Interface engineering of advanced heterostructure through electrochemical synthesis for water splitting

Peng, Dongdong

2021

Peng, D. (2021). Interface engineering of advanced heterostructure through electrochemical synthesis for water splitting. Doctoral thesis, Nanyang Technological University, Singapore. <https://hdl.handle.net/10356/153323>

<https://hdl.handle.net/10356/153323>

<https://doi.org/10.32657/10356/153323>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 17:47:56 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**INTERFACE ENGINEERING OF ADVANCED
HETEROSTRUCTURE THROUGH ELECTROCHEMICAL
SYNTHESIS FOR WATER SPLITTING**

PENG DONGDONG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

**INTERFACE ENGINEERING OF ADVANCED
HETEROSTRUCTURE THROUGH ELECTROCHEMICAL
SYNTHESIS FOR WATER SPLITTING**

PENG DONGDONG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2021

Statement of Originality

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

18/11/2021

.....

Date

NTU NTU NTU NTU NTU NTU NTU NTU

NTU NTU NTU NTU NTU NTU NTU NTU

NTU NTU *Peng Dongdong* NTU NTU NTU

NTU NTU NTU NTU NTU NTU NTU NTU

.....

Peng Dongdong

Supervisor Declaration Statement

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

18/11/2021

Date

Assoc Prof Huang Yizhong

Authorship Attribution Statement

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

Chapter 4 is published as Peng, D., Zhang, B., Wu, J., Huang, K., Cao, X., Lu, Y., ... & Huang, Y. (2020). Growth of lattice coherent Co₉S₈/Co₃O₄ Nano - Heterostructure for Maximizing the Catalysis of Co - Based Composites. ChemCatChem.

The contributions of the co-authors are as follows:

- A/Prof Huang Yizhong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Cao Xun.
- I co-designed the study with A/Prof Yizhong and performed all the laboratory work at the School of Materials Science and Engineering and the Singapore Synchrotron Light Source. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.

18/11/2021

.....
Date

Peng Dongdong

Abstract

Green energy has played a key role in solving the current energy crisis and environmental issues. For various green energy resources including solar energy, wind energy, tidal energy, hydropower and so on, hydrogen produced from water splitting is abundant and cost-effective clean energy upon the active electrocatalyst. In this thesis, the electrocatalyst is prepared by electrodeposition that has been proven to be an economical, easy and efficient synthesis method when compared with other fabrication methods including solvothermal method and wet chemical method.

Firstly, a facile electrochemical method to grow $\text{Co}_9\text{S}_8/\text{Co}_3\text{O}_4$ heterostructured nanocomposite with N_2 purging and subsequent annealing is carried out and reported. The gas purging is involved during the growth in order to decrease hydroxide ions (generated by the reduction of nitrate ion) concentration near electrode surface and benefit the formation of heterostructure electrocatalyst. It consists of two epitaxial phases (i.e. Co_9S_8 and Co_3O_4), that are oriented along {020} lattice plane enabling the rapid mass transport and charge transfer during HER and OER. In addition, the intrinsic high energy state interface and other factors such as small size and good conductivity contribute to the significantly improved electrocatalytic activity towards water splitting and excellent durability. As a result, to produce $10 \text{ mA}\cdot\text{cm}^{-2}$ OER current density, the composite only requires an overpotential of 250 mV with a low Tafel slope of $73.54 \text{ mV}\cdot\text{dec}^{-1}$. In fact, it offers better electrochemical redox performance than the state-of-the-art Co-based nanocomposites. Besides, this special composite is also examined to deliver high HER performance with superior durability in alkaline solution.

Subsequently, an exclusive cost-effective and highly efficient OER catalyst has been successfully fabricated by simple electrodeposition followed by dealloying. The catalyst presents a core-shell structure in which the highly conductive dendritic FeCoCu alloy is the core that is covered by the $\text{FeOOH}/\text{Co}(\text{OH})_2$ nanosheets as the shell. The whole catalyst is supported on the copper nanotubes (Cu NTs). This design enables the formation of a

hierarchical catalyst with small R_{ct} and large ECSA which afford the enhanced intrinsic properties and high exposure of active sites. The catalyst is demonstrated to offer excellent OER performance with the current density reaching to $10 \text{ mA} \cdot \text{cm}^{-2}$ at a small overpotential of 250 mV, which is more competitive than most FeCo-based OER catalysts reported. In addition, this catalyst is also highly resistant to the corrosive attack in alkaline medium, and maintains almost the same performance after 12 h of stability test. This work provides an easy and economic design for fabricating highly efficient and durable OER catalyst, showing the potential for the large scale-up in industrial application.

Lastly, a high performance hierarchical quaternary nano-porous nanostructure FeCoNiCu catalyst has been developed via electrodeposition approach followed by the electrochemical etching process. Effect of different electrodeposition time on the catalytic performance is systemically studied, and it is found that FeCoNiCu electrode at 5 min electrodeposition time demonstrates the best performance with lowest Tafel slope of 57 mV/dec and is higher than the performance of similar catalysts reported in literature. Such good performance is attributed to the nanoporous structure and the mixture of FeO(OH), Ni(OH)₂ and Co(OH)₂ hydroxyl-grouped phases.

Lay Summary

To meet the increasing demand for renewable energies, various green energy resources including solar energy and wind energy have been developed. However, intermittence is one of the common issues for the renewable energy resources mentioned above. Water splitting is known to play a key role in solving the issue considering its advantage in energy conversion and storage. However, the large-scale application of water splitting mainly depends on the development of high-efficient and low-cost catalyst for the reaction.

Electrochemical methods are usually very simple and easy to carry out. Besides, they are also highly controllable and easy to adjust the parameters such as potential and current. Thus, they are more advantageous than solvothermal and wet chemical methods which usually require special equipment and not environmentally friendly. In addition, the composition of products prepared by electrochemical approach can be specified when subject to gas purging. The present work reports a product that is claimed to be highly active towards OER and HER when gas purging is applied. Without gas purging, the product is determined to be only active towards OER.

In addition to gas-assisted electrodeposition, there are also alternative electrochemical methods allowing the fabrication of efficient and stable electrocatalyst. In the present work, electrochemical dealloying is used to synthesize metal-metal (oxy)hydroxide heterostructure which is highly active towards OER.

Besides, the performance of the catalyst can be further improved when nickel is incorporated into the electrolyte, producing quaternary phases in the product. It is the synergistic effect between these three phases mentioned above that improves the electrocatalytic activity of the product. In other words, a highly efficient electrocatalyst can be produced through simple and economical electrochemical dealloying method.

Acknowledgements

This dissertation would not have been possible without funding from the RSS scholarship, AcRF grant MOE Singapore and National Natural Science Foundation of China.

I would like to express special gratitude to my supervisor, Prof Huang Yizhong for his continual guidance and encouragement.

I am also grateful to Prof Wu Junsheng for his continual support in experimental materials and valuable advices.

Thanks all the technicians in FACTS for patiently guiding me operate all kinds of equipment, collect and analyze data.

I also want to thank all the colleagues in my group for their friendship.

Many thanks for the continual support and understanding from my family members.

Table of Contents

Abstract.....	i
Lay Summary.....	i
Acknowledgements.....	iii
Table of Contents.....	v
Table Captions.....	ix
Figure Captions	xi
Abbreviations.....	xxi
Chapter 1.....	1
1.1 Hypothesis/Problem Statement	2
1.2 Objectives and Scope.....	3
1.3 Dissertation overview	4
1.4 Findings and Outcomes/Originality	5
References	7
Chapter 2.....	9
2.1 Overview	10
2.2 Interface engineering of noble-metal based heterostructures.....	10
2.2.1 Interface engineering of Platinum (Pt)-based heterostructures	11
2.2.2 Interface engineering of Ruthenium (Ru)-based heterostructures	14
2.2.3 Interface engineering of Palladium (Pd)-based heterostructures	19
2.3 Interface engineering of non-noble metal based heterostructures.....	21
2.3.1 Interface engineering of Transition Metal Carbide (TMC)/carbon-based heterostructures	21
2.3.2 Interface engineering of Transition Metal Sulfide-based heterostructures.....	26
2.3.3 Interface engineering of Transition Metal Phosphide-based heterostructures	31
2.4 Interface engineering of cobalt-based heterostructures for water splitting.....	35
2.4.1 Interface engineering of Cobalt Selenides (CoSeS)-based heterostructures for water splitting	35
2.4.2 Interface engineering of Cobalt Sulfides-based heterostructures for water splitting.....	37
2.4.3 Interface engineering of Cobalt Oxides-based heterostructures for water splitting	39
2.4.4 Interface engineering of Cobalt Hydroxides-based heterostructures for water splitting .	41
References	47
Chapter 3.....	59

3.1	Rationale for selection of synthetic methods.....	60
3.2	Synthesis methods.....	61
3.2.1	Gas-assisted electrodeposition	61
3.2.2	Dealloying.....	61
3.3	Characterization and analysis	62
3.3.1	Transmission Electron Microscopy (TEM)	62
3.3.2	Scanning Electron Microscopy (SEM).....	64
3.3.3	Powder X-ray Diffraction (XRD)	66
3.3.4	X-ray Photoelectron Spectroscopy (XPS)	69
3.3.5	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	70
3.3.6	Electrochemical measurements.....	71
	Reference.....	73
Chapter 4.....		75
4.1	Introduction	76
4.2	Materials preparation.....	77
4.3	Characterization methods	78
4.4	Principle outcomes	78
4.4.1	The electrochemical synthesis	78
4.4.2	CoMn LDH synthesized without N ₂ purging.....	79
4.4.3	Co ₉ S ₈ /Co ₃ O ₄ nano-heterostructure synthesized with N ₂ purging.....	83
4.4.4	Catalytic performance of CoMn LDH and Co ₉ S ₈ /Co ₃ O ₄ nano-heterostructure.....	87
	Reference.....	95
Chapter 5.....		99
5.1	Introduction	100
5.2	Materials preparation.....	101
5.3	Characterization methods.....	103
5.4	Principal outcomes.....	103
5.4.1	The electrochemical synthesis of CuNTs.....	103
5.4.2	The XPS study of dealloyed Fe-Co-Cu metal-(oxy)hydroxide.....	113
5.4.3	Electrochemical behavior of dealloyed Fe-Co-Cu metal-(oxy) hydroxide in 1M KOH	114
	Reference.....	121
Chapter 6.....		127
6.1	Introduction	128
6.2	Materials preparation	129
6.3	Principal outcomes.....	131

6.3.1 Electrochemical synthesis of copper nanoarrays	131
6.3.2 Synthesis of dealloyed FeCoNiCu.....	134
6.3.3 OER performance of dealloyed FeCoNiCu	136
6.4 Conclusion.....	136
References	138
Chapter 7.....	143
7.1 Conclusions	144
7.2 Future work	145
7.2.1 Porous FeCoNi (FCN)-dendritic FeCoCu	145
7.2.2 3D electrically reduced copper foam coated with Ni	146
7.3 Outcomes reflected in the original hypothesis.....	147

Table Captions

Table 4.1 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) results of CoOS-3 heterostructure after 1000 cycles

Table 4.2 Comparison of OER performance with other state-of-art electrocatalysts [S1-S7]

Table 5.1 Summary of Inductively coupled plasma mass spectrometry (ICP-MS) results (unit:cps)

Table 5.2 Summary of performance of previous FeCo based catalysts

Table 5.3 Summary of fitted results

Figure Captions

Figure 2.1 Interface and phase characterizations of Pt₃Ni₃ NWs-S. Representative (a) high-resolution TEM (HRTEM) image of Pt₃Ni₃ NWs-S and (b, c) the magnified HRTEM images recorded from regions b and c marked in a. The yellow dashed curve highlights the NiS_x particle on the surface of the Pt₃Ni NWs.

Figure 2.2 HAADF-STEM images of (a) Pt₃Ni₃ NWs/C-air and (b) Pt₃Ni₃ NWs/C-H₂. HAADF-STEM image and EDS elemental mappings of (c) Pt₃Ni₃ NWs/C-air and (d) Pt₃Ni₃ NWs/C-H₂. (e) HRTEM image of Pt₃Ni₃ NWs/C-air and (f) the magnified HRTEM image recorded from regions f marked in (e).

Figure 2.3 STM images (60 nm by 60 nm) and CV traces for (A) Pt(111), (B) Pt(111) with 2D Pt islands, and (C) Pt(111) modified with 3D Ni(OH)₂ clusters in 0.1 M KOH electrolyte. (D) HER activities for Pt(111), Pt-islands/Pt(111), and Ni(OH)₂/Pt(111) surfaces in alkaline solution (a, b, and c, respectively). Corresponding HER activities for Pt(111) and Pt-islands/Pt(111) electrodes in acid solutions (a' and b') are shown to emphasize large initial differences between kinetics of the HER in alkaline versus acid solutions. The inset shows XANES spectra for Ni(OH)₂ on Pt(111) shown for three different potentials: HER (−0.1 V), Hupd (0.1 V), and near OER (1.2 V). Also shown is the reference spectrum for Ni(OH)₂. No shift in the edge energy in XANES spectra between HER and Hupd regions is observed.

Figure 2.4 (a) Chemical state analysis of Ru, Co, and P components in pristine Ru, pristine CoP, Ru/CoP and RuCoP catalysts. The adsorption energies of (b) hydrogen, (c) water, and (d) OH on Ru, Ru/CoP and RuCoP catalysts. The dark pink, orange, dark green, white, and red spheres represent cobalt, phosphorus, Ru, hydrogen, and oxygen atoms, respectively.

Figure 2.5 Structural characterization and high-resolution transmission electron microscopy analysis of the Ru@C₂N catalyst. a, XRD pattern of Ru@C₂N. b, TEM image of Ru@C₂N. Inset: corresponding particle size distribution of the Ru nanoparticles. Scale bar, 20 nm. c, d, Atomic-resolution TEM image of Ru@C₂N (c) and corresponding FFT pattern (d). Scale bar, 1 nm. e, Electron energy-loss spectroscopy spectrum of Ru@C₂N. f, STEM image and STEM-EDS element mapping of Ru@C₂N. Scale bars, 20 nm. g, N₂ adsorption/desorption isotherms of Ru@C₂N. Top inset: corresponding pore size distribution.

Figure 2.6 (a,c,e) HAADF-STEM images and the (b,d,f) corresponding FFT patterns of Ru nanoparticles showing (a) fcc; (c) mixed fcc/hcp; and (e) hcp structure. The red and blue dots in panels a, c, e mark the typical atomic arrangements of fcc and hcp structures along different zone

axes. The green circles in panel d inset indicate the shared diffraction plans of the fcc and hcp structures.

Figure 2.7 SEM images of the as-synthesized a) Pd NPs and b) core/shell Pd/Fe₃O₄ NPs. c) XANES spectra of Pd K-edge Pd/Fe₃O₄ NPs and standard samples. The inset is the corresponding EXAFS $k^3\chi(R)$ spectra. d) XANES spectra of the Fe K-edge Pd/Fe₃O₄ NPs and standard samples. The inset is the corresponding EXAFS $k^3\chi(R)$ spectra.

Figure 2.8 (a) HRTEM image of RMoS₂Pd with clear fringes and (b) zoomed part highlighted in (a); the inset shows the arrangement of atoms in the 1T phase.

Figure 2.9 Nanostructured hydrogen-evolving cathode f-MWCNTs@Pd/TiO₂. (a) Schematic representation of the synthetic protocols yielding the f-MWCNTs@Pd/TiO₂ electrocatalysts. (b) STEM tomographic reconstruction of f-MWCNTs@Pd/TiO₂. Here the region of high density corresponding to the Pd particles is rendered with a violet mesh (raw data). The Pd particles are then localized by placing spherical markers centered in the regions of high density (yellow spheres). Scale bar, 100 nm. (c) General scheme for the HER proposed mechanism by f-MWCNTs@Pd/TiO₂ at neutral pH. Water absorption and dissociation occurs at the hydrophilic, porous, TiO₂ outer layer (blue shell), promoting the formation of Had (grey) intermediates on the catalytic Pd sites (black).

Figure 2.10 Schematic illustration for the preparation of N-MoxC@C HSs from Mo Ss with dicyandiamide at tunable temperature.

Figure 2.11 Synthetic route toward mNC-Mo₂C@rGO nanosheets through a strategy of interface self-assembly in solution.

Figure 2.12 (a) Schematic illustration of the formation mechanism of nanocrystalline M₃C (M: Fe, Co, Ni) on VA-GNRs. (b and c) SEM images of VA-GNRs with “teepee” structure. (d) Typical SEM image of M₃C-GNRs; (e-g) SEM images of M₃C (M: Fe, Co, Ni) NCs grown on the tips of VA-GNRs.

Figure 2.13 Schematic illustration showing the influence of different carbon precursors. Gaseous carbon precursor (for example, CH₄) and non-volatile solid carbon precursor (for example, CNT) may have different impacts on the chemical composition and microstructure of the carburization product.

Figure 2.14 Schematic illustration of heterostructure Ni₉S₈@MoS₂ hybrid

Figure 2.15 Schematic diagram of the fabrication procedure of NiS₂/MoS₂-RGO nanocomposites

Figure 2.16 a) Schematic illustration of the preparation of NiTe/NiS heterojunction nanoarrays. b) FESEM, c) TEM, and d) HRTEM images of the NiTe. e) FESEM, f) TEM, and g) HRTEM images of the NiTe/NiS. h–k) HAADF-STEM image and STEM-EDS mappings of NiTe/NiS.

Figure 2.17 Illustration of the fabrication of 3D-networked heterostructured Ni₂P–Ni₃S₂ HNAs/NF composites

Figure 2.18 a) XRD spectra of the bare NF, NiCoP/NF, NiFe LDH@NiCoP/NF, and NiFe LDH/NF. b) SEM image of the as-synthesized NiCoP/NF nanowires, where the inset shows a high-resolution image of the NiCoP nanowires. c) SEM image of the as-synthesized NiFe LDH@NiCoP/NF nanowires, where the inset shows a high-resolution image of the NiFe LDH@NiCoP nanowires. d) TEM image of an NiCoP nanowire. e) TEM image of an NiFe LDH@NiCoP nanowire. f) EDX mapping images of the NiFe LDH@NiCoP nanowire. g) HRTEM image of the NiFe LDH@NiCoP nanowire highlighting the interface between nanowire and nanosheets. h) SAD pattern of the interface of the NiFe LDH@NiCoP. i–k) XPS patterns of the Ni 2p_{3/2}, Co 2p_{3/2}, and P 2p for NiCoP/NF and NiFe LDH@NiCoP/NF, respectively.

Figure 2.19 (a, e, and h) SEM and (b, f, and i) TEM and (c, g, and j) HRTEM images of FeNiP/PG, FeNiP/GC/PG and FeNiP/RGO. (d) HAADF-STEM elemental mapping of FeNiP/PG. The insets in (a, e, and h) are the structural models of FeNiP/PG, FeNiP/GC/PG and FeNiP/RGO.

Figure 2.20 Schematic illustration of the synthesis process of CoSe₂/FeSe₂@C

Figure 2.21 (a, d) SEM and (b, e) TEM images, and (c, f) elemental mapping of (a–c) CoNiSe₂/NF and (d–f) CoNiSe₂@CoNi-LDHs/NF. In panel e, the defects (e.g., faultage, malposition, and interfaces) on CoNiSe₂@CoNi-LDHs are marked.

Figure 2.22 Schematic illustration for the formation of heterogeneous CoS₂/CoS porous nanosheets.

Figure 2.23 a) The schematic synthesis of the NiCo₂S₄/FeOOH heterostructure. Color scheme for chemical representation: red for Co, green for Ni, purple for Fe, blue for O, white for S, and grey for H. X-ray diffraction (XRD) patterns of b) precursor-2, c) different precursors for comparison, and d) NiCo₂S₄/Fe.

Figure 2.24 Crystal structures of (a) CoO and (b) Co₃O₄ (Navy blue, dark green and red balls indicate Co²⁺, Co³⁺, and O²⁻ ions, respectively).

Figure 2.25 SEM images of $\text{Co}_3\text{O}_4/\text{NF}$ (a), $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ -12 h (b), $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ -24 h (c) and $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ -36 h (d).

Figure 2.26 a) XRD patterns of CFP, CFP/ NiCo_2O_4 , CFP/ CuS , and CFP/ $\text{NiCo}_2\text{O}_4/\text{CuS}$. b) Low- and high-magnification (inset) SEM images of CFP/ NiCo_2O_4 . c) Low- and high-magnification (inset) SEM images of CFP/ $\text{NiCo}_2\text{O}_4/\text{CuS}$. d) HRTEM and TEM images (inset) of CFP/ $\text{NiCo}_2\text{O}_4/\text{CuS}$. e) SAED pattern of CFP/ $\text{NiCo}_2\text{O}_4/\text{CuS}$. f) SEM image and EDS elemental mapping images of S, Cu, C, Ni, Co, and O for CFP/ $\text{NiCo}_2\text{O}_4/\text{CuS}$

Figure 2.27 The schematic representation of cobalt hydroxide structure

Figure 2.28 (a) Schematic of the synthesis of $\text{Co}(\text{OH})_2/\text{SFM-NF}$. (b) XRD pattern of SFM, SFM-NF and $\text{Co}(\text{OH})_2/\text{SFM-NF}$. (c) Raman spectra of SFM-NF and $\text{Co}(\text{OH})_2/\text{SFM-NF}$ samples.

Figure 2.29 Schematic diagram for the fabrication of $\text{CoFe}@\text{NiFe}/\text{NF}$ architecture

Figure 3.1 Illustration of gas-assisted electrodeposition

Figure 3.2 Illustration of dealloying

Figure 3.3 Schematic illustration of image formation in TEM

Figure 3.4 Schematic illustration of major components of SEM

Figure 3.5 Schematic illustration of X-ray diffractometer

Figure 3.6 Schematic illustration of Bragg's law

Figure 3.7 Schematic illustration of energy levels

Figure 3.8 Schematic illustration of ICP-MS

Figure 3.9 Detailed explanation of cyclic voltammetry taking Fc as an example

Figure 3.10 A typical EIS diagram with R and C in parallel connection

Figure 4.1 Schematic illustration of electrochemical synthesis of Co-based electrocatalysts under different conditions

Figure 4.2 CV curves of electrodeposition: (a) without N₂ purging before or during electrodeposition; (b) 30 min rigorous N₂ purging (1 bar) before and mild N₂ purging (0.1 bar) during electrodeposition.

Figure 4.3 Characterization of a sample obtained without N₂ purging before or during electrodeposition: (a) SEM observation; (b) corresponding EDS spectrum; (c) TEM image and (inset) corresponding SAED; (d) HRTEM image and (inset) the FFT pattern of the square region; (e) STEM mapping and (f) XRD pattern.

Figure 4.4 SEM observation of the electrodeposited Ni foam without N₂ purging before or during the electrodeposition: a), b) low and c) high magnification image; d) SEM image and corresponding elemental mapping data

Figure 4.5 XPS spectra of electrodeposited Ni foam without N₂ purging before or during electrodeposition: (a) survey; (b) Co; (c) Mn and (d) O

Figure 4.6 Characterization of sample obtained with 30 min N₂ purging before electrodeposition and continuous but mild N₂ purging during the electrodeposition: (a) SEM observation; (b) corresponding XRD pattern; (c) low magnification TEM image and (inset) the SAED pattern; (d) the corresponding EDX; (e) HRTEM images (inset of c) the FFT pattern of the square region); (f) Inverse FFT (IFFT) image.

Figure 4.7 SEM observation of the electrodeposited Ni foam with N₂ purging before and during the electrodeposition: a), b) low and c) high magnification image; d) SEM image and corresponding elemental mapping data

Figure.4.8 XPS spectra of electrodeposited Ni foam with 30min rigorous N₂ purging (1 bar) before and mild N₂ purging (0.01 bar) during electrodeposition: (a) survey; (b) Co; (c) S and (d) O

Figure 4.9 The cross-section of the electrodeposited Ni foam a) without N₂ purging before or during electrodeposition, b) 30 min rigorous N₂ purging (1 bar) before and mild N₂ purging (0.1 bar) during electrodeposition

Figure 4.10 Performance test of electrodeposited Ni foams prepared by different under different conditions: (a) Nyquist plots and LSV curves for HER, (b) corresponding Tafel slopes and (c) stability performance in 1 M KOH (without i-R compensation); (d) LSV curves for OER, (e) corresponding Tafel slopes and (f) stability test in 1 M KOH (without i-R compensation).

Figure 4.11 OER performance of electrodeposited Ni (CoOS-3) after stability test ($100\text{mA}\cdot\text{cm}^{-2}$, 12h): a) Nyquist plot, b) Linear scan voltammetry curves, c) low magnification SEM image d) high magnification image

Figure 4.12 HER performance of electrodeposited Ni (CoOS-3) after stability test ($10\text{mA}\cdot\text{cm}^{-2}$, 12h): a) Nyquist plot, b) Linear scan voltammetry curves, c) low magnification SEM image d) high magnification image

Figure 4.13 Cyclic voltammograms (CV) of (a) CoOS-1, (b) CoOS-2, (c) CoOS-3, (d) CoOS-4, (e) CoMn-LDH and (f) the anodic charging current measured at 1.15 V vs Ag/AgCl plotted against different scan rates

Figure 4.14 XRD pattern CoOS-3 heterostructure after 1000 cycles

Figure 4.15 TEM characterization of CoOS-3 heterostructure after 1000 cycles: (a) TEM image and corresponding SAED image; (b) HRTEM image and corresponding FFT image

Figure 4.16 XPS characterization of CoOS-3 heterostructure after 1000 cycles: (a) survey; (b) Co; (c) S and (d) O

Figure 5.1 Schematic illustration of electrochemical synthesis of hierarchical CS FeCoCu@Cu NTs

Figure 5.2 SEM images and corresponding XRD patterns of Cu foam after electrooxidation in 3M NaOH solution for different times: (a) 100 s; (b) 350 s; (c) 700 s; (d) 960 s; (e) 1200 s

Figure 5.3 SEM observation of pure Cu foam after pretreatment in 37% HCl for 10 min: (a), (b) and (c) SEM images of Cu foam in different magnifications; (d) and (e): EDS elemental mapping images; (f) corresponding EDS spectrum

Figure 5.4 TEM image and corresponding Selected Area Electron Diffraction pattern of $\text{Cu}(\text{OH})_2$ nanotube

Figure 5.5 SEM images and corresponding XRD patterns of (a1-a4): $\text{CuO}_x\text{Cu}_2\text{O}$ nanotube array; (b1-b4): Cu nanotube array (CNTA)

Figure 5.6 FeCoCu@Cu NTs (3min): SEM images (a-c) and corresponding XRD pattern (d); TEM images (e-f), HRTEM image (g) and corresponding FFT image (h); STEM EDX elemental mapping (i-l)

Figure 5.7 SEM EDS mapping images of CNTA FeCoCu

Figure 5.8 The STEM EDS Spectrum of CNTA FeCoCu

Figure 5.9 Characterization of CS FeCoCu@Cu NTs: (a-c) SEM images with different magnifications; (d) corresponding XRD pattern; (e-g) TEM images with different magnifications; (h) corresponding FFT pattern; (I-M) STEM EDX mapping images

Figure 5.10 EDX Mapping of CuNTA_FeCoCu 3(min) after selective corrosion

Figure 5.11 High resolution XPS spectra of Fe 2p (a), Co 2p (b), Cu 2p (c) and O 1s (d) for FeCoCu@Cu NTs

Figure 5.12 High resolution XPS spectra of Fe 2p (a), Co 2p (b) and O 1s (c) for CS FeCoCu@Cu NTs

Figure 5.13 Figure 7 High resolution XPS spectra of Fe 2p (a), Co 2p (b), and O 1s (c) for CS FeCoCu@3D CNTA after stability test (12 h)

Figure 5.14 Electrochemical characterization after dealloying in 1M KOH: (a) OER performance; (b) and (c) corresponding overpotential and Tafel slope; (d) EIS spectra; (e) equivalent circuits used to fit the EIS spectra in (d); (f) fitted EIS spectra; (g) summary of charge transfer resistance (R_{ct}) calculated from fitting; (h) stability test for CS FeCoCu@Cu NTs; (i) OER performance after the stability test

Figure 6.1 SEM images Cu foam after electrooxidation in 3M NaOH solution (a-a2); after annealing at 200 C in Ar for 2h (b-b2).

Figure 6.2 XRD patterns of Cu foam after electrooxidation in 3M NaOH solution (a-a2); after annealing at 200 C in Ar for 2h (b-b2).

Figure 6.3 SEM images (a,b,c) and corresponding XRD patterns (d) of Cu foam after electrochemical reduction.

Figure 6.4 SEM images (a,b,c) of electrodeposited FeCoNiCu

Figure 6.5 SEM images with different magnifications of dealloyed FeCuNiCu on Cu foam after electrodeposition.

Figure 6.6 (a) XRD pattern of FeCuNiCu on Cu foam after electrodeposition; (b) TEM images with corresponding FFT pattern.

Figure 6.7 Electrochemical characterization after selective corrosion: (a) OER performance; (b) EIS spectra; (c) stability test for 12 hrs.

Figure 7.1 Porous FCN on Ni foam

Figure 7.2 Porous FCN-dendritic FeCoCu

Figure 7.3 E-reduced copper foam coated with Ni

Abbreviations

ANSTO	Australian Nuclear Science and Technology Organization
ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BSE	Backscattered Electron
BVS	Bond Valence Sum
EDS	Energy Dispersive X-ray Spectroscopy
EPMA	Electron Probe Microanalysis
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
HER	Hydrogen Evolution Reaction
LSV	Linear Sweep Voltammetry
LDH	Layered Double Hydroxides
OER	Oxygen Evolution Reaction
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XANES	X-ray Absorption Near Edge Structure
Z	Atomic Number

Chapter 1

Introduction

This chapter mainly focuses on the overview of the thesis, starting with the proposition of the hypotheses and the introduction of corresponding objectives and scope. Subsequently, the separate overview for each chapter is also presented, followed by the summary of major results that the thesis is obtained.

