Interface engineering towards transition metal based nanocomposites for water splitting

Yin, Shengming

2017

Yin, S. (2017). Interface engineering towards transition metal based nanocomposites for water splitting. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/72989>

<https://doi.org/10.32657/10356/72989>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**INTERFACE ENGINEERING TOWARDS TRANSITION METAL BASED
NANOCOMPOSITES FOR WATER SPLITTING**

YIN SHENGMING

School of Chemical and Biomedical Engineering

2017

**INTERFACE ENGINEERING TOWARDS TRANSITION METAL BASED
NANOCOMPOSITES FOR WATER SPLITTING**

YIN SHENGMING

School of Chemical and Biomedical Engineering

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

2017

ACKNOWLEDGEMENTS

Here I would like to express my sincere gratitude to my Ph.D. supervisor Prof. Xu Rong for the continuous supporting of my research, her guidance on my project, and the encouragement to explore different areas that interest me. Prof. Xu's academic rigor, dedicated attitude and great passion in research have great effects on me and inspire me to conquer any difficulty in my graduate research. I sincerely appreciate her guidance, encouragement, generosity and patience. It is a great honor to be mentored by her.

Besides my supervisor, I also would like to thank my lab mates, Dr. Wang Yabo, Dr. Hong Jindui, Dr. Amin Yoosefi Booshehri, Dr. Zhou Tianhua, Dr. Pan Yunxiang, Dr. Zou Yinjun, Dr. Xu you, Dr. Tu Wenguang, Dr. Sheng Yuan and Mr. Wu Shuyang. It is their efforts that help create a harmonious academic environment and they are always kind enough to offer help in research work and life. I was enjoying working with all of them. Also, my thanks go to the technical staffs and professional officers in our school. They have done excellent job on keeping our research work running smoothly.

Last but not the least, I would like to thank my family, especially my mother for her unconditioned love and support throughout all these years. Life is not easy for her since she has to live all by herself. I hope I can spend more time with her and bring her a good life in the future. Besides, I would give my thankfulness to Miss Su Zijun for accompanying me along the way. She brings color to my life and I am happy to have her by my side.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	I
TABLE OF CONTENTS.....	II
LIST OF FIGURES	V
LIST OF TABLES.....	XI
LIST OF SCHEMATICS.....	XII
LIST OF ABBREVIATIONS.....	XIII
ABSTRACT.....	XV
CHAPTER 1 INTRODUCTION	1
1.1 Background and motivations.....	1
1.2 Objective and scope	2
1.3 Major contributions of the thesis.....	3
CHAPTER 2 LITERATURE REVIEW	5
2.1 Photocatalytic water splitting.....	5
2.1.1 Basic principle of photocatalytic water splitting	5
2.1.2 Semiconductors for photocatalytic water splitting	6
2.1.3 Non-noble metal containing co-catalysts for photocatalytic H ₂ evolution....	8
2.1.4 Non-noble metal containing co-catalysts for photocatalytic O ₂ evolution..	12
2.2 Electrocatalytic water splitting.....	12
2.2.1 Electrocatalytic activity evaluation	12
2.2.2 Non-noble metal containing electrocatalysts for H ₂ evolution.....	13
2.2.3 Non-noble metal containing electrocatalysts for O ₂ evolution.....	19
2.3 Summary of literature review.....	23
CHAPTER 3 HIGHLY EFFICIENT NOBLE METAL FREE PHOTOCATALYTIC HYDROGEN EVOLUTION SYSTEM CONTAINING MoP AND CdS QUANTUM DOTS	24
3.1 Introduction	24
3.2 Experimental	25
3.2.1 Materials and reagents	25
3.2.2 Materials synthesis	25
3.2.3 Materials characterization.....	27
3.2.4 Photocatalytic activity measurement	28
3.2.5 Electrochemical measurement	29

3.3 Results and discussion.....	29
3.3.1 Properties of MoP catalyst.....	29
3.3.2 Effect of reaction conditions on phase structure and morphology of MoP.....	32
3.3.3 Electrocatalytic hydrogen evolution reaction (HER) activity	35
3.3.4 Photocatalytic hydrogen evolution activity	37
3.3.5 Characterization of photocatalyst after reaction.....	43
3.4 Conclusion.....	45
CHAPTER 4 Co _x P-ZnO/CdS QUANTUM DOTS NANOCOMPOSITE AS AN ARTIFICIAL PHOTOCATALYST FOR EFFICIENT HYDROGEN EVOLUTION	46
4.1 Introduction	46
4.2 Experimental	47
4.2.1 Materials and reagents	47
4.2.2 Materials synthesis	47
4.2.3 Materials characterization.....	48
4.2.4 Photocatalytic activity measurement	48
4.3 Results and discussion.....	48
4.3.1 Structure and morphology of Co _x P-ZnO	48
4.3.2 Photocatalytic hydrogen evolution activity of Co _x P-ZnO.....	52
4.4 Conclusion.....	59
CHAPTER 5 CoP ON MESOPOROUS CARBON NANOTUBE FOR EFFICIENT HYDROGEN EVOLUTION	60
5.1 Introduction	60
5.2 Experimental	61
5.2.1 Materials and reagents	61
5.2.2 Preparation of Co@P-NCNTs	61
5.2.3 Materials characterization.....	62
5.2.4 Electrochemical measurements	62
5.3 Results and discussion.....	64
5.3.1 Characterization of Co-P/NCNT	64
5.3.2 Acid leaching of Co-P/NCNT	69
5.3.3 Electrocatalytic activity of A-Co-P/NCNT	72
5.3.4 Stability of A-Co-P/NCNT	74
5.4 Conclusion.....	77

CHAPTER 6 HIGHLY EFFICIENT OXYGEN EVOLUTION CATALYST CONSISTING OF INTERCONNECTED AMORPHOUS Ni-Fe LAYERED DOUBLE HYDROXIDE AND CARBON NANODOMAIN	78
6.1 Introduction	78
6.2 Experimental	79
6.2.1 Materials and reagents	79
6.2.2 Preparation of Ni _x Fe _{1-x} /C	79
6.2.3 Physical characterization	80
6.2.4 Electrode preparation.....	81
6.2.5 Electrochemical measurements	82
6.2.6 Turnover frequency (TOF) calculation.....	83
6.3 Results and discussion.....	83
6.3.1 Electrocatalyst characterization	83
6.3.2 <i>In situ</i> growth of nanocarbon and metal-carbon interaction.....	89
6.3.3 Electrocatalytic activity and stability	95
6.3.4 Characterization of catalyst after OER durability test.....	99
6.4 Conclusions	103
CHAPTER 7 CONCLUSIONS AND OUTLOOK	104
7.1 Conclusions	104
7.2 Outlook.....	105
LIST OF PUBLICATION	108
REFERENCE.....	111

