydrogen generation in alkaline electrolyte (pH=14); meanwhile Ni(OH)₂/NF, NiFe-LDHs/NF, NiV-LDHs/NF require 193 mV, 157 mV, 145 mV, respectively.

Figure 6.9 (a) HER polarization curves of NiFeV-LDHs/NF, Ni(OH)₂/NF, NiFe-LDHs/NF, and NiV-LDHs/NF in 1.0 M KOH at scan rate of 1.0 mV s⁻¹ and their corresponding (b) Tafel slopes. (c) The overpotentials of above samples at the current density of 10 mA cm⁻². (d) Chronopotentiometry measurements of NiFeV-LDHs/NF electrode at the current density of 30 mA cm⁻² in 1.0 M KOH solution.

The HER electrocatalysis durability is also crucial for practical application. Figure 4.9d reveals the chronopotentiometry test for the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode performed in 1.0 M KOH at the current density of -30 mA cm⁻². An insignificant voltage increase of just above 1% over 15 hours and the post analysis studies (Figure 4.10a-b) suggest that the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs own an excellent stability and HER durability in strong alkaline solution (pH=14). Also, the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode exhibits almost 100% Faradaic efficiency under constant current of -10 mA for 60 minutes (Figure 4.7b)

Figure 6.10 (a) XRD spectrum and (b) SEM image of NiFeV-LDHs/NF after 15 hours of HER testing.

The above results and discussions indicate that the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs}$ is a highly active and stable electrocatalyst for both OER and HER in strong alkaline medium (pH=14). Hence, a homemade two-electrode set up with $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ as both anode and cathode was employed to investigate the electrocatalytic activity toward water electrolysis in 1.0 M KOH solution.

Figure 6.11 Homemade two-electrode system during water splitting test with NiFeV-LDHs/NF served as both anode and cathode.

During water splitting, bubbles were clearly observed on surfaces of both electrodes (Figure 4.11). The voltage to reach a current density of 10 mA cm^{-2} is found to be 1.591

V, surpassing the state-of-the-art $\text{IrO}_2/\text{NF-Pt/C/NF}$ which requires 1.738 mV (Figure 4.12a). In chronopotentiometry test, the cell remains stable overpotential (less than 2% increment) at 30 mA cm^{-2} after 15 hours of operation (Figure 4.12b). The overpotential at 10 mA cm^{-2} obtained using a two-electrode system (361 mV) is very similar to that of the three-electrode system (356 mV, combining HER and OER), between which the 5 mV difference is due to the different testing configurations.³¹ This performance of $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ electrodes is remarkably impressive compared to that of reported bifunctional catalysts and even benchmark catalysts

Figure 6.12 (a) Polarization curves of the water electrolysis using NiFeV-LDHs/NF as bifunctional electrocatalyst compared with $\text{IrO}_2/\text{NF} \parallel \text{Pt/C/NF}$ in a two-electrode system at the scan rate of 1.0 mV s^{-1} (b) Chronoamperometric response (inset: image taken during water splitting).

In light of the excellent electrochemical properties toward OER, HER, and overall water splitting of the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ catalyst, it is necessary to estimate the electrochemically effective surface area (ECSA) since higher active surface area results in higher number of active sites and normally better catalytic activity. As shown in Figure 4.13a-h, the electrochemical results reveal that the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ has a C_{dl} of 126.2 mF cm^{-2} , which is higher than NiFe-LDHs/NF (39.5 mF cm^{-2}), NiV-LDHs/NF (96.3 mF cm^{-2}), and $\text{Ni(OH)}_2/\text{NF}$ (41.4 mF cm^{-2}). This implies that $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ has a larger electroactive surface area, which partially facilitates the reactions.