1.1 Hypothesis/Problem Statement

Transition metals have been widely used as electrocatalysts in energy-related fields such as water splitting, CO₂ reduction and methanol and ethanol oxidation[1-3] due to their high-efficiency and earth-abundance. However, their performances in real applications is still not competitive when compared to traditional precious electrocatalysts such as platinum (Pt) and palladium (Pd)[4, 5]. In this case, various strategies have been employed to further improve their performances. Recently intensive research effort has been devoted to the phase engineering of transition-metal electrocatalysts[6-8]. There are numerous ways including alkali metal intercalation[9, 10] and electron beam irradiation that have been used to engage phase engineering[11]. However, both methods mentioned above are not suitable for large-scale applications since they usually require special equipment in addition to the high energy consumption. Therefore, the hypothesis proposed based on problems above is stated below:

Electrochemical synthesis is used in combination with gas purging to achieve controllable phase engineering. The gas purging is assumed to assist the electrodeposition with the control of the specific phase formation. The method is quite economic and efficient, suitable for large-scale application in industry.

In addition to gas-purging assisted electrodeposition, there is also alternative way to further improve the performance of electrocatalysts. Usually there are two effective ways to promote the performance of electrocatalysts. The first is to increase the number of active sites exposed to the electrolyte and the second is to promote the intrinsic electrocatalytic property of electrocatalysts. Electrochemical dealloying enables to achieve both targets. It is essentially a selective corrosion process of the alloy where the electrochemically more active element will be dissolved and removed away. The more noble element will remain and diffuse through the interface. Finally, a porous core-shell structure with numerous pores is formed. In this structure, many more active sites could be created and exposed to electrolytes. Furthermore, the intrinsic electrocatalytic property of electrocatalysts is also significantly improved due to the formation of different phases on the interface. The thesis employs electrochemical dealloying to synthesize the highly efficient electrocatalysts (Fe-

Co-Cu metal-(oxy)hydroxide) with numerous pores and phase boundaries. Phase engineering could be easily achieved through electrochemical dealloying. The hypothesis is that the porous core-shell structure ought to present the long-term stability and be suitable for practical application.

In addition to Fe-Co-Cu metal-(oxy)hydroxide, the performance of electrocatalysts can be further improved by the addition of Ni into the dealloyed Fe-Co-Cu metal-(oxy)hydroxide, forming the three-phase synergistic system. However, the addition of Ni needs to be very careful as it may be harmful to the original synergistic two-phase system and the new synergistic three-phase system may not be formed in the end. Besides, the newly formed synergistic three-phase system may be vulnerable to the harsh environment in reality. Considering this hypothesis based on the problem stated above, Fe-Co-Ni-Cu metal-(oxy)hydroxide is finally obtained through electrochemical dealloying which affords the excellent performance and satisfies the practical application.

1.2 Objectives and Scope

The major objective of this thesis is to fabricate highly efficient and robust electrocatalysts through electrochemical phase engineering. The synthesis used here is electrodeposition which is efficient and economic. The detailed objectives are listed below according to the hypotheses mentioned above.

First, the $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure was prepared through the gas-purging assisted electrodeposition. The composition and morphology of this heterostructure can be finely tuned through the control of gas purging. The performance dependence of this heterostructure on its composition and morphology will be studied to unveil their relationship. In addition, the formation mechanism of this heterostructure is also investigated through the electrochemical method such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) and it was found that the hydroxide ions (OH^-) play a key role in the formation of $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure.

Second, the phase engineering can also be achieved by simpler method-electrochemical dealloying. The core-shell structure with numerous pores can be obtained through selective corrosion of the electrochemically more active element in the alloy and the diffusion of noble elements on the interface. Therefore, much more active sites can be initiated on the surface of this porous core-shell structure which are exposed to the electrolyte. Besides, the intrinsic property of this electrocatalyst can also be significantly promoted at the same time due to the formation of synergistic two-phase system. Herein, the synergistic two-phase system consists of two phases-iron cobalt (oxy)hydroxide which is highly efficient for water splitting.

Third, the performance of this electrocatalyst can be further improved by the addition of another element-Ni forming the synergistic three-phase system, more advanced than the synergistic two-phase system.

1.3 Dissertation overview

The thesis addresses how to achieve phase engineering through efficient and economic method-gas-purging assisted electrodeposition. Meanwhile, the thesis also shows how to obtain highly efficient electrocatalyst through simple electrochemical dealloying, which does not require additional gas purging. Finally, the thesis presents how to further improve the performance of electrocatalyst by the addition of Ni, forming the synergistic three phase system.

The study of phase engineering through electrodeposition contributes to the study of fabrication of highly efficient and low-cost electrocatalysts for water splitting. Besides, the mechanism behind phase engineering is also revealed through electrochemical methods such as cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

Chapter 1 offers a reasoning for the thesis and provides a summary of goals and scope.

Chapter 2 outlines a literature review about the study of phase engineering of transition

metal based electrocatalysts, especially the current progress on the study of Fe, Co and Ni based electrocatalysts for phase engineering.

Chapter 3 describes the reasoning of various methods used in this thesis. Besides, it also introduces the underlying principles of these methods for characterization and data analysis.

Chapter 4 introduces the details of gas-purging assisted synthesis of $\text{Co}_3\text{O}_4\text{-Co}_9\text{S}_8$ heterostructure, followed by revelation of the mechanism behind the formation of this heterostructure.

Chapter 5 introduces the more advanced synthesis method to fabricate the highly efficient Fe-Co-Cu metal-(oxy)hydroxide which is also economic enough for practical application.

Chapter 6 elaborates the effect of addition of another element-Ni to the synergistic two-phase system, further improving the electrochemical performance.

Chapter 7 summarizes the major points of the whole thesis and provides the perspectives. Besides, the opportunities and further work that could be finished in the near future is also summed up.

1.4 Findings and Outcomes/Originality

There are several new findings for this research:

1. The gas-purging assisted electrodeposition has been proven to be very effective in fine tuning the composition and morphology of the electrocatalyst, thus maximizing its performance towards water splitting. The formation mechanism of $\text{Co}_3\text{O}_4\text{-Co}_9\text{S}_8$ heterostructure is also revealed to be closely related to the generation of hydroxide ions (OH^-).
2. The performance of electrocatalysts can be further improved by simplified electrochemical dealloying which is economic and efficient. The electrocatalyst thus obtained possesses core-shell structure with numerous pores, which is quite beneficial

for increasing the number of intrinsic active sites.

3. The addition of Ni to the synergistic two-phase system has successfully led to the formation of synergistic three-phase system which is more electrocatalytically active when compared to the two-phase system.

References

- [1] M. Asadi, K. Kim, C. Liu, A.V. Addepalli, P. Abbasi, Nanostructured transition metal dichalcogenide electrocatalysts for CO₂ reduction in ionic liquid, *Electrochemistry*, 353 (2016) 467-470.
- [2] D. Li, J. Shi, C. Li, Transition-Metal-Based Electrocatalysts as Cocatalysts for Photoelectrochemical Water Splitting: A Mini Review, *Small*, 14 (2018) e1704179.
- [3] A.N. Vyas, G.D. Saratale, S.D. Sartale, Recent developments in nickel based electrocatalysts for ethanol electrooxidation, *International Journal of Hydrogen Energy*, 45 (2020) 5928-5947.
- [4] L. Han, S. Dong, E. Wang, Transition-Metal (Co, Ni, and Fe)-Based Electrocatalysts for the Water Oxidation Reaction, *Advanced materials*, 28 (2016) 9266-9291.
- [5] G.M. Alvarenga, H.M. Villullas, Transition metal oxides in the electrocatalytic oxidation of methanol and ethanol on noble metal nanoparticles, *Current Opinion in Electrochemistry*, 4 (2017) 39-44.
- [6] D. Voiry, A. Mohite, M. Chhowalla, Phase engineering of transition metal dichalcogenides, *Chemical Society reviews*, 44 (2015) 2702-2712.
- [7] D. Voiry, A. Goswami, R. Kappera, C. e Silva Cde, D. Kaplan, T. Fujita, M. Chen, T. Asefa, M. Chhowalla, Covalent functionalization of monolayered transition metal dichalcogenides by phase engineering, *Nat Chem*, 7 (2015) 45-49.
- [8] D. Wang, X. Zhang, S. Bao, Z. Zhang, H. Fei, Z. Wu, Phase engineering of a multiphasic 1T/2H MoS₂ catalyst for highly efficient hydrogen evolution, *Journal of Materials Chemistry A*, 5 (2017) 2681-2688.
- [9] A.N. Enyashin, G. Seifert, Density-functional study of Li_xMoS₂ intercalates (0 ≤ x ≤ 1), *Computational and Theoretical Chemistry*, 999 (2012) 13-20.
- [10] M. Kan, J.Y. Wang, X.W. Li, S.H. Zhang, Y.W. Li, Y. Kawazoe, Q. Sun, P. Jena, Structures and Phase Transition of a MoS₂ Monolayer, *The Journal of Physical Chemistry C*, 118 (2014) 1515-1522.
- [11] Y.C. Lin, D.O. Dumcenco, Y.S. Huang, K. Suenaga, Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS₂, *Nature nanotechnology*, 9 (2014) 391-396.

Chapter 2

Literature Review

This chapter provides the literature review on the study of interface engineering of cobalt-based heterostructures by using electrochemical synthesis. Recent progress on the development of noble-metal based heterostructures obtained through interface engineering is discussed first. Afterwards, noble-metal free based heterostructures is also summarized. Finally, a detailed analysis of cobalt-based heterostructures is conducted. The questions regarding the thesis subject are also answered here.

2.1 Overview

Global energy crisis has long been the big challenge that the society is facing and there is an urgent need to solve this problem nowadays due to a series of side effects including global warming and environmental pollution it brought[1]. One of the key factors in solving this problem lies in the replacement of traditional fossil fuels with renewable energy including solar energy, hydro power, wind energy and biomass energy[2-4], all of which are green and carbon-free energy sources. However, there are still some intrinsic drawbacks like intermittence for all the renewable energy sources mentioned above to overcome in the practical application[5, 6]. In this case, other techniques especially water splitting (including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)) can be quite competitive in avoiding the disadvantages[7, 8]. Water splitting has proven to be advantageous as an energy storage technique and the final product of reaction is hydrogen and oxygen, both of which are carbon-free and environmentally friendly[9, 10]. Furthermore, as a fuel with high energy density, hydrogen is also widely used in various fields such as fuel cells and aviation[11, 12].

The large-scale application of water splitting largely depends on the development of low-cost, efficient and reliable electrocatalysts for the reaction[13, 14]. Therefore, intensive research effort has been devoted to this field[15-17]. Traditionally noble metals and noble metals oxides have been used as benchmark electrocatalyst for water splitting[18]. Nevertheless, the scarcity and reliability of electrocatalysts have hindered their industrial-scale application[19, 20]. In this case, a variety of strategies have been proposed and interface engineering has emerged as one of the most promising methods since it can promote the efficiency and reliability of electrocatalysts simultaneously[21, 22].

2.2 Interface engineering of noble-metal based heterostructures

The general definition of heterostructure can be defined as follows: a unique structure formed by stacking different components or compositions[23]. Consequently, abundant interfaces will be formed on the contact area of different

components. Although there is tremendous research effort dedicated to the development of non-noble-metal based electrocatalysts, the noble-metal (including Pt, Ru and Ir) based electrocatalysts remains to be the state-of-art catalysts due to their excellent efficiency[24]. However, their practical application is quite limited because of the high cost and low reliability in working conditions which is usually harsh environment. In this case, heterostructured interface engineering has been proposed as an effective strategy to promote electrocatalysts' performance while significantly reducing the mass loading at the same time[23].

2.2.1 Interface engineering of Platinum (Pt)-based heterostructures

One of the commonly used methods for the heterostructured interface engineering is the combination of noble metals with proper supports such as non-noble metals or other functional materials[25]. When the noble metal is connected with another metal forming the heterostructure, this kind of heterostructure can be classified as noble-metal-based metal/metal heterojunction. Besides, the heterostructure can be classified as metal/metal compound heterojunction when the noble metal is combined with metal compound. Finally, there is another type of heterojunction which is metal/organic molecule which is comprised of metal and organic molecule[26].

In order to maximize the effect of interface engineering strategy, reasonable selection of heterostructured component is quite important. The specific method used to synthesize the heterostructure is also crucial for industrial application in which a facile, cost-effective, and efficient method is highly desired. Pt/PtTe NWs heterojunction, for instance, was successfully synthesized by Yu et al[27]. The method used for the synthesis is facile "precursor solution-aging". In detail, Te was used as a template during the Pt nanoparticles growth. In combination with the coexistence of PtCl_4^{2-} ions and Pt_mCl_n complexes, Pt NPs can be controllably formed on the PtTe nanowires, generating abundant interface structures that function as active sites during catalytic reaction. Besides, it can also act as ideal

location for charge transfer. Based on the various characterization including in situ UV-vis spectroscopies as well as DFT calculations, it is concluded that the surface charge polarization has greatly contributed to the significantly enhanced electrocatalytic activity for oxygen reduction. Wang et al. also prepared platinum-nickel/nickel sulfide heterojunction through direct sulfuring of platinum-nickel nanowires, thus forming abundant interfaces between these two different components (see Figure 2.1)[24]. Consequently, only a very small overpotential (70 mV) is required to reach the current density of $37.2 \text{ mA}\cdot\text{cm}^{-2}$, remarkably outperforming over the commercial Pt/C. This significant promotion is believed to be achieved by the synergistic effect between the two different components comprising the heterojunction. According to the DFT calculations, the water dissociation is greatly facilitated by NiS, which is beneficial for generating H^+ . Besides, the production of H_2 is accelerated by the existence of Pt_3Ni . Similarly, interface engineered Pt-Ni NWs was also prepared by Wang et al. through simple post annealing in a controllable way. The Pt-Ni NWs obtained (see Figure 3.2) has demonstrated excellent HER performance, delivering the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the overpotential of 40 mV in alkaline media. This superior performance is considered to originate from the unique phase/interface structures generated by interface engineering[28].

In addition to Pt-Ni NWs, composite materials were prepared by Ram et al. who directly grew $\text{Ni}(\text{OH})_2$ clusters on the modified Pt(111) surface (denoted as $\text{Ni}(\text{OH})_2/\text{Pt-islands}/\text{Pt}(111)$) (see Figure 2.3)[29]. The rationale behind this design is that $\text{Ni}(\text{OH})_2$ as a metal hydroxide facilitates the dissociation of water while the modified metal (Pt-island/Pt(111) in this case) is beneficial for hydrogen adsorption. The electrocatalytic performance of the heterojunction has been significantly improved when compared to the single component, highlighting the importance of heterojunction. In detail, the synergistic effect between $\text{Ni}(\text{OH})_2$ and Pt is considered to have greatly contributed to the remarkable promotion in reaction rate of HER.

Figure 2.1 Interface and phase characterizations of Pt_3Ni_3 NWs-S. Representative (a) high-resolution TEM (HRTEM) image of Pt_3Ni_3 NWs-S and (b, c) the magnified HRTEM images recorded from regions b and c marked in a. The yellow dashed curve highlights the NiS_x particle on the surface of the Pt_3Ni NWs.

Figure 2.2 HAADF-STEM images of a) Pt_3Ni_3 NWs/C-air and b) Pt_3Ni_3 NWs/C-H2. HAADF-STEM image and EDS elemental mappings of c) Pt_3Ni_3 NWs/C-air and d) Pt_3Ni_3 NWs/C-H2. e) HRTEM image of Pt_3Ni_3 NWs/C-air and f) the magnified HRTEM image recorded from regions f marked in (e).

Figure 2.3 STM images (60 nm by 60 nm) and CV traces for (A) Pt(111), (B) Pt(111) with 2D Pt islands, and (C) Pt(111) modified with 3D Ni(OH)₂ clusters in 0.1 M KOH electrolyte. (D) HER activities for Pt(111), Pt-islands/Pt(111), and Ni(OH)₂/Pt(111) surfaces in alkaline solution (a, b, and c, respectively). Corresponding HER activities for Pt(111) and Pt-islands/Pt(111) electrodes in acid solutions (a' and b') are shown to emphasize large initial differences between kinetics of the HER in alkaline versus acid solutions. The inset shows XANES spectra for Ni(OH)₂ on Pt(111) shown for three different potentials: HER (−0.1 V), Hupd (0.1 V), and near OER (1.2 V). Also shown is the reference spectrum for Ni(OH)₂. No shift in the edge energy in XANES spectra between HER and Hupd regions is observed.

2.2.2 Interface engineering of Ruthenium (Ru)-based heterostructures

Ruthenium (Ru) as noble metal is much cheaper than platinum (Pt). Therefore, the development of Ru-based electrocatalysts to replace platinum (Pt)-based electrocatalysts is highly desired and intensive research interest has thus been aroused. Xu et al. has successfully prepared two types of ruthenium-based heterostructures: ruthenium/cobalt phosphide (Ru/CoP) and ruthenium cobalt phosphide (RuCoP) (see Figure 2.4)[30]. As expected, the electrocatalytic performance is significantly promoted. The reason behind this remarkable improvement is followings: (1) the number of active sites is greatly increased through the formation of heterostructure; (2) the existence of numerous defects

and strain also contributes to the enhancement of electrocatalytic activity; (3) the effect of electronic coupling plays a major role in the performance promotion.

Javeed et al. also prepared ruthenium-based heterostructure for HER through polycondensation reaction followed by annealing (see Figure 2.5)[31]. In detail, the heterojunction (Ru@CN) is comprised of ruthenium (Ru) and nitrogen-doped holey carbon (CN). It also has demonstrated excellent HER performance, delivering the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the overpotential of 22 mV, which is superior to other related catalysts including Ni@C₂N, Pt@C₂N and commercial Pt/C. This remarkable improvement is attributed to the enhanced attraction to H₂O, which will substantially increase the H₂O capture rate. Consequently, the process of H₂O dissociation will become much easier, greatly facilitating the reaction kinetics.

Similarly, anomalously structured Ru/C₃N₄/C heterostructure was synthesized by Zheng et al. through solution-based freeze-drying followed by annealing(see Figure 2.6)[32]. The heterojunction thus obtained has demonstrated excellent electrocatalytic activity, delivering the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at a very small overpotential of 79 mV in alkaline media. This performance is superior to that of all the precious metals including Pt in the same conditions. The remarkable enhancement in performance is considered to come from the formation of anomalous Ru nanoparticles in fcc phase. In details, Pt has thermodynamically demonstrated the ideal free energy of hydrogen adsorption ($\Delta G_{H^*}^{Pt}$) which is near zero. This is in good agreement with its excellent performance in acidic solution, in which the HER proceeds through the Heyrovsky step. However, Ru/C₃N₄/C heterostructure has displayed superior electrocatalytic activity than Pt in alkaline media, which is mainly due to the different pathway HER proceeds. In alkaline media, the dissociation of water to generate protons is a critical reaction in Volmer step:

For Pt, this step is kinetically slow due to the large energy barrier on its surface. In contrast, the Ru surface has demonstrated much smaller energy barrier, remarkably promoting the reaction kinetics of water dissociation.

Figure 2.4 (a) Chemical state analysis of Ru, Co, and P components in pristine Ru, pristine CoP, Ru/CoP and RuCoP catalysts. The adsorption energies of (b) hydrogen, (c) water, and (d) OH on Ru, Ru/CoP and RuCoP catalysts. The dark pink, orange, dark green, white, and red spheres represent cobalt, phosphorus, Ru, hydrogen, and oxygen atoms, respectively.

Figure 2.5 Structural characterization and high-resolution transmission electron microscopy analysis of the Ru@C₂N catalyst. a, XRD pattern of Ru@C₂N. b, TEM image of Ru@C₂N. Inset: corresponding particle size distribution of the Ru nanoparticles. Scale bar, 20 nm. c, d, Atomic-resolution TEM image of Ru@C₂N (c) and corresponding FFT pattern (d). Scale bar, 1 nm. e, Electron energy-loss spectroscopy spectrum of Ru@C₂N. f, STEM image and STEM-EDS element mapping of Ru@C₂N. Scale bars, 20 nm. g, N₂ adsorption/desorption isotherms of Ru@C₂N. Top inset: corresponding pore size distribution.

Figure 2.6 (a,c,e) HAADF-STEM images and the (b,d,f) corresponding FFT patterns of Ru nanoparticles showing (a) fcc; (c) mixed fcc/hcp; and (e) hcp structure. The red and blue dots in panels a, c, e mark the typical atomic arrangements of fcc and hcp structures along different zone axes. The green circles in panel d inset indicate the shared diffraction plans of the fcc and hcp structures.

2.2.3 Interface engineering of Palladium (Pd)-based heterostructures

Liao et al. has synthesized Pd/FeO_x(OH)_{2-2x} heterostructure (see Figure 2.7) NPs through the chemical reduction followed by electrochemical cycling[33]. The heterostructure thus obtained possesses core/shell structure. Besides, electrochemical test in alkaline media has shown that it is highly active towards HER, which also exceeds the corresponding performance of commercial Pt/C and Pd/C. In the heterostructure obtained, FeO_x(OH)_{2-2x} shell is proven to facilitate the dissociation of water in alkaline media. In addition, the Pd core is beneficial for the H recombination. In this case, the performance of this heterostructure is determined by the coverage balance of Pd and FeO_x(OH)_{2-2x}, which will reach the maximum performance at the FeO_x(OH)_{2-2x} coverage of 40%.

Pandey et al. also synthesized RGO/MoS₂/Pd heterostructure (see Figure 2.8) for overall water splitting in alkaline media[34]. The heterojunction obtained has demonstrated excellent electrocatalytic activity towards both HER and OER. For HER, it can deliver the current density of 10 mA·cm⁻² at the small overpotential of 86 mV. The corresponding value for OER is 245 mV. The significantly improved performance is considered to originate from the synergistic effect between RGO/MoS₂ and Pd nanoparticles anchored on it. To be specific, the structural formation of 1T MoS₂ with plentiful of edge sites and S vacancies can greatly improve the HER kinetics. In addition, the small charge transport resistance also accelerates the HER process.

Similarly, a palladium/titanium dioxide supported on functionalized multi-walled carbon nanotubes f-MWCNTs@Pd/TiO₂ heterostructure has been successfully fabricated by Giovanni et al., see Figure 2.9[35]. This heterostructure possesses a unique hierarchical structure with co-axial arrangement. Consequently, it has shown excellent HER performance which is superior to that of state-of-the-art electrocatalysts. This remarkable performance is attributed to the merging of individual components. To the specific, the hydrophilic nature of TiO₂ layer, together with existence of abundant OH groups, have counterbalanced the hydrophobic nature of f-CNTs. Besides, it is also beneficial for water adsorption and dissociate reactions. On the other hand, the conductive nanocarbon tube core will also facilitate the electron transfer as well as the mass transfer.

Figure 2.7 SEM images of the as-synthesized a) Pd NPs and b) core/shell Pd/Fe₃O₄ NPs. c) XANES spectra of Pd K-edge Pd/Fe₃O₄ NPs and standard samples. The inset is the corresponding EXAFS $k^3\chi(R)$ spectra. d) XANES spectra of the Fe K-edge Pd/Fe₃O₄ NPs and standard samples. The inset is the corresponding EXAFS $k^3\chi(R)$ spectra.

Figure 2.8 (a) HRTEM image of RMoS2Pd with clear fringes and (b) zoomed part highlighted in (a); the inset shows the arrangement of atoms in the 1T phase.

Figure 2.9 Nanostructured hydrogen-evolving cathode f-MWCNTs@Pd/TiO₂. (a) Schematic representation of the synthetic protocols yielding the f-MWCNTs@Pd/TiO₂ electrocatalysts. (b) STEM tomographic reconstruction of f-MWCNTs@Pd/TiO₂. Here the region of high density corresponding to the Pd particles is rendered with a violet mesh (raw data). The Pd particles are then localized by placing spherical markers centered in the regions of high density (yellow spheres). Scale bar, 100 nm. (c) General scheme for the HER proposed mechanism by f-MWCNTs@Pd/TiO₂ at neutral pH. Water absorption and dissociation occurs at the hydrophilic, porous, TiO₂ outer layer (blue shell), promoting the formation of Had (grey) intermediates on the catalytic Pd sites (black).

2.3 Interface engineering of non-noble metal based heterostructures

2.3.1 Interface engineering of Transition Metal Carbide (TMC)/carbon-based heterostructures

Interface engineering is a key factor in promoting the electrocatalytic activity and the major reason can be ascribed to the fundamental mechanism underlying it[36]. First, the number of active sites can be significantly increased with the formation of abundant interfaces. Secondly, the electronic structure can also be finely tuned due to the charge redistribution.

Finally, the energy barrier of different reaction intermediates can be reduced or optimized on the interfaces. Transition metal carbides (TMCs) have attracted considerable research interest recently due to their unique physiochemical properties which make them efficient catalysts towards water splitting[37]. For instance, TMCs usually possess precious-metal-like electronic structure, rendering them intrinsic catalytic activities like Pt-based catalysts[38]. In addition, they have demonstrated good electrical conductivity as well as corrosion resistance which gives them excellent durability in electrolyte. Until now, numerous carbon-based materials have been incorporated to the TMCs to form various heterostructures with excellent catalytic activity[39-47]. For example, graphene[48, 49], reduced graphene oxide (rGO)[47, 50], carbon nanotubes (CNTs)[51, 52] including single-walled nanotubes and multi-walled nanotubes and porous carbon[40, 53] have all been successfully combined with TMCs to form heterostructures with unique physical and chemical properties.

As a typical transition metal, molybdenum (Mo) has also displayed Pt-like d-electrons structure[54]. Therefore, its derivatives including molybdenum oxide[55], molybdenum carbide[43], molybdenum sulfide[56] have been reported as highly active catalysts for water splitting. Among them, molybdenum carbide (Mo_xC) has stood out as one of the most promising candidates due to its unique properties including high electrical conductivity and Pt-like d-band electronic density[57]. In this case, intensive research efforts have been dedicated to the development of Mo_xC -based catalysts. For instance, Xiong et al. has successfully synthesized the carbon-wrapped molybdenum carbide heterophase sheets ($\text{N-Mo}_x\text{C}@\text{C HSs}$)(see Figure 2.10)[58]. The heterophase consist of $\gamma\text{-MoC}$ and $\beta\text{-Mo}_2\text{C}$, both of which are highly active for HER. As expected, the heterostructure thus obtained has shown desirable HER performance in acidic media, delivering the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the small overpotential of 172 mV. The corresponding Tafel slope is only 60 mV dec⁻¹, indicating the remarkably enhanced reaction kinetics. This excellent catalytic performance is ascribed to the formation of abundant interfaces generated through the interface engineering, which will significantly increase the number of active sites exposed to the electrolyte. The unique design strategy

of the heterostructure also enables short diffusion distance and facilitated charge transfer channels. To be specific, a quadplex synergistic effect is summarized as follows:

- (1) The intrinsic activity of Mo_xC can be greatly promoted due to the synergistic effect between the $\gamma\text{-MoC}$ and $\beta\text{-Mo}_2\text{C}$ phases.
- (2) The synergistic effect between Mo_xC and N-doped C shell can significantly increase the number of active sites as well as the conductivity of Mo_xC .

Similarly, carbon/ Mo_2C /reduced graphene oxide nanohybrids ($\text{mNC-Mo}_2\text{C}@r\text{GO}$) were also prepared by Hou et al. through self-assembly approach (see Figure 2.11)[59]. The nanohybrids thus obtained have displayed excellent catalytic activity towards HER in alkaline media, delivering the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the small overpotential of 95 mV. The corresponding Tafel slope is only 49.8 mV/dec, suggesting the fast reaction kinetics. After detailed characterization and analysis, the highly active activity is attributed to the strong interaction between Mo_2C and N-doped carbon matrix, which will significantly improve the intrinsic activity of the heterostructure through the formation of numerous interfaces which act as active sites.

In addition to molybdenum-based carbides, Iron, cobalt, and nickel-based carbides have also been investigated as potential candidates for active catalysts. For instance, Fan et al. has prepared M_3C (M: Fe, Co, Ni) supported on vertically aligned graphene nanoribbons (VA-GNRs) through hot filament chemical vapor deposition (HF-CVD) approach (see Figure 2.12)[49]. The M_3C -VA-GNRs thus obtained shows a large cathodic current density as well as small Tafel slope at small overpotential. This remarkably enhanced electrocatalytic activity is attributed to the strong interaction between M_3C and GNR. In detail, the electronic configuration is redistributed due to the unique host-electronic interaction, which will accelerate the reaction kinetics and facilitate a fast electron transfer. In addition, the close interconnection between M_3C and GNR guarantees the homogeneous distribution of M_3C NCs, thus maintaining the high exposure of active sites to the electrolyte.

Apart from these popular transition metal carbides mentioned above, the unpopular tungsten carbide (W_2C) has also been studied as an alternative to the Pt-based catalysts[52]. It was reported by Gong et al. that the ultrasmall (sub-2 nm) and phase-pure W_2C nanoparticles are anchored on the multi-walled carbon nanotubes (MWCNTs) by selectively choosing MWCNTs as the solid carbon source (see Figure 2.13). There are several obvious advantages by choosing MWCNTs as the carbon precursor. Firstly, the formation of W_2C phase instead of WC is favored due to the carbon-deficient environment resulting from the slow diffusion of carbon. Secondly, the extensive coking and sintering of products can also be avoided. Consequently, the catalyst (W_2C /MWCNTs) thus obtained has shown outstanding electrocatalytic activity. The thesis first uses electrochemical synthesis. The thesis first uses electrochemical synthesis. The thesis first uses electrochemical synthesis. The thesis first uses electrochemical synthesis towards HER, delivering the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 123 mV.

Figure 2.10 Schematic illustration for the preparation of N-Mo_xC@C HSs from Mo Ss with dicyandiamide at tunable temperature.

Figure 2.11 Synthetic route toward mNC-Mo₂C@rGO nanosheets through a strategy of interface self-assembly in solution.