LIST OF FIGURES

Figure 3-1 Photograph of probe sonicator.....	27
Figure 3-2 XRD pattern of as-prepared MoP-2CA-650 sample before sonication.	30
Figure 3-3 (a, b) SEM images of as-prepared MoP-2CA-650 sample before sonication; (c) EDS spectrum of as-prepared MoP-2CA-650 sample before sonication.	30
Figure 3-4 (a) SEM; (b, c) TEM and (d) HRTEM images of MoP-2CA-650 sample after probe sonication.....	31
Figure 3-5 (a) XPS survey spectrum of MoP-2CA-650 sample; high resolution XPS spectrum of (b) Mo 3d and (c) P 2p in the as-prepared MoP-2CA-650 sample.	32
Figure 3-6 (a) XRD patterns of MoP samples prepared at different temperatures. TEM images of MoP samples prepared at (b) 550 °C, (c) 600 °C, (d) 650 °C and (e) 700 °C	33
Figure 3-7 (a) XRD patterns of MoP samples prepared at 650.....	34
Figure 3-8 Raman spectra of different samples recorded at 633 nm (MoP-2CA-aged refers to MoP-2CA stored at ambient condition for 0.5 year).	35
Figure 3-9 The polarization curves of (a) MoP-2CA prepared at different temperatures and (b) MoP-650 prepared with different CA:Mo ratios.	36
Figure 3-10 (a) XRD patterns, (b) TEM image and (c) UV-vis and PL spectra of as-prepared CdS QDs.	37
Figure 3-11 (a) TEM and (b, c) HRTEM images of MoP/CdS QDs composite with a molar ratio of 1.75:1 for CdS:MoP.	38
Figure 3-12 (a) Time course of H ₂ evolution using MoP-2CA samples prepared at different temperatures as co-catalysts; (b) Time course of H ₂ evolution using MoP-xCA samples prepared at 650 °C as co-catalysts; (c) PL emission spectra of various samples at an excitation wavelength of 360 nm at 77 K.....	40
Figure 3-13 Time course of H ₂ evolution using MoP-2CA-650 samples prepared with (a) different ramping rate; (b) different calcination duration; (c) different amount of MoP while the amount of CdS QDs was fixed at 50 μmol; (d) different amount of	

CdS QDs while the amount of MoP was fixed at 60 μmol ; (e) H_2 evolution rate of CdS/MoP-650 at different pH values of the reaction solution.....	41
Figure 3-14 (a) stability test (b) long duration irradiation test and (c) AQE of the optimized MoP/CdS QDs system.	42
Figure 3-15 (a) XRD patterns, (b, c) Raman spectrum and (d, e) HRTEM images of MoP/CdS QDs after photoreaction.	45
Figure 3-16 High resolution XPS spectra of (a) Mo, (b) P and (c) S in the MoP/CdS QDs after photoreaction.	45
Figure 4-1 (a) XRD patterns of ZnO, 3% Co_xP -ZnO, CoP and Co_2P ; (b) XRD patterns of Co_xP prepared without ZnO.	49
Figure 4-2 TEM and HRTEM images of 3% Co_xP -ZnO.	50
Figure 4-3 (a) XPS survey spectrum of 3% Co_xP -ZnO; (b) high resolution Co 2p spectrum of 3% Co_xP -ZnO; (c) high resolution Zn 3s and P 2p spectra of 3% Co_xP -ZnO.	51
Figure 4-4 Co K-edge X-ray absorption near edge spectrum (XANES) of 3% Co_xP -ZnO.	51
Figure 4-5 UV-vis spectra of 0.3% Co_xP -ZnO, 3% Co_xP -ZnO, ZnO and CdS.	52
Figure 4-6 TEM and HRTEM image of Co_xP -ZnO/CdS QDs.....	53
Figure 4-7 (a) Time course of photocatalytic H_2 evolution of Co_xP hybridized with different metal oxides; (b) H_2 evolution rate of Co_xP hybridized with different metal oxides. Reaction conditions: 5 mg Co_xP -ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).	54
Figure 4-8 H_2 evolution rate over Co_xP -ZnO with different loading percentage. Reaction conditions: 5 mg Co_xP -ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).	55
Figure 4-9 (a) Photocatalytic H_2 evolution activity with different amount of 3% Co_xP -ZnO (20 mg CdS QDs; 20 v/v% LA solution); (b) photocatalytic H_2 evolution activity with different amount of CdS QDs (5 mg 3% Co_xP -ZnO; 20 v/v% LA solution); (c) photocatalytic H_2 evolution activity with different LA concentration (20 mg CdS QDs and 5 mg 3% Co_xP -ZnO); (d) photocatalytic H_2 evolution activity with different	

amount of 3% Co _x P-ZnO (20 mg CdS QDs; 30 v/v% LA solution).	56
Figure 4-10 AQE of the optimized Co _x P-ZnO/CdS QDs system. Reaction conditions: 5 mg 3% Co _x P-ZnO, 20 mg CdS QDs, 100 mL LA solution (30 v/v%).	57
Figure 4-11 Stability test of Co _x P-ZnO/CdS QDs system. Reaction conditions: 5 mg 0.3% Co _x P-ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).	58
Figure 4-12 PL emission spectra of CdS QDs and 3% Co _x P-ZnO/CdS QDs at an excitation wavelength of 360 nm at 77 K.	58
Figure 5-1 Electrochemical system with three-electrode configuration and proton exchange membrane.....	63
Figure 5-2 (a, b) SEM images of CoNA MWs at different magnifications, inset: photograph of CoNA MWs; (c, d) SEM and TEM image of CoNA/DPA NWs; inset: photograph of CoNA/DPA NWs.....	65
Figure 5-3 (a) XRD pattern of Co-P/NCNT; (b, c) SEM image of Co-P/NCNT under different magnifications; inset: photograph of Co-P/NCNT.....	65
Figure 5-4 (a) TEM image of Co-P/NCNT; (b, c) HRTEM images of Co-P/NCNT; (d) HAADF-STEM image and (e) elemental mapping of Co-P/NCNT.....	66
Figure 5-5 N ₂ absorption and desorption isotherms of Co-P/NCNT. Inset: pore size distribution curve of Co-P/NCNT.....	67
Figure 5-6 (a) C 1s; (d) N 1s; (c) Co 2p and (d) P 2p high resolution XPS spectra of Co-P/NCNT.....	68
Figure 5-7 (a) Raman spectrum and (b) TGA result of Co-P/NCNT.	69
Figure 5-8 (a) XRD pattern of A-Co-P/NCNT; (b) TGA result of A-Co-P/NCNT.....	70
Figure 5-9 (a-e) C 1s, N 1s, Co 2p, P 2p and Pt 4f high resolution XPS spectra of A- Co-P/NCNT; (f) Raman spectrum of A-Co-P/NCNT.	71
Figure 5-10 (a, b) SEM image and TEM image of A-Co-P/NCNT; (c) HAADF- STEM image of A-Co-P/NCNT; (d) elemental mapping result for A-Co-P/NCNT.	72
Figure 5-11 (a) CV scan of A-Co-P/NCNT in H ₂ SO ₄ ; (b) polarization curves of various electrocatalysts; (c, d) ECSA plot and EIS spectra of various electrocatalysts; and (e) Tafel slope of A-Co-P/NCNT and Pt/C.	74