Figure 6.13 Cyclic voltammograms (CV) of (a) $\text{Ni}_{0.5}\text{Fe}_{0.25}\text{V}_{0.25}\text{-LDHs/NF}$, (b) $\text{Ni}_{0.67}\text{Fe}_{0.165}\text{V}_{0.165}\text{-LDHs/NF}$, (c) $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$, (d) $\text{Ni}_{0.8}\text{Fe}_{0.1}\text{V}_{0.1}\text{-LDHs/NF}$, (e) $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-LDHs/NF}$, (f) $\text{Ni}_{0.75}\text{V}_{0.25}\text{-LDHs/NF}$ and (g) $\text{Ni(OH)}_2\text{/NF}$ are taken in a potential window (0.3–0.4 V vs. Hg/HgO) at various scan rates of 2, 4, 6, 8, 10, and 12

mV s^{-1} in 1.0 M KOH solution. (f) The capacitive current ($j_{\text{anodic}} - j_{\text{cathodic}}$) at 0.35 V vs. Hg/HgO as a function of various scan rates for of above samples

Nonetheless, it has not escaped our notice that compared to the best double metal LDHs in this study, $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF has only 1.3-fold higher in ECSA; with such small increase of active sites, the current density at 280 mV OER overpotential is well above six times larger (178.5 mA cm^{-2} compared to 28.2 mA cm^{-2}). This analysis suggests that such significant enhancement cannot be only attributed to the marginally increased effective surface area but also higher intrinsic activity of the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF electrode.

The ECSAs of NiFeV-LDHs/NF with different compositions were further examined in details. The C_{dl} of $\text{Ni}_{0.5}\text{Fe}_{0.25}\text{V}_{0.25}$ -, $\text{Ni}_{0.66}\text{Fe}_{0.167}\text{V}_{0.167}$ -, $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ - and $\text{Ni}_{0.8}\text{Fe}_{0.1}\text{V}_{0.1}$ -LDHs/NF electrodes were 89.4 mF cm^{-2} , 82.8 mF cm^{-2} , 126.2 mF cm^{-2} , and 60.3 mF cm^{-2} , respectively (Figure 4.13h). The $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}$ -LDHs/NF electrode possesses the optimum ECSA, implying that the number of surface active sites can be increased by optimizing the ratio of three metal in the system. It is also noted that although the current density of NiFeV-LDHs/NF with different ratio show an increase trend along with ECSA, only doubling the ECSA (from 60.3 mF cm^{-2} to 126.2 mF cm^{-2}) leads to more than 8 times current density improvement (from $\sim 21.5 \text{ mA cm}^{-2}$ to 178.5 mA cm^{-2}) (Figure 4.14). This is a solid evidence that optimizing Ni, Fe, and V ratio not only boost the surface active sites, but also increase the intrinsic activity.

Figure 6.14 Plot of current density at 280 mV OER overpotential versus ECSA ($2C_{\text{dl}}$) of NiFeV-LDHs/NF electrodes with different compositions.

To further investigate the kinetics of the as-obtained catalysts, electrochemical impedance spectroscopy (EIS) measurements were carried out at a potential of 1.53 V (*vs.* RHE) in the frequency range from 100 kHz to 0.1 Hz in 1.0 M KOH solution. Figure 4.15 shows the Nyquist plots that were fitted by a reported electrical analog.³² The x-intercepts at high frequency region indicate the solution resistance, which were used for Ohmic correction in this study. The charge-transfer resistance (R_{ct}), corresponding to the semicircular diameter in the EIS spectrum, of $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ electrode is only $0.50\ \Omega$, slightly smaller than those of other control samples, *i.e.* $0.57\ \Omega$ ($\text{Ni}(\text{OH})_2/\text{NF}$), $0.52\ \Omega$ (NiV-LDHs/NF), and $0.64\ \Omega$ (NiFe-LDHs/NF). These small resistances are ascribed to the superb electrical contact between the catalyst and conductive Ni foam support. In addition, the smaller R_{ct} of the optimized $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ electrode indicates faster charge transfer ability compared to other control electrodes.