Figure 2.12 (a) Schematic illustration of the formation mechanism of nanocrystalline M₃C (M: Fe, Co, Ni) on VA-GNRs. (b and c) SEM images of VA-GNRs with "teepee" structure. (d) Typical SEM image of M₃C-GNRs; (e-g) SEM images of M₃C (M: Fe, Co, Ni) NCs grown on the tips of VA-GNRs.

Figure 2.13 Schematic illustration showing the influence of different carbon precursors. Gaseous carbon precursor (for example, CH₄) and non-volatile solid carbon precursor (for example, CNT) may have different impacts on the chemical composition and microstructure of the carburization product.

2.3.2 Interface engineering of Transition Metal Sulfide-based heterostructures

In addition to transition-metal-carbides-based heterostructures, transition-metal-sulfide-based heterostructures have also attracted great interest. Among all the transition metal sulfides, molybdenum sulfide (MoS₂) has been intensively investigated due to its outstanding catalytic activity[60]. As a typical 2D layered material, the edge area of MoS₂ has been verified to be the active sites for HER due to the existence of abundant unsaturated S atoms. These defected S atoms are the ideal position for the adsorption/desorption of H proton since its corresponding adsorption free energy is close to zero[61].

Nickel sulfides have long been studied as a promising candidate for efficient water electrolysis[62-64]. However, the deficient number of active sites as well as the instability in electrolyte have both hindered its widespread application in industry[65, 66]. In this case, the combination of nickel sulfides with MoS₂ is expected to promote the catalytic performance due to the numerous interfaces to be formed. For instance, Xu et al. has

successfully prepared $\text{Ni}_9\text{S}_8@\text{MoS}_2$ heterostructure through Li^+ intercalation followed by hydrothermal reaction at 220°C for 24 h (see Figure 2.14)[67]. The product thus obtained has shown a small onset overpotential of 88 mV and a low Tafel slope of $49 \text{ mV}\cdot\text{dec}^{-1}$. After experimental characterization and analysis, this excellent HER performance is attributed to the strong interaction between the Ni_9S_8 and MoS_2 which comprises the heterostructure. To be specific, the electrical coupling between these two phases together with the abundant active sites from the edge positions of MoS_2 have contributed to the greatly enhanced catalytic activity towards HER. Besides, the synergistic effect mentioned above will also enable a faster electron transfer from Ni to Mo, which can significantly improve the intrinsic activity of heterostructure.

To further improve the electrical conductivity of NiS_2 , the highly conductive carbon materials have been employed as the support. For example, Wang et al. has combined the $\text{NiS}_2\text{-MoS}_2$ heterostructure with the highly conductive reduced graphene oxide (rGO) through hydrothermal reaction followed by annealing. The final product thus obtained is denoted as $\text{NiS}_2/\text{MoS}_2\text{-RGO}$, which shows remarkable HER performance in a wide pH range (see Figure 2.15)[68]. The highly enhanced catalytic activity is ascribed to the abundant active sites created due to the formation of massive interfaces in the heterostructure. In addition, the excellent conductivity provided by rGO has also contributed to the improved HER performance.

Besides MoS_2 , nickel sulfide has also been combined to other compounds to further improve its properties. For instance, it was report by Xue et al. that NiTe can be combined with NiS to form NiTe/NiS heterostructure (see Figure 2.16) through facile approach[69]. The heterostructure thus obtains has displayed outstanding OER performance in 1.0 M KOH, reaching the current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ at the overpotential of only 257 mV. The Tafel slope is also as low as $49 \text{ mV}\cdot\text{dec}^{-1}$, indicating the highly enhanced reaction kinetics. This excellent performance is considered to come from the strong coupling between NiS and NiTe . To be specific, the massive interfaces created will induce the modulation of electronic structure. According to the DFT calculation, the d-band center of Ni will be regulated due to the electron transfer

from NiTe to NiS. Consequently, the binding energy of *OOH intermediates will be largely reduced, resulting in a lowered reaction barrier of OER.

Figure 2.14 Schematic illustration of heterostructure $\text{Ni}_9\text{S}_8@\text{MoS}_2$ hybrid

Figure 2.15 Schematic diagram of the fabrication procedure of NiS₂/MoS₂-RGO nanocomposites

Figure 2.16 a) Schematic illustration of the preparation of NiTe/NiS heterojunction nanoarrays. b) FESEM, c) TEM, and d) HRTEM images of the NiTe. e) FESEM, f) TEM, and g) HRTEM images of the NiTe/NiS. h–k) HAADF-STEM image and STEM-EDS mappings of NiTe/NiS.

2.3.3 Interface engineering of Transition Metal Phosphide-based heterostructures

In addition to transition metal carbides and sulfides, transition metal phosphides (TMPs) have also attracted intensive attention due to their advantageous properties regarding electrical conductivity and quick charge transfer, making them promising candidates for catalytic water electrolysis[70, 71]. However, the performance of TMPs can be further enhanced when they are integrated with other compounds, forming the TMP-based heterostructured catalysts[72-78]. For instance, Zeng et al. have integrated Ni_2P with Ni_3S_2 which anchored nickel foam, generating 3D-networked $\text{Ni}_2\text{P}/\text{Ni}_3\text{S}_2$ heterostructure ($\text{Ni}_2\text{P}-\text{Ni}_3\text{S}_2$ HNAs/NF) (see Figure 2.17)[65]. The product thus obtained has demonstrated highly active toward HER and OER in alkaline media, delivering the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 80 mV and 210 mV for HER and OER, respectively. This significantly enhanced catalytic activity is attributed to the strong coupling between Ni_2P and Ni_3S_2 , leading to the regulated electronic structure which is beneficial for the reaction kinetics. Besides, the hydrogen adsorption energy is also reduced accordingly, largely promoting the intermediates adsorption.

Similarly, Zhang et al. have also synthesized a 3D heterostructure through hydrothermal approach [76]. However, the heterostructure here also possesses a unique hierarchical structure. To be specific, NiCo hydroxide nanowires was firstly grown on Ni foam followed by the in-situ phosphatization, producing NiCoP nanowires. Subsequently, NiFe LDH nanosheets were loaded on these NiCoP nanowires, forming the hierarchical NiFe-LDH@NiCoP/NF heterostructure (see Figure 2.18). The product thus obtained has proven to be highly active towards both HER and OER in alkaline media, delivering the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 120 mV and 220 mV in 1M KOH for HER and OER, respectively. The experimental characterization reveals that the inner structure of heterojunction has become more advanced and massive interfaces have also been created, generating abundant active sites exposed to the electrolyte. Furthermore, the electronic structure has also been optimized due to the strong coupling effect between NiCoP and NiFe LDH, remarkably enhancing the catalytic activity of the heterostructure.

Both works introduced above have used Ni foam as the current collector. In contrast, Bu et al. has employed a newly developed method-microwave-assisted thermal conversion to prepare the FeNiP/P-doped graphene (FeNiP/PG, see Figure 2.19)[79]. This novel approach is also able to synthesize heterostructure with adjustable component. In this work, FeNiP/graphitized carbon/ P-doped graphene (FeNiP/GC/PG) heterostructure can also be fabricated when metal organic framework/graphene is used as the precursor. This newly developed strategy possesses great advantages over transitional heating treatment, allowing for the fine tuning of graphitized carbon formation on FeNiP. It is verified in this work that the catalytic activity of FeNiP and their derivatives including oxy/hydroxides is higher than that of graphitized carbon, which is contrary to what has been considered for long time. To be specific, the FeNiP/PG heterostructure can deliver the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 229 mV and 173 mV for OER and HER, respectively.

Figure 2.17 Illustration of the fabrication of 3D-networked heterostructured $\text{Ni}_2\text{P}-\text{Ni}_3\text{S}_2$ HNAs/NF composites

Figure 2.18 a) XRD spectra of the bare NF, NiCoP/NF, NiFe LDH@NiCoP/NF, and NiFe LDH/NF. b) SEM image of the as-synthesized NiCoP/NF nanowires, where the inset shows a high-resolution image of the NiCoP nanowires. c) SEM image of the as-synthesized NiFe LDH@NiCoP/NF nanowires, where the inset shows a high-resolution image of the NiFe LDH@NiCoP nanowires. d) TEM image of an NiCoP nanowire. e) TEM image of an NiFe LDH@NiCoP nanowire. f) EDX mapping images of the NiFe LDH@NiCoP nanowire. g) HRTEM image of the NiFe LDH@NiCoP nanowire highlighting the interface between nanowire and nanosheets. h) SAD pattern of the interface of the NiFe LDH@NiCoP. i-k) XPS patterns of the Ni 2p_{3/2}, Co 2p_{3/2}, and P 2p for NiCoP/NF and NiFe LDH@NiCoP/NF, respectively.

Figure 2.19 (a, e, and h) SEM and (b, f, and i) TEM and (c, g, and j) HRTEM images of FeNiP/PG, FeNiP/GC/PG and FeNiP/RGO. (d) HAADF-STEM elemental mapping of FeNiP/PG. The insets in (a, e, and h) are the structural models of FeNiP/PG, FeNiP/GC/PG and FeNiP/RGO.

2.4 Interface engineering of cobalt-based heterostructures for water splitting

Cobalt has recently received great research interest due to its high catalytic activity towards OER and cobalt-based catalysts for water splitting have been intensively investigated[80]. However, these catalysts developed so far are far from satisfactory for practical application due to various issues including instability, large overpotential, degradation and so on[81]. Therefore, new strategies have been advanced to overcome these drawbacks. Among them, cobalt-based heterogeneous catalysts have emerged as one of the most promising candidates for efficient and stable cobalt-based catalysts for water electrolysis.

2.4.1 Interface engineering of Cobalt Selenides (CoSe₂)-based heterostructures for water splitting

It was reported by Shao-Horn et al. that the catalyst's intrinsic activity of OER is usually very high if the corresponding e_g orbital is occupied in near unity[82]. According to this prediction, the cubic CoSe₂ should possess high catalytic activity towards OER since its Co3d electrons ($t_{2g}^6 e_g^1$) is quite near to this desirable e_g filling[83]. It was confirmed by Xie et al. that CoSe₂ possessed metallic properties, facilitating the charge transport during reaction. However, the actual catalytic activity of CoSe₂ was far from good enough for industrial application due to the insufficient exposure of active sites. In this case, it is reasonable to combine other compounds with CoSe₂ so that its OER performance can be further promoted.

For example, Li et al. have prepared CoSe₂/FeSe₂@C heterostructure (see Figure 2.20) through template-assisted synthesis strategy[84]. The MOF-derived heterostructure has demonstrated excellent OER performance, reaching the current density of 10 mA·cm⁻² at the small overpotential of 291 mV with a low Tafel slope of 62 mV·dec⁻¹, which is superior to the RuO₂ benchmark electrocatalyst. Furthermore, this heterostructure has also shown good durability in alkaline media, indicating its dramatic corrosion resistance to the electrolyte attack. After detailed experimental characterizations and analysis, it was found that this remarkable OER performance can be attributed to several factors. Firstly, the

heterostructure possesses high surface area and easy electron transfer due to the unique structure ($\text{CoSe}_2/\text{FeSe}_2$ supported on carbon nanorods); Secondly, there is systematic synergistic effect among the three components consisting of $\text{CoSe}_2/\text{FeSe}_2/\text{C}$ heterostructure, leading to massive defective vacancies and strong electronic coupling, all of which greatly improves the intrinsic activity of the heterostructure.

In addition to single-metal selenide, bimetallic selenides have also been investigated and combined with other compounds to form heterostructures. For instance, Yang et al. have synthesized $\text{CoNiSe}_2/\text{CoNi-LDHs/NF}$ heterostructure (see Figure 2.21) by electrodepositing CoNi-LDHs nanosheets on CoNiSe_2 nanorods (prepared by hydrothermal approach). The heterostructure thus obtained has shown dramatic catalytic activity towards overall water splitting, achieving the geometric current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the low cell voltage of 1.44 V. According to the experimental characterizations including in-sit Raman analysis as well as DFT calculations, this significantly promoted catalytic performance can be ascribed to the highly enhanced water molecules adsorption and dissociation on the interfaces between CoNiSe_2 and CoNi-LDHs , verifying the strong coupling effect between these two components of heterostructure.

Figure 2.20 Schematic illustration of the synthesis process of $\text{CoSe}_2/\text{FeSe}_2/\text{C}$

Figure 2.21 (a, d) SEM and (b, e) TEM images, and (c, f) elemental mapping of (a–c) CoNiSe₂/NF and (d–f) CoNiSe₂@CoNi-LDHs/NF. In panel e, the defects (e.g., faultage, malposition, and interfaces) on CoNiSe₂@CoNi-LDHs are marked.

2.4.2 Interface engineering of Cobalt Sulfides-based heterostructures for water splitting

In terms of electrical conductivity, cobalt sulfides are generally superior to their oxides[85]. Cobalt sulfides including CoS₂[86] and Co₉S₈[87] have also received great research interest due to their excellent electrochemical performance. However, the single cobalt sulfide often lacks sufficient active sites as well as long durability. In this case, combining it with other compounds have been investigated and proven to be an effective strategy to further enhance its performance. For example, Hu et al. have successfully fabricated CoS₂/CoS nanosheets heterostructure (see Figure 2.22) with porous structure. The as-prepared heterostructure has shown remarkable catalytic activity towards OER, achieving current density of 10 mA·cm⁻² at the small overpotential of 269 mV with a low Tafel slope of 52 mV·dec⁻¹ in alkaline media. Besides, it has also presented good stability when compared to the benchmark catalyst-RuO₂. This dramatically enhanced OER performance can be attributed to the following two factors:

- (1) The 3D hierarchical structure with pores has greatly facilitated the exposure of active sites and mass/charge transfer.

(2) The synergistic effect between CoS_2 and CoS has moderately regulated the electrons interaction, thus resulting optimized electronic structure which improves the intrinsic activity of the heterostructure.

In addition to CoS_x , NiCo_2S_4 has also received intensive attention due to its high electrocatalytic activity[88, 89]. To further enhance its catalytic performance, it has also been combined with other compounds to form heterostructures. For instance, Li et al. have synthesized $\text{NiCo}_2\text{S}_4/\text{FeOOH}$ nanowire arrays (see Figure 2.23) through hydrothermal approach followed by sulfur anion exchange. The as-synthesized heterostructure has exhibited excellent OER performance, reaching the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 200 mV, outperforming the benchmark catalyst of RuO_2 and IrO_2 . According to the experimental results and DFT calculations, this dramatic OER performance can be ascribed to the unique 1D porous structure which greatly facilitates the sufficient exposure of active sites, especially those on the interface between NiCo_2S_4 and FeOOH . Besides, it is also quite beneficial for the mass transport, reducing the diffusion length. Furthermore, the synergistic effect between NiCo_2S_4 and FeOOH on the electronic interaction will finally optimally regulate the surface binding energies of intermediates including O^* and OOH^* , remarkably accelerating the reaction kinetics.

Figure 2.22 Schematic illustration for the formation of heterogeneous CoS_2/CoS porous nanosheets.

Figure 2.23 a) The schematic synthesis of the $\text{NiCo}_2\text{S}_4/\text{FeOOH}$ heterostructure. Color scheme for chemical representation: red for Co, green for Ni, purple for Fe, blue for O, white for S, and grey for H. X-ray diffraction (XRD) patterns of b) precursor-2, c) different precursors for comparison, and d) $\text{NiCo}_2\text{S}_4/\text{Fe}$.

2.4.3 Interface engineering of Cobalt Oxides-based heterostructures for water splitting

Cobalt oxides have been extensively investigated for various applications due to its advantages including environmental friendliness, earth abundance and low price[90]. There are many types of cobalt oxides including CoO , Co_2O_3 and Co_3O_4 . Correspondingly, their crystal structures also differ in various forms. For example, Figure 2.24 shows the typical structure of CoO and Co_3O_4 , both of which are

thermodynamically stable[91]. So far, cobalt oxides have been applied in various fields including energy conversion and storage, especially water splitting due to its high electrocatalytic activity[92-94]. However, there are still many issues to be solved before they can be widely used in industry. One of the most challenging problems is their inferior charge conductivity, which hinders a fast reaction kinetics[95]. In this case, intensive research efforts have been devoted to solving the issues mentioned above and the combination with other compounds which are property-complementary has proven to be an effective approach. For instance, Du et al. have successfully fabricated $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ heterostructure (see Figure 2.25) through hydrothermal method. To be specific, Co_3O_4 nanowires were firstly in situ grown on Ni foam through co-precipitation. Subsequently, the as-prepared Co_3O_4 nanowires was sulfurized with sodium sulfide (Na_2S) at 100°C and the product thus obtained was $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ heterostructure as verified by XRD and TEM results. The synthesis mechanism was also investigated and found to be different in the two steps. The first step was dominated by the anion exchange while the Ostwald ripening became prevalent in the second step. The Ostwald ripening was further investigated by controlling the sulfurization and it was found that the layer of Co_3S_4 covered on the surface Co_3O_4 nanowires became thicker as the sulfurization time went longer. Therefore, the Ostwald ripening was also time-dominant reaction. Furthermore, the final product thus obtained possessed the typical core-shell structure in which the first grown Co_3O_4 nanowires acted as “core” while the Co_3S_4 covering the surface of Co_3O_4 nanowires acted as the “shell”. The performance of final product was examined by various electrochemical methods including Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS). It turned out that the $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ heterostructure was highly active towards OER and HER, reaching the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the small overpotential of 270 mV and 143 mV for OER and HER, respectively. When assembled as water electrolyser, the potential required to achieve $10 \text{ mA}\cdot\text{cm}^{-2}$ was only 1.53 V, indicating its excellent bifunctional catalytic activity towards water splitting. This dramatic performance was ascribed to the formation of abundant interfaces which greatly facilitates creation and exposure of actives.

Besides, the electron transfer process was also significantly enhanced due to the construction of core-shell structure.

In addition to CoO_x ($x=1, 2, 3$, and 4) type cobalt oxide, nickel cobaltite (NiCo_2O_4) with spinel structure has also demonstrated superior OER performance when compared to Co_3O_4 . The major reason is it possesses better electrical conductivity and larger surface area[96, 97]. In spite of this, the performance of NiCo_2O_4 still needs to be further promoted before it can be practically used in industry[98-100]. In this case, An et al. have combined the NiCo_2O_4 with CuS to fabricate $\text{NiCo}_2\text{O}_4/\text{CuS}/\text{CFP}$ heterostructure (see Figure 2.26)[101]. The synthesis method used here is a facile hydrothermal approach in which cobalt nitrate, nickel nitrate, and urea were heated at $120\text{ }^\circ\text{C}$ for 16 h followed by annealing at $300\text{ }^\circ\text{C}$ for 2 h. The product thus obtained was $\text{CFP}/\text{NiCo}_2\text{O}_4$. Afterwards, the $\text{CFP}/\text{NiCo}_2\text{O}_4$ was further heated with copper chloride and sodium dodecylbenzene sulfonate at $100\text{ }^\circ\text{C}$ for 4 h. Finally, the heating process of $100\text{ }^\circ\text{C}$, 4 h was repeated with thioacetamide and the product of $\text{CFP}/\text{NiCo}_2\text{O}_4/\text{CuS}$ was then obtained. The final product thus obtained has shown dramatic HER performance in acidic media, achieving the current density of $10\text{ mA}\cdot\text{cm}^{-2}$ at a very small overpotential of 72.3 mV with a low Tafel slope of 41 mV dec^{-1} . Furthermore, when assembled in a water electrolyser, it can generate $10\text{ mA}\cdot\text{cm}^{-2}$ when the applied potential was only 1.5 V. The excellent performance can be attributed to the significant increase of exposed active sites on the interfaces of $\text{CFP}/\text{NiCo}_2\text{O}_4/\text{CuS}$ heterostructure. Moreover, the strong electrical coupling between NiCo_2O_4 and CuS as well as CFP and NiCo_2O_4 , which had optimally regulated the electronic structure of the heterostructure, reducing the energy barriers for adsorption/desorption of intermediates.

2.4.4 Interface engineering of Cobalt Hydroxides-based heterostructures for water splitting

Cobalt hydroxides ($\text{Co}(\text{OH})_2$) usually possesses layered structure, see Figure 2.27[102,103]. In general, there are two different polymorphs of $\text{Co}(\text{OH})_2$ including α - $\text{Co}(\text{OH})_2$ and β -

Co(OH)_2 which possess different physiochemical properties. For instance, the interlayer distance of $\alpha\text{-Co(OH)}_2$ is larger than that of $\beta\text{-Co(OH)}_2$. The major reason for this difference is the intercalated anions and water molecules between interlayers. In addition, the $\beta\text{-Co(OH)}_2$ is more thermodynamically more stable than $\alpha\text{-Co(OH)}_2$ which can be simply transformed into $\beta\text{-Co(OH)}_2$ in strong alkaline media[104, 105]. Cobalt (oxy)hydroxides have long been considered to be catalytically active towards OER[106-109]. Cobalt hydroxides have also received great research interest due to their unique properties including proper electronic configuration and tunable morphologies[110-112]. However, the catalytic performance of cobalt hydroxide itself is not good enough for practical application in industry. In this case, the combination of cobalt hydroxides with another complementary components has proved to be an effective strategy in promoting the practical performance. For instance, He et al. have fabricated $\text{Co(OH)}_2/\text{SFM-NF}$ heterostructure (see Figure 2.28) through electrostatic spinning followed by atomic layer deposition (ALD)[113]. In detail, electrostatic spinning was first carried out to fabricate the primary nanofibers. The nanofibers thus obtained were subsequently calcined at 1000 °C for continuous 5 h to generate $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) nanofibers. Afterwards, ALD-ZnO thin film was deposited on the $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) nanofibers through atomic layer deposition. The thickness of ZnO film can be finely tuned by adjusting the cycling number. As a result, it was found that the optimal thickness was about 10 nm. The catalytic performance of the heterostructure thus obtained has been evaluated in alkaline media through electrochemical measurements including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). It turned out that the $\text{Co(OH)}_2/\text{SFM-NF}$ heterostructure was a good bifunctional for water splitting, achieving the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the overpotential of 384 mV and 322 mV for OER and HER, respectively, outperforming the single SFM nanofibers. Furthermore, the heterostructure has also shown remarkable catalytic activity when assembled as a cell, requiring only 1.6 V to deliver the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ which can stabilize for over 68 h. This excellent performance can be attributed to the enlarged electrochemical surface area and massive active sites created during the formation of heterostructure. Both advantages can further be ascribed to the synergistic effect between the two components of heterostructure including Co(OH)_2 and SFM.

In addition to cobalt hydroxides, cobalt-based layered double hydroxides have also presented to be active catalysts towards water splitting. Nevertheless, its catalytic performance still cannot meet the requirement for practical application. Therefore, cobalt-based layered double hydroxides have also been combined with other complementary compounds to further improve its performance[114, 115]. For example, Yang et al. have successfully synthesized CoFe@NiFe/NF heterostructure (see Figure 2.29) through hydrothermal method followed by electrodeposition[116]. To be specific, iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and urea ($\text{CH}_4\text{N}_2\text{O}$) were hydrothermally heated at 120 °C for 6 h to obtain CoFe-LDH/NF nanosheets array. Subsequently, electrodeposition was carried out with the CoFe-LDH/NF nanoarray to fabricate NiFe-LDH covering the surface of CoFe-LDH so that CoFe@NiFe/NF heterostructure was finally obtained. The catalytic performance of CoFe@NiFe/NF heterostructure was assessed by various electrochemical methods including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) and it turned out to be highly active towards both OER and HER, achieving the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 190 mV and 240 mV for OER and HER, respectively. Furthermore, only a low voltage of 1.59 V was required to generate the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ when the heterostructure was assembled as a cell, which outperforms most of other reported cells. This excellent catalytic performance can be attributed to the intensive coupling effect between CoFe-LDH and NiFe-LDH. To be specific, this coupling effect will largely improve the charge transfer and optimally regulate the binding energies at the interface where massive active sites were created during the formation of heterostructure. Besides, the 3D porous structure as well as the core-shell construction in the heterostructure has also dramatically promoted the exposure of active sites and mass transport, thus enhancing the reaction kinetics.

In addition to couple with LDH, cobalt-based LDHs have also been integrated with other compounds such as sulfides[117] and nitrides[118] and both heterostructures thus formed have demonstrated superior water splitting performance to their single components.

Figure 2.24 Crystal structures of (a) CoO and (b) Co₃O₄ (Navy blue, dark green and red balls indicate Co²⁺, Co³⁺, and O²⁻ ions, respectively).

Figure 2.25 SEM images of Co₃O₄/NF (a), Co₃O₄@Co₃S₄/NF-12 h (b), Co₃O₄@Co₃S₄/NF-24 h (c)

and $\text{Co}_3\text{O}_4@\text{Co}_3\text{S}_4/\text{NF}$ -36 h (d).

Figure 2.26 a) XRD patterns of CFP, CFP/NiCo₂O₄, CFP/CuS, and CFP/NiCo₂O₄/CuS. b) Low- and high-magnification (inset) SEM images of CFP/ NiCo₂O₄. c) Low- and high-magnification (inset) SEM images of CFP/NiCo₂O₄ /CuS. d) HRTEM and TEM images (inset) of CFP/NiCo₂O₄/CuS. e) SAED pattern of CFP/NiCo₂O₄/CuS. f) SEM image and EDS elementals mapping images of S, Cu, C, Ni, Co, and O for CFP/NiCo₂O₄ /CuS

Figure 2.27 The schematic representation of cobalt hydroxide structure

Figure 2.28 (a) Schematic of the synthesis of $\text{Co(OH)}_2/\text{SFM-NF}$. (b) XRD pattern of SFM, SFM-NF and $\text{Co(OH)}_2/\text{SFM-NF}$. (c) Raman spectra of SFM-NF and $\text{Co(OH)}_2/\text{SFM-NF}$ samples.

Figure 2.29 Schematic diagram for the fabrication of CoFe@NiFe/NF architecture

References

- [1] H. Li, X. Wang, Phase Control in Inorganic Nanocrystals through Finely Tuned Growth at an Ultrathin Scale, *Acc Chem Res*, 52 (2019) 780-790.
- [2] N.L. Panwar, S.C. Kaushik, S. Kothari, Role of renewable energy sources in environmental protection: A review, *Renewable and Sustainable Energy Reviews*, 15 (2011) 1513-1524.
- [3] J. Potočník, Renewable Energy Sources and the Realities of Setting an Energy Agenda, *Science*, 315 (2011) 1513-1524.
- [4] S. Jenniches, Assessing the regional economic impacts of renewable energy sources – A literature review, *Renewable and Sustainable Energy Reviews*, 93 (2018) 35-51.
- [5] J. Benedek, T.-T. Sebestyén, B. Bartók, Evaluation of renewable energy sources in peripheral areas and renewable energy-based rural development, *Renewable and Sustainable Energy Reviews*, 90 (2018) 516-535.
- [6] J. Jurasz, F.A. Canales, A. Kies, M. Guezgouz, A. Beluco, A review on the complementarity of renewable energy sources: Concept, metrics, application and future research directions, *Solar Energy*, 195 (2020) 703-724.
- [7] L. Li, P. Wang, Q. Shao, X. Huang, Metallic nanostructures with low dimensionality for electrochemical water splitting, *Chemical Society reviews*, 49 (2020) 3072-3106.
- [8] S. Anantharaj, S. Noda, Amorphous Catalysts and Electrochemical Water Splitting: An Untold Story of Harmony, *Small*, 16 (2020) e1905779.
- [9] J. Joo, T. Kim, J. Lee, S.I. Choi, K. Lee, Morphology-Controlled Metal Sulfides and Phosphides for Electrochemical Water Splitting, *Advanced materials*, 31 (2019) e1806682.
- [10] C. Zhu, Q. Shi, S. Feng, D. Du, Y. Lin, Single-Atom Catalysts for Electrochemical Water Splitting, *ACS Energy Letters*, 3 (2018) 1713-1721.
- [11] Crabtree, G. W, M.S. Dresselhaus, M.V. Buchanan, The hydrogen economy, *Phys Today*, 57 (2004).
- [12] K. Alanne, S. Cao, Zero-energy hydrogen economy (ZEH 2 E) for buildings and communities including personal mobility, *Renewable and Sustainable Energy Reviews*, 71 (2017) 697-711.
- [13] I. Roger, M.A. Shipman, M.D. Symes, Earth-abundant catalysts for electrochemical and photoelectrochemical water splitting, *Nature Reviews Chemistry*, 1 (2017).
- [14] J. Yu, Q. He, G. Yang, W. Zhou, Z. Shao, M. Ni, Recent Advances and Prospective in Ruthenium-Based Materials for Electrochemical Water Splitting, *ACS Catalysis*, 9 (2019) 9973-10011.