Figure 5-12 (a) XRD patterns of A-Co-P/NCNT prepared at 700 °C and 800 °C; (b) Raman spectrum of A-Co-P/NCNT-800; (c) N ₂ absorption-desorption isotherms of A-Co-P/NCNT-800.	74
Figure 5-13 (a) chronopotentiometry of A-Co-P/NCNT on GC electrode; (b) polarization curves of A-Co-P/NCNT before and after stability test.....	75
Figure 5-14 (a-d) Co 2p, C 1s, N 1s and P 2p high resolution XPS spectra of A-Co-P/NCNT after stability test; Raman spectrum of A-Co-P/NCNT after stability test. ..	76
Figure 5-15 (a) TEM image, (b) HAADF-STEM image and (c) elemental mapping result of A-Co-P/NCNT after stability test.	76
Figure 6-1 (a) XRD patterns of Ni _x Fe _{1-x} /C samples prepared with different Ni/Fe ratio; SEM images of (b) Ni/C, (c) Ni _{0.75} Fe _{0.25} /C, (d) Ni _{0.67} Fe _{0.33} /C and (e) Ni _{0.5} Fe _{0.5} /C.	84
Figure 6-2 TEM images of (a) Ni/C, (b) Ni _{0.75} Fe _{0.25} /C, (c) Ni _{0.67} Fe _{0.33} /C and (d) Ni _{0.5} Fe _{0.5} /C.	85
Figure 6-3 (a) HRTEM image of Ni _{0.67} Fe _{0.33} /C; (b) enlarged image of red circled area in (a); (c) HRTEM image of Ni _{0.5} Fe _{0.5} /C.	86
Figure 6-4 (a) HAADF-STEM image of Ni _{0.67} Fe _{0.33} /C, (b) Ni, Fe, O, C elemental mapping results of Ni _{0.67} Fe _{0.33} /C.....	86
Figure 6-5 (a) AFM image and height profile of Ni _{0.67} Fe _{0.33} /C; (b) Photographs of colloidal solution of Ni _{0.67} Fe _{0.33} /C dispersed in deionized water with laser irradiation.	87
Figure 6-6 (a) XRD patterns of Ni _{0.75} Fe _{0.25} /C prepared at different temperatures; (b-d) TEM images of Ni _{0.75} Fe _{0.25} /C-160, Ni _{0.75} Fe _{0.25} /C-180 and Ni _{0.75} Fe _{0.25} /C-200.	87
Figure 6-7 (a) XRD patterns of samples prepared with Ni/Fe ratio of 3:1 using different ligands; (b-d) SEM images of Ni _{0.75} Fe _{0.25} /C-MNBI, Ni _{0.75} Fe _{0.25} /C-BIM and Ni _{0.75} Fe _{0.25} /C-MIM; (e, f) XRD pattern and SEM image of sample prepared without ligand.....	88
Figure 6-8 (a) UV-vis spectra of NiFe, MNBI and NiFe-MNBI in DMF; (b) optical images of NiFe-MNBI solution before and after stored in ambient atmosphere irradiated with a laser beam.	90

Figure 6-9 (a) Raman spectra of Ni/C, Ni _{0.75} Fe _{0.25} /C, Ni _{0.67} Fe _{0.33} /C and Ni _{0.5} Fe _{0.5} /C prepared at 160 °C; (B) Raman spectra of Ni _{0.75} Fe _{0.25} /C-160, Ni _{0.75} Fe _{0.25} /C-180 and Ni _{0.75} Fe _{0.25} /C-200; (c) Raman spectra of Ni _{0.75} Fe _{0.25} /C-BMNI, Ni _{0.75} Fe _{0.25} /C-BIM and Ni _{0.75} Fe _{0.25} /C-MIM; (d-f) C 1s, N 1s and S 2p high resolution XPS spectra of Ni _{0.67} Fe _{0.33} /C.	92
Figure 6-10 (a-c) Ni 2p, Fe 2p and O 1s high resolution XPS spectra of Ni _{0.67} Fe _{0.33} /C; (d) comparison of Ni 2p and Fe 2p high resolution XPS spectra between Ni _{0.67} Fe _{0.33} /C and NiFe-LDH.	93
Figure 6-11 (a, b) Ni and Fe K-edge X-ray absorption near edge structure (XANES) spectra of Ni _{0.67} Fe _{0.33} /C and NiFe-LDH as a reference; (c) enlarged Fe K-edge XANES spectrum; (d, e) Magnitude of k3-weighted Fourier transform of Ni and Fe edge of extended X-ray absorption fine structure (EXAFS) of Ni _{0.67} Fe _{0.33} /C and NiFe-LDH.	95
Figure 6-12 (a) CV curves of the electrocatalysts before (dotted line) and after (solid line) activation, scan rate: 20 mV/s, (b) polarization curves of the Ni _x Fe _{1-x} /C electrocatalysts, Ir/C and NiFe-LDH, scan rate: 5 mV/s, (c) calculated TOFs from current density at η of 300 mV and overpotential at j of 10 mA/cm ² , (d) Tafel slopes of Ni _x Fe _{1-x} /C electrocatalysts and Ir/C; (e) ECSA of Ni _x Fe _{1-x} /C electrocatalysts and NiFe-LDH; (f) EIS of Ni _x Fe _{1-x} /C electrocatalysts.	98
Figure 6-13 (a) Chronopotentiometry test for Ni _{0.67} Fe _{0.33} /C on CFP electrode, (b) polarization curves of Ni _{0.67} Fe _{0.33} /C on CFP before and after test in (a), (c) CV cycling test for Ni _{0.67} Fe _{0.33} /C on GC electrode, and (d) polarization curves of Ni _{0.67} Fe _{0.33} /C before and after test in (c).	99
Figure 6-14 (a) TEM image of Ni _{0.67} Fe _{0.33} /C after OER, inset: SAED; (b) HRTEM image of Ni _{0.67} Fe _{0.33} /C after OER; (c) elemental mapping result for Ni _{0.67} Fe _{0.33} /C after OER.....	100
Figure 6-15 (a) XRD pattern and (b) Raman spectrum of Ni _{0.67} Fe _{0.33} /C after OER; (c) comparison of FTIR spectra between Ni _{0.67} Fe _{0.33} /C before and after OER; (d) C 1s high resolution XPS spectrum of Ni _{0.67} Fe _{0.33} /C after OER.....	101
Figure 6-16 (a) Raman spectrum in the range of 200-1000 cm ⁻¹ , (b, c, d) Ni 2p, Fe 2p	

and O 1s high resolution XPS spectra, (e) Ni K-edge XANES and (f) Fe K-edge XANES of Ni _{0.67} Fe _{0.33} /C after OER durability test.	102
--	-----

LIST OF TABLES

Table 2-1 Comparison of representative metal sulfides/phosphides containing photocatalytic H ₂ evolution systems.....	11
Table 2-2 Comparison of non-noble metal based HER catalysts in 0.5 M H ₂ SO ₄	19
Table 2-3 Comparison of Ni based OER electrocatalysts from recent publications. ...	22
Table 3-1 Brunaur-Emmett-Teller (BET) surface areas of different MoP samples.....	35
Table 6-1 Bulk and surface elemental composition and BET surface area of various samples.....	92
Table 6-2 Local structure parameters around Ni and Fe estimated by EXAFS analysis.	95