Figure 6.15 EIS spectrum measured at 300 mV overpotential of $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$, $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-LDHs/NF}$, $\text{Ni}_{0.75}\text{V}_{0.25}\text{-LDHs/NF}$, $\text{Ni}(\text{OH})_2/\text{NF}$.

To the best of our knowledge, the $\text{Ni}_{0.75}\text{Fe}_{0.125}\text{V}_{0.125}\text{-LDHs/NF}$ electrode exhibits an outstanding OER performance, which is better than most of reported LDHs including the state-of-the-art NiFe-LDHs . The exceptional catalytic activity is attributed to the

synergistically combination of Fe and V in Ni-based layered hydroxide that leads the better intrinsic catalytic activity and higher active surface area. The porous structure of the nanosheets gives enough space for electrolyte penetration and diffusion; as well as provide higher number of active sites by boosting the accessible ECSA. In addition, the *in-situ* growth of the hydroxide onto conductive Ni foam substrate benefits the charge transfer, lowering significantly the resistance of the system.

6.4 Conclusion

In summary, NiFeV-LDHs/NF with different molar ratio have been prepared by one-step hydrothermal treatment and demonstrated for the first time as highly active water splitting electrodes that outperform most of reported LDHs. Among all composition investigated, Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF delivers the best performance. To achieve a current density of 10 mA cm⁻², it requires overpotentials of only 231 mV for OER and 125 mV for HER with a Tafel slope of 39.4 mV dec⁻¹ and 62.0 mV dec⁻¹, respectively, in alkaline medium (pH=14). When integrated as both anode and cathode in water electrolysis, a modest voltage of 1.591 V is obtained to reach 10 mA cm⁻². The electrode also exhibits outstanding durability and stability for 15 hours of operation at 30 mA cm⁻². These excellent features come from the synergistic effect of ternary metals system and ultrathin porous nature of NiFeV-LDHs nanosheets. This work opens up a new route to acquire the optimal low-cost Ni-based hydroxides materials for overall water splitting to eliminate the use of precious transition metal catalysts.

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Chapter 7

Conclusions and Future Works

In this chapter, a general summary of the findings on engineering of Ni-based layered double hydroxides and their phosphide/sulfide derivatives in this dissertation is presented. After that, conclusions and originality drawn from these findings are highlighted. Lastly, possible future works are recommended.

7.1 Conclusions

With the depletion of fossil fuel and the rise of environmental pollution, solar-light-coupled water electrolysis for hydrogen generation has arisen as one of the best solution. However, electrocatalysts, which are the key component in water splitting devices, are still relied on noble group metals. Low-cost, earth-abundant, electrocatalytically active, and stable alternatives are highly desirable. Recent advances in materials science have shown the capability of Ni-based layered double hydroxides (LDHs) towards alkaline water electrolysis by virtue of the low overpotentials and decent stability. Nonetheless, the high electronic resistance (hindering electron transportation) and limited BET surface area are holding them back from industrialization. In this dissertation, rational designs and engineers of Ni-based layered double hydroxides for efficient electrochemical water splitting are presented.

Firstly, the semiconductor-to-conductor transition of NiS_2 after Cu incorporation is proposed and confirmed by DFT calculations and temperature-dependent resistivity measurements, respectively. Such transition facilitated reaction kinetics, reduced the loss of electron transport during electrocatalysis, increased the density of active sites, and gave rise to intrinsic activities. Further calculations also confirmed the advantages of Cu incorporation by reducing Gibbs free energy of H adsorption of both Ni sites and S sites. Besides, Cu-doped NiS_2 surface offers even more favorable water dissociation than that of Pt (111), making the former perform well in alkaline conditions. Thus, the modulated Cu- NiS_2 illustrates remarkable improvement in electrocatalytic activity toward HER and OER.