- [15] Q. Hu, G. Li, Z. Han, Z. Wang, X. Huang, H. Yang, Q. Zhang, J. Liu, C. He, Recent progress in the hybrids of transition metals/carbon for electrochemical water splitting, *Journal of Materials Chemistry A*, 7 (2019) 14380-14390.
- [16] A.G. Wallace, M.D. Symes, Decoupling Strategies in Electrochemical Water Splitting and Beyond, *Joule*, 2 (2018) 1390-1395.
- [17] C. Zhang, H. Nan, H. Tian, W. Zheng, Recent advances in pentlandites for electrochemical water splitting: A short review, *J Alloy Compd*, 838 (2020) 155685.
- [18] C. Li, J.B. Baek, Recent Advances in Noble Metal (Pt, Ru, and Ir)-Based Electrocatalysts for Efficient Hydrogen Evolution Reaction, *ACS Omega*, 5 (2020) 31-40.
- [19] Z. Chen, X. Duan, W. Wei, S. Wang, B.-J. Ni, Iridium-based nanomaterials for electrochemical water splitting, *Nano Energy*, 78 (2020) 105270.
- [20] Y. Li, Y. Sun, Y. Qin, W. Zhang, L. Wang, M. Luo, H. Yang, S. Guo, Recent Advances on Water - Splitting Electrocatalysis Mediated by Noble - Metal - Based Nanostructured Materials, *Advanced Energy Materials*, 10 (2020) 1903120.
- [21] B. Zhang, J. Liu, J. Wang, Y. Ruan, X. Ji, K. Xu, C. Chen, H. Wan, L. Miao, J. Jiang, Interface engineering: The $\text{Ni}(\text{OH})_2$ / MoS_2 heterostructure for highly efficient alkaline hydrogen evolution, *Nano Energy*, 37 (2017) 74-80.
- [22] Y. Liu, S. Jiang, S. Li, L. Zhou, Z. Li, J. Li, M. Shao, Interface engineering of (Ni, Fe) S_2 @ MoS_2 heterostructures for synergetic electrochemical water splitting, *Applied Catalysis B: Environmental*, 247 (2019) 107-114.
- [23] H. Wang, W. Fu, X. Yang, Z. Huang, J. Li, H. Zhang, Y. Wang, Recent advancements in heterostructured interface engineering for hydrogen evolution reaction electrocatalysis, *Journal of Materials Chemistry A*, 8 (2020) 6926-6956.
- [24] P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao, X. Huang, Precise tuning in platinum-nickel/nickel sulfide interface nanowires for synergistic hydrogen evolution catalysis, *Nature communications*, 8 (2017) 14580.
- [25] Y. Liu, S. Liu, Y. Wang, Q. Zhang, L. Gu, S. Zhao, D. Xu, Y. Li, J. Bao, Z. Dai, Ru Modulation Effects in the Synthesis of Unique Rod-like $\text{Ni}@\text{Ni}_2\text{P}$ -Ru Heterostructures and Their Remarkable Electrocatalytic Hydrogen Evolution Performance, *Journal of the American Chemical Society*, 140 (2018) 2731-2734.
- [26] Y. Li, S. Guo, Noble metal-based 1D and 2D electrocatalytic nanomaterials: Recent progress, challenges and perspectives, *Nano Today*, 28 (2019) 100774.
- [27] H.-H. Li, M.-L. Xie, C.-H. Cui, D. He, M. Gong, J. Jiang, Y.-R. Zheng, G. Chen, Y. Lei, S.-H. Yu, Surface Charge Polarization at the Interface: Enhancing the Oxygen Reduction via

- Precise Synthesis of Heterogeneous Ultrathin Pt/PtTe Nanowire, *Chem Mater*, 28 (2016) 8890-8898.
- [28] P. Wang, K. Jiang, G. Wang, J. Yao, X. Huang, Phase and Interface Engineering of Platinum-Nickel Nanowires for Efficient Electrochemical Hydrogen Evolution, *Angewandte Chemie*, 55 (2016) 12859-12863.
- [29] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A.P. Paulikas, V. Stamenkovic, N.M. Markovic, Enhancing hydrogen evolution activity in water splitting by tailoring, *Science*, 334 (2011) 1256-1260.
- [30] J. Xu, T. Liu, J. Li, B. Li, Y. Liu, B. Zhang, D. Xiong, I. Amorim, W. Li, L. Liu, Boosting the hydrogen evolution performance of ruthenium clusters through synergistic coupling with cobalt phosphide, *Energy & Environmental Science*, 11 (2018) 1819-1827.
- [31] J. Mahmood, F. Li, S.M. Jung, M.S. Okyay, I. Ahmad, S.J. Kim, N. Park, H.Y. Jeong, J.B. Baek, An efficient and pH-universal ruthenium-based catalyst for the hydrogen evolution reaction, *Nature nanotechnology*, 12 (2017) 441-446.
- [32] Y. Zheng, Y. Jiao, Y. Zhu, L.H. Li, Y. Han, Y. Chen, M. Jaroniec, S.Z. Qiao, High Electrocatalytic Hydrogen Evolution Activity of an Anomalous Ruthenium Catalyst, *Journal of the American Chemical Society*, 138 (2016) 16174-16181.
- [33] H. Liao, C. Wei, J. Wang, A. Fisher, T. Sritharan, Z. Feng, Z.J. Xu, A Multisite Strategy for Enhancing the Hydrogen Evolution Reaction on a Nano-Pd Surface in Alkaline Media, *Advanced Energy Materials*, 7 (2017) 1701129.
- [34] A. Pandey, A. Mukherjee, S. Chakrabarty, D. Chanda, S. Basu, Interface Engineering of an RGO/MoS₂/Pd 2D Heterostructure for Electrocatalytic Overall Water Splitting in Alkaline Medium, *ACS Appl Mater Interfaces*, 11 (2019) 42094-42103.
- [35] G. Valenti, A. Boni, M. Melchionna, M. Cargnello, L. Nasi, G. Bertoni, R.J. Gorte, M. Marcaccio, S. Rapino, M. Bonchio, P. Fornasiero, M. Prato, F. Paolucci, Co-axial heterostructures integrating palladium/titanium dioxide with carbon nanotubes for efficient electrocatalytic hydrogen evolution, *Nature communications*, 7 (2016) 13549.
- [36] R. Zhao, Q. Li, X. Jiang, S. Huang, G. Fu, J.-M. Lee, Interface engineering in transition metal-based heterostructures for oxygen electrocatalysis, *Materials Chemistry Frontiers*, 5 (2021) 1033-1059.
- [37] M. Kuang, W. Huang, C. Hegde, W. Fang, X. Tan, C. Liu, J. Ma, Q. Yan, Interface engineering in transition metal carbides for electrocatalytic hydrogen generation and nitrogen fixation, *Materials Horizons*, 7 (2020) 32-53.

- [38] P. Yu, F. Wang, T.A. Shifa, X. Zhan, X. Lou, F. Xia, J. He, Earth abundant materials beyond transition metal dichalcogenides: A focus on electrocatalyzing hydrogen evolution reaction, *Nano Energy*, 58 (2019) 244-276.
- [39] R. Ma, Y. Zhou, Y. Chen, P. Li, Q. Liu, J. Wang, Ultrafine Molybdenum Carbide Nanoparticles Compositied with Carbon as a Highly Active Hydrogen-Evolution Electrocatalyst, *Angewandte Chemie*, 54 (2015) 14723-14727.
- [40] J. Jia, W. Zhou, Z. Wei, T. Xiong, G. Li, L. Zhao, X. Zhang, H. Liu, J. Zhou, S. Chen, Molybdenum carbide on hierarchical porous carbon synthesized from Cu-MoO₂ as efficient electrocatalysts for electrochemical hydrogen generation, *Nano Energy*, 41 (2017) 749-757.
- [41] C. Wu, D. Liu, H. Li, J. Li, Molybdenum Carbide-Decorated Metallic Cobalt@Nitrogen-Doped Carbon Polyhedrons for Enhanced Electrocatalytic Hydrogen Evolution, *Small*, 14 (2018) e1704227.
- [42] X. Xu, F. Nosheen, X. Wang, Ni-Decorated Molybdenum Carbide Hollow Structure Derived from Carbon-Coated Metal–Organic Framework for Electrocatalytic Hydrogen Evolution Reaction, *Chem Mater*, 28 (2016) 6313-6320.
- [43] C. Tang, W. Wang, A. Sun, C. Qi, D. Zhang, Z. Wu, D. Wang, Sulfur-Decorated Molybdenum Carbide Catalysts for Enhanced Hydrogen Evolution, *ACS Catalysis*, 5 (2015) 6956-6963.
- [44] M. Liu, Y. Yang, X. Luan, X. Dai, X. Zhang, J. Yong, H. Qiao, H. Zhao, W. Song, X. Huang, Interface-Synergistically Enhanced Acidic, Neutral, and Alkaline Hydrogen Evolution Reaction over Mo₂C/MoO₂ Heteronanorods, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 14356-14364.
- [45] W. Yuan, Q. Huang, X. Yang, Z. Cui, S. Zhu, Z. Li, S. Du, N. Qiu, Y. Liang, Two-Dimensional Lamellar Mo₂C for Electrochemical Hydrogen Production: Insights into the Origin of Hydrogen Evolution Reaction Activity in Acidic and Alkaline Electrolytes, *ACS Appl Mater Interfaces*, 10 (2018) 40500-40508.
- [46] P. Xiao, Y. Yan, X. Ge, Z. Liu, J.-Y. Wang, X. Wang, Investigation of molybdenum carbide nano-rod as an efficient and durable electrocatalyst for hydrogen evolution in acidic and alkaline media, *Applied Catalysis B: Environmental*, 154-155 (2014) 232-237.
- [47] J.S. Li, Y. Wang, C.H. Liu, S.L. Li, Y.G. Wang, L.Z. Dong, Z.H. Dai, Y.F. Li, Y.Q. Lan, Coupled molybdenum carbide and reduced graphene oxide electrocatalysts for efficient hydrogen evolution, *Nature communications*, 7 (2016) 11204.
- [48] J. Wang, H. Xia, Z. Peng, C. Lv, L. Jin, Y. Zhao, Z. Huang, C. Zhang, Graphene Porous Foam Loaded with Molybdenum Carbide Nanoparticulate Electrocatalyst for Effective Hydrogen Generation, *ChemSusChem*, 9 (2016) 855-862.

- [49] X. Fan, Z. Peng, R. Ye, H. Zhou, X. Guo, M3C (M Fe, Co, Ni) Nanocrystals Encased in Graphene nanoribbons: An Active and Stable Bifunctional Electrocatalyst for Oxygen Reduction and Hydrogen Evolution Reactions, *ACS nano*, 9 (2015) 7407-7418.
- [50] S. Wang, L. Liao, Z. Shi, J. Xiao, Q. Gao, Y. Zhang, B. Liu, Y. Tang, Mo₂C/Reduced-Graphene-Oxide Nanocomposite: An Efficient Electrocatalyst for the Hydrogen Evolution Reaction, *ChemElectroChem*, 3 (2016) 2110-2115.
- [51] W.F. Chen, C.H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J.T. Muckerman, Y. Zhu, R.R. Adzic, Highly active and durable nanostructured molybdenum carbide electrocatalysts for hydrogen production, *Energy & Environmental Science*, 6 (2013) 943.
- [52] Q. Gong, Y. Wang, Q. Hu, J. Zhou, R. Feng, P.N. Duchesne, P. Zhang, F. Chen, N. Han, Y. Li, C. Jin, Y. Li, S.T. Lee, Ultrasmall and phase-pure W₂C nanoparticles for efficient electrocatalytic and photoelectrochemical hydrogen evolution, *Nature communications*, 7 (2016) 13216.
- [53] S. Li, C. Cheng, A. Sagaltchik, P. Pachfule, C. Zhao, A. Thomas, Metal-Organic Precursor-Derived Mesoporous Carbon Spheres with Homogeneously Distributed Molybdenum Carbide/Nitride Nanoparticles for Efficient Hydrogen Evolution in Alkaline Media, *Adv Funct Mater*, 29 (2019) 1807419.
- [54] L. Lin, S. Yao, R. Gao, X. Liang, Q. Yu, Y. Deng, J. Liu, M. Peng, Z. Jiang, S. Li, Y.W. Li, X.D. Wen, W. Zhou, D. Ma, A highly CO-tolerant atomically dispersed Pt catalyst for chemoselective hydrogenation, *Nature nanotechnology*, 14 (2019) 354-361.
- [55] C. Jian, Q. Cai, W. Hong, J. Li, W. Liu, Edge-Riched MoSe₂/MoO₂ Hybrid Electrocatalyst for Efficient Hydrogen Evolution Reaction, *Small*, 14 (2018) e1703798.
- [56] R. Ge, W. Li, J. Huo, T. Liao, N. Cheng, Y. Du, M. Zhu, Y. Li, J. Zhang, Metal-ion bridged high conductive RGO-M-MoS₂ (M = Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) composite electrocatalysts for photo-assisted hydrogen evolution, *Applied Catalysis B: Environmental*, 246 (2019) 129-139.
- [57] R. Ge, J. Huo, M. Sun, M. Zhu, Y. Li, S. Chou, W. Li, Surface and Interface Engineering: Molybdenum Carbide-Based Nanomaterials for Electrochemical Energy Conversion, *Small*, 17 (2021) e1903380.
- [58] T. Xiong, J. Jia, Z. Wei, L. Zeng, Y. Deng, W. Zhou, S. Chen, N-doped carbon-wrapped Mo C heterophase sheets for high-efficiency electrochemical hydrogen production, *Chem Eng J*, 358 (2019) 362-368.

- [59] D. Hou, S. Zhu, H. Tian, H. Wei, X. Feng, Y. Mai, Two-Dimensional Sandwich-Structured Mesoporous $\text{Mo}_2\text{C}/\text{Carbon}/\text{Graphene}$ Nanohybrids for Efficient Hydrogen Production Electrocatalysts, *ACS Appl Mater Interfaces*, 10 (2018) 40800-40807.
- [60] Y. Li, Z. Yin, M. Cui, X. Liu, J. Xiong, S. Chen, T. Ma, Interface engineering of transitional metal sulfide– MoS_2 heterostructure composites as effective electrocatalysts for water-splitting, *Journal of Materials Chemistry A*, 9 (2021) 2070-2092.
- [61] F. Yu, L. Yu, I.K. Mishra, Y. Yu, Z.F. Ren, H.Q. Zhou, Recent developments in earth-abundant and non-noble electrocatalysts for water electrolysis, *Materials Today Physics*, 7 (2018) 121-138.
- [62] Y. Guo, T. Park, J.W. Yi, J. Henzie, J. Kim, Z. Wang, B. Jiang, Y. Bando, Y. Sugahara, J. Tang, Y. Yamauchi, Nanoarchitectonics for Transition-Metal-Sulfide-Based Electrocatalysts for Water Splitting, *Advanced materials*, 31 (2019) e1807134.
- [63] Z. Chen, X. Duan, W. Wei, S. Wang, B.-J. Ni, Recent advances in transition metal-based electrocatalysts for alkaline hydrogen evolution, *Journal of Materials Chemistry A*, 7 (2019) 14971-15005.
- [64] X. Zheng, X. Han, Y. Zhang, J. Wang, C. Zhong, Y. Deng, W. Hu, Controllable synthesis of nickel sulfide nanocatalysts and their phase-dependent performance for overall water splitting, *Nanoscale*, 11 (2019) 5646-5654.
- [65] L. Zeng, K. Sun, X. Wang, Y. Liu, Y. Pan, Z. Liu, D. Cao, Y. Song, S. Liu, C. Liu, Three-dimensional-networked $\text{Ni}_2\text{P}/\text{Ni}_3\text{S}_2$ heteronanoflake arrays for highly enhanced electrochemical overall-water-splitting activity, *Nano Energy*, 51 (2018) 26-36.
- [66] L. An, J. Feng, Y. Zhang, R. Wang, H. Liu, G.-C. Wang, F. Cheng, P. Xi, Epitaxial Heterogeneous Interfaces on $\text{N-NiMoO}_4/\text{NiS}_2$ Nanowires/Nanosheets to Boost Hydrogen and Oxygen Production for Overall Water Splitting, *Adv Funct Mater*, 29 (2019) 1805298.
- [67] X. Xu, W. Zhong, L. Zhang, G. Liu, Y. Du, Synergistic effect of MoS_2 and Ni_9S_8 nanosheets as an efficient electrocatalyst for hydrogen evolution reaction, *J Colloid Interf Sci*, 556 (2019) 24-32.
- [68] L. Wang, T. Guo, S. Sun, Y. Wang, X. Chen, K. Zhang, D. Zhang, Z. Xue, X. Zhou, Tree-Like $\text{NiS}_2/\text{MoS}_2\text{-RGO}$ Nanocomposites as pH Universal Electrocatalysts for Hydrogen Evolution Reaction, *Catalysis Letters*, 149 (2019) 1197-1210.

- [69] Z. Xue, X. Li, Q. Liu, M. Cai, K. Liu, M. Liu, Z. Ke, X. Liu, G. Li, Interfacial Electronic Structure Modulation of NiTe Nanoarrays with NiS Nanodots Facilitates Electrocatalytic Oxygen Evolution, *Advanced materials*, 31 (2019) e1900430.
- [70] H. Du, R.M. Kong, X. Guo, F. Qu, J. Li, Recent progress in transition metal phosphides with enhanced electrocatalysis for hydrogen evolution, *Nanoscale*, 10 (2018) 21617-21624.
- [71] J.F. Callejas, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Synthesis, Characterization, and Properties of Metal Phosphide Catalysts for the Hydrogen-Evolution Reaction, *Chem Mater*, 28 (2016) 6017-6044.
- [72] K. Xu, H. Cheng, H. Lv, J. Wang, L. Liu, S. Liu, X. Wu, W. Chu, C. Wu, Y. Xie, Controllable Surface Reorganization Engineering on Cobalt Phosphide Nanowire Arrays for Efficient Alkaline Hydrogen Evolution Reaction, *Advanced materials*, 30 (2018).
- [73] L. Wang, C. Gu, X. Ge, J. Zhang, H. Zhu, J. Tu, Anchoring Ni₂P Sheets on NiCo₂O₄ Nanocone Arrays as Optimized Bifunctional Electrocatalyst for Water Splitting, *Advanced Materials Interfaces*, 4 (2017) 1700481.
- [74] H. Guo, Q. Feng, K. Xu, J. Xu, J. Zhu, C. Zhang, T. Liu, Self - Templated Conversion of Metallogel into Heterostructured TMP@Carbon Quasiaerogels Boosting Bifunctional Electrocatalysis, *Adv Funct Mater*, 29 (2019) 1903660.
- [75] H. Li, Q. Li, P. Wen, T.B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D.L. Carroll, G.L. Donati, P.M. Lundin, Y. Qiu, S.M. Geyer, Colloidal Cobalt Phosphide Nanocrystals as Trifunctional Electrocatalysts for Overall Water Splitting Powered by a Zinc-Air Battery, *Advanced materials*, 30 (2018).
- [76] H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S.L. Schweizer, A.W. Maijenburg, R.B. Wehrspohn, Bifunctional Heterostructure Assembly of NiFe LDH Nanosheets on NiCoP Nanowires for Highly Efficient and Stable Overall Water Splitting, *Adv Funct Mater*, 28 (2018) 1706847.
- [77] Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu, Q. Xu, Co₂P-CoN Double Active Centers Confined in N-Doped Carbon Nanotube: Heterostructural Engineering for Trifunctional Catalysis toward HER, ORR, OER, and Zn-Air Batteries Driven Water Splitting, *Adv Funct Mater*, 28 (2018) 1805641.
- [78] S. Dutta, A. Indra, H. Han, T. Song, An Intriguing Pea-Like Nanostructure of Cobalt Phosphide on Molybdenum Carbide Incorporated Nitrogen-Doped Carbon Nanosheets for Efficient Electrochemical Water Splitting, *ChemSusChem*, 11 (2018) 3956-3964.

- [79] F. Bu, W. Chen, M.F. Aly Aboud, I. Shakir, J. Gu, Y. Xu, Microwave-assisted ultrafast synthesis of adjustable bimetal phosphide/graphene heterostructures from MOFs for efficient electrochemical water splitting, *Journal of Materials Chemistry A*, 7 (2019) 14526-14535.
- [80] J. Wang, W. Cui, Q. Liu, Z. Xing, A.M. Asiri, X. Sun, Recent Progress in Cobalt-Based Heterogeneous Catalysts for Electrochemical Water Splitting, *Advanced materials*, 28 (2016) 215-230.
- [81] Y. Sun, J.P. Bigi, N.A. Piro, M.L. Tang, J.R. Long, C.J. Chang, Molecular cobalt pentapyridine catalysts for generating hydrogen from water, *Journal of the American Chemical Society*, 133 (2011) 9212-9215.
- [82] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles, *Science*, 334 (2011) 1383-1385.
- [83] Y. Liu, H. Cheng, M. Lyu, S. Fan, Q. Liu, W. Zhang, Y. Zhi, C. Wang, C. Xiao, S. Wei, B. Ye, Y. Xie, Low overpotential in vacancy-rich ultrathin CoSe₂ nanosheets for water oxidation, *Journal of the American Chemical Society*, 136 (2014) 15670-15675.
- [84] W. Li, Y. Niu, X. Wu, F. Wu, T. Li, W. Hu, Heterostructured CoSe₂/FeSe₂ Nanoparticles with Abundant Vacancies and Strong Electronic Coupling Supported on Carbon Nanorods for Oxygen Evolution Electrocatalysis, *ACS Sustainable Chemistry & Engineering*, 8 (2020) 4658-4666.
- [85] A. Pramanik, S. Maiti, M. Sreemany, S. Mahanty, Carbon Doped MnCo₂S₄ Microcubes Grown on Ni foam as High Energy Density Faradaic Electrode, *Electrochimica Acta*, 213 (2016) 672-679.
- [86] T. Liu, Y. Liang, Q. Liu, X. Sun, Y. He, A.M. Asiri, Electrodeposition of cobalt-sulfide nanosheets film as an efficient electrocatalyst for oxygen evolution reaction, *Electrochemistry Communications*, 60 (2015) 92-96.
- [87] S.B. Kale, A.C. Lokhande, R.B. Pujari, C.D. Lokhande, Cobalt sulfide thin films for electrocatalytic oxygen evolution reaction and supercapacitor applications, *J Colloid Interface Sci*, 532 (2018) 491-499.
- [88] W. Liu, J. Zhang, Z. Bai, G. Jiang, M. Li, K. Feng, L. Yang, Y. Ding, T. Yu, Z. Chen, A. Yu, Controllable Urchin-Like NiCo₂S₄ Microsphere Synergized with Sulfur-Doped Graphene as Bifunctional Catalyst for Superior Rechargeable Zn-Air Battery, *Adv Funct Mater*, 28 (2018) 1706675.
- [89] W. Zhu, M. Ren, N. Hu, W. Zhang, Z. Luo, R. Wang, J. Wang, L. Huang, Y. Suo, J. Wang, Traditional NiCo₂S₄ Phase with Porous Nanosheets Array Topology on Carbon Cloth: A

- Flexible, Versatile and Fabulous Electrocatalyst for Overall Water and Urea Electrolysis, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 5011-5020.
- [90] J. Mei, T. Liao, G.A. Ayoko, J. Bell, Z. Sun, Cobalt oxide-based nanoarchitectures for electrochemical energy applications, *Progress in Materials Science*, 103 (2019) 596-677.
- [91] X. Wang, W. Tian, T. Zhai, C. Zhi, Y. Bando, D. Golberg, Cobalt(ii,iii) oxide hollow structures: fabrication, properties and applications, *Journal of Materials Chemistry*, 22 (2012) 23310.
- [92] Q. He, E.J. Cairns, Review—Recent Progress in Electrocatalysts for Oxygen Reduction, *J Electrochem Soc*, 162 (2015) F1504-F1539.
- [93] J. Lee, B. Jeong, J.D. Ocon, Oxygen electrocatalysis in chemical energy conversion and storage technologies, *Current Applied Physics*, 13 (2013) 309-321.
- [94] C.R. Raj, A. Samanta, S.H. Noh, S. Mondal, T. Okajima, T. Ohsaka, Emerging new generation electrocatalysts for the oxygen reduction reaction, *Journal of Materials Chemistry A*, 4 (2016) 11156-11178.
- [95] H.-J. Qiu, L. Liu, Y.-P. Mu, H.-J. Zhang, Y. Wang, Designed synthesis of cobalt-oxide-based nanomaterials for superior electrochemical energy storage devices, *Nano Res*, 8 (2014) 321-339.
- [96] S. Liu, L. Hu, X. Xu, A.A. Al-Ghamdi, X. Fang, Nickel Cobaltite Nanostructures for Photoelectric and Catalytic Applications, *Small*, 11 (2015) 4267-4283.
- [97] M. Yang, W. Lu, R. Jin, X.-C. Liu, S. Song, Y. Xing, Superior Oxygen Evolution Reaction Performance of $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4/\text{Ni}$ Foam Composite with Hierarchical Structure, *ACS Sustainable Chemistry & Engineering*, (2019).
- [98] Z. Zhuang, W. Sheng, Y. Yan, Synthesis of monodisperse $\text{Au}@\text{Co}_3\text{O}_4$ core-shell nanocrystals and their enhanced catalytic activity for oxygen evolution reaction, *Advanced materials*, 26 (2014) 3950-3955.
- [99] X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang, Z. Lin, Hierarchical NiCo_2O_4 Hollow Microcuboids as Bifunctional Electrocatalysts for Overall Water-Splitting, *Angewandte Chemie*, 55 (2016) 6290-6294.
- [100] J. Yang, C. Yu, S. Liang, S. Li, H. Huang, X. Han, C. Zhao, X. Song, C. Hao, P.M. Ajayan, J. Qiu, Bridging of Ultrathin NiCo_2O_4 Nanosheets and Graphene with Polyaniline: A Theoretical and Experimental Study, *Chem Mater*, 28 (2016) 5855-5863.
- [101] L. An, L. Huang, P. Zhou, J. Yin, H. Liu, P. Xi, A Self-Standing High-Performance Hydrogen Evolution Electrode with Nanostructured $\text{NiCo}_2\text{O}_4/\text{CuS}$ Heterostructures, *Adv Funct Mater*, 25 (2015) 6814-6822.

- [102] Q. Liu, E. Wang, G. Sun, Layered transition-metal hydroxides for alkaline hydrogen evolution reaction, *Chinese Journal of Catalysis*, 41 (2020) 574-591.
- [103] H. Ebrahimzade, G.R. Khayati, M. Schaffie, Preparation and kinetic modeling of β -Co(OH)₂ nanoplates thermal decomposition obtained from spent Li-ion batteries, *Advanced Powder Technology*, 28 (2017) 2779-2786.
- [104] R.S. Jayashree, P.V. Kamath, Electrochemical synthesis of α -cobalt hydroxide, *Journal of Materials Chemistry*, 9 (1998) 961-963.
- [105] X. Liu, R. Yi, N. Zhang, R. Shi, X. Li, G. Qiu, Cobalt hydroxide nanosheets and their thermal decomposition to cobalt oxide nanorings, *Chem Asian J*, 3 (2008) 732-738.
- [106] Z. Liang, C. Zhang, Y. Xu, W. Zhang, H. Zheng, R. Cao, Dual Tuning of Ultrathin α -Co(OH)₂ Nanosheets by Solvent Engineering and Coordination Competition for Efficient Oxygen Evolution, *ACS Sustainable Chemistry & Engineering*, 7 (2018) 3527-3535.
- [107] R. Subbaraman, D. Tripkovic, K.C. Chang, D. Strmcnik, A.P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic, N.M. Markovic, Trends in activity for the water electrolyser reactions on 3d M(Ni,Co,Fe,Mn) hydr(oxy)oxide catalysts, *Nature materials*, 11 (2012) 550-557.
- [108] K. Yan, Z. Liang, Z. Li, M. Zhang, Y. Huang, Y. Wang, HMTA-assisted formation of hierarchical Co-based materials built by low-dimensional substructures as water oxidation electrocatalysts, *CrystEngComm*, 20 (2018) 5249-5255.
- [109] M.A. Sayeed, T. Herd, A.P. O'Mullane, Direct electrochemical formation of nanostructured amorphous Co(OH)₂ on gold electrodes with enhanced activity for the oxygen evolution reaction, *Journal of Materials Chemistry A*, 4 (2016) 991-999.
- [110] S. Wan, J. Qi, W. Zhang, W. Wang, S. Zhang, K. Liu, H. Zheng, J. Sun, S. Wang, R. Cao, Hierarchical Co(OH)F Superstructure Built by Low-Dimensional Substructures for Electrocatalytic Water Oxidation, *Advanced materials*, 29 (2017).
- [111] H. Jiang, Q. He, X. Li, X. Su, Y. Zhang, S. Chen, S. Zhang, G. Zhang, J. Jiang, Y. Luo, P.M. Ajayan, L. Song, Tracking Structural Self-Reconstruction and Identifying True Active Sites toward Cobalt Oxychloride Precatalyst of Oxygen Evolution Reaction, *Advanced materials*, 31 (2019) e1805127.
- [112] R. Liu, Y. Wang, D. Liu, Y. Zou, S. Wang, Water-Plasma-Enabled Exfoliation of Ultrathin Layered Double Hydroxide Nanosheets with Multivacancies for Water Oxidation, *Advanced materials*, 29 (2017).

- [113] B. He, K. Tan, Y. Gong, R. Wang, H. Wang, L. Zhao, Coupling amorphous cobalt hydroxide nanoflakes on $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_5$ perovskite nanofibers to induce bifunctionality for water splitting, *Nanoscale*, 12 (2020) 9048-9057.
- [114] J. Wang, F. Xu, H. Jin, Y. Chen, Y. Wang, Non-Noble Metal-based Carbon Composites in Hydrogen Evolution Reaction: Fundamentals to Applications, *Advanced materials*, 29 (2017).
- [115] M.I. Jamesh, Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electrocatalyst for overall water splitting in alkaline media, *Journal of Power Sources*, 333 (2016) 213-236.
- [116] R. Yang, Y. Zhou, Y. Xing, D. Li, D. Jiang, M. Chen, W. Shi, S. Yuan, Synergistic coupling of CoFe-LDH arrays with NiFe-LDH nanosheet for highly efficient overall water splitting in alkaline media, *Applied Catalysis B: Environmental*, 253 (2019) 131-139.
- [117] Y. Liu, Y. Bai, W. Yang, J. Ma, K. Sun, Self-supported electrode of NiCo-LDH/ NiCo_2S_4 /CC with enhanced performance for oxygen evolution reaction and hydrogen evolution reaction, *Electrochimica Acta*, 367 (2021) 137534.
- [118] M. Arif, G. Yasin, M. Shakeel, M.A. Mushtaq, W. Ye, X. Fang, S. Ji, D. Yan, Hierarchical CoFe-layered double hydroxide and $\text{g-C}_3\text{N}_4$ heterostructures with enhanced bifunctional photo/electrocatalytic activity towards overall water splitting, *Materials Chemistry Frontiers*, 3 (2019) 520-531.