LIST OF SCHEMATICS

Scheme 2-1 Schematic of heterogeneous photocatalytic water splitting.	5
Scheme 2-2 (a-c) band alignment in Type I, II, III heterojunction; and (d) schematic of Z-scheme water splitting system.	8
Scheme 3-1 Schematic illustration of photocatalytic H ₂ evolution over MoP/CdS QDs system.	43
Schematic 4-1 (a) Schematic illustration of photocatalytic H ₂ evolution over Co _x P-ZnO/CdS QDs system; (b) band structure of Co _x P-ZnO/CdS QDs system.	59
Schematic 5-1 Illustration of fabrication procedure of the Co NPs embedded N, P co-doped CNT.	64
Schematic 6-1 Schematic representation of the synthesis for the preparation of amorphous NiFe-LDH interconnected by highly disordered N-doped nanocarbon.	89

LIST OF ABBREVIATIONS

AQE	Apparent quantum efficiency
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
BIM	Benzimidazole
Cat	Catalyst
CB	Conduction band
CNT	Carbon Nanotube
CV	Cyclic voltammetry
CA	Citrate acid
DMF	Dimethylformamide
e^-	Electron
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectrum
ECSA	Electrochemical active surface area
EA	Elemental analysis
FESEM	Field emission scanning electron microscopy
FWHM	Full width at half maximum
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GCE	Glassy carbon electrode
h^+	Hole
HAADF	High-angle annular dark filed
HER	Hydrogen evolution reaction
IPA	Isopropyl alcohol
ICP	Inductively coupled plasma
LA	L-(+)-lactic acid
LSV	Linear sweep voltammetry
MOF	Metal-organic framework

MNBI	2-mercapto-5-nitro-benzimidazole
MIM	2-methyl imidazole
NHE	Normal hydrogen electrode
NWs	Nanowires
OER	Oxygen evolution reaction
PV	Photovoltaic
PL	Photoluminescence
PDA	Polydopamine
QDs	Quantum dots
rGO	Reduced graphene oxide
RHE	Reversible hydrogen electrode
RDE	Rotating disk electrode
SC	Semiconductor
SCE	Saturated calomel electrode
SSLS	Singapore Synchronic Light Source
STEM	Scanning transmission electron microscopy
TPR	Temperature programmed reduction
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TOF	Turnover frequency
UV-vis	Ultraviolet-visible spectroscopy
VB	Valence band
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
XANES	X-ray absorption near edge structure
XAFS	X-ray absorption fine structure

ABSTRACT

Hydrogen (H_2) is a promising energy source to replace fossil fuels and the key to solving current energy and environment problems. Hydrogen production from water splitting via photocatalysis or electrolysis is considered to be an economical and environmentally friendly approach to convert clean energy into chemical fuels. The main difficulty of water splitting is the lack of low-cost, stable and efficient catalysts. The works presented in this thesis are focused on the development of highly efficient noble metal free catalysts for both hydrogen evolution and oxygen evolution reactions via photocatalytic and electrocatalytic water splitting. In these multi-step processes, more than one component are generally required to accomplish light absorption and charge separation (for photocatalytic reaction), charge carrier transportation and surface redox reaction. The overall efficiency of the process is strongly affected by the interplay among the components as well as the interfacial properties. Therefore, the overall aim of this thesis works is to assemble appropriate functional components with engineered interfaces to achieve remarkably enhanced photocatalytic and electrocatalytic performances for water splitting.

In the first part of the research works, MoP particulates were synthesized and dispersed into nanosized particles using probe sonicator. The MoP nanoparticle as a co-catalyst exhibits 4 times of improved photocatalytic hydrogen evolution reaction (HER) activity compared to the bulk form due to the small particle size with increased surface area and better integration with the semiconductor light absorber, CdS quantum dots (QDs). The nanosized dimension of CdS QDs facilitate the charge migration from bulk to surface where holes are consumed by lactic acid. More importantly, the good dispersion of CdS QDs in solution allows them to be trapped in the cluster of MoP nanoparticles. An intimate interface between CdS QDs and MoP is thus formed, which is favorable for the efficient charge transfer from CdS QDs to MoP. Besides, the metallic property and good HER activity of MoP lead to efficient and stable H_2 evolution.

Next, to further reduce the particle size of metal phosphides and improve the

interface between light absorber and co-catalysts, metal oxide (ZnO) was introduced as a low-cost metal oxide support to disperse and stabilize CoP on its surface. The interface between metal oxides and CdS QDs is formed via electrostatic interactions since ZnO is positively charged whereas CdS QDs is negatively charged. Besides, the band structure alignment between ZnO and CdS QDs facilitate the charge transfer from CdS QDs to ZnO, which was further transferred to CoP. The excellent HER activity of CoP and the engineered interface result in the highly efficient and stable H₂ production under visible light irradiation. Apparent quantum efficiency of this system can reach as high as 66% at 420 nm and no activity loss is observed for this system after 144 h photocatalytic reaction.

The third part of the research work is focused on the development of a noble metal free HER electrocatalyst that has an activity close to that of Pt. CoNA/PDA (NA: Nitrilotriacetic acid; PDA: Polydopamine) core/shell nanowires were first synthesized by coating PDA on the surface of CoNA nanowires (NWs). N, P co-doped carbon nanotube is obtained through phosphidation of CoNA/PDA NWs with subsequent pyrolysis in N₂ atmosphere. CoNA NWs decomposed to Co nanoparticles wrapped by several graphene layers. CoP is formed at the cobalt/carbon interface. After activation, the wrapped nanoparticles become accessible and less stable Co nanoparticles are removed by acidic solution. The CoP nanoparticles stabilized by N–Co–P bonding are exposed which exhibit a high HER activity and stability.

Lastly, research efforts of this thesis work were also spent to tackle the other half of the water splitting reaction, oxygen evolution reaction (OER), since the sluggish kinetics of OER is the bottleneck of the overall performance of water splitting. In this part of the work, a promising OER catalyst, Ni-Fe layered double hydroxide (LDH) was chosen and its intrinsic high OER activity was harnessed by blending ultra-fine NiFe-LDH nanocrystals with conductive carbon. The NiFe-LDH/C hybrid was fabricated by a novel one-pot solvothermal method using molecule precursors of metal cations and organic ligand. The resultant NiFe-LDH/C nanosheet consists of poorly crystallized NiFe-LDH (< 5 nm) interconnected with N doped carbon nanodomains. The *in situ* formation of both components leads to a self-confined growth and fine blending

of NiFe-LDH nanocrystals and carbon domains. Such a unique structure results in improved electrical conductivity, increased active sites and enhanced electrochemical active surface area. In addition, the strong interaction between metal centers and carbon leads to the local electronic structure modification of metal centers. These factors contribute together to the development of a highly efficient and stable NiFe-LDH based OER catalyst.

In summary, the research efforts in this thesis were spent on designing efficient and noble metal free photocatalysts and electrocatalysts for water splitting reactions. In particular, engineering suitable interfaces is a key focus. Detailed materials characterization and structural analyses were carried out to understand the key factors contributing to the high performances of the catalysts. Through such efforts, several promising transition-metal based catalysts have been developed with high efficiency for HER and OER reactions. It is believed that the findings from this work would contribute to the advancement of the energy research field and the development of practical catalysts for water splitting utilizing solar energy directly or electricity from clean energy.