In the second part, a combined-strategy of cation tuning and surface engineering for the fabrication of highly active, earth-abundant, and robust LDHs-derived Ni_2P is reported. First principle calculations suggest the effectiveness of V doping and O_2 plasma, which enhance the DOS at Fermi level and make the Ni sites more susceptible to OH^- adsorption. Furthermore, the O_2 plasma helps to enhance the wettability of the catalyst toward aqueous solution and induce a higher specific surface area; thus, higher number of active sites and lower charge transfer resistance are attained. Consequently, the catalyst shows desirable catalytic performance towards OER and HER. When employed for two-

electrode water electrolysis, the catalyst demonstrates a low voltage of 1.56 V at 10 mA cm⁻² with good stability and durability, outperforming the benchmark IrO₂ || Pt/C.

Finally, it was experimentally proven that the incorporation of vanadium into Ni-based LDHs (specifically NiFe-LDHs in this study) has a positive effect on HER, OER, and water splitting performance. Lower charge transfer resistance, and more importantly, higher intrinsic catalytic activity were obtained after vanadium doping. To further overcome the problem of low conductivity of LDHs materials, nickel foam (NF) was employed as conductive substrate during the growth, eliminating the use of polymeric binders (which contributes to additional resistance). In addition, the use of three dimensional substrate reduces aggregation of LDHs nanosheets; hence, higher density of active sites were obtained. Among all molar ratio investigated, the Ni_{0.75}Fe_{0.125}V_{0.125}-LDHs/NF electrode depicts the optimized performance with small overpotentials and Tafel slopes towards OER, HER and water splitting. More importantly, remarkable durability, stability and Faradaic efficiencies are also achieved.

The realizations of noble metal-free Ni-based LDHs and their sulfide/phosphide derivatives performing on par with IrO₂ || Pt couple in strong alkaline conditions offers a key step toward large scale implementation of solar-light-coupled water electrolyzers.

7.2 Recommendation for future work

In the view of current research findings, Ni-based LDHs and the phosphide/sulfide derivatives have shown their huge potential for practical implementation. In this part, recommendation for future works to further develop this family of materials towards efficient electrochemical water splitting are presented.

7.2.1 Explore the potential of Ni-based LDHs and their derivatives in other energy research fields

In addition to storing energy *via* H₂, rechargeable metal-air batteries such as zinc-air and lithium-air have also attracted lots of attention due to their much high theoretical specific capacities (820 mA h g⁻¹ for Zn-air batteries and 3828 mA h g⁻¹ Li-air ones) theoretical

energy densities (up to 1086 Wh kg⁻¹ for Zn-air batteries and 11400 Wh kg⁻¹ for Li-air ones).¹⁻² In those batteries, electrocatalysts play an important role to facilitate charge and discharge processes. Particularly, the high charging voltage, which is due to sluggish oxygen evolution reaction, is the bottleneck of this technology. This is where Ni-based LDHs and their derivatives with superior OER catalytic activity as seen in Chapter 4-6 can come in and make a difference.

Dai *et al.* were the first to employ their own developed NiFe-LDHs hybridized with multi-walled CNTs (NiFe-LDHs/CNT) for rechargeable Zn-air battery (Figure 7.1).³ After mixing with CoO nanocrystals on N-doped CNTs (CoO/N-CNT), which is only active towards oxygen reduction reaction (ORR), the battery showed the modest charging voltage of only ~1.93 V at current density of 10 mA cm⁻² (Figure 7.1h), outperforming the state-of-the-art Pt/C+Ir/C mixture. However, performance degradation was observed (Figure 7.1h-i), which is most likely due to carbon being oxidized at highly oxidative OER condition.