Chapter 3

Experimental Methodology

In this chapter, the preparation methods, characterizations and analysis of cobalt-based heterostructure were outlined. First, the rationale for the selection of synthetic methods is elaborated. The fundamentals underlying the selected preparation approaches are then explained in detail. Finally, the principles of various characterization and analysis methods are elucidated.

3.1 Rationale for selection of synthetic methods

In the first part, gas-assisted electrodeposition was chosen as the synthetic method because it possesses a variety of advantages when compared to other approaches. First, it is quite a facile and simple method since it usually occurs at room temperature and atmospheric pressure; secondly, it is cost-effective since no special equipment such as heating furnace or high-pressure autoclave is required for this method. Furthermore, it is easy to take advantage of well-established electrochemical equipment in industry. Therefore, this method is usually low-cost and economic; Thirdly, this method is also highly controllable during synthesis. In general, there are three key parameters in electrodeposition including potential, current and time. It is quite easy to set up these parameters before experiment. Moreover, all these parameters can also be freely changed during experiment. For gas-assisted electrodeposition, another important parameter is the gas flux which can be simply controlled by adjusting the rate of gas flow. Finally, electrodeposition is also a versatile method. It can be used for synthesizing almost all the transition metal related compounds including transition metals themselves, transition metal oxide, transition metal hydroxide, transition metal sulfide, transition metal phosphide, transition metal selenide, etc. by simply adjusting the electrolyte employed and corresponding parameters. Furthermore, various electrochemical methods including chrono amperometry, chrono potentiometry and cyclic voltammetry (CV) can be used for the synthesis.

In the second and third part, selective corrosion (dealloying) was chosen as the synthesis approach. Dealloying is traditionally a corrosion phenomenon that had been observed long time ago. However, it has received renewed attention due to its ability to fabricate nanoporous materials. Typically, dealloying is a chemical or electrochemical process in which the less noble component(s) of an alloy is (are) etched away while the noble one(s) remains connected to each other with pores and nanoscale ligands homogeneously distributed across these remained parts. Dealloying is quite an important fabrication method for preparation of nanoporous metals (NPMs) which have various applications such as energy conversion/storage[1-3], actuators[4-6] and water splitting[7, 8] due to their unique physiochemical properties. Furthermore, NPMs fabricated through dealloying also

possess several extra advantages in composition and structure. First, there are usually abundant possibilities in compositional variations such as metals, alloys, sulfides and so forth. Moreover, all these possibilities can be finely tuned with predetermined composition. Secondly, there are usually massive 3D ligaments/channels inherited from the dealloying process, which is quite beneficial for application like energy conversion and water splitting. Thirdly, there are also numerous pores interconnected with each other and the pores diameter can be easily controlled by adjusting the precursors and dealloying conditions. Last but not least, dealloying presents to be the most promising technique for commercialization when compared to other preparation methods such as templating, chemical reduction and laser etching. The major reason behind this is the extremely low cost and ease of large-scale production[9].

3.2 Synthesis methods

3.2.1 Gas-assisted electrodeposition

As illustrated in Figure 3.1, electrodeposition was carried out in a traditional three-electrode system where the sample, platinum plate and Ag/AgCl electrode acted as working electrode, counter electrode, and reference electrode, respectively. Additionally, there is also a gas channel besides the working electrode. All the three electrodes are connected to the electrochemical workstation which is controlled by the computer. The gas channel was separately controlled by a gas valve. Besides, chrono amperometry was used to conduct the electrodeposition.

3.2.2 Dealloying

The equipment used for dealloying is quite similar to that of gas-assisted electrodeposition except that it does not have the gas channel (see Figure 3.2). Cyclic voltammetry (CV) was employed to carry out the dealloying.

Three-electrode system

Figure 3.1 Illustration of gas-assisted electrodeposition

Three-electrode system

Figure 3.2 Illustration of dealloying

3.3 Characterization and analysis

3.3.1 Transmission Electron Microscopy (TEM)

TEM is a very popular characterization method that uses electron beams as the incident beam to interact with the specimen (usually the very thin, <100 nm). The electron beam is generated by the electron gun, positioning at the top of the chamber column which is under

high vacuum environment ($<10^{-4}$ Pa) all the time so that the particles in air will not scatter the electrons. The electron beam will then go through condenser lens which can accelerate and adjust it to the parallel beam. Subsequently, the parallel beam will interact with the specimen positioned below the condenser lens and all the signals after the interaction will be focused on the back focal plane of the objective lens below the specimen, forming the primary beam. This primary beam will then go through a series of electromagnetic lens including intermediate lens and projector lens for further magnification and finally be captured by the fluorescent screen or electronic detector. The whole process is illustrated in Figure 3.3[10].

For TEM imaging, there are usually three basic types including low-magnification TEM, high-resolution TEM (HRTEM) and diffraction. For low-magnification TEM, the image contrast comes from the transmitted electrons. In details, the thick regions in specimen will allow less electrons transmitted through when compared to the thin areas. As a result, the thick region will appear darker than the thin areas since the low-magnification image will only collect the transmitted electrons. For HRTEM, the contrast come from the phase difference in specimen. To be more specific, it results from the wave interference with itself. HRTEM is usually used to observe the atomic structure of the specimen. Furthermore, it can also be employed to study the crystalline structures with the assistance of specialized computer simulation. For diffraction imaging, the electron beam is a wave itself. At the same time, the atomic lattice just acts as the grating. Therefore, the electron beam will interfere with the atomic lattice grating and elastic scattering is one of the results of wave interference. The scattered electrons can be collected by the detector and displayed as interference pattern including distinct dots pattern and rings. One of the important applications of this kind of diffraction is selected area electron diffraction (SAED) in which the SAED aperture is applied to ensure the diffraction only occur at the selected area. There will be strong distinct dots pattern or rings when the electron beam interferes constructively with the atomic lattice (when the requirement for Bragg's law is satisfied). The interference pattern thus obtained will be focused on the back focal plane of the objective lens and be further magnified by intermediate lens and projector lens until collected by the detector.

Figure 3.3 Schematic illustration of image formation in TEM

3.3.2 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) is a versatile tool in characterizing the surface morphology and analysis of chemical composition of materials. A detailed illustration of its major components is presented in Figure 3.4[11]. As presented in the figure, these major components include electron gun, electromagnetic lens, detectors and etc. , and all the electron column mentioned above is under high vacuum environment so that the electrons starting from electron gun will not be scatter by air. Besides, the electron diameter is too large to form a high-resolution image. Therefore, electromagnetic lenses are employed to focus the electron beam from electron gun, forming the primary beam. The primary beam

focused by the electromagnetic lenses will then interact with the specimen, generating various signals including secondary electrons (SEs), backscattered electrons (BSEs), characteristic X-rays, etc. The detectors above the specimen will then collect these signals and output these signals after further processing and analysis.

The interaction between primary beam and specimen is the fundamental part for the SEM image formation. This interaction can be classified into two basic types: elastic scattering and inelastic scattering. If the electrons in primary beam are deflected by the nucleus of atoms in a wide angle, then there will be negligible energy loss and the signal thus generated is called “back scattered electron”. This type of signal is quite useful for compositional analysis in SEM since there is a much higher chance for heavy element to deflect the electrons in primary beam. In this case, there will be an obvious atomic mass contrast when BSEs is used for imaging. There are various types of signals in inelastic scattering if the atoms of specimen impacted is ionized and energy loss is thus caused. Among all these signals, secondary electrons possess low-energy level (typically 3-5 eV) and can only escape from the near surface region (a few nanometers). Therefore, they can accurately reflect the surface information of the specimen. They are usually used to characterize the surface morphology and topology of the specimen in SEM. There are obvious differences between secondary electrons and backscattered electrons. First, backscattered electrons are produced by the deflection of nucleus, with negligible energy loss. In contrast, secondary electrons come from the “excitation” of outer shell electrons. Second, secondary electrons are usually “excited” in the near-surface region while the backscattered electrons can penetrate deep through the specimen. In this case, the SEs can be used to produce high-resolution image while the picture produced by BSEs is much inferior in resolution. Third, the SEs are usually in low energy level (3-5 eV) while the BSEs are in much higher energy level (about 50 eV).

In addition to secondary electrons, there is another useful signal called “characteristic X-rays” which is produced by inelastic scattering. When the inner shell electrons are knocked out by the primary beam, the outer shell electrons will fall inside to maintain the charge balance. And characteristic X-rays are thus generated due to the different energy level between inner shell and outer shell. This kind of signal can be used to determine the exact

atomic number of elements analyzed. The EDS mode in SEM has taken advantage of this signal and can be used to qualitatively and semi-quantitatively analyze the elements in specimen.

Figure 3.4 Schematic illustration of major components of SEM

3.3.3 Powder X-ray Diffraction (XRD)

X-ray diffraction is a powerful technique that has wide applications in various industries including pharmaceuticals, geological science, and microelectronics industry. It is usually carried out with a X-ray diffractometer shown in Figure 3.5[12]. As displayed in the figure,

it consists of four major components including X-ray source, system optics including the slits, sample stage and detector. The X-ray source is usually an X-ray cathode tube in which high voltage is applied to draw electrons to the anode or target. The electrons starting from the filament will bombard the target materials like copper to generate characteristic X-rays. Subsequently, these characteristic X-rays will go through the monochromators so that only X-rays with identical wavelength will remain, which is also an ideal condition for powder X-ray diffraction and analysis. After other optical processing, the monochromatic X-rays will finally reach the sample and interfere with the numerous crystal planes in the specimen since the spacings of these planes is similar to the wavelength of X-rays used here. A lot of these interference will cancel out each other. However, there will be constructive interference pattern produced as long as the distance of crystal planes and angle fulfill the Bragg's law: $n\lambda = 2d\sin\theta$, see Figure 3.6[13]. For most powder diffractometers, the dominant geometry is Bragg-Brentano parafocusing geometry. Diffractometers adopting this geometry can provide spectrums with high-resolution and high intensity, which makes it easy for data analysis. However, accurate alignment and careful sample preparation are required for the experiment. In general, there are two basic configurations for powder diffractometers in Bragg-Brentano geometry. The first is θ - 2θ mode: The X-ray source is fixed while the rotates at the rate of θ/min , the detector moves at the speed of $2\theta/\text{min}$. The second is θ - θ mode: the position of sample is fixed. Both the X-ray source and detector rotates at the speed of θ/min .

In addition to Bragg-Brentano (BB) geometry, there is another parallel beam (PB) geometry adopted by the diffractometer. In PB geometry, there is not much requirement for sample flatness and roughness, which is a big constraint in BB geometry. Besides, the distance requirement that the source-to-sample distance must be kept constant and the same as the detector-to-sample distance is also removed. In this case, it is possible to do measurement with much different sample sizes and shapes.

Figure 3.5 Schematic illustration of X-ray diffractometer

Figure 3.6 Schematic illustration of Bragg's law

3.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a powerful surface technique that could be used to identify the chemical elements of the material's surface as well as the surrounding chemical environment like the oxidation state as well as which element it is bonded with. XPS is based on the photoelectric effect discovered in 1887. When the material is irradiated by X-ray, photoelectrons will be emitted from the specimen surface. The fundamental physical laws governing XPS can be described as the following equation.

$$BE = h\nu - KE - \phi_{spec} \quad (1)$$

BE here represent the binding energy to be calculated, $h\nu$ is the energy of incident X-ray, KE is the kinetic energy of the emitted photoelectron and ϕ_{spec} is the work function of spectrometer which is a constant. All the elements in equation (1) can be either measured (like KE and $h\nu$) or already known (like ϕ_{spec}), thus it is easy to the characteristic binding energy, see Figure 3.7[14].

Figure 3.7 Schematic illustration of energy levels

3.3.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a versatile technique that has been widely geochemistry. It is capable of detecting the element abundance in a high sensitivity of one part per trillion (ppt). Besides, it can also analyze the isotope ratio of a specific element. All the tasks can be done by ionizing the sample in inductively coupled plasma and subsequently introduced to the mass spectrometer for further analysis (separation and quantification). Various samples including natural water and solids like dust, soil and other matters can be analyzed by ICP-MS although the solids must be dissolved in solution first before ionization. The ICP-MS instrumentation usually include sample introduction part, inductively coupled plasma, vacuum system, ion optics and ion detection system, see Figure 3.8[15]. The sample introduction section and inductively coupled plasma are usually operated in air while other parts are operated under high vacuum (10^{-4} - 10^{-9} mbar). Based on the specific types of mass spectrometer that ICP combines with, the ICPMS can be classified into multi-collector (MC) ICP-MS, sector field mass spectrometry (ICP-SFMS) and quadrupole ICP-MS. (MC) ICP-MS is characterized with multiple detectors to collect the isotope signals so that the isotope ratio can be calculated and analyzed in a very high precision. ICP-SFMS can provide high mass resolution results in higher sensitivity when compared to quadrupole ICP-MS. In contrast, quadrupole ICP-MS is capable of rapidly doing the measurement and providing the outcome based on the entire periodic table.

Figure 3.8 Schematic illustration of ICP-MS

3.3.6 Electrochemical measurements

3.3.6.1 Cyclic voltammetry (CV)

Cyclic voltammetry is a typical potentiodynamic technique that has been widely used in electrochemistry. It is usually employed to investigate the analyte in solution or electrolyte and the traditional three-electrode system is adopted in the analysis. The potential is measured between the working electrode and reference and the current is measured between the working electrode and counter electrode. And the potential is plotted against the current to get the cyclic voltammogram (see Figure 3.9)[16]. As illustrated in Figure 3.9, the redox couple of ferrocenium (Fc^+) and ferrocene (Fc) is taken as an example. Figure H and Figure I have shown the cyclic voltammogram and corresponding potentiodynamic curve of Fc^+ vs Fc , respectively. Figure A-G have revealed the concentration distribution of Fc^+ (blue) and Fc (red) from the electrode surface to the solution. The scan starts from A where only oxidate Fc^+ exist and is homogeneously distributed across the bulk electrolyte. The scan starting from A is a cathodic scan, so the oxidate Fc^+ is reduced to reductant Fc . In this case, the oxidate A will gradually be consumed although new Fc^+ will diffuse from the solution to the electrode surface. As the scan continues, the concentration of Fc^+ will reduce over time while the concentration of Fc will increase. The current flow also increases even as the potential applied decrease due to the generation of Faradic current from the redox reaction. At stage B, the concentration of Fc^+ is equal to that of Fc at the electrode surface. At critical stage C, the concentration of Fc^+ is well below the concentration of Fc at the electrode surface, the current reaches its maxima will start to decrease even the absolute value of potential applied continues to grow. When the scan reaches stage D, all the Fc^+ is depleted and the concentration of Fc has reached its peak across the solution. After stage D, the inverse scan starts followed by the oxidation of Fc to Fc^+ . The processes of D-F are quite similar to processes A-D except that the reaction taking place is oxidation reaction ($\text{Fc} \rightarrow \text{Fc}^+$). When the scan finally reaches stage G, a complete cycle is finished.

Figure 3.9 Detailed explanation of cyclic voltammetry taking Fc as an example

3.3.6.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a versatile tool that has broad application in various fields including corrosion, lithium-ion batteries, and biochemistry, etc. It is also quite different from other electrochemical techniques such as cyclic voltammetry since it is a frequency-domain technique in which frequency is the major parameter. Unlike other electrochemical methods using potential sweeps to make the system deviate from equilibrium, EIS uses small perturbations to achieve the same purpose. The obvious advantage for this is that small perturbations lead to small deviation from equilibrium, which is then assumed to have a linear relationship. In this case, the further data analysis is significantly simplified.

Figure 3.10 A typical EIS diagram with R and C in parallel connection

Reference

- [1] Q. Chen, Y. Ding, M. Chen, Nanoporous metal by dealloying for electrochemical energy conversion and storage, MRS Bulletin, 43 (2018) 43-48.

- [2] J. Zhang, C.M. Li, Nanoporous metals: fabrication strategies and advanced electrochemical applications in catalysis, sensing and energy systems, *Chemical Society reviews*, 41 (2012) 7016-7031.
- [3] Y. Yang, G. Ruan, C. Xiang, G. Wang, J.M. Tour, Flexible three-dimensional nanoporous metal-based energy devices, *Journal of the American Chemical Society*, 136 (2014) 6187-6190.
- [4] H.J. Jin, X.L. Wang, S. Parida, K. Wang, M. Seo, J. Weissmuller, Nanoporous Au-Pt alloys as large strain electrochemical actuators, *Nano letters*, 10 (2010) 187-194.
- [5] E. Detsi, M.S. Sellès, P.R. Onck, J.T.M. De Hosson, Nanoporous silver as electrochemical actuator, *Scripta Materialia*, 69 (2013) 195-198.
- [6] J. Biener, A. Wittstock, L.A. Zepeda-Ruiz, M.M. Biener, V. Zielasek, D. Kramer, R.N. Viswanath, J. Weissmuller, M. Baumer, A.V. Hamza, Surface-chemistry-driven actuation in nanoporous gold, *Nature materials*, 8 (2009) 47-51.
- [7] J. Oh, T.G. Deutsch, H.-C. Yuan, H.M. Branz, Nanoporous black silicon photocathode for H₂ production by photoelectrochemical water splitting, *Energy & Environmental Science*, 4 (2011) 1690.
- [8] C.H. Bak, K. Kim, K. Jung, J.-B. Kim, J.-H. Jang, Efficient photoelectrochemical water splitting of nanostructured hematite on a three-dimensional nanoporous metal electrode, *J. Mater. Chem. A*, 2 (2014) 17249-17252.
- [9] X. Wu, G. He, Y. Ding, Dealloyed nanoporous materials for rechargeable lithium batteries, *Electrochemical Energy Reviews*, 3 (2020) 541-580.
- [10] B. Fultz, J. Howe, *Transmission Electron Microscopy and Diffractometry of Materials*, Springer Science & Business Media 2012.
- [11] A. Ul-Hamid, *A Beginners guide to scanning electron microscopy*, Springer International Publishing 2018.
- [12] P.D. Hatton, S.B. Wilkins, T.A. Beale, T.K. Johal, D. Prabhakaran, A.T. Boothroyd, Resonant soft X-ray diffraction - in extremis, *J Synchrotron Radiat*, 12 (2005) 434-441.
- [13] C. Stan, C. Beavers, M. Kunz, N. Tamura, X-Ray Diffraction under Extreme Conditions at the Advanced Light Source, *Quantum Beam Science*, 2 (2018) 4.
- [14] F.A. Stevie, C.L. Donley, Introduction to x-ray photoelectron spectroscopy, *Journal of Vacuum Science & Technology A*, 38 (2020) 063204.
- [15] M. Schönbachler, *Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*, 2016, pp. 1-6.
- [16] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A Practical Beginner's Guide to Cyclic Voltammetry, *Journal of Chemical Education*, 95 (2017) 197-206.

Chapter 4

Growth of Lattice Coherent Co₉S₈/Co₃O₄ Nano-Heterostructure for Maximizing the Catalysis of Co-Based Composites

Gas purging during electrodeposition has significant influence on microstructures and compositions of products obtained. Co-Mn LDH was electrodeposited on Ni foam without gas purging, whereas electrodeposition with N₂ purging followed by annealing formed highly efficient Co₉S₈/Co₃O₄ heterostructure for water splitting. This remarkable distinction is mainly due to the decrease of concentration of hydroxide ions (produced by the reduction of NO₃⁻) near electrode surface owing to the enhanced ion transport brought by N₂ purging. The heterostructure thus obtained has shown superior performance for water splitting, especially for oxygen evolution reaction (OER). The corresponding 250 mV overpotential (@ 10 mA·cm⁻²) and 73.54 mV·dec⁻¹ Tafel slope for OER exceed the state-of-the-art Co-based composites. It has also demonstrated excellent durability in alkaline media, indicating its promising potential for practical application in industry.

*This section published/submitted substantially as "Growth of Lattice Coherent Co₉S₈/Co₃O₄ Nano - Heterostructure for Maximizing the Catalysis of Co - Based Composites." ChemCatChem 12(2020). Reproduced with permission. Copyright (2020) Chemistry Europe.

4.1 Introduction

Electrochemical water splitting including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) has been considered to be one of the most promising techniques to meet the increasing energy demand in an efficient and eco-friendly way.[1-12] However, the traditional state-of-the-art electrocatalysts for water splitting are noble metal (Pt) or metal oxides (IrO_2 , RuO_2), which are not suitable for large-scale application due to their scarcity and high cost[13-16]. Therefore, intensive efforts have been devoted to develop the earth-abundant and efficient electrocatalysts.

Among all these catalysts developed so far, cobalt-based catalysts have demonstrated to be a promising candidate for replacing those electrocatalysts[17]. For instance, Fang et al. have successfully synthesized cobalt-manganese layered double hydroxide (Co-Mn LDH) by co-precipitation method, which was reported to be highly active toward OER[18]. In addition, Li et al. reported that the hierarchically porous Co_3O_4 derived from the zeolitic imidazolate framework (ZIF-67-Co) by calcination can act as efficient OER electrocatalyst[19]. Similarly, cobalt pentlandite (Co_9S_8) was also found to be a good candidate for electrocatalytic water splitting. Using Co-NSOMOF as precursor, Du et al. synthesized Co/ Co_9S_8 nanoparticles as excellent bifunctional electrocatalysts for water splitting. Using Co-NSOMOF as precursor, Du et al. synthesized Co/ Co_9S_8 nanoparticles as excellent bifunctional electrocatalysts for water splitting[20]. Liu et al. demonstrated that Co_9S_8 nanosheets supported on doped reduced graphene oxide (rGO) have exhibited exceptional OER performance due to the synergistic catalysis between these two phases[21]. Here a much simpler and low-cost synthesis method – electrodeposition is employed to fabricate highly efficient cobalt-based bifunctional electrocatalysts. The products obtained can be fine-tuned by controlling the nitrogen purging before and during the electrodeposition. One of the electrocatalysts with best performance turns out to be a heterostructure composed of Co_3O_4 and Co_9S_8 and have exhibited excellent electrocatalytic activity due to the synergistic effect.

4.2 Materials preparation

Unless otherwise pointed out, all the chemicals used here were purchased from Sigma-Aldrich. Nickel foam (purchased from Sigma-Aldrich) was used as substrate for electrodeposition. Prior to use, it was pre-treated with sequential ultrasonication in concentrated hydrochloric acid (37%, HCl), absolute ethanol, and deionized (DI) water for 10 min each. After pre-treatment, the substrate was further cleaned by blow drying with nitrogen gas.

Cyclic voltammetry (CV) was used to carry out the electrodeposition. The corresponding scan range and scan rate were -1.2-0.2 V and 5 mV/s, respectively. The electrodes here were the commonly used three-electrode system in which the platinum plate, silver/silver chloride (3.5 M KCl) and the sample acts as counter electrode, reference electrode and working electrode, respectively. Each sample had gone through 5 cycles of CV for the electrodeposition. For electrolyte, cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$) were employed as precursors and thiourea was used as sulphur source. To investigate the effect of concentration, a series of electrolyte with various concentration of manganese nitrate tetrahydrate (ranging from 20 mM, 15 mM, 10 mM to 5 mM) were prepared accordingly. The concentration of cobalt chloride hexahydrate and thiourea were kept constant at 5 mM and 0.5 M, respectively. The samples thus obtained are denoted as CoOS-4, CoOS-3, CoOS-2 and CoOS-1, respectively. In certain circumstances, rigorous nitrogen purging (1 bar) was conducted for 30 min before electrodeposition and kept during electrodeposition but at a mild speed (0.1 bar). For the sample fabricated without N_2 purging, it is denoted as CoMn-LDH. In order to enhance the crystallinity of the specimens obtained with N_2 purging, all of them were annealed at 300 °C for 2 h at argon atmosphere. i-R compensation was also carried out in the performance tests to correct the effect of solution resistance on the electrocatalytic activity.

4.3 Characterization methods

Scanning electron microscope (SEM, JSM-7800F, JEOL), transmission electron microscope as well as scanning transmission electron microscope (TEM & STEM, JEM-2100F, JEOL) and X-ray diffraction (XRD, Bruker D8 Advance & Shimadzu thin film) were employed here to investigate the morphology and composition of the materials obtained. The performance of the sample towards water splitting was evaluated by electrochemical impedance spectroscopy (EIS) as well as linear sweep voltammetry (LSV) using the electrochemical station (Autolab, PGSTAT 302N). In addition, X-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos) was also used to analyze the surface information especially the elemental composition and valence.

4.4 Principle outcomes

4.4.1 The electrochemical synthesis

In present work, a rather simple and low-cost synthesis method (i. e. electrodeposition) is used to synthesize highly efficient bifunctional electrocatalysts, see Figure 4.1. The products obtained can be fine-tuned by controlling the nitrogen purging prior to and during the electrodeposition. Figure 1 shows two sets of CV curves with 5 cycles for each electrodeposition, which were collected without N_2 purging (Figure 4.2a), and with 30 min rigorous N_2 purging before electrodeposition and continuous mild N_2 purging during electrodeposition (Figure 4.2b). The pressures corresponding to rigorous and mild purging are 1 bar and 0.01 bar, respectively. Both curves show oxidation and reduction peak in forward and reverse scan. In spite of the similar curvature, the peaks are positioned differently in these two curves. For the curve without N_2 purging, except for the first two peaks, the peak positions of oxidation and reduction are 0.06 V and -0.34 V, respectively. In contrast, the corresponding peak positions change to 0.26 V and -0.24 V with N_2 purging. The shift in redox peaks indicates that the major reactions occurring on the electrode surface has changed.

Figure 4.1 Schematic illustration of electrochemical synthesis of Co-based electrocatalysts under different conditions

Figure 4.2 CV curves of electrodeposition: (a) without N₂ purging before or during electrodeposition; (b) 30 min rigorous N₂ purging (1 bar) before and mild N₂ purging (0.1 bar) during electrodeposition.

4.4.2 CoMn LDH synthesized without N₂ purging

Figure 4.3a shows that the surface of electrodeposited Ni foam without N₂ purging before or during electrodeposition is uniformly covered with free standing and ultrathin

nanosheets (less than 10 nm), as further displayed in Figure 4.4(a-c). However, the lateral size of the nanosheets is approximately 500 nm. Energy dispersive spectroscopy (EDS) attached on the SEM was used to investigate the elemental composition of these nanosheets and the presence of five elements (i. e. Co, Mn, O, S and Cl) was confirmed (see Figure 4.3b). All these elements are uniformly distributed across these nanosheets (see Figure 4.4d). TEM observation was also carried out to further analyze the lattice structure of Mn-Co LDH nanosheets obtained. Figure 4.3c shows the typical ultrathin nanosheet morphology. The selected area electron diffraction (SAED) pattern (i. e. the inset in Figure 4.3c) demonstrates the polycrystalline structure of the Mn-Co LDH nanosheets, which is further confirmed by the high resolution TEM (HRTEM) image (Figure 4.3d). In addition, the existence of the five elements (Co, Mn, O, Cl and S) mentioned above is again confirmed by STEM elemental mapping in Figure 4.3e. XRD characterization was also conducted to further investigate the crystalline structure and phase identity of the nanosheets with the result presented in Figure 4.3f. The peaks at about 19°, 32°, 36.5° and 50°, 55° and 58.5° are assigned to (006), (009), (012), (018), (110) and (113) lattice planes of Mn-Co LDH, respectively[22]. The other three remained peaks positioned at 45°, 52° and 77° are indexed to (111), (200) and (202) lattice planes of Ni foam substrate. Based on the results above, it is clear that only Mn-Co LDH will be formed during electrodeposition if no N₂ is purged before or during the electrochemical synthesis. This is also in good agreement with the elemental composition mentioned above. It is also reasonable to deduce that S²⁻ and Cl⁻ act as intercalation anions between the layers to balance the charges. Besides, XPS analysis was also conducted and the results are summarized in Figure 4.5. As revealed in the figure, in addition to the existence of three major elements (Co, Mn and O), the formation of Mn³⁺ is also confirmed[23]. In this case, it is obvious that the redox peaks in Figure 4.2a are produced by the redox of Mn. Based on the results mentioned above, the possible formation mechanism is proposed here[6]:

Figure 4.3 Characterization of a sample obtained without N_2 purging before or during electrodeposition: (a) SEM observation; (b) corresponding EDS spectrum; (c) TEM image and (inset) corresponding SAED; (d) HRTEM image and (inset) the FFT pattern of the square region; (e) STEM mapping and (f) XRD pattern.

Figure 4.4 SEM observation of the electrodeposited Ni foam without N_2 purging before or during the electrodeposition: a), b) low and c) high magnification image; d) SEM image and corresponding elemental mapping data

Figure 4.5 XPS spectra of electrodeposited Ni foam without N_2 purging before or during electrodeposition: (a) survey; (b) Co; (c) Mn and (d) O

4.4.3 Co₉S₈/Co₃O₄ nano-heterostructure synthesized with N₂ purging

In contrast, when subjected to N₂ purging starting with 30 min rigorous speed (1 bar) prior to electrodeposition followed by mild speed (0.01 bar) during the electrodeposition, remarkably different nanosheets in terms of the composition and microstructure were formed. These nanosheets have a very small size (around 100 nm) (see Figure 4.6 & Figure 4.7) and consist of Co₉S₈ and Co₃O₄ according to the XRD pattern (Figure 3b). The characteristic peaks generated from Co₉S₈ are located at 15.5°, 17.9°, 25.4°, 29.8°, 31.18°, 47.6°, 52.1°, 61.9° and 65° corresponding to (111), (200), (220), (311), (222), (511), (440) (622) and (444) lattice planes, respectively (PDF #04-007-5239). The rest of the peaks positioned at 19.4°, 31.9°, 37.6° and 39.4° are all diffracted from Co₃O₄ and attributed to the lattice planes of (111), (220), (311), and (222) in sequence (PDF # 04-022-7118).