CHAPTER 1 INTRODUCTION

1.1 Background and motivations

The energy and environment problems have become more and more severe over the recent years due to the overuse of fossil fuels and uncontrolled CO₂ emission from the combustion of fossil fuels. It is of utmost urgency to develop technologies that utilize renewable and clean energy sources to address these concerns.¹ H₂ is an ideal energy carrier as it is able to generate the highest energy per unit weight compared to other fuels like hydrocarbons with zero emission of greenhouse gases. It is considered to be a promising energy source to replace fossil fuels. However, the practical usage of H₂ as the main energy source requires development in H₂ production, storage and end use. Currently, 96% of the global H₂ production is from fossil fuels by steam reforming, which places a heavy burden on environment as a great amount of greenhouse gases are emitted during the production.² Therefore, it is important to produce H₂ from a clean energy.

Solar energy is an abundant, decentralized and inexhaustible energy. The total amount of sunlight that shines on the earth surface for one hour (4.3×10^{20} J) is almost equal to world annual energy consumption (4.1×10^{20} J in 2005). It has been harnessed as thermal energy for heating³ or converted into electricity by photovoltaics (PVs). During past two decades, great advances have been witnessed in the development photovoltaics (PVs) and the PV efficiency reaches as high as 35%.⁴ However, due to the daily and seasonal variability of sunlight, it is preferred that solar energy is stored in a stable and constant form other than electricity which allows it to be easily transported and used upon demand.

Water splitting is a process that could convert the electricity emerged from solar energy or other renewable energy like wind energy or geothermal energy into chemical bond like H₂, which allows us to solve the energy and environmental crisis. Two half reactions, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are involved in the water splitting process. They can be described as following:

Suitable catalysts could reduce the overpotential of these reactions and consequently increase the efficiency of water splitting.⁵

Photocatalytic water splitting is also a promising method which could convert solar energy directly into H_2 . In photocatalysis, a light absorber (semiconductor or molecular dye) is used to generate excited charges. The electrons are used to reduce water into H_2 whereas holes are used to oxidize water into O_2 . Even though the catalytic process (HER and OER) could proceed on bare semiconductor surface, highly efficient water splitting could only be achieved with the help of suitable co-catalysts.⁶

Nanocomposites have been widely used for water splitting. For example, heterojunctions between semiconductors (SC-SC) are designed to absorb broader spectrum of solar energy or promote charge separation;⁷ nanocomposite of semiconductor and catalyst (SC-Cat) is constructed to accelerate the surface catalytic reactions;⁸ nanocomposites between catalyst and carbon material (Cat-C) are developed to enhance the electrical property of catalyst for better electrocatalytic performance.⁹ The interface between different components in the composite needs to be well constructed to achieve an excellent performance.

1.2 Objective and scope

During recent years, both HER and OER half-reactions have been extensively studied. However, noble metals are still widely used as the most efficient electrocatalysts for water splitting (e.g., Pt, Rh_2O_3 for HER, Ir, RuO_2 for OER). The high price and scarcity of these noble metals limit their practical applications in water splitting. The overall objective of this thesis was to develop efficient, robust and low-cost catalysts for both HER and OER reactions which are vital to the production of H_2 fuel from clean energy. The scopes of this thesis are summarized as follows:

(1) Firstly, efficient and stable photocatalytic systems for H_2 production were constructed using transition metal phosphides (MoP and CoP) as the co-catalyst and CdS quantum dots (QDs) as light absorber. CdS QDs exhibit suitable band structures

for visible light absorption with sufficient conduction band (CB) potential to drive HER. The nanosized dimension of CdS QDs leads to shorter charge transportation length and lower possibility for charge recombination. The good dispersion of CdS QDs in water facilitates the formation of interface between CdS QDs and the co-catalyst. Metal phosphides have shown to be excellent electrocatalysts for HER but had been rarely applied as the co-catalyst in photocatalytic reaction before this thesis work. The photocatalytic systems constructed using these components with engineered interface display excellent photocatalytic activity and high stability for H₂ evolution. These works are presented in Chapters 3 (MoP/CdS QDs) and 4 (CoP/CdS QDs).

(2) The findings from Chapter 4 indicate that CoP is a highly promising catalyst for H₂ evolution. Therefore, further research efforts were spent on developing highly active and stable CoP electrocatalyst for HER. A novel HER catalyst, N, P co-doped carbon nanotube (CNT) supported metal phosphide has been synthesized. CNT stabilizes the nanosized catalysts via surface bond and enhances the electrical property. The as-prepared catalyst shows an excellent HER activity which approaches that of Pt with good stability. This work is presented in Chapter 5.

(3) In water splitting process, the overall efficiency remains bottlenecked by the sluggish OER kinetics. Therefore, the development of efficient noble metal free OER catalysts is a critically important task to boost the performance of electrocatalytic water splitting for practical use. A nanocomposite consisting of interconnected Ni-Fe layered double hydroxide (LDH) and N doped carbon was fabricated by a novel *in situ* self-confined solution growth method. The resultant NiFe-LDH/C is a highly active and stable OER electrocatalyst with comparable performance with those of the best OER catalysts ever reported. The work is presented in Chapter 6.

1.3 Major contributions of the thesis

Contributions of this thesis to the field of hybrid material for water splitting are summarized as following:

(1) It was found that MoP particulates prepared using the conventional temperature programmed reduction process can be easily dispersed to nanoparticles by probe

sonication. After hybridization of nanosized MoP with CdS QDs, an intimate interface is formed. MoP/CdS QDs nanocomposite exhibits excellent quantum efficiency for H₂ evolution under visible light. This study is the first example showing CdS QDs could be used as the light absorber with metal phosphides as the catalyst for highly efficient photocatalytic H₂ production.

(2) Co_xP nanoparticles can be dispersed and stabilized on the surface of ZnO. The positively charged surface of ZnO allows an efficient assembly of negatively charged CdS QDs on its surface via electrostatic interaction. Intimate interface and alignment between band structure of CdS QDs and ZnO are favorable for charge carrier transfer, leading to efficient H₂ production. The obtained quantum efficiency of 66% is among the best reported values for noble metal free photocatalytic H₂ production systems.

(3) CoP/N, P co-doped CNT is prepared using PDA as carbon precursor and CoNA nanowires as a template. After acid leaching, non-stabilized Co nanoparticles are dissolved by acidic solution and ultra-small CoP nanoparticles stabilized by N–Co–P surface bond is exposed. A-Co-P/NCNT exhibits a high HER activity and good stability. The superior activity is attributed to the enhanced ECSA due to the mesoporous structure of carbon nanotube, improved electrical conductivity of hetero-atom doped carbon nanotube and active N–Co–P surface state. This material shows potential to be used as alternative to replace noble metal based electrocatalysts for HER.