Figure 7.1 (a–c) Schematic structure, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of CoO/N-CNT. (d–f) Schematic structure, SEM and TEM images of NiFe-LDHs/CNT. (g–i) CoO/N-CNT and NiFe-LDHs/CNT hybrid electrocatalysts are mixed in a single cathode for rechargeable Zn-air battery: (g) A schematic structure of the battery. (h) Cycling data at 5 and 10 mA cm^{-2} , respectively, in short cycle periods (200 seconds per cycle, 100 seconds discharge followed by 100 seconds charge). (i) Cycling data at 20 mA cm^{-2} in long cycle periods (20 hours per cycle, 10 hours discharge followed by 10 hours charge). Scale bars are 200 nm, 5 nm, 200 nm, and 20 nm in b, c, e, and f, respectively.³

Another issue to consider is that unlike Zn-air batteries, the discharge product in Li-air batteries are insoluble in electrolyte and tend to accommodate at the pores of catalytic material at cathode. Therefore, high specific surface area materials with large pores are required to avoid premature discharge termination.⁴

In these respects, our strategies of vanadium doping and post-treatment by sulfidation/phosphidation or plasma might improve the conductivity of the electrocatalysts without the need for additional carbon, enhance the wettability towards electrolyte of interest to fasten kinetics, and create pore structures to boost the specific surface area. Thus, better batteries performance by means of lower charging voltage, higher stability and durability, and faster reaction kinetics can be achieved, which has not been reported so far.

7.2.2 Understand the role of edges, basal planes, and dopants on the catalytic properties of Ni-based LDHs and their derivatives.

Comprehensive understanding on the active sites would pave the way to further develop electrocatalysts with superior performance. Taking the well-investigated HER catalyst – MoS₂ as an example, it is proven by Jaramillo *et al.* that the basal plane of MoS₂ is catalytically inactive towards HER while the metallic edges are extremely active.⁵ Since then, a large number of publications with numerous strategies to increase the density of exposed edges (exfoliation, engineering surface structure) have been reported for the same purpose of activity enhancement.⁶⁻⁷

Regarding Ni-based LDHs, despite high catalytic activities and durability towards HER, OER, and water splitting, there are still lots of room for improvement and questions need to answer. Should effort be devoted to find scalable method to exfoliate LDHs in order to increase the edge density? What are the role of second and third metal species in multi-metal Ni-based LDHs?

To address those concerns, in-depth studies like the case of above-mentioned MoS₂ would be of great interest.

Firstly, micro-electrolytic cell is built up based on the work by Chhowalla *et al.* to measure the electrocatalytic activities of a single NiFe-LDHs nanosheet (Figure 7.2).⁸ In

this cell, counter electrode and reference electrode are Pt wire and Ag/AgCl with micro-sized tip, respectively; and a Cr/Au pad contacting a single NiFe-LDHs nanosheet is the working electrode (Figure 7.2a-b). With the help of precise electron beam lithography (EBL) patterning, electrocatalytic performance of only the basal plane (with the edges covered, Figure 7.2c) or only the edges (with the basal plane covered, Figure 7.2d) can be measured. Entire substrate except the area of interest of NiFe-LDHs nanosheet is covered with photoresist layer to ensure that the current measured is due to that area only. By this way, the region that responsible for high catalytic activity can be identified; thus, laying the foundation to engineer Ni-based LDHs. Furthermore, similar measurements on a single NiFeV-LDHs nanosheet can further explain the enhanced catalytic activity observed after vanadium incorporation, which was seen in Chapter 6.

Figure 7.2 Electrochemical set-up for the HER, OER measurement on single-layer materials. (a) Photograph of the electrochemical micro-cell. (b) Schematic of the micro-cell showing single layer nanosheet deposited on Si/SiO₂ substrate and contacted by Auelectrode (working electrode). Platinum wire and Ag/AgCl electrodes with micro-

sized tip are employed as counter and reference electrode, respectively. Everything is covered with poly methylmethacrylate (PMMA) photoresist layer except a window on top of the edges of the nanosheet. Only the nanosheet is in contact with the electrolyte if interest. Edge-exposed and edge-covered nanosheet can be fabricated and tested. (c-d) Optical microscope images of (c) edge covered nanosheet or (d) edge exposed nanosheet.⁸