XPS analysis was also carried out and it was found that cobalt exists in three different oxidation states (Co⁺, Co²⁺ and Co³⁺)[24, 25], which is in good agreement with the XRD results described above. Besides, the existence of three major elements including Co, S and O is also verified (see Figure 4.8). Therefore, it is cobalt ions that mainly contribute to the redox peaks in Figure 4.2b. The proposed reaction mechanism is as follow[6]:

Similarly, OH⁻ was generated during the reduction of NO₃⁻ [see Eq. (4)]. Meanwhile, Co²⁺ was oxidized and reduced to Co³⁺ [see Eq. (5)] and Co⁺, respectively [see Eq. (6)]. The existing cobalt ions will then combine with the OH⁻ to form hydroxides including Co(OH)₂ [see Eq. (7)] and Co(OH)₃ [see Eq. (8)] as intermediates which will be further dehydrated to Co₃O₄ [see Eq. (9)]. Alternatively, the cobalt ions (Co⁺ and Co²⁺) can also react with thiourea to form Co(TU)⁺ [see Eq. (10)] and Co(TU)₂²⁺ [see Eq. (11)] as intermediates, respectively. These two products will then react with each other to form Co₉S₈ [see Eq. (12)]. Therefore, it is reasonable to conclude that the decrease of hydroxides ions, which is caused by the enhanced ion transport due to N₂ purging, is beneficial for the formation of Co₉S₈/Co₃O₄ heterostructure instead of CoMn LDH. Furthermore, the SAED (inset of Figure 4.6c) suggests the polycrystalline structure of the nanosheets and the elemental analysis of the nanosheets using EDS reveals that there is lack of Mn in the nanosheets (Figure 4.6d & Figure 4.6d), which is in good agreement with XRD analysis. Besides, the nanosheets also show porous structure (see Figure 4.6a). More detailed lattice structure is analysed from the HRTEM images (see Figure 4.6e). Two phases are identified according to the corresponding FFT pattern. For further analysis, the squared area marked in Figure 3e were used to produce inverse FFT image (see Figure 4.6f). The two phases including Co₃O₄ (red colour) and Co₉S₈ (blue colour) are clearly shown in the figure and completely coherent in the lattice plane of {020}. It is this well-orientated lattice structure that provides an excellent path facilitating the mass transport and ion transport during HER and OER. On the one hand, the interfaces between the two phases are able to significantly reduce the activation energy barrier needed to be overcome for the onset of reactions. On the other hand, the strong absorption of intermediates formed during reaction accelerates the overall process of water splitting.

In addition, N₂ purging also has significant influence on the growth kinetics of the films, which is confirmed by measuring the thickness of electrodeposited film through the cross-section image produced by focus ion beam (FIB). The average thickness of Mn-Co LDH film is about 2 μm (see Figure 4.9a) while the average thickness of Co₉S₈/Co₃O₄ decreases to only 1 μm (see Figure 4.9b), indicating that nitrogen purging resulting in the slower growth of the composite film, thus allowing for the exposure of more active sites.

Figure 4.6 Characterization of sample obtained with 30 min N_2 purging before electrodeposition and continuous but mild N_2 purging during the electrodeposition: (a) SEM observation; (b) corresponding XRD pattern; (c) low magnification TEM image and (inset) the SAED pattern; (d) the corresponding EDX; (e) HRTEM images (inset of c) the FFT pattern of the square region); (f) Inverse FFT (IFFT) image.

Figure 4.7 SEM observation of the electrodeposited Ni foam with N_2 purging before and during the electrodeposition: a), b) low and c) high magnification image; d) SEM image and corresponding elemental mapping data

Figure 4.8 XPS spectra of electrodeposited Ni foam with 30min rigorous N_2 purging (1 bar) before and mild N_2 purging (0.01 bar) during electrodeposition: (a) survey; (b) Co; (c) S and (d) O

Figure 4.9 The cross-section of the electrodeposited Ni foam a) without N_2 purging before or during electrodeposition, b) 30 min rigorous N_2 purging (1 bar) before and mild N_2 purging (0.1 bar) during electrodeposition

4.4.4 Catalytic performance of CoMn LDH and $\text{Co}_9\text{S}_8/\text{Co}_3\text{O}_4$ nano-heterostructure

To investigate the electrocatalytic performance of samples, electrochemical measurements were performed to evaluate the catalytic activities towards water splitting in 1 M KOH. The results are summarized in Figure 4.10. It was found that the molar ratio of manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) to cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in electrolyte has significant effect on the electrocatalytic activity of the samples. This is probably due to the change of molar ratio of Co_9S_8 to Co_3O_4 in the heterostructure. For example, when the molar ratio of Mn to Co reaches 3 in electrolyte, it is capable of generating $10 \text{ mA} \cdot \text{cm}^{-2}$ at a low overpotential of 235.04 mV (see Figure 4.10a) with the Tafel slope of $164.44 \text{ mV} \cdot \text{dec}^{-1}$ (see Figure 4.10b), much better than the pure CoMn LDH. Meanwhile, it has shown extraordinary OER performance, much higher than that of pure CoMn LDH. When the molar ratio of Mn to Co in electrolyte is also 3, it only requires the overpotential of 330 mV to reach the current density of $100 \text{ mA} \cdot \text{cm}^{-2}$, with the corresponding Tafel slope of $73.54 \text{ mV} \cdot \text{dec}^{-1}$ (see Figure 4.10d and Figure 4.10e). Furthermore, only 250 mV of overpotential is needed if the target current density is set to the commonly used $10 \text{ mA} \cdot \text{cm}^{-2}$. In ECSA measurements (see Figure 4.11), CoOS-3 also

possesses the largest ECSA when compared to other samples, further confirming its high electrocatalytic activity. Besides, the corresponding loading mass is only 0.2 mg/cm⁻², indicating the high specific activity. In contrast, the corresponding values for pure CoMn LDH are 450 mV and 117.42 mV·dec⁻¹ (@ 100 mA·cm⁻²), respectively.

Meanwhile, it also possesses excellent stability in 1 M KOH regarding HER&OER (See Figure 4.10c & Figure 4.10f and Figure 4.12 & Figure 4.13). This is further proven by XRD, HRTEM, XPS and ICPMS (see Figure 4.14, Figure 4.15, Figure 4.16 and Table 4.1) results collected after cyclic measurement. This extraordinary performance can be attributed to the following factors:

(i) the interface formed between Co₉S₈ and Co₃O₄ which could remarkably facilitate the adsorption of intermediates produced in reaction and is beneficial for the proton reduction as well as oxygen oxidation on the electrode; (ii) the intrinsic property of higher energy state in the interface largely reduces the energy barrier needed to be overcome for the adsorption of the intermediates; (iii) the porous structure is capable of greatly enhancing the permeating of electrolyte as well as the mass transport, thus facilitating the overall electrochemical reaction; (iv) the remarkably improved conductivity (see EIS spectrum in Figure 4.10a).

In summary, the present work reports a facile, efficient and cost-effective electrochemical method to synthesize Co₉S₈/Co₃O₄ nano-heterostructure with N₂ purging and subsequent annealing. The gas purging will directly result in the decrease of hydroxide ions concentration near electrode surface, which is beneficial for the formation of heterostructure. It offers better electrocatalytic performance than the state of the art Co-based nanocomposites (see Table 4.2 in supplementary information), indicating its promising potential for practical application.

Figure 4.10 Performance test of electrodeposited Ni foams prepared by different under different conditions: (a) Nyquist plots and LSV curves for HER, (b) corresponding Tafel slopes and (c) stability performance in 1 M KOH (without i-R compensation); (d) LSV curves for OER, (e) corresponding Tafel slopes and (f) stability test in 1 M KOH (without i-R compensation).

Figure 4.11 OER performance of electrodeposited Ni (CoOS-3) after stability test ($100\text{mA}\cdot\text{cm}^{-2}$, 12h): a) Nyquist plot, b) Linear scan voltammetry curves, c) low magnification SEM image d) high magnification image

Figure 4.12 HER performance of electrodeposited Ni (CoOS-3) after stability test ($10\text{mA}\cdot\text{cm}^{-2}$, 12h): a) Nyquist plot, b) Linear scan voltammetry curves, c) low magnification SEM image d) high magnification image

Figure 4.13 Cyclic voltammograms (CV) of (a) CoOS-1, (b) CoOS-2, (c) CoOS-3, (d) CoOS-4, (e) CoMn-LDH and (f) the anodic charging current measured at 1.15 V vs Ag/AgCl plotted against different scan rates

Figure 4.14 XRD pattern CoOS-3 heterostructure after 1000 cycles Figure 4.15 TEM characterization of CoOS-3 heterostructure after 1000 cycles: (a) TEM image and corresponding SAED image; (b) HRTEM image and corresponding FFT image

Figure 4.16 XPS characterization of CoOS-3 heterostructure after 1000 cycles: (a) survey; (b) Co; (c) S and (d) O

Table 4.1 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) results of CoOS-3 heterostructure after 1000 cycles

Element	Before cycling	After 1000 cycles
Co	0.0115 ppb	0.0166 ppb

Table 4.2 Comparison of OER performance with other state-of-art electrocatalysts

Materials	Overpotential	Target Current Density	Tafel slope	Reference
CoO	269 mV	10 mA·cm ⁻²	64.4 mV·dec ⁻¹	[26]
Co ₃ O ₄	303 mV	100 mA·cm ⁻²	75.6 mV·dec ⁻¹	[27]
Co ₉ S ₈	299 mV	10 mA·cm ⁻²	67 mV·dec ⁻¹	[28]
Ni _x Co _{3-x} O ₄	420 mV	10 mA·cm ⁻²	59 mV·dec ⁻¹	[29]
Co ₃ O ₄ /NiCo ₂ O ₄	340 mV	10 mA·cm ⁻²	88 mV·dec ⁻¹	[30]
CoCo-NS	353 mV	10 mA·cm ⁻²	45 mV·dec ⁻¹	[31]
CeO ₂ /CoSe ₂	288 mV	10 mA·cm ⁻²	44 mV·dec ⁻¹	[32]

Reference

- [1] R. Parsons, The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen, *Transactions of the Faraday Society*, 54 (1958) 1053-1063.
- [2] H. Zhu, J. Zhang, R. Yanzhang, M. Du, Q. Wang, G. Gao, J. Wu, G. Wu, M. Zhang, B. Liu, J. Yao, X. Zhang, When cubic cobalt sulfide meets layered molybdenum disulfide: a core-shell system toward synergetic electrocatalytic water splitting, *Advanced materials*, 27 (2015) 4752-4759.
- [3] A. Yamaguchi, R. Inuzuka, T. Takashima, T. Hayashi, K. Hashimoto, R. Nakamura, Regulating proton-coupled electron transfer for efficient water splitting by manganese oxides at neutral pH, *Nature communications*, 5 (2014) 4256.
- [4] S. Chen, S.-Z. Qiao, Hierarchically Porous Nitrogen-Doped Graphene- NiCo_2O_4 Hybrid Paper as an Advanced Electrocatalytic Water-Splitting Material.pdf, *ACS nano*, 7 (2013) 10190-10196.
- [5] J. Wang, W. Cui, Q. Liu, Z. Xing, A.M. Asiri, X. Sun, Recent Progress in Cobalt-Based Heterogeneous Catalysts for Electrochemical Water Splitting, *Advanced materials*, 28 (2016) 215-230.
- [6] S. Anantharaj, S.R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, Recent Trends and Perspectives in Electrochemical Water Splitting with an Emphasis on Sulfide, Selenide, and Phosphide Catalysts of Fe, Co, and Ni: A Review, *ACS Catalysis*, 6 (2016) 8069-8097.
- [7] J. Masa, P. Weide, D. Peeters, I. Sinev, W. Xia, Z. Sun, C. Somsen, M. Muhler, W. Schuhmann, Amorphous Cobalt Boride (Co_2B) B) as a Highly Efficient Nonprecious Catalyst for Electrochemical Water Splitting: Oxygen and Hydrogen Evolution, *Advanced Energy Materials*, 6 (2016).
- [8] H.N. Nong, H.S. Oh, T. Reier, E. Willinger, M.G. Willinger, V. Petkov, D. Teschner, P. Strasser, Oxide-supported $\text{IrNiO}(x)$ core-shell particles as efficient, cost-effective, and stable catalysts for electrochemical water splitting, *Angewandte Chemie*, 54 (2015) 2975-2979.
- [9] J. Zhang, L. Dai, Nitrogen, Phosphorus, and Fluorine Tri-doped Graphene as a Multifunctional Catalyst for Self-Powered Electrochemical Water Splitting, *Angewandte Chemie*, 55 (2016) 13296-13300.
- [10] X. Li, X. Hao, A. Abudula, G. Guan, Nanostructured catalysts for electrochemical water splitting: current state and prospects, *Journal of Materials Chemistry A*, 4 (2016) 11973-12000.

- [11] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting, *Journal of Materials Chemistry A*, 4 (2016) 17587-17603.
- [12] G. Ming, D.-Y. Wang, C.-C. Chen, B.-J. Hwang, H. Dai, A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction, 9 (2016) 28-46.
- [13] W. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum-Acid vs Alkaline Electrolytes.pdf, *J Electrochem Soc*, 157 (2010) B1529-B1536.
- [14] N. Cheng, S. Stambula, D. Wang, M.N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T.K. Sham, L.M. Liu, G.A. Botton, X. Sun, Platinum single-atom and cluster catalysis of the hydrogen evolution reaction, *Nature communications*, 7 (2016) 13638.
- [15] D.V. Esposito, S.T. Hunt, A.L. Stottlemeyer, K.D. Dobson, B.E. McCandless, R.W. Birkmire, J.G. Chen, Low-cost hydrogen-evolution catalysts based on monolayer platinum on tungsten monocarbide substrates, *Angewandte Chemie*, 49 (2010) 9859-9862.
- [16] M.D. Scanlon, X. Bian, H. Vrubel, V. Amstutz, K. Schenk, X. Hu, B. Liu, H.H. Girault, Low-cost industrially available molybdenum boride and carbide as "platinum-like" catalysts for the hydrogen evolution reaction in biphasic liquid systems, *Phys Chem Chem Phys*, 15 (2013) 2847-2857.
- [17] G. Huang, Z. Xiao, R. Chen, S. Wang, Defect Engineering of Cobalt-Based Materials for Electrocatalytic Water Splitting, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 15954-15969.
- [18] F. Song, X. Hu, Ultrathin cobalt-manganese layered double hydroxide is an efficient oxygen evolution catalyst, *Journal of the American Chemical Society*, 136 (2014) 16481-16484.
- [19] L. Li, T. Tian, J. Jiang, L. Ai, Hierarchically porous Co₃O₄ architectures with honeycomb-like structures for efficient oxygen generation from electrochemical water splitting, *Journal of Power Sources*, 294 (2015) 103-111.
- [20] J. Du, R. Wang, Y.R. Lv, Y.L. Wei, S.Q. Zang, One-step MOF-derived Co/Co₉S₈ nanoparticles embedded in nitrogen, sulfur and oxygen ternary-doped porous carbon: an efficient electrocatalyst for overall water splitting, *Chem Commun (Camb)*, 55 (2019) 3203-3206.
- [21] H. Liu, C.Y. Xu, Y. Du, F.X. Ma, Y. Li, J. Yu, L. Zhen, Ultrathin Co₉S₈ nanosheets vertically aligned on N,S/rGO for low voltage electrolytic water in alkaline media, *Sci Rep*, 9 (2019) 1951.

- [22] J. Zhao, J. Chen, S. Xu, M. Shao, D. Yan, M. Wei, D.G. Evans, X. Duan, CoMn-layered double hydroxide nanowalls supported on carbon fibers for high-performance flexible energy storage devices, *Journal of Materials Chemistry A*, 1 (2013).
- [23] J. Zhao, J. Chen, S. Xu, M. Shao, Q. Zhang, F. Wei, J. Ma, M. Wei, D.G. Evans, X. Duan, Hierarchical NiMn Layered Double Hydroxide/Carbon Nanotubes Architecture with Superb Energy Density for Flexible Supercapacitors, *Adv Funct Mater*, 24 (2014) 2938-2946.
- [24] X. Hong, Q. Liu, X. Gao, C. He, X. You, X. Zhao, X. Liu, M. Ye, Rational design of coralloid Co_9S_8 -CuS hierarchical architectures for quantum dot-sensitized solar cells, *Journal of Materials Chemistry C*, 6 (2018) 11384-11391.
- [25] X. Liu, H. Liu, Y. Zhao, Y. Dong, Q. Fan, Q. Kuang, Synthesis of the Carbon-Coated Nanoparticle Co_9S_8 and Its Electrochemical Performance as an Anode Material for Sodium-Ion Batteries, *Langmuir*, 32 (2016) 12593-12602.
- [26] Y. Li, P. Hasin, Y. Wu, $\text{Ni}_{(x)}\text{Co}_{(3-x)}\text{O}_{(4)}$ nanowire arrays for electrocatalytic oxygen evolution, *Advanced materials*, 22 (2010) 1926-1929.
- [27] C. Wang, T. Wang, J. Liu, Y. Zhou, D. Yu, J.-K. cheng, F. Han, Q. Li, J. Chen, Y. Huang, Facile synthesis of silk-cocoon S-rich cobalt polysulfide as an efficient catalyst for the hydrogen evolution reaction, *Energy & Environmental Science*, 11 (2018) 2467-2475.
- [28] C. Zhang, S. Bhoyate, P.K. Kahol, K. Siam, T.P. Poudel, S.R. Mishra, F. Perez, A. Gupta, G. Gupta, R.K. Gupta, Highly Efficient and Durable Electrocatalyst Based on Nanowires of Cobalt Sulfide for Overall Water Splitting, *Chemnanomat*, 4 (2018) 1240-1246.
- [29] W. Gu, L. Hu, X. Zhu, C. Shang, J. Li, E. Wang, Rapid synthesis of Co_3O_4 nanosheet arrays on Ni foam by in situ electrochemical oxidization of air-plasma engraved $\text{Co}(\text{OH})_2$ for efficient oxygen evolution, *Chem Commun (Camb)*, 54 (2018) 12698-12701.
- [30] H. Hu, B. Guan, B. Xia, X.W. Lou, Designed Formation of $\text{Co}_{(3)}\text{O}_{(4)}/\text{NiCo}_{(2)}\text{O}_{(4)}$ Double-Shelled Nanocages with Enhanced Pseudocapacitive and Electrocatalytic Properties, *Journal of the American Chemical Society*, 137 (2015) 5590-5595.
- [31] F. Song, X. Hu, Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis, *Nature communications*, 5 (2014) 4477.
- [32] Y.R. Zheng, M.R. Gao, Q. Gao, H.H. Li, J. Xu, Z.Y. Wu, S.H. Yu, An efficient $\text{CeO}_2/\text{CoSe}_2$ Nanobelt composite for electrochemical water oxidation, *Small*, 11 (2015) 182-188.

Chapter 5

Exclusively dealloyed FeCoCu metal-(oxy)hydroxide supported by copper nanotube arrays for highly efficient oxygen evolution reaction

Considering the sluggish kinetics of oxygen evolution reaction (OER), a cost-effective, efficient and robust catalyst is critical for the wide adoption of electrochemical water splitting. Herein, a dendritic cobalt-iron-copper (CoFeCu) metal-(oxy)hydroxide core-shell structure supported on three dimensional copper nanotubes was prepared through dealloying process. The as-prepared electrode has superseded the state-of-the-art amongst the CoFe-based catalysts with outstanding performance (reaching the low overpotential of 250 mV @ 10 mA·cm⁻²). The dealloying process performed on the dendritic CoFeCu@Cu NTs in the alkaline solution leads to an exclusive morphological and compositional nanostructure. It enables the acceleration of mass transport as well as the adsorption and desorption and brings about the remarkably improved intrinsic property towards OER. Meanwhile, the Cu NTs and dendritic structure supported on it have significantly increased the electrochemical surface area and amount of active sites. The formation of interface between the CoFeCu metal and CoFe (oxy)hydroxide is also beneficial for the electron transfer, which highly promotes the reaction kinetics and thus improve the intrinsic catalytic activities.

5.1 Introduction

With the ever-increasing energy demands and aggravation of negative impacts resulting from the relentless consumption of traditional fossil fuels, intensive efforts have been executed on the renewable energy sources in recent researches [1-4]. Among all these energy resources, solar energy is one of the most promising candidates due to its abundance, ubiquitousness and greenness. However, one of the biggest disadvantages of solar energy is its intermittence (not shining at night or in cloudy and rainy days), thus hindering its uninterrupted operation in practical application [5, 6]. In this case, water splitting has provided an ideal solution as the excess electricity can be used to energize the production of high-purity hydrogen and oxygen, while the former is also a clean and highly efficient fuel widely used to regenerate electricity in fuel cells or heat in industry [7, 8]. Near zero emission can be achieved in the whole process, making huge contribution to the carbon neutrality goal. In addition, water splitting can also serve as an important energy storage technique for other forms of renewable energy sources including wind energy, tidal energy as well as hydro power, all of which have to overcome the drawback of intermittence to some extent.

Water splitting can be separated into two half-reactions including the hydrogen evolution reaction (HER) at cathode and oxygen evolution reaction (OER) at anode [9]. OER is a more complex reaction involving a four-electron transfer process, while only two electrons are transferred in HER. Consequently, a higher overpotential is usually required for OER. Therefore, the quality of OER catalyst will largely determine the overall efficiency of water splitting [1, 10]. For now, the state-of-the-art OER catalysts come from the noble metal oxides (RuO_2 and IrO_2). Both of them are too costly to be widely used in industry [11]. Thus, the earth-abundant catalysts have been extensively investigated as an alternative due to their unique properties of cost-effectiveness, high efficiency, and robustness. Among them, transition metal oxides and hydroxides (oxyhydroxides) have shown superior performance toward OER [12-14]. For example, CoOx converted from Co(OH)_2 through the coordination interaction shows extraordinary performance in 1M KOH [15]. The performance of $\alpha\text{-Co(OH)}_2/\text{CoOOH}$ is also significantly improved due to the defects and

oxyhydroxide fragments produced during electrochemical etching [16]. Similarly, much research effort has also focused on $\text{Ni}(\text{OH})_2/\text{NiOOH}$ and found that it was highly active for OER in alkaline media due to the coupling effect between these two phases [17-20]. Furthermore, the multiple-metal based catalysts have shown far superior catalytic performance than that of single-metal based catalysts [21]. The synergistic effect among different components was reported to have contributed to this significant improvement [22, 23]. There are various ways including hydrothermal and wet chemical approach to fabricate the multi-metal based catalysts mentioned above. However, the catalysts thus obtained would have to overcome some intrinsic shortcomings, especially the large crystallite size [24]. As a result, the formation of large crystallites will notably reduce the surface area exposed, resulting in limited electrochemically active sites. Kyung et al [25] had successfully avoided this drawback by utilizing the facile and easy electrodeposition method to synthesize the desirable catalyst. There are generally two ways to improve the performance of catalysts and one of them is to promote the intrinsic property whilst the other is to increase the number of active sites in specific area. Herein, maximizing the electrochemical surface area (ECSA) and active site exposure is achieved by the creation of an array of copper nanotubes (Cu NTs) coated with dendritic FeCoCu alloy forming a core-shell nanostructure as a catalyst in the present work. The dealloying of this core-shell nanostructure enables to deliver an exclusive morphological and compositional catalyst, which is claimed to engage the acceleration of mass transport as well as the adsorption and desorption and bring about the remarkably improved intrinsic property towards OER.

5.2 Materials preparation

The chemicals used in the experiment include cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium citrate tribasic dihydrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$), sodium hypophosphite monohydrate ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium chloride (NaCl), hydrochloric acid (HCl), absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$) and acetone. All these reagents were purchased from Sigma Aldrich and used as obtained.

The detailed fabrication process furnished as following:

1) The pre-treatment of copper foam

Here, copper foam was cut into the size of $1\text{ cm} \times 1\text{ cm}$ so that the exposed area is 1 cm^2 . Before it can be used for experiment, the pre-treatment was conducted to ensure that the metal oxide layer as well as other impurities and contaminations are thoroughly removed. Firstly, the copper foam was sequentially cleaned ultrasonically in acetone, isopropyl alcohol and ethanol for 5 min. Afterwards, it was rinsed with enough DI water to remove the remained ethanol, followed by dipping in HCl solution (37%) for 10 min. Finally, abundant DI water and ethanol were used to eliminate any remained HCl and then the pre-treated sample was blow-dried with N_2 .

2) The preparation of an array of copper nanotubes (Cu NTs)

The pre-treated copper foam was anodized in 3M NaOH at the constant current density of $45\text{ mA} \cdot \text{cm}^{-2}$ for 750 s to produce $\text{Cu}(\text{OH})_2$ nanotube array. Then it was annealed at 150°C for 4 h to get CuO nanotube array. Finally, it was further reduced to Cu nanotube array by simple electrochemical reduction (under -1.4 V for 1 h).

3) The synthesis of dendritic FeCoCu@Cu NTs

After the successful preparation of Cu NTs, FeCoCu alloy was deposited on it through cathodic reduction. The corresponding electrolyte contains $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The molar ration of Co, Fe and Cu is 8:2.5:4 and the pH value was adjusted to 9 with 5 M NaOH. Besides, a buffer solution consisting of 0.2 M $\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$, 0.55 M $\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$ and 0.45 M $(\text{NH}_4)_2\text{SO}_4$ was also included in the electrolyte to ensure the stabilization of pH value. Similarly, FeCo@Cu NTs, FeCu@Cu NTs and CoCu@Cu NTs were also synthesized according to the procedure described above.

4) The fabrication of Core-Shell FeCoCu@Cu NTs (CS FeCoCu@Cu NTs)

CS FeCoCu@Cu NTs was obtained by electrochemical oxidation of FeCoCu@Cu NTs in 1 M KOH at a fixed potential range (Cyclic voltammetry scan (1.0-1.8 V), 10 cycles). Besides, CS FeCo@Cu NTs, CS FeCu@Cu NTs and CS CoCu@Cu NTs were also fabricated accordingly for comparison.

5.3 Characterization methods

Scanning electron microscope (SEM) (FESEM JSM-7600F coupled with EDX, JEOL) and (scanning) transmission electron microscope (TEM/STEM, JEM-2100F coupled with EDX, JEOL) observation were carried out to characterize the morphology, elemental composition, and crystallinity of the samples. The X-ray diffraction (XRD) pattern was acquired to analyze the crystallographic structure (XRD-6000, Shimadzu). XPS measurement (Kratos AXIS Supra) was also conducted to investigate the chemical state of surface elements. In addition, various electrochemical tests (performed with Autolab PGSTAT 302N) including electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), chronoamperometry (CA) and chronopotentiometry (CP) were conducted to evaluate the OER performance of samples obtained. A traditional three-electrode system including working electrode (the specimen), reference electrode (Ag/AgCl with saturated KCl) and counter electrode (platinum plate) was used for all the tests mentioned above. Besides, for LSV measurement, the potential was converted to refer to the reversible hydrogen electrode (RHE) according to the following equation:

$$E_{RHE} = E_{recorded} + 0.0592 \times pH + E^{\circ}(Ag/AgCl) \quad (1)$$

Finally, the Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Element Series HR-ICP-MS, Thermo Fisher) was also used to evaluate the trace amount of elements in the solution.

5.4 Principal outcomes

5.4.1 The electrochemical synthesis of CuNTs

The detailed fabrication process is illustrated in Figure 5.1. Figure 5.2 illustrates the detailed synthetic approach that uses CP technique to perform a consecutive anodic oxidation of the Cu foam in NaOH solution. when compared with the pre-treated surface of Cu foam prior to oxidation (see Figure 5.3). Further oxidation leads to morphological change from nano-feather (Figure 5.2 (b1)-(b3)), nanotube (Figure 5.2 (c1)-(c3)), nanobelt

(Figure 5.2 (d1)-(d3)) to nanosheets (Figure 5.2 (e1)-(e3)) after 350 s, 700 s, 960 s and 1200 s respectively. The transformation in morphology is mainly due to the relaxation of hydrogen bond interaction between the nanostructures[26]. The compositional change of oxidized Cu foam was analyzed synchronously with their respective XRD patterns presented in Figure 5.2 (a4-e4). Figure 5.2 (a4) reveals that the initial oxide grown before 100 s was pure cuprous oxide (Cu_2O) which was further oxidized to $\text{Cu}(\text{OH})_2$ at 350 s (Figure 5.2 (b4)). The specific reaction route can be depicted as the following steps[26]:

At 700 s, a small amount of $\text{Cu}(\text{OH})_2$ was reduced to Cu_2O (Figure 5.2 (c4)) which was then further oxidized to CuO at 960 s. At 1200 s, the entire foam surface was covered by pure CuO . This time-dependent morphological and compositional changes provide an opportunity to select the desirable nanostructure as the support for synthesizing highly efficient catalyst. In this work, $\text{Cu}(\text{OH})_2$ with a nanotubular morphology was chosen since its perfect three dimensional structure is expected to greatly facilitate the exposure of active sites. The as-synthesized $\text{Cu}(\text{OH})_2$ was further analyzed by TEM. The low magnification bright field TEM image (see Figure 5.4) also confirms the formation of tubular $\text{Cu}(\text{OH})_2$. As presented in the SAED pattern (Figure 5.4 inset), the preferential growth direction turns out to be $[1\ 0\ 0]$. This is also in good agreement with Bravais-Friedel-Donnay-Harker law[27, 28] since the $[1\ 0\ 0]$ direction is supposed to be the direction with fastest growth rate according to the law.