(4) A simple solvothermal method has been developed to synthesize amorphous NiFe-LDH nanocrystals of less than 5 nm interconnected with N doped carbon nanodomains in ultrathin nanosheets. The NiFe-LDH nanocrystals and carbon nanodomains are *in situ* formed in solution starting from the metal-ligand molecular precursor. The incorporation of carbon nanodomain not only improves the electronic property of this composite but also enhances the exposure of surface redox sites. These factors contribute to the harnessing of the high intrinsic activity of NiFe-LDH towards a much improved OER activity with good durability. The use of metal-ligand molecular precursor for one-pot synthesis of strongly coupled metal-carbon hybrid under mild condition is believed a promising strategy for preparation of high-performance catalysts.

CHAPTER 2 LITERATURE REVIEW

2.1 Photocatalytic water splitting

2.1.1 Basic principle of photocatalytic water splitting

In heterogeneous photocatalytic water splitting, a semiconductor (SC) is used as photocatalyst to absorb light and split water on its surface. When SC is irradiated under sunlight or simulated light source, electron-hole pairs are generated with the electron (e^-) in the conduction band (CB) and the hole (h^+) in the valence band (VB). These photo-generated charge carriers can migrate to the surface of the photocatalyst where redox reactions (HER and OER) occur. Overall, three main steps are included in the photocatalytic water splitting as shown in Scheme 2-1. **i.** SC absorbs photons with certain energy to generate electron-hole pairs; **ii.** Charges carriers migrate to the surface; **iii.** Water is reduced or oxidized.

Scheme 2-1 Schematic of heterogeneous photocatalytic water splitting.

Several points are key to the overall photocatalytic process. Firstly, only incident photons with an energy larger than the bandgap of the SC can be absorbed. To make the photocatalyst work under visible light ($\lambda \geq 420$ nm) which contains a large portion of the solar spectrum, the bandgap energy of SC should be smaller than 2.95 eV. Secondly, the efficient charge separation and migration to surface are important for utilizing

excited charge carriers. SC with high crystallinity or suitable crystal structure would be beneficial for the charge separation and transportation. A reduction in particle size may decrease the migration path for charge carriers and leads to the reduced possibility for recombination. Thirdly, e^- and h^+ should have sufficient redox potentials to make HER and OER thermodynamically favorable. Therefore, the minimum of CB should be more negative than the redox potential of H^+/H_2 (0 V vs NHE) while the maximum of VB should be more positive than the redox potential of O_2/H_2O (1.23 V vs NHE). As a result, the minimum bandgap energy of SC for water splitting is 1.23 eV.¹⁰ Lastly, co-catalysts, which exhibit excellent performance for HER or OER, could be used to accelerate the redox reactions, promote the charge separation and migration by forming junctions with the photocatalyst.

2.1.2 Semiconductors for photocatalytic water splitting

TiO_2 is the first reported photocatalyst for water splitting which works under UV irradiation.¹¹ Since then, TiO_2 and TiO_2 based metal oxides have been widely studied.¹²⁻¹⁶ Other binary metal oxides like ZrO_2 ,¹⁷ Ga_2O_3 ,¹⁸ Nb_2O_5 ,¹⁹ Ta_2O_5 ²⁰ and ternary metal oxides such as $BaZrO_3$,²¹ $La_2Zr_2O_7$,²² $K_4Nb_6O_{17}$,²³ $Sr_2Nb_2O_7$,²⁴ $NaTaO_3$,²⁵ $SrTa_2O_6$,²⁶ are also capable of splitting water under light irradiation. Among these photocatalysts, NiO loaded La-doped $NaTaO_3$ exhibits an apparent quantum efficiency of 56% at 270 nm for overall water splitting, which is the highest quantum efficiency for pure water splitting.²⁷ Metal oxides have many advantages such as low cost, non-toxic and high stability, but they usually have a large bandgap due to its valence band consisting of O 2p orbital is located at a position more positive than 3.0 eV vs NHE (normal hydrogen electrode). Element doping is used to optimize the band structure to allow visible light absorption.²⁸⁻³³ Some metal oxides possess the ability to absorb visible lights with intrinsic narrow bandgap like Cu_2O ,³⁴ Fe_2O_3 ,³⁵ WO_3 ,³⁶ $BiVO_4$,³⁷ Ag_3PO_4 .³⁸ But the band structure of these SCs are unfavorable for overall water splitting. They are mostly used for half reactions or as photoelectrodes.

Metal sulfides have been studied as promising visible light active photocatalysts for water splitting as they exhibit narrower bandgap compared with that of metal oxides.¹⁰

Photo-corrosion is the main drawback of metal sulfides, so sacrificial reagents such as $\text{S}^{2-}/\text{SO}_3^{2-}$ and lactic acid (LA) are used. CdS is widely used for water splitting under visible light due to its narrow bandgap of 2.4 eV.^{39, 40} Nearly 100% quantum efficiency has been achieved over co-catalysts loaded CdS and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$.^{41, 42} CdS quantum dot (QD) is considered as a promising photocatalyst since its band structure can be precisely controlled by tuning the size of the QD. Furthermore, the good water dispersity of CdS QDs could enhance the absorption of visible light. The nanosized dimension of CdS QDs leads to shorter charge transportation length and lower possibility for charge recombination.⁴³⁻⁴⁷

Ta_3N_5 and C_3N_4 are also reported to be active for water splitting under visible light.⁴⁸⁻⁵⁰ Polymeric C_3N_4 , which is chemically stable and composed of earth abundant carbon and nitrogen only, is an ideal photocatalyst for solar energy conversion. Modification methods have been applied to improve its performance.⁵¹⁻⁵⁴ GaN-ZnO solid solution is another typical and efficient photocatalyst which is capable of decomposing water into H_2 and O_2 simultaneously and stoichiometrically when $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ is loaded as a cocatalyst.⁵⁵⁻⁵⁷

Nanocomposites of two semiconductors (SC-SC) are used to promote charge separation and improve efficiency. Three typical band alignment schemes are shown in Scheme 2-2. Type I heterojunction results in accumulation of photoexcited e^- and h^+ in SC-B; Type II and type III heterojunctions result in enhanced charge separation.⁷ A special type, Z scheme, is also shown in Scheme 2-2. A redox couple (Red./Ox.) are added into this system. Ox. is reduced to Red. by e^- at the surface of SC-B while Red. is oxidized to Ox. by h^+ at the surface of SC-A. Z scheme system allows a better utilization of solar spectrum as two semiconductors with narrow bandgap are used in such system. And overall water splitting could be achieved over Z scheme system.⁵⁸⁻⁶⁰

Scheme 2-2 (a-c) band alignment in Type I, II, III heterojunction; and (d) schematic of Z-scheme water splitting system.^{7, 55}

2.1.3 Non-noble metal containing co-catalysts for photocatalytic H_2 evolution

The loading of co-catalysts (Cat) is key to the construction of an efficient photocatalyst for water splitting. In a SC-Cat nanocomposite, photogenerated e^- in SC can migrate to Cat, resulting in efficient charge separation. Subsequently, co-catalysts can accelerate the redox reaction rate by lowering the activation energy.^{8, 61} So far, the most effective and commonly used co-catalysts for HER are Pt, Rh and Pd; while RuO_2 and IrO_x are widely used for OER. However, the high price and scarcity of noble metal limit the practical application of photocatalytic water splitting. As a result, it is important to develop noble metal free co-catalysts for photocatalytic water splitting reactions.