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List of Publications

1. Ultrathin Porous NiFeV Ternary Layer Hydroxide Nanosheets as a Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting
K. N. Dinh, P. L. Zheng, Z. F. Dai, Y. Zhang, R. Dangol, Y. Zheng, B. Li, Y. Zong, and Q. Y. Yan,* *Small*, **2018**, 14(8), 1703257.
2. O₂ Plasma and Cation Tuned Nickel Phosphide Nanosheets for Highly Efficient Overall Water Splitting
K. N. Dinh, X. L. Sun, Z. F. Dai, Y. Zheng, P. L. Zheng, J. Yang, J. W. Xu, Z. G. Wang, and Q. Y. Yan,* *Nano Energy*, **2019**, 54, 82.
3. Highly Efficient and Stable Hydrogen Production in All pH Range by Two-Dimensional Structured Metal-Doped Tungsten Semicarbides
E. H. Ang,† **K. N. Dinh**† (co-first author), X. L. Sun, Y. Huang, J. Yang, Z. L. Dong, X. C. Dong, W. Huang, Z. G. Wang, H. Zhang,* and Q. Y. Yan,* *Research*, **2019**, 2019, 4029516 (Co-first Author)
4. Performance-improved Li-O₂ battery by tailoring phases of Mo_xC porous nanorods as an efficient cathode
H. Yu,† **K. N. Dinh**† (co-first author), Y. M. Sun, H. S. Fan, Y. H. Wang, Y. Jing, S. Z. Li, M. Srinivasan, and Q. Y. Yan,* *Nanoscale*, **2018**, 10, 14877 (Co-first Author)
5. Nanostructured metallic transition metal carbides, nitrides, phosphides, and borides for energy storage and conversion
K. N. Dinh, Q. H. Liang, C-F. Du, J. Zhao, A. I. Y. Tok, H. Mao,* and Q. Y. Yan,* *Nano Today*, **2019**, 25, 99
6. Self-Assemble and In Situ Formation of Ni_{1-x}Fe_xPS₃ Nanomosaic-Decorated MXene Hybrids for Overall Water Splitting
C.-F. Du, **K. N. Dinh**, Q. H. Liang, Y. Zheng, Y. B. Luo, J. L. Zhang, Q. Y. Yan,* *Adv. Energy Mater.*, **2018**, DOI: 10.1002/aenm.201801127
7. Synthesis, characterizations, and utilization of oxygen-deficient metal oxides for lithium/sodium-ion batteries and supercapacitors
L. Wang, X. Xie, **K. N. Dinh**, Q. Y. Yan,* and J. M. Ma,* *Coord. Chem. Rev.*, **2019**, 397, 138

8. Synergy of Nb Doping and Surface Alloy Enhanced on Water–Alkali Electrocatalytic Hydrogen Generation Performance in Ti-Based MXene
C-F. Du, X. L. Sun, H. Yu, Q. H. Liang, **K. N. Dinh**, Y. Zheng, Y. B. Luo, Z. G. Wang, and Q. Y. Yan,* *Adv. Sci.*, **2019**, 6, 1900116
9. Facile Synthesis of Amorphous Ternary Metal Borides–Reduced Graphene Oxide Hybrid with Superior Oxygen Evolution Activity
J. M. V. Nsanzimana, R. Dangol, V. Reddu, S. Duo, Y. C. Peng, **K. N. Dinh**, Z. F. Huang, Q. Y. Yan, and X. Wang,* *ACS Appl. Mater. Interfaces*, **2018**, 11, 846.
10. Few-layer NiPS₃ nanosheets as bifunctional materials for Li-ion storage and oxygen evolution reaction
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11. Constructing multi-functional heterostructure of Fe₂O₃@Ni₃Se₄ nanotubes
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12. Scalable Synthesis of SnS₂/S-Doped Graphene Composites for Superior Li/Na-Ion Batteries
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