Figure 5.1 Schematic illustration of electrochemical synthesis of hierarchical CS FeCoCu@Cu NTs

Figure 5.2 SEM images and corresponding XRD patterns of Cu foam after electrooxidation in 3M NaOH solution for different times: (a) 100 s; (b) 350 s; (c) 700 s; (d) 960 s; (e) 1200

s

Figure 5.3 SEM observation of pure Cu foam after pretreatment in 37% HCl for 10 min: (a), (b) and (c) SEM images of Cu foam in different magnifications; (d) and (e): EDS elemental mapping images; (f) corresponding EDS spectrum

Figure 5.4 TEM image and corresponding Selected Area Electron Diffraction pattern of $\text{Cu}(\text{OH})_2$ nanotube

Subsequent annealing and electrochemical reduction turned the support into copper nanotubes (denoted as Cu NTs, see Figure 5.5). The electroplating was then carried out to deposit FeCoCu alloy over the surface of Cu NTs. The plated surfaces of Cu NTs were observed in SEM as shown in Figure 5.6a-b. They are seen in high magnification to be covered by a thin layer that is made up of small nanoparticles with the average size of around 50 nm and dendrites (Figure 5.6c). A number of nanoneedles grow outwards from the thin layer and are vertical to the Cu nanotube. When viewed in TEM, the coated Cu NTs appear dendrite-like structure (Figure 5.6d). The dendrites are nanoneedles and are about 2 μm long with a very sharp tip (Figure 5.6c). The tip area was examined by high-resolution TEM (HRTEM) to be crystalline, as demonstrated by Figure 5.6f, which is a real lattice image. The corresponding reciprocal lattice is shown in Figure 5.6g. It is an image taken at an orientation of $[1\ 1\ 1]$ zone axis of FeCoCu alloy. This alloy has a body centered cubic (bcc) structure. Such phase crystal structure was further proven by XRD pattern as shown in Figure 5.6h. The phase consists of three elements (Fe, Co, and Cu) which are uniformly distributed across the entire dendritic structure as confirmed from the elemental analysis (Figure 5.6i-l and Figure 5.7). The atomic ratio of these three elements is estimated from the corresponding EDX spectrum to be roughly 1:3:4.5 (Fe/Co/Cu) (Figure 5.8).

Figure 5.5 SEM images and corresponding XRD patterns of (a1-a4): CuO-Cu₂O nanotube array; (b1-b4): Cu nanotube array (CNTA)

Figure 5.6 FeCoCu@Cu NTs (3min): SEM images (a-c) and corresponding XRD pattern (d); TEM images (e-f), HRTEM image (g) and corresponding FFT image (h); STEM EDX elemental mapping (i-l)

Figure 5.7 SEM EDS mapping images of CNTA FeCoCu

Figure 5.8 The STEM EDS Spectrum of CNTA FeCoCu

After the electrodeposition, electrochemically dealloying of the core-shell (CS) FeCoCu@Cu NTs was performed. It is a widely used method to selectively attack and remove the elements with high electrochemical activity in alloys[29-31]. As shown in Figure 5.9 a-c, the dendritic structure was well retained after being subjected to dealloying and the surface of the alloy is homogeneously covered by nanosheets (about 500 nm in lateral size and 10 nm in thickness). Corresponding XRD pattern (Figure 5.9 d) indicates that the shell consists of two phases (i.e. FeOOH and Co(OH)₂). Both were in-situ grown from the metallic core, which could be verified by the TEM characterization (Figure 5.9 e-h). The core shell structure is clearly shown in Figure 5.9 f as labelled. Besides, the FFT pattern (Figure 5.9h) derived from the square region in the HRTEM image (Figure 5.9 g), reveals that the shell is comprised of coherent phases of FeOOH and Co(OH)₂. They are closely connected to the metallic core with continuous lattice across the interface (see Figure 5.9 g), indicating that the shell was originated from the core and formed during the dealloying process. As mentioned above, the formation process of FeOOH/Co(OH)₂ shell is closely associated with the elimination of chemically more active elements under experimental conditions. In detail, cyclic voltammetry (CV) activation was conducted for continuous 10 cycles in 1 M KOH solution, so that the chemically more active element (Cu in this case) is easier to be oxidized and dissolved in the alkaline solution[32]:

This could be corroborated by the elemental analysis after dealloying. Although all the four elements including Fe, Co, Cu and O are uniformly distributed in microscale (see Figure 5.10), copper is free from the shell (i.e. FeCo (oxy)hydroxide layer), as viewed from Figure 5.9 i-m. This result is also in good agreement with the XRD pattern and HRTEM analysis above. Furthermore, the electrolytes before and after dealloying were analyzed by ICP-MS and the concentration of Cu in the solution has substantially increased by 17 times from 655 cps to 11900 cps (see Table 5.1). In contrast, the concentration increase of Fe and Co is only about 2 times (from 265 cps to 719 cps) and 1 time (from 32.7 cps to 68.7 cps) respectively, thus highlighting the selective dissolution of Cu as described in equation 4 and 5.

Figure 5.9 Characterization of CS FeCoCu@Cu NTs: (a-c) SEM images with different magnifications; (d) corresponding XRD pattern; (e-g) TEM images with different magnifications; (h) corresponding FFT pattern; (i-M) STEM EDX mapping images

Figure 5.10 EDX Mapping of CuNTA_FeCoCu 3(min) after selective corrosion

Table 5.1 Summary of Inductively coupled plasma mass spectrometry (ICP-MS) results (unit: cps)

Element	Before SC	After SC
Fe	265	719
Co	32.7	68.7
Cu	655	11900

5.4.2 The XPS study of dealloyed Fe-Co-Cu metal-(oxy)hydroxide

In order to study the surface state of the elements, XPS characterization was carried out on FeCoCu@Cu NTs and CS FeCoCu@Cu NTs and the results were summarized in Figure 5.11 and Figure 5.12, respectively. As displayed in Figure 5.11a, there is a Fe 2p_{3/2} peak at 707.9 eV which can be indexed to Fe⁰ [33]. Similarly, Co 2p_{3/2} peak at 778.2 eV (Figure 5.11b) and Cu 2p_{3/2} peak at 933 eV (Figure 5.11c) are contributed by Co⁰ and Cu⁰, respectively [34, 35]. The results above clearly indicate the formation of trimetallic FeCoCu alloy. Besides, O 1s peak is also observed at 529.3 eV (Figure 5.11d) which is attributed to the presence of O²⁻ [35] due to the oxidation of alloy surface upon exposure to the air. After dealloying, the Fe 2p_{3/2} peak shifts to 712.5 eV along with a satellite peak at 720.3 eV (Figure 5.6a), which corresponds well to Fe³⁺ [21, 36]. In addition, two major Co 2p_{3/2} peaks are observed at 781.3 eV and 797 eV accompanied with two satellite peaks at 786 eV and 802.5 eV (Figure 5.12b), suggesting the formation of Co²⁺ [37]. Apart from those, a significant change is observed in the O 1s spectra. As shown in Figure 5.12c, there are two splitted O 1s peaks positioned at 531.1 eV and 529.3 eV, which can be assigned to OH⁻ and O²⁻, respectively [38], attributed from the formation of FeOOH/Co(OH)₂ shell as proven by the XRD and HRTEM results. The catalyst also shows similar XPS spectra after stability test (see Figure 5.13).

5.4.3 Electrochemical behavior of dealloyed Fe-Co-Cu metal-(oxy) hydroxide in 1M KOH

To investigate the catalytic performance of the CS FeCoCu@Cu NTs, electrochemical tests were conducted in 1 M KOH solution. According to the LSV curves shown in Figure 5.14 a, CS FeCoCu@Cu NTs demonstrates significantly higher activity towards OER when compared to other catalysts including CS FeCo@Cu NTs, CS FeCu@Cu NTs, CS CoCu@Cu NTs, Cu NTs, and pure Cu foam. Specifically, to reach $10 \text{ mA} \cdot \text{cm}^{-2}$, the overpotential required is only 250 mV (see Figure 5.14b), which is lower than that of most FeCo-based metal oxides and (oxy)hydroxides (see Table 5.2). In contrast, a much higher overpotential of 290 mV is needed for CS FeCo@Cu NTs, suggesting the importance of dealloying of Cu in promoting the OER performance through dealloying. The overpotentials for other catalysts in this work are summarized in Figure 5.14b and are significantly higher. The incorporation of Cu enables the formation of dendritic FeCoCu parent alloy, remarkably enlarging the ECSA of the sample. Subsequent dealloying also leads to the in-situ growth of metal (oxy)hydroxide nanosheets homogeneously covering the whole dendritic structure, which further increases the exposure of active sites. Consequently, the reaction kinetics of OER is expected to be greatly improved, which is corroborated by the calculation of Tafel slope from LSV curves. As displayed in Figure 5.14c, the CS FeCoCu@Cu NTs shows the smallest Tafel slope ($85 \text{ mV} \cdot \text{dec}^{-1}$) compared to other catalysts, indicating the fastest reaction rate produced by the unique structure introduced above.

Subsequent dealloying also leads to the in-situ growth of metal (oxy)hydroxide nanosheets homogeneously covering the whole dendritic structure, which further increases the exposure of active sites. Consequently, the reaction kinetics of OER is expected to be greatly improved, which is corroborated by the calculation of Tafel slope from LSV curves. As displayed in Figure 5.14c, the CS FeCoCu@Cu NTs shows the smallest Tafel slope ($85 \text{ mV} \cdot \text{dec}^{-1}$) compared to other catalysts, indicating the fastest reaction rate produced by the unique structure introduced above.

To further study the electrochemical kinetics of catalysts during OER, EIS measurements

were conducted in the frequency range of 10^5 - 10^{-2} Hz with the results summarized in Figure 5.14d. It clearly shows that the smallest impedance comes from CS FeCoCu@Cu NTs. To reveal more details regarding the reaction kinetics, all the EIS results were fitted with the equivalent circuits shown in Figure 5.14e. There are three different circuits corresponding to different catalysts to ensure that all the EIS curves could be properly fitted. To be specific, equivalent circuit 1 was used for pure Cu foam since the interface between electrode surface (Cu foam) and electrolyte was the site where OER occurs, and there is a single time constant circuit from the time domain perspective [39, 40]. The circuit consists of three different parts including R_s , R_{ct} and C , representing the solution resistance, charge transfer resistance and electric double layer capacitance, respectively. For Cu NTs, OER also occurs on the Cu nanotube surfaces, suggesting two time constants in the equivalent circuit. Thus, equivalent circuit 2 (R_p represents polarization resistance) was used for the fitting of Cu NTs. Finally, for all core-shell (labelled with CS) samples, OER takes place at two sites. However, if the diffusion process of reactants and products in the electrolyte as well as the interfacial heterogeneity are considered, the equivalent circuit used should be different from that of Cu NTs. In this case, equivalent circuit 3 is considered with the capacitance replaced by constant phase element (CPE) that could better simulate the actual electrochemical behavior of an imperfect electric double layer (EDL) [41, 42]. The fitted results were collected and shown in Figure 5.14f and Table 5.3. As indicated in Figure 5.14f, the CS FeCoCu@Cu NTs presents the smallest impedance. In detail, one of the key components in the equivalent circuit is R_{ct} which is directly correlated to the reaction kinetics. According to the fitted results in Figure 5.14g and Table 5.3, CS FeCoCu@Cu NTs again demonstrates the smallest value (7.7Ω) among all the catalysts, indicating the fastest reaction kinetics, which in alignment with the smallest Tafel slopes in Figure 5.14c. This fact clearly shows that the significantly improved reaction kinetics is brought by the introduction of the morphological and compositional core-shell structure through dealloying. To be specific, the formation of interface between core and shell benefits the alleviation of activation polarization, and thus largely reduces the energy barrier needed to overcome during the initial stage of reaction.

Figure 5.11 High resolution XPS spectra of Fe 2p (a), Co 2p (b), Cu 2p (c) and O 1s (d) for FeCoCu@Cu NTs

Figure 5.12 High resolution XPS spectra of Fe 2p (a), Co 2p (b) and O 1s (c) for CS FeCoCu@Cu NTs

Figure 5.13 Figure 7 High resolution XPS spectra of Fe 2p (a), Co 2p (b), and O 1s (c) for CS FeCoCu@3D CNTA after stability test (12 h)

Figure 5.14 Electrochemical characterization after dealloying in 1M KOH: (a) OER performance; (b) and (c) corresponding overpotential and Tafel slope; (d) EIS spectra; (e) equivalents circuits used to fit the EIS spectra in (d); (f) fitted EIS spectra; (g) summary of charge transfer resistance (R_{ct}) calculated from fitting; (h) stability test for CS FeCoCu@Cu NTs; (i) OER performance after the stability test

Table 5.2 Summary of performance of previous FeCo based catalysts

Catalyst	Electrolyte	Overpotential @ 10 $\text{mA}\cdot\text{cm}^{-2}$ (mV)	Tafel slope (mV/dec)	Reference
FeCoNi@FeNC	1M KOH	330	57	[43]
NiCoFeB nanochains	1M KOH	284	46	[44]
CoFe-H	1M KOH	280	24	[45]
CoFeP NSs	1M KOH	305	49.6	[46]
Co ₃ FePx/C	1M KOH	260	58	[47]
Co-Fe-P foam	1M KOH	294	96	[48]

Table 5.3 Summary of fitted results

Sample	$R_s(\Omega)$	$R_p(\Omega)$	$R_{ct}(\Omega)$	CPE1(Mho,*) or C1 (mF,#)	CPE2(Mho,*) or C2(mF,#)
Cu foam	1.5	N.A.	6233	2.55 #	N.A.
Cu NTs	1.12	10.8	143	201 #	185 #
CS FeCoCu@Cu NTs	0.926	7.73	7.73	3.18 *	2.02 *
CS FeCo@Cu NTs	1.26	19.6	19.6	0.995 *	2.95 *
CS FeCu@Cu NTs	1.05	73.1	73.1	3.83 *	1.11 *
CS CoCu@Cu NTs	1.76	16.8	16.8	3.37 *	1.41 *

In addition to R_{ct} , ECSA is another key parameter in evaluating the performance of a catalyst. Theoretically ECSA is positively correlated to the capacitance of EDL which is reflected by the value of CPE here. As mentioned above, the introduction of CPE is to simulate the actual behavior of EDL in electrolyte, which is different from that of an ideal capacitor [49]. The major reason for this deviation is considered to be the interfacial heterogeneity and roughness resulting from the core-shell structure and Cu NTA [44, 50], . The resistance of CPE (ZCPE) can be defined by the following equation when it is used to study the behavior an EDL [42, 43, 49]:

$$Z_{CPE} = [Q(R_s^{-1} + R_{ct}^{-1})^{\alpha-1}]^{1/\alpha} \quad (6)$$

where R_s is the solution resistance and α is the CPE exponent (varying between 0 and 1). The CPE is considered to be a pure capacitor when α equals to 1. According to the equivalent circuit shown in Figure 5.14e, there are two CPE components in equivalent circuit 3, both of which originate from the electrode-electrolyte interface. In detail, the first CPE is believed to be derived from the interface between shell ($\text{FeOOH}/\text{Co}(\text{OH})_2$) and electrolyte while the second is from the interface between core (FeCoCu alloy) and electrolyte. In spite of the different origins, both of them contribute to the capacitive behavior of the EDL, which is closely associated with the ECSA. As displayed in Table 5.3, the sum of two CPEs in CS FeCoCu@Cu NTs demonstrates to be the largest (5.2 Mho)

among all the CS catalysts. Herein, it is clear that CS FeCoCu@Cu NTs possesses the largest ECSA among all the catalysts, suggesting that it has exposed the highest number of active sites to the electrolyte. Along with the superior performance, CS FeCoCu@Cu NTA also presented to be robust in alkaline solution (1 M KOH) according to the stability test (see Figure 5.14h), the CP profile shows that the potential was held consistent for continuous 12 h. The OER performance after stability test shows no obvious performance degradation (see Figure 5.14i), which also verifies the excellent robustness of the catalyst under operating conditions.

An exclusive cost-effective and highly efficient OER catalyst has been successfully fabricated by simple electrodeposition followed by dealloying. The catalyst presents a core-shell structure in which the highly conductive dendritic FeCoCu alloy is the core that is covered by the FeOOH/Co(OH)₂ nanosheets as the shell. The whole catalyst is supported on the copper nanotubes (Cu NTs). This design enables the formation of a hierarchical catalyst with small R_{ct} and large ECSA which afford the enhanced intrinsic properties and high exposure of active sites. The catalyst is demonstrated to offer excellent OER performance with the current density reaching to $10 \text{ mA} \cdot \text{cm}^{-2}$ at a small overpotential of 250 mV, which is more competitive than most FeCo-based OER catalysts reported. In addition, this catalyst is also highly resistant to the corrosive attack in alkaline medium and maintains almost the same performance after 12 h of stability test. This work provides an easy and economic design for fabricating highly efficient and durable OER catalyst, showing the potential for the large scale-up in industrial application.

Reference

- [1] J. Song, C. Wei, Z.F. Huang, C. Liu, L. Zeng, X. Wang, Z.J. Xu, A review on fundamentals for designing oxygen evolution electrocatalysts, *Chemical Society reviews*, 49 (2020) 2196-2214.
- [2] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, *Nature*, 488 (2012) 294-303.
- [3] A.M. Appel, J.E. Bercaw, A.B. Bocarsly, H. Dobbek, D.L. DuBois, M. Dupuis, J.G. Ferry, E. Fujita, R. Hille, P.J. Kenis, C.A. Kerfeld, R.H. Morris, C.H. Peden, A.R. Portis, S.W. Ragsdale, T.B. Rauchfuss, J.N. Reek, L.C. Seefeldt, R.K. Thauer, G.L. Waldrop, *Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO₂ fixation*, *Chemical reviews*, 113 (2013) 6621-6658.
- [4] Z. Chen, T.F. Jaramillo, T.G. Deutsch, A. Kleiman-Shwarscstein, A.J. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, H.N. Dinh, Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols, *Journal of Materials Research*, 25 (2011) 3-16.
- [5] J.H. Montoya, L.C. Seitz, P. Chakthranont, A. Vojvodic, T.F. Jaramillo, J.K. Nørskov, *Materials for solar fuels and chemicals*, *Nature materials*, 16 (2016) 70-81.
- [6] N.S. Lewis, D.G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *PNAS*, 103 (2006) 15729-15735.
- [7] J. Kibsgaard, I. Chorkendorff, Considerations for the scaling-up of water splitting catalysts, *Nature Energy*, 4 (2019) 430-433.
- [8] B. You, Y. Sun, Innovative Strategies for Electrocatalytic Water Splitting, *Acc Chem Res*, 51 (2018) 1571-1580.
- [9] Q. Shi, C. Zhu, D. Du, Y. Lin, Robust noble metal-based electrocatalysts for oxygen evolution reaction, *Chemical Society reviews*, 48 (2019) 3181-3192.
- [10] L. Han, S. Dong, E. Wang, Transition-Metal (Co, Ni, and Fe)-Based Electrocatalysts for the Water Oxidation Reaction, *Advanced materials*, 28 (2016) 9266-9291.
- [11] J. Lim, S. Yang, C. Kim, C.W. Roh, Y. Kwon, Y.T. Kim, H. Lee, Shaped Ir-Ni bimetallic nanoparticles for minimizing Ir utilization in oxygen evolution reaction, *Chem Commun (Camb)*, 52 (2016) 5641-5644.
- [12] A. Singh, L. Spiccia, Water oxidation catalysts based on abundant 1st row transition metals, *Coordination Chemistry Reviews*, 257 (2013) 2607-2622.

- [13] J.R. Galán-Mascarós, Water Oxidation at Electrodes Modified with Earth-Abundant Transition-Metal Catalysts, *ChemElectroChem*, 2 (2015) 37-50.
- [14] M.S. Burke, L.J. Enman, A.S. Batchellor, S. Zou, S.W. Boettcher, Oxygen Evolution Reaction Electrocatalysis on Transition Metal Oxides and (Oxy)hydroxides: Activity Trends and Design Principles, *Chem Mater*, 27 (2015) 7549-7558.
- [15] W. Xu, F. Lyu, Y. Bai, A. Gao, J. Feng, Z. Cai, Y. Yin, Porous cobalt oxide nanoplates enriched with oxygen vacancies for oxygen evolution reaction, *Nano Energy*, 43 (2018) 110-116.
- [16] P.F. Liu, S. Yang, L.R. Zheng, B. Zhang, H.G. Yang, Electrochemical etching of α -cobalt hydroxide for improvement of oxygen evolution reaction, *Journal of Materials Chemistry A*, 4 (2016) 9578-9584.
- [17] S. Klaus, Y. Cai, M.W. Louie, L. Trotochaud, A.T. Bell, Effects of Fe Electrolyte Impurities on $\text{Ni}(\text{OH})_2/\text{NiOOH}$ Structure and Oxygen Evolution Activity, *The Journal of Physical Chemistry C*, 119 (2015) 7243-7254.
- [18] I.M. Sadiq, A.M. Mohammad, M.E. El-Shakre, M.S. El-Deab, Electrocatalytic activity of nickel oxide nanoparticles-modified electrodes: Optimization of the loading level and operating pH towards the oxygen evolution reaction, *International Journal of Hydrogen Energy*, 37 (2012) 68-77.
- [19] J. Ren, J. Yan, Z. Zhou, X. Wang, X. Gao, High-temperature electrochemical performance of spherical $\text{Ni}(\text{OH})_2$ coated with $\text{Lu}(\text{OH})_3$, *International Journal of Hydrogen Energy*, 31 (2006) 71-76.
- [20] Y.-F. Li, A. Selloni, Pathway of Photocatalytic Oxygen Evolution on Aqueous TiO_2 Anatase and Insights into the Different Activities of Anatase and Rutile, *ACS Catalysis*, 6 (2016) 4769-4774.
- [21] P. Zhang, L. Li, D. Nordlund, H. Chen, L. Fan, B. Zhang, X. Sheng, Q. Daniel, L. Sun, Dendritic core-shell nickel-iron-copper metal/metal oxide electrode for efficient electrocatalytic water oxidation, *Nature communications*, 9 (2018) 381.
- [22] J.B. Gerken, S.E. Shaner, R.C. Massé, N.J. Porubsky, S.S. Stahl, A survey of diverse earth abundant oxygen evolution electrocatalysts showing enhanced activity from Ni-Fe oxides containing a third metal, *Energy Environ. Sci.*, 7 (2014) 2376-2382.
- [23] B.M. Hunter, J.D. Blakemore, M. Deimund, H.B. Gray, J.R. Winkler, A.M. Muller, Highly active mixed-metal nanosheet water oxidation catalysts made by pulsed-laser ablation in liquids, *Journal of the American Chemical Society*, 136 (2014) 13118-13121.

- [24] M. Gong, H. Dai, A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts, *Nano Res*, 8 (2014) 23-39.
- [25] K.H. Kim, J.Y. Zheng, W. Shin, Y.S. Kang, Preparation of dendritic NiFe films by electrodeposition for oxygen evolution, *RSC Advances*, 2 (2012) 4759-4767.
- [26] X. Wu, H. Bai, J. Zhang, F.e. Chen, G. Shi, Copper Hydroxide Nanoneedle and Nanotube Arrays Fabricated by Anodization of Copper, *J. Phys. Chem. B*, 109 (2005) 22836-22842.
- [27] P.HARTMAN, W.G.PERDOK, On the Relations Between Structure and Morphology of Crystals, *Acta Cryst.*, 8 (1954) 49.
- [28] W. Zhang, X. Wen, S. Yang, Controlled Reactions on a Copper Surface- Synthesis and Characterization of Nanostructured Copper Compound Films, *Inorganic Chemistry*, 42 (2003) 5005-5014.
- [29] E. Detsi, J.B. Cook, B. Lesel, C. Turner, Y.L. Liang, S. Robbennolt, S.H. Tolbert, Mesoporous Ni₆₀Fe₃₀Mn₁₀-alloy based metal/metal oxide composite thick films as highly active and robust oxygen evolution catalysts dagger, *Energy Environ Sci*, 9 (2016) 540-549.
- [30] E. Detsi, M. van de Schootbrugge, S. Punzhin, P.R. Onck, J.T.M. De Hosson, On tuning the morphology of nanoporous gold, *Scripta Materialia*, 64 (2011) 319-322.
- [31] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of nanoporosity in dealloying, *Nature*, 410 (2001).
- [32] G. BRAUER, H. Sauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press 1963.
- [33] L. Fan, P. Zhang, B. Zhang, Q. Daniel, B.J.J. Timmer, F. Zhang, L. Sun, 3D Core-Shell NiFeCr Catalyst on a Cu Nanoarray for Water Oxidation: Synergy between Structural and Electronic Modulation, *ACS Energy Letters*, 3 (2018) 2865-2874.
- [34] M.M. Najafpour, S. Mehrabani, R. Bagheri, Z. Song, J.-R. Shen, S.I. Allakhverdiev, An aluminum/cobalt/iron/nickel alloy as a precatalyst for water oxidation, *International Journal of Hydrogen Energy*, 43 (2018) 2083-2090.
- [35] Y. Zhou, Z. Wang, Z. Pan, L. Liu, J. Xi, X. Luo, Y. Shen, Exceptional Performance of Hierarchical Ni-Fe (hydr)oxide@NiCu Electrocatalysts for Water Splitting, *Advanced materials*, 31 (2019) e1806769.
- [36] Y. Pei, Y. Ge, H. Chu, W. Smith, P. Dong, P.M. Ajayan, M. Ye, J. Shen, Controlled synthesis of 3D porous structured cobalt-iron based nanosheets by electrodeposition as asymmetric electrodes for ultra-efficient water splitting, *Applied Catalysis B: Environmental*, 244 (2019) 583-593.

- [37] J. Wang, W. Cui, Q. Liu, Z. Xing, A.M. Asiri, X. Sun, Recent Progress in Cobalt-Based Heterogeneous Catalysts for Electrochemical Water Splitting, *Advanced materials*, 28 (2016) 215-230.
- [38] F. Qin, Z. Zhao, M.K. Alam, Y. Ni, F. Robles-Hernandez, L. Yu, S. Chen, Z. Ren, Z. Wang, J. Bao, Trimetallic NiFeMo for Overall Electrochemical Water Splitting with a Low Cell Voltage, *ACS Energy Letters*, 3 (2018) 546-554.
- [39] V. Sedlakova, J. Sikula, J. Majzner, P. Sedlak, T. Kuparowitz, B. Buerger, P. Vasina, Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion, *Journal of Power Sources*, 286 (2015) 58-65.
- [40] M. Kaus, J. Kowal, D.U. Sauer, Modelling the effects of charge redistribution during self-discharge of supercapacitors, *Electrochimica Acta*, 55 (2010) 7516-7523.
- [41] Z. Chu, R. Jobman, A. Rodríguez, G.L. Plett, M.S. Trimboli, X. Feng, M. Ouyang, A control-oriented electrochemical model for lithium-ion battery. Part II: Parameter identification based on reference electrode, *Journal of Energy Storage*, 27 (2020) 101101.
- [42] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, Determination of effective capacitance and film thickness from constant-phase-element parameters, *Electrochimica Acta*, 55 (2010) 6218-6227.
- [43] P. Córdoba-Torres, T.J. Mesquita, O. Devos, B. Tribollet, V. Roche, R.P. Nogueira, On the intrinsic coupling between constant-phase element parameters α and Q in electrochemical impedance spectroscopy, *Electrochimica Acta*, 72 (2012) 172-178.
- [44] M. Birla Singh, R. Kant, Theory of Anomalous Dynamics of Electric Double Layer at Heterogeneous and Rough Electrodes, *The Journal of Physical Chemistry C*, 118 (2014) 5122-5133.
- [45] W. Liu, H. Liu, L. Dang, H. Zhang, X. Wu, B. Yang, Z. Li, X. Zhang, L. Lei, S. Jin, Amorphous Cobalt-Iron Hydroxide Nanosheet Electrocatalyst for Efficient Electrochemical and Photo-Electrochemical Oxygen Evolution, *Adv Funct Mater*, 27 (2017) 1603904.
- [46] H. Xu, J. Wei, C. Liu, Y. Zhang, L. Tian, C. Wang, Y. Du, Phosphorus-doped cobalt-iron oxyhydroxide with untrafine nanosheet structure enable efficient oxygen evolution electrocatalysis, *J Colloid Interface Sci*, 530 (2018) 146-153.
- [47] J. Han, G. Chen, X. Liu, N. Zhang, S. Liang, R. Ma, G. Qiu, Cobalt iron phosphide nanoparticles embedded within a carbon matrix as highly efficient electrocatalysts for the oxygen evolution reaction, *Chem Commun (Camb)*, 55 (2019) 9212-9215.

- [48] H. Kim, S. Oh, E. Cho, H. Kwon, 3D Porous Cobalt–Iron–Phosphorus Bifunctional Electrocatalyst for the Oxygen and Hydrogen Evolution Reactions, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 6305-6311.
- [49] P. Córdoba-Torres, T.J. Mesquita, R.P. Nogueira, Relationship between the Origin of Constant-Phase Element Behavior in Electrochemical Impedance Spectroscopy and Electrode Surface Structure, *The Journal of Physical Chemistry C*, 119 (2015) 4136-4147.
- [50] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, N.S. Ferriols, P. Bogdanoff, E.C. Pereira, Doubling Exponent Models for the Analysis of Porous Film Electrodes by Impedance Relaxation of TiO₂ Nanoporous in Aqueous Solution, *J. Phys. Chem. B*, 104 (2000) 2287-2298.

Chapter 6

Electrochemically dealloyed FeCoNiCu as highly efficient catalyst for OER

A low-cost and efficient electrocatalyst for water oxidation was fabricated through simple and economical method-electrochemical synthesis. The as-prepared electrocatalyst is based on FeCoNiCu supported on 3D copper nanoarray. and has demonstrated excellent performance for oxygen evolution reaction (OER), reaching the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ at the small overpotential of 230 mV. This remarkable performance is attributed to the unique 3D porous structure of dealloyed FeCoNiCu as well as the 3D copper nanoarray, which greatly facilitates the mass transport process. Besides, the synergistic effect among the three phases in dealloyed FeCoNiCu has also greatly contributed to the enhanced electrocatalytic activity. This work has proposed an economical and easy approach to synthesize highly efficient electrocatalyst for OER.

6.1 Introduction

Because of the world's huge consumption of non-renewable energy and the demand for energy from the economy, it is important to find an alternative electrochemical energy conversion and storage [1-4]. Water decomposition technology has also recently gained increasing attention because it efficiently breaks down water into oxygen and hydrogen for use in fuel cell applications [5, 6]. At the same time, clean energy sources such as solar, tidal, and wind energy, etc. cannot be used directly due to intermittent characteristics, and water decomposition technology can be used to store these clean energy sources in the form of oxygen and hydrogen [7, 8].