(1) Transition metal

Earth abundant and low-cost transition metals like Co,⁶² Ni,⁶³ and Cu⁶⁴ have been applied as co-catalysts for photocatalytic H_2 evolution which are deposited by *in situ* photoreduction, chemical reduction and impregnation-calcination/reduction methods. Such metal co-catalysts are in the form of atom clusters or nanoparticles distributed on the surface of SC. The photocatalytic activity of transition metal loaded photocatalysts is moderate compared to Pt loaded photocatalysts.

(2) Transition metal oxides

Transition metal oxides, such as NiO,⁶⁵ NiO_x,⁶⁶ CuO⁶⁷ and Cu₂O⁶⁸ are well-known as noble metal free co-catalysts for photocatalytic H₂ evolution. The oxides are typically prepared by an incipient wetness impregnation method. NiO-loaded La-doped SrTiO₃ exhibits the highest activity for overall water splitting with apparent quantum efficiency of 56% at 270 nm.²⁷ Sreethawong *et al.* reported that CuO-loaded TiO₂ showed a photocatalytic H₂ evolution rate two times higher than NiO-loaded TiO₂.⁶⁷ Xu *et al.* reported that CuO/TiO₂ exhibited a photocatalytic H₂ evolution rate of 99823 μmol/h/g in water-glycerol mixture, which is even higher than that of some Pt- or Pd-loaded TiO₂.⁶⁹

(3) Transition metal hydroxides

Recently, Co(OH)₂,⁷⁰ Ni(OH)₂⁷¹ and Cu(OH)₂⁷² have been developed as efficient and low-cost co-catalysts for photocatalytic H₂ evolution. Metal hydroxides loaded photocatalysts can be prepared by simple precipitation method. A proposed mechanism attributes the metal clusters formed *in situ* by photoexcited e⁻ to be the true co-catalysts. The redox potential of the reduction of metal hydroxide is lower than the CB of photocatalyst and facilitates the charge carrier migration from photocatalyst to metal hydroxides.

(4) Transition metal sulfides

To date, transition metal sulfides such as FeS,⁷³ CoS,⁷⁴ NiS,⁷⁵ NiS₂, CuS,⁷⁶ MoS₂,⁷⁷ MoS₃⁷⁸ and WS₂⁷⁹ have emerged as cost-effective co-catalysts for photocatalytic H₂ evolution. Some of them show even better activity than Pt. For example, highly dispersed and ultrafine NiS nanoparticles were deposited on CdS via hydrothermal method, forming NiS/CdS nanocomposite. The H₂ evolution rate achieved as high as 2.18 mmol/h over optimized NiS/CdS under visible light (λ ≥ 420 nm) illumination, which exceeded the rate of 0.4 mmol/h obtained over Pt/CdS.⁷⁵ MoS₂ is well known for its excellent HER activity which stems from its exposed edge sites. MoS₂ has also been reported as an efficient co-catalyst. MoS₂/CdS showed a higher H₂ evolution rate than Pt/CdS, suggesting that the intimate interface formed between MoS₂ and CdS was of great importance for enhancing its photocatalytic activity.⁷⁷ MoS₂/Zn_xCd_{1-x}S can be

prepared via a facile and energy saving photo-assisted deposition approach and the nanocomposite exhibited a good performance for H₂ evolution.⁸⁰ Tungsten carbide (WC) is also developed as the co-catalyst for photocatalytic H₂ evolution.^{81, 82} As prepared WC/CdS photocatalyst showed a comparable H₂ evolution rate to that of Pt/CdS. Besides, WC/CdS photocatalyst is active for overall water splitting as WC is inactive for hydrogen oxidation reaction, which prevents the back reaction in water splitting.

(5) Transition metal phosphides

Very recently, metal phosphides like Ni₂P,⁸³ CoP,⁸⁴ FeP,⁸⁵ and MoP⁸⁶ have been studied as efficient HER electrocatalysts. It was reported that the phosphorous (P) in metal phosphides exhibits a weak “ligand effect” in metal-P bonds and facilitates H₂ release from the active sites, which mimics the role of sulfur in MoS₂.⁸⁶ Metal phosphides exhibit low onset potential with small Tafel slope and their HER activity are superior among noble metal free electrocatalysts. However, limited studies have been conducted using metal phosphides as the co-catalyst for photocatalytic H₂ evolution. FeP/P25 is active for H₂ production under full arc light irradiation due to the large bandgap of TiO₂.⁸⁵ Sun *et al.* prepared CoP nanowires (NWs) using Co(CO₃)_{0.5}(OH)·0.11H₂O nanowires as precursor and NaH₂PO₂ as P source. Sensitized by a fluorescence based dye, CoP NWs can split water to H₂ but the evolution rate is slow.⁸⁷ Fu *et al.* prepared Ni₂P and CoP nanoparticles (NPs) which were stabilized by poly(vinylpyrrolidone) (PVP) in aqueous solution. The mixture of metal phosphide NPs and CdS nanorods (NRs) was capable of evolving H₂ under visible light with long-term stability.^{88, 89} Ni₂P, CoP and Cu₃P were prepared by converting respective metal hydroxides into phosphides using NaH₂PO₂. Then the phosphides were mixed together with bulk CdS for photocatalytic H₂ evolution. The best photocatalyst exhibited a QE of 25.1% under LED visible light irradiation.⁹⁰ Recently, Du's group reported that Ni₂P- and MoP-loaded CdS NRs were efficient photocatalysts for H₂ evolution.^{91, 92} Ni₂P/CdS NRs prepared by solvothermal method showed a stable and high H₂ evolution activity. MoP/CdS NRs was prepared by post calcination of MoP with large particles size and CdS NRs and exhibited only moderate H₂ evolution activity. It is supposed that the

moderate photocatalytic activity of MoP/CdS NRs may be attributed to the fact that MoP with large particle size has a relatively low surface area and the interface between MoP and CdS NRs is not optimized. Therefore, further improvement of MoP/CdS composite may be achieved by using MoP nanoparticles and CdS QDs, which has not been studied by other researchers. The activity of metal sulfides/phosphides containing photocatalytic H₂ evolution systems are listed in Table 2-1.

Table 2-1 Comparison of representative metal sulfides/phosphides containing photocatalytic H₂ evolution systems.