Generally, water splitting consists of HER and OER reactions. OER is more difficult and complex than HER's dual electron transfer because OER needs to transfer four electrons[9]. This results in OERs using greater overpotential to improve the entire water decomposition process and efficiency[10]. Traditional noble metal catalysts such as RuO₂, Pt and IrO₂, although highly catalytic, limit commercial applications due to their price and scarcity[11]. So, in recent years, more and more research has focused on ordinary metals that can replace traditional precious metals. Transition metals are increasingly favored by researchers because of their abundant storage and efficient catalytic efficiency[12-14]. To date, extensive research has been conducted on transitional metal-based materials, such as metal oxide [15-17], carbide [18], sulfide [19, 20], (oxy)hydroxide [21, 22], etc. Among them, transitional metal hydroxides have attracted much attention, especially in multimetal compounds, because of synergistic effect among various metal ions, tuneable adsorption energy, and electronic structure[23]. Therefore, transition metal catalysts are considered to be able to achieve better catalytic performance than that of noble metal such Ir based in basic media [24]. For instance, substitution of Co in CoOOH with Fe increases the OER activity by at least 10-folds compared to pure CoOOH catalytic performance, FeOOH is more catalytic active, but with poor electrical conductivity, meanwhile could easily dissolve in alkaline solution. While CoOOH is a good electronic conductor and has excellent electrochemical stability. The combination of FeOOH and CoOOH will have a synergy effect [25] [26]. Similarly, the partial replacement of Ni with Fe can significantly improve the catalytic performance [27, 28], better than that of either of them alone, with

evidence that Fe can change the electronic structure of NiOOH [29-33]. In addition, studies have shown that though NiO_xH_y nanosheets alone have excellent catalytic performance, but its catalytic stability is not good, which makes incorporating of Fe promising [34, 35]. Further studies have also shown that amorphous Ni-Fe oxide catalysts demonstrate better OER performance than that of Co-Fe, Ni-Co, Fe-Mn, Cu-Fe, and Cu-Ni. Besides, Ni/Fe ratio is crucial for catalytic performance [36]. For example, Fe₆Ni₁₀ exhibits better OER performance with an overpotential of 286 mV at 10 mA cm⁻² than other Ni/Fe ratios such as 1/10, 2/10, 10/10, 10/6, and 10/2. This is consistent with other reports that OER catalytic activity is highest when the Ni/Fe ratio is 3/7 [37], but the synthesis method used here is reactive magnetron co-sputtering technique instead of aerosol-spray-assisted approach that was used previously. As known, synthesis methods that can prepare OER catalysts with nanoparticle size and uniform multiple metal composition ratio is critical to the final performance of catalysts [38]. So far, such synthesis methods include electrodeposition method [39-46], magnetron sputtering [37], metal organic decomposition [47-51] and thermal decomposition [52]. However, despite impressive progress has been made and extensive research has been conducted, till now, electrochemical studies on synthesis of triple metal Fe, Co and Ni by electrodeposition have rarely been seen.

Herein, we have prepared FeCoNi three metals catalyst with 3D hierarchical porous structure by electrodeposition approach for high-performance OER application. The test results show that this catalyst demonstrates excellent OER catalytic performance, with FeCoNiCu electrodeposited for 5 min showing the better performance compared to other time. The following synthesis of bimetallic catalysts such as FeNiCu, CoNiCu, FeCoCu with same electrodeposition time duration of 5 mins was conducted. It is found that FeCoNiCu exhibits better performance than bimetallic catalysts in terms of electrochemical stability, onset potential and Tafel slope. Furthermore, TEM result shows that FeOOH, CoOOH, and NiOOH phases are distributed uniformly within the particles.

6.2 Materials preparation

1) Chemicals used

The chemicals used include 37% hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), potassium hydroxide (KOH), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nickel chloride (NiCl_2), sodium citrate tribasic dihydrate ($\text{HOC}(\text{COONa})(\text{CH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$), sodium hypophosphite monohydrate ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$), isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), ammonium sulfate and acetone.

2) Pre-treatment

The copper foam was first cut into $1\text{cm} \times 1\text{cm}$ size to ensure that the exposure area is 1cm^2 . Afterwards, the cut copper foam was sequentially treated by acetone, isopropyl alcohol and absolute ethanol for 5 min in ultrasonic machine to remove any remained oil or organic substance. Then, it was etched in 37% HCl for 10 min to remove the surface layer of metal oxides followed by enough washing of DI water and absolute ethanol sequentially. In the last step, the copper foam was air blow dried for use.

3) The preparation of 3D copper nanotube array (3D Cu NTA)

The pre-treated copper foam was anodized in 3M NaOH at the constant current density of $45\text{ mA} \cdot \text{cm}^{-2}$ for 750 s to produce $\text{Cu}(\text{OH})_2$ nanotube array. Then it was annealed at 150°C for 4 h to get CuO nanotube array. Finally, it was further reduced to Cu nanotube array by simple electrochemical reduction (under -1.4 V for 1 h).

4) Electrodeposition

The pre-treated copper foam was used as the working electrode while platinum plate and silver/silver chloride electrode were used as counter electrode and reference electrode, respectively. The three-electrode system mentioned above was then used to electrodeposit FeCoNiCu alloy onto the working electrode with the assistance of electrolyte consisting of iron, cobalt, nickel and copper with a molar ratio of 2.5:8:2.5:4. Besides, a buffer solution consisting of 0.2 M sodium citrate tribasic dihydrate, 0.55 M sodium hypophosphite monohydrate and 0.45 M ammonium sulfate was also included in the electrolyte to stabilize the pH value.

5) Dealloying

The electrodeposited working electrode was then dealloyed in 1M KOH using cyclic voltammetry method for 10 cycles. The potential range is 0-1V vs Ag/AgCl, the copper was completely dealloyed. The working electrode was obtained after 10 cycles of dealloying process which was then used to carry out various performance tests including OER.

6.3 Principal outcomes

6.3.1 Electrochemical synthesis of copper nanoarrays

To get a 3D copper nanostructure with large surface area, the pre-treated foam copper was firstly electrochemically oxidized using a current of 750 seconds forming the copper hydroxide array shown in Fig. 6.1. As seen from Fig. 1a1, the dense fur structured $\text{Cu}(\text{OH})_2$ is neatly grown on Cu foam. The fur structure fibers is $\text{Cu}(\text{OH})_2$ identified from XRD pattern (Fig. 6.2a). The sample subsequently underwent heating at 150 °C to obtain copper oxide tubular structure. From Fig. 6.1b1, the tubular structure appears slightly randomly ordered, but the shape remains almost the same. XRD in Fig.6.2b indicates that the material is CuO mixed with Cu_2O .

Figure 6.1 SEM images of Cu foam after electrooxidation in 3M NaOH solution (a-a2); after annealing at 200 C in Ar for 2h (b-b2).

The obtained 3D copper oxide structure sample was continued to be electrochemically reduced, generating a structure of the 3D hierarchical porous copper nanofibers structure as shown in Figure 6.3. The previous long copper oxide fibers become bent after electrochemical reduction and the surface is no longer smooth with nano particles less than 100 nanometers in size (Fig. 6.3b). These are beneficial to the subsequent electrochemical coating of alloy metal. It is observed that the majority of sample has been converted to Cu with a trace amount of Cu_2O that is still preserved after electrochemical reduction.

Figure 6.2 XRD patterns of Cu foam after electrooxidation in 3M NaOH solution (a-a2); after annealing at 200 C in Ar for 2h (b-b2).

Figure 6.3 SEM images (a,b,c) and corresponding XRD patterns (d) of Cu foam after electrochemical reduction.

6.3.2 Synthesis of dealloyed FeCoNiCu

After obtaining the conductive 3D copper structure, the electrodeposition of alloy was carried out. Many particles are observed to grow on the copper wire surface forming a core-shell structure (Fig.6.4).

Figure 6.4 SEM images (a,b,c) of electrodeposited FeCoNiCu

The final step is to selectively corrode the copper elements inside, with the aim of creating more active sites. After the selective corrosion of the copper element, it is of interest to see that the appearance has changed from the previous particles to the porous flower structure (Fig.6.5d). This could be due to the Kirkendall effect arising by interdiffusion of Cu element laterally from within to outside reconstructing alloy particles on surface of Cu wires during electrochemical etching process[53-55].

The phase structure of the dealloyed FeCuNiCu catalyst was characterized by XRD. The diffraction pattern in Fig.6.6a shows that phases of FeO(OH), Ni(OH)₂ and Co(OH)₂ are present. These phases are further verified by TEM characterization in Fig. 6b. Based on the FFT pattern derived from the three regions, three phases of FeO(OH), Ni(OH)₂ and Co(OH)₂, are closely connected within one particle. Such close connection between different phases contributes the good catalytic performance.

Figure 6.5 SEM images with different magnifications of dealloyed FeCuNiCu on Cu foam after electrodeposition.

Figure 6.6 (a) XRD pattern of FeCuNiCu on Cu foam after electrodeposition; (b) TEM images with corresponding FFT pattern.

6.3.3 OER performance of dealloyed FeCoNiCu

Electrochemical behavior of the as prepared electrodes via electrodeposition was measured using linear sweep voltammogram (LSV) in 1 M KOH aqueous solution (pH 13.0), as shown in Fig. 6.6a. The j -V curves of copper foam is shown as references. The anodic current together with a large number of bubbles presented on the electrode surface displays that the oxygen gas is evolved due to water oxidation reaction. The onset potential (at $j = 0.1 \text{ mAcm}^{-2}$) for OER of the investigated samples are compared. Other samples all show much higher electrocatalytic activity than that of Cu foam. The onset potential of the FeCoNiCu electrode shifts negatively with the increase of electrodeposition time and reaches the maximum at 5 min. Further extending the electrodeposition time will lower catalytic activity. It is noticed that other bimetal catalysts such as FeCoCu, FeNiCu, and CoNiCu with the same electrodeposition time of 5 min, offer inferior performance. CoNiCu without addition of Fe, in particular, has the lowest catalytic activity compared with other bimetal catalysts, in good agreement with the literature that Fe can help improve the catalytic activity[36, 37]. Fig.6.6b is the Tafel plot for different electrocatalysts. It is observed that FeCoNiCu electrode at 5 min displays a linear dependence on the logarithm of current density with a slope of 57 mV/dec, which is smaller than those of other catalysts. The EIS result shows the similar resistance of these catalysts. The stability testing of FeCoNiCu electrode was further conducted in alkaline solution of 1M KOH with the CP profile demonstrating that potential is stabilized for 12 h testing, suggesting the good stability of FeCoNiCu catalyst.

6.4 Conclusions

In summary, we have developed high performance hierarchical nano-porous nanostructure three metal FeCoNiCu catalyst via a electrodeposition approach followed by the electrochemical etching process. Effect of different electrodeposition time on the catalytic performance was systemically studied, and it is found that FeCoNiCu electrode at 5 min electrodeposition time demonstrates the best performance with lowest Tafel slope of 57 mV/dec, one of the best performances in literature. Such good performance can be

attributed to the nanoporous structure and close connection of FeO(OH), Ni(OH)₂ and Co(OH)₂ phases.

Fig. 6.7 Electrochemical characterization after selective corrosion: (a) OER performance; (b) EIS spectra; (c) stability test for 12 h.

References

- [1] Z.W. Seh, J. Kibsgaard, C.F. Dickens, I. Chorkendorff, J.K. Nørskov, T.F.J.S. Jaramillo, Combining theory and experiment in electrocatalysis, Insights into materials design, 355 (2017).
- [2] H. Jin, C. Guo, X. Liu, J. Liu, A. Vasileff, Y. Jiao, Y. Zheng, S.-Z.J.C.r. Qiao, Emerging two-dimensional nanomaterials for electrocatalysis, 118 (2018) 6337-6408.
- [3] Y. Jiao, Y. Zheng, M. Jaroniec, S.Z.J.C.S.R. Qiao, Design of electrocatalysts for oxygen-and hydrogen-involving energy conversion reactions, 44 (2015) 2060-2086.
- [4] S. Park, Y. Shao, J. Liu, Y.J.E. Wang, E. Science, Oxygen electrocatalysts for water electrolyzers and reversible fuel cells: status and perspective, 5 (2012) 9331-9344.
- [5] J. Kibsgaard, I.J.N.E. Chorkendorff, Considerations for the scaling-up of water splitting catalysts, 4 (2019) 430-433.
- [6] B. You, Y.J.A.o.c.r. Sun, Innovative strategies for electrocatalytic water splitting, 51 (2018) 1571-1580.
- [7] J.H. Montoya, L.C. Seitz, P. Chakthranont, A. Vojvodic, T.F. Jaramillo, J.K.J.N.m. Nørskov, Materials for solar fuels and chemicals, 16 (2017) 70-81.
- [8] N.S. Lewis, D.G.J.P.o.t.N.A.o.S. Nocera, Powering the planet: Chemical challenges in solar energy utilization, 103 (2006) 15729-15735.
- [9] Q. Shi, C. Zhu, D. Du, Y.J.C.S.R. Lin, Robust noble metal-based electrocatalysts for oxygen evolution reaction, 48 (2019) 3181-3192.
- [10] L. Han, S. Dong, E.J.A.m. Wang, Transition - metal (Co, Ni, and Fe) - based electrocatalysts for the water oxidation reaction, 28 (2016) 9266-9291.
- [11] J. Lim, S. Yang, C. Kim, C.-W. Roh, Y. Kwon, Y.-T. Kim, H.J.C.C. Lee, Shaped Ir–Ni bimetallic nanoparticles for minimizing Ir utilization in oxygen evolution reaction, 52 (2016) 5641-5644.
- [12] A. Singh, L.J.C.C.R. Spiccia, Water oxidation catalysts based on abundant 1st row transition metals, 257 (2013) 2607-2622.
- [13] J.R.J.C. Galón - Mascarós, Water oxidation at electrodes modified with earth - abundant transition - metal catalysts, 2 (2015) 37-50.

- [14] M.S. Burke, L.J. Enman, A.S. Batchellor, S. Zou, S.W.J.C.o.M. Boettcher, Oxygen evolution reaction electrocatalysis on transition metal oxides and (oxy) hydroxides: activity trends and design principles, 27 (2015) 7549-7558.
- [15] M. Gong, W. Zhou, M.J. Kenney, R. Kapusta, S. Cowley, Y. Wu, B. Lu, M.C. Lin, D.Y. Wang, J.J.A.C. Yang, Blending Cr₂O₃ into a NiO–Ni electrocatalyst for sustained water splitting, 127 (2015) 12157-12161.
- [16] Y. Wang, M. Chen, Y. Xie, P. Wei, H.F. Schaefer III, G.H.J.J.o.t.A.C.S. Robinson, Stabilization of Silicon–Carbon Mixed Oxides, 137 (2015) 8396-8399.
- [17] Y. Liu, C. Ma, Q. Zhang, W. Wang, P. Pan, L. Gu, D. Xu, J. Bao, Z.J.A.M. Dai, 2D electron gas and oxygen vacancy induced high oxygen evolution performances for advanced Co₃O₄/CeO₂ nanohybrids, 31 (2019) 1900062.
- [18] C. Niether, S. Faure, A. Bordet, J. Deseure, M. Chatenet, J. Carrey, B. Chaudret, A.J.N.E. Rouet, Improved water electrolysis using magnetic heating of FeC–Ni core–shell nanoparticles, 3 (2018) 476-483.
- [19] P. Ganesan, M. Prabu, J. Sanetuntikul, S.J.A.c. Shanmugam, Cobalt sulfide nanoparticles grown on nitrogen and sulfur codoped graphene oxide: an efficient electrocatalyst for oxygen reduction and evolution reactions, 5 (2015) 3625-3637.
- [20] Y. Lin, G. Chen, H. Wan, F. Chen, X. Liu, R.J.S. Ma, 2D Free - Standing Nitrogen - Doped Ni - Ni₃S₂@ Carbon Nanoplates Derived from Metal - Organic Frameworks for Enhanced Oxygen Evolution Reaction, 15 (2019) 1900348.
- [21] J.X. Feng, H. Xu, Y.T. Dong, S.H. Ye, Y.X. Tong, G.R.J.A.C.I.E. Li, FeOOH/Co/FeOOH hybrid nanotube arrays as high - performance electrocatalysts for the oxygen evolution reaction, 55 (2016) 3694-3698.
- [22] J.X. Feng, S.H. Ye, H. Xu, Y.X. Tong, G.R.J.A.M. Li, Design and synthesis of FeOOH/CeO₂ heterolayered nanotube electrocatalysts for the oxygen evolution reaction, 28 (2016) 4698-4703.
- [23] J.S. Kim, B. Kim, H. Kim, K.J.A.E.M. Kang, Recent progress on multimetal oxide catalysts for the oxygen evolution reaction, 8 (2018) 1702774.
- [24] Y. Yang, Y. Song, S. Mo, M.J.C.E.J. Liu, Efficient and durable FeCoNi-(Oxy) hydroxide anode: Stoichiometric ration regulated morphology-, defect-and valence-dependent water oxidation performance, 417 (2021) 127934.

- [25] M.S. Burke, M.G. Kast, L. Trotochaud, A.M. Smith, S.W.J.J.o.t.A.C.S. Boettcher, Cobalt–iron (oxy) hydroxide oxygen evolution electrocatalysts: the role of structure and composition on activity, stability, and mechanism, 137 (2015) 3638-3648.
- [26] P. Zhang, L. Li, D. Nordlund, H. Chen, L. Fan, B. Zhang, X. Sheng, Q. Daniel, L. Sun, Dendritic core-shell nickel-iron-copper metal/metal oxide electrode for efficient electrocatalytic water oxidation, *Nature communications*, 9 (2018) 381.
- [27] D.A.J.J.o.T.E.S. Corrigan, The catalysis of the oxygen evolution reaction by iron impurities in thin film nickel oxide electrodes, 134 (1987) 377.
- [28] L. Trotochaud, S.L. Young, J.K. Ranney, S.W.J.J.o.t.A.C.S. Boettcher, Nickel–iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation, 136 (2014) 6744-6753.
- [29] J.B. Gerken, S.E. Shaner, R.C. Massé, N.J. Porubsky, S.S. Stahl, A survey of diverse earth abundant oxygen evolution electrocatalysts showing enhanced activity from Ni–Fe oxides containing a third metal, *Energy Environ. Sci.*, 7 (2014) 2376-2382.
- [30] B.M. Hunter, J.D. Blakemore, M. Deimund, H.B. Gray, J.R. Winkler, A.M. Muller, Highly active mixed-metal nanosheet water oxidation catalysts made by pulsed-laser ablation in liquids, *Journal of the American Chemical Society*, 136 (2014) 13118-13121.
- [31] M.W. Louie, A.T.J.J.o.t.A.C.S. Bell, An investigation of thin-film Ni–Fe oxide catalysts for the electrochemical evolution of oxygen, 135 (2013) 12329-12337.
- [32] D.A. Corrigan, R.S. Conell, C.A. Fierro, D.A.J.J.o.P.C. Scherson, In-situ Moessbauer study of redox processes in a composite hydroxide of iron and nickel, 91 (1987) 5009-5011.
- [33] D. Friebe, M.W. Louie, M. Bajdich, K.E. Sanwald, Y. Cai, A.M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R.J.J.o.t.A.C.S. Alonso-Mori, Identification of highly active Fe sites in (Ni, Fe) OOH for electrocatalytic water splitting, 137 (2015) 1305-1313.
- [34] J. Deng, M.R. Nellist, M.B. Stevens, C. Dette, Y. Wang, S.W.J.N.I. Boettcher, Morphology dynamics of single-layered Ni (OH)₂/NiOOH nanosheets and subsequent Fe incorporation studied by in situ electrochemical atomic force microscopy, 17 (2017) 6922-6926.
- [35] S. Ida, D. Shiga, M. Koinuma, Y.J.J.o.t.A.C.S. Matsumoto, Synthesis of hexagonal nickel hydroxide nanosheets by exfoliation of layered nickel hydroxide intercalated

- with dodecyl sulfate ions, 130 (2008) 14038-14039.
- [36] L. Kuai, J. Geng, C. Chen, E. Kan, Y. Liu, Q. Wang, B.J.A.C.I.E. Geng, A reliable aerosol - spray - assisted approach to produce and optimize amorphous metal oxide catalysts for electrochemical water splitting, 53 (2014) 7547-7551.
- [37] D. Zhang, L. Meng, J. Shi, N. Wang, S. Liu, C.J.E.A. Li, One-step preparation of optically transparent Ni-Fe oxide film electrocatalyst for oxygen evolution reaction, 169 (2015) 402-408.
- [38] M. Gong, H. Dai, A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts, Nano Res, 8 (2014) 23-39.
- [39] K.H. Kim, J.Y. Zheng, W. Shin, Y.S. Kang, Preparation of dendritic NiFe films by electrodeposition for oxygen evolution, RSC Advances, 2 (2012) 4759-4767.
- [40] X. Lu, C.J.N.c. Zhao, Electrodeposition of hierarchically structured three-dimensional nickel-iron electrodes for efficient oxygen evolution at high current densities, 6 (2015) 1-7.
- [41] S. Cattarin, I. Frateur, P. Guerriero, M.J.E.a. Musiani, Electrodeposition of $\text{PbO}_2 + \text{CoO}_x$ composites by simultaneous oxidation of Pb^{2+} and Co^{2+} and their use as anodes for O_2 evolution, 45 (2000) 2279-2288.
- [42] M.D. Merrill, R.C.J.T.J.o.P.C.C. Dougherty, Metal oxide catalysts for the evolution of O_2 from H_2O , 112 (2008) 3655-3666.
- [43] Y. Yang, H. Fei, G. Ruan, C. Xiang, J.M.J.A.n. Tour, Efficient electrocatalytic oxygen evolution on amorphous nickel-cobalt binary oxide nanoporous layers, 8 (2014) 9518-9523.
- [44] B.J. Trześniewski, O. Diaz-Morales, D.A. Vermaas, A. Longo, W. Bras, M.T. Koper, W.A.J.J.o.t.A.C.S. Smith, In situ observation of active oxygen species in Fe-containing Ni-based oxygen evolution catalysts: the effect of pH on electrochemical activity, 137 (2015) 15112-15121.
- [45] C.G. Morales-Guio, L. Liardet, X.J.J.o.t.A.C.S. Hu, Oxidatively electrodeposited thin-film transition metal (oxy) hydroxides as oxygen evolution catalysts, 138 (2016) 8946-8957.
- [46] L. Wang, X. Ge, Y. Li, J. Liu, L. Huang, L. Feng, Y.J.J.o.M.C.A. Wang, Nickel enhanced the catalytic activities of amorphous copper for the oxygen evolution reaction,

- 5 (2017) 4331-4334.
- [47] R.D. Smith, M.S. Prévot, R.D. Fagan, Z. Zhang, P.A. Sedach, M.K.J. Siu, S. Trudel, C.P.J.S. Berlinguette, Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis, 340 (2013) 60-63.
- [48] R.D. Smith, M.S. Prévot, R.D. Fagan, S. Trudel, C.P.J.J.o.t.A.C.S. Berlinguette, Water oxidation catalysis: electrocatalytic response to metal stoichiometry in amorphous metal oxide films containing iron, cobalt, and nickel, 135 (2013) 11580-11586.
- [49] C. Zhang, R.D. Fagan, R.D. Smith, S.A. Moore, C.P. Berlinguette, S.J.J.o.M.C.A. Trudel, Mapping the performance of amorphous ternary metal oxide water oxidation catalysts containing aluminium, 3 (2015) 756-761.
- [50] C. Zhang, C.P. Berlinguette, S.J.C.C. Trudel, Water oxidation catalysis: an amorphous quaternary Ba-Sr-Co-Fe oxide as a promising electrocatalyst for the oxygen-evolution reaction, 52 (2016) 1513-1516.
- [51] X. Duan, C. Wang, J.C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang, A. Pan, J. Jiang, R. Yu, Y. Huang, X. Duan, Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions, *Nature nanotechnology*, 9 (2014) 1024-1030.
- [52] A.T. Marshall, R.G.J.E.A. Haverkamp, Electrocatalytic activity of IrO₂-RuO₂ supported on Sb-doped SnO₂ nanoparticles, 55 (2010) 1978-1984.
- [53] W. Xiao, J. Zhou, L. Yu, D. Wang, X.W.J.A.C. Lou, Electrolytic formation of crystalline silicon/germanium alloy nanotubes and hollow particles with enhanced lithium - storage properties, 128 (2016) 7553-7557.
- [54] K.-N. Tu, U.J.A.P.L. Gösele, Hollow nanostructures based on the Kirkendall effect: Design and stability considerations, 86 (2005) 093111.
- [55] H.H. Li, S.H.J.A.M. Yu, Recent advances on controlled synthesis and engineering of hollow alloyed nanotubes for electrocatalysis, 31 (2019) 1803503.

Chapter 7

Conclusions and Recommendations

In this chapter, general conclusions including implications, impact and outstanding questions were drawn. In specific, $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure was synthesized by gas-assisted electrodeposition and it has demonstrated excellent overall water splitting ability, better than the state-of-the-art electrocatalysts. This outstanding performance was attributed to the numerous interfaces formed between these two phases, promoting active sites exposure as well as optimizing the electronic structure. Afterwards, dealloyed FeCoCu was successfully synthesized by electrodeposition followed by dealloying. The dealloyed FeCoCu has displayed remarkable OER performance, thanks to the synergistic effect between different phases in dealloyed FeCoCu. The synergistic effect in dealloyed FeCoNiCu was also discussed. Besides, future work about the mechanism studies of synergistic effect is also discussed. Finally, there is a summary of major outcomes to illustrate that how the outcomes will be reflected in the hypothesis.

7.1 Conclusions

The influence of gas-assisted electrodeposition of $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure was studied and found to be an effective strategy to fabricate efficient electrocatalyst for both HER and OER. Then, the electrochemical synthesis of dealloyed FeCoCu was investigated by cyclic voltammetry (CV) method. Their OER performance have both demonstrated to be excellent, better than the state-of-the-art electrocatalyst. To further improve the OER performance, nickel was added to the FeCoCu system and the dealloyed FeCoNiCu has displayed superior OER performance when compared to FeCoCu system, highlighting the synergistic effect of three phases consisting of dealloyed FeCoNiCu.

Firstly, the gas-assisted electrodeposition of $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure was studied by controlling the gas purging. It was found that there was no formation of $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure when gas purging was stopped. That is mainly because the concentration of hydroxide ions (OH^-) will become higher near the electrode-electrolyte interface, prompting the formation of metal hydroxides, rather than metal oxides. However, when gas purging was applied, the generated OH^- from NO_3^- will diffuse through the interface and the concentration of OH^- will not increase significantly. This is beneficial for the formation of cobalt oxide as well cobalt sulfide. In other words, the gas purging will directly promote the formation of $\text{Co}_3\text{O}_4/\text{Co}_9\text{S}_8$ heterostructure.

Secondly, the dealloyed FeCoCu consists of two different phases which will prompt a synergistic effect to each other. The FeCoCu itself is comprised of dendritic crystal structure, significantly enlarging the surface area. The remained FeCoCu alloy has provided fast channel for electron transfer. The dendritic structure from FeCoCu has largely promoted the diffusion of reactants and intermediates, accelerating the processing. Meanwhile, there is obvious synergistic effect between FeOOH and $\text{Co}(\text{OH})_2$ consisting of dealloyed FeCoCu. All of these factors have contributed to the improved OER performance.

Lastly, in order to further improve the OER performance, Ni was added into the FeCoCu system, forming FeCoNiCu system. After dealloying, there are three phases including

FeOOH , $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$, all of which are synergistic to each other. This greatly improves the reaction kinetics, making it an efficient electrocatalyst for OER.

7.2 Future work

7.2.1 Porous FeCoNi (FCN)-dendritic FeCoCu

As can be seen from Fig.7.1 and Fig.7.2, porous FeCoNi alloy was first electrodeposited on the 3D Ni foam, acting as perfect current collector. Besides, itself also possesses excellent OER capabilities. Afterwards, dendritic FeCoCu was electrodeposited onto the FCN, see Fig.7.2. As shown in the figure, the dendritic structure is beneficial for the diffusion of reactants and intermediates, accelerating mass transport and thus reaction kinetics. Besides, it can also enlarge the surface area exposure. Last but not least, the interaction between FCN and dendritic FeCoCu will provide a synergistic effect, enhancing their OER performance. The detailed analysis of this material and the clarification of its OER mechanism will be in progress in future.

Figure 7.1 Porous FCN on Ni foam

Figure 7.2 Porous FCN-dendritic FeCoCu

7.2.2 3D electrically reduced copper foam coated with Ni

As shown in Fig.7.3, the 3D E-reduced copper foam was coated with Ni. There is obvious agglomerate on the tip of E-reduced copper foam, indicating that tip position is the current collector. The Ni coated E-reduced copper foam can be a perfect supported for various electrocatalysts. On the one hand, it is perfect electron conductor, proving fast channel for electron transfer, which is quite beneficial for electrocatalysis. On the other hand, it provides 3D nanoporous structure, which is beneficial for mass transport and charge transfer. Last but not least, nickel itself is also active electrocatalyst for OER. Its performance will be further enhanced when combining with other active electrocatalysts. These are only primary results and more work will be implemented in the future.

Figure 7.3 E-reduced copper foam coated with Ni

7.3 Outcomes reflected in the original hypothesis

All hypotheses mentioned above are proved and the specific details are as follows:

Gas-purging-assisted electrodeposition is proven to be useful in controlling the phases thus formed. When gas-purging is performed, $\text{Co}_9\text{S}_8/\text{Co}_3\text{O}_4$ heterostructure is formed. The product obtained changes to Co-Mn LDH without gas-purging.

The second hypothesis is that there is alternative ways to improve the performance. Electrochemical dealloying has been proven to be quite useful in achieving this goal.

The incorporation of Ni can further improve the performance is the last hypothesis, which is verified in Chapter 6.