Photocatalysts	Light source	Sacrificial agent	H ₂ evolution Activity	Quantum efficiency	Ref
FeP/TiO ₂	200 W Hg(Xe) arc, >365 nm	MeOH-H ₂ O	1.9 $\mu\text{mol}/\text{mg}/\text{h}$	8.7%	85
P _{HIV} /CoP	500 W Xe, >420 nm	TEOA	160.7 μmol^{a}	--	87
CoP/CdS	30 $\times$ 3W WLED source, >420 nm	Lactic Acid	251 $\mu\text{mol}/\text{h}$	25.1%	90
Ni ₂ P/CdS	30 $\times$ 3W WLED source, >420 nm	Lactic Acid	143 $\mu\text{mol}/\text{h}$	14.3%	90
Cu ₃ P/CdS	30 $\times$ 3W WLED source, >420 nm	Lactic Acid	77 $\mu\text{mol}/\text{h}$	7.7%	90
Ni ₂ P/CdS NRs	30 $\times$ 3W WLED source, >420 nm	Lactic Acid	130 $\mu\text{mol}/\text{h}^{\text{b}}$	--	88
Ni ₂ P/CdS NRs	300 W Xe, >420 nm	Na ₂ S-Na ₂ SO ₃	1.2 mmol/mg/h	41%	91
Co ₂ P/CdS NRs	30 $\times$ 3W WLED source, >420 nm	DL-mandelic acid	15 $\mu\text{mol}/\text{h}$	6.8%	89
MoP/CdS NRs	300 W Xe, >420 nm	Lactic Acid	163 $\mu\text{mol}/\text{mg}/\text{h}$	16.7%	92
MoS ₂ /CdS	300 W Xe, >420 nm	Lactic Acid	1.28 mmol/h	28.1	93
MoS ₂ /CdS	300 W Xe, >420 nm	Lactic Acid	1.31 mmol/h	--	94
MoS ₃ -CdS/CdSe NRs	500 W Hg/Xe arc, 450 nm	TEOA	10 $\mu\text{mol}/\text{h}$	10%	78

a: H₂ evolution measured in 40 min;

b: Calculated by the amount of H₂ evolved in the first 2 h.

2.1.4 Non-noble metal containing co-catalysts for photocatalytic O₂ evolution

O₂ evolution half reaction is a more challenging step because it involves a four-electron transfer process coupled to the removal of four protons from water molecules to form an oxygen–oxygen bond. As discussed above, RuO₂ and IrO_x are widely used as co-catalysts for photocatalytic O₂ evolution.

In recent years, cost-effective co-catalysts like CoO_x,⁹⁵ Co₃O₄,⁹⁶ Co-Pi,⁹⁷ MnO_x,⁹⁸ and NiO_x for photocatalytic O₂ evolution have been exploited. Co-based co-catalysts have received much attention due to their outstanding performance for O₂ evolution. For example, the optimized CoO_x/LaTiO₂N shows a high QE of 27.1% at 440 nm, exceeding the values reported for previous photocatalysts for O₂ evolution.⁹⁹ Amorphous cobalt-oxide-phosphate (Co-Pi) is one of the most promising OER catalysts. Originally reported by Kanan and Nocera, Co-Pi contains Co(III) ions, oxide and phosphate, and requires an overpotential of only 0.41 V at pH 7 to oxidize water (measured at 1 mA/cm²).¹⁰⁰ Co-Pi can also enhance the O₂ evolution as the co-catalyst in photocatalytic process via a simple photo deposition method.⁹⁷ Metal (oxy)hydroxides have recently been widely studied as the co-catalysts for photocatalytic O₂ evolution. A dual layer NiOOH/FeOOH deposited BiVO₄ has been reported as an excellent photoanode with good stability.³⁷

2.2 Electrocatalytic water splitting

2.2.1 Electrocatalytic activity evaluation

Some important parameters can be used to elucidate the catalytic activity of a electrocatalyst.¹⁰¹

(1) Total electrode activity

The total electrode activity can be estimated by performing cyclic voltammetry (CV) or linear sweep voltammetry (LSV). A slow scan rate should be applied for CV or LSV to eliminate the non-Faradaic capacitive current from the total, especially for carbon-containing catalysts. The obtained currents are normalized to the geometric electrode area. The overpotential that electrocatalyst needs to yield a current density of 10 mA/cm² (which is the current density expected for a 12.3% efficient solar water-

splitting device) is normally used to compare the activities between different catalysts.

(2) Tafel plot

Tafel plot depicts the dependence of steady-state current densities over overpotentials. Generally, the overpotential (η) is logarithmically related to the current density (j) and the linear portion of the Tafel plot is fit to the Tafel equation: $\eta = a + b \log j$; where b is the Tafel slope, which is generally related to the catalytic mechanism of the electrode reaction. A catalytic material having a small Tafel slope (b) is desirable.

(3) Stability

Good structural and catalytic stabilities of a electrocatalyst are important in practical applications. Two methods are used to determine the electrocatalytic stability of a catalyst. One method is to measure the current variation with time (*i.e.* the i - t curve). The other method is to conduct the recycling experiment by performing consecutive CV scans.

(4) Faradaic efficiency

For a HER catalyst, Faradaic efficiency is defined as the ratio of the experimentally detected H_2 amount to the theoretical H_2 amount, which can be calculated from the current density based on a 100% Faradaic yield.

(5) Turnover frequency

Turnover frequency (TOF) is defined as the number of reactant that a catalyst can convert to a desired product per catalytic site per unit of time, which can exhibit the intrinsic activity of each catalytic site. It is very difficult to get a precise TOF value for many solid-state (heterogeneous) catalytic materials as the number of catalytic active sites is hard to determined. To make a safe estimation, the TOF can be calculated based on the total catalytic species present in the material. This will obviously result in underestimated TOF compared with the real TOF value of the active site. However, when similar materials are compared, such results could still be relevant and useful.

2.2.2 Non-noble metal containing electrocatalysts for H_2 evolution

(1) Metal carbides

In 1973, R. B. Levy and M. Boudart discovered that tungsten carbide possessed some

platinum-like catalytic behaviors because of its similar d-band electronic density states to platinum.¹⁰² Since then, metal carbides have been studied as promising noble metal free HER catalysts.

In 2012, Hu's group reported that commercial β -Mo₂C exhibited high activity for HER in both acidic and basic solutions.¹⁰³ In addition, Leonard *et al.* found that HER activity of distinct phases of molybdenum carbides increased in the order of α -MoC_{1-x} < η -MoC < γ -Mo < β -Mo₂C in acidic solution.¹⁰⁴ Furthermore, fine structural modification was conducted. Mo₂C NWs were prepared by pyrolysis of MoO_x-amine hybrid precursor under inert atmosphere.¹⁰⁵ The excellent activity is attributed to its large surface area, nanosized crystallites and porous structure. Carbon materials are used as effective supports to construct Mo₂C-carbon composite for HER. Mo₂C-carbon nanotubes (CNT) with superior activity and stability were synthesized by *in situ* carburization of ammonium molybdate on carbon nanotubes.¹⁰⁶ Mo₂C-graphene and Mo₂C-nanocarbon-nanotubes have been prepared as excellent HER catalysts.^{107, 108} The introduction of graphene and CNT-graphene supports could avoid aggregation of nanocrystals and facilitate charge transfer.

Tungsten carbides (including WC and W₂C) are another group of metal carbide that are active and stable for HER in acidic solution.¹⁰⁹ Tungsten carbides are typically prepared in a carbon-rich reaction system. The activity of tungsten carbides strongly depends on the surface carbon coverage, the particle size, lattice defects and so on. Tungsten carbide nanocrystals prepared using template exhibit high HER activity and stability.^{82, 110} However, tungsten carbides generally show a poor stability in neutral and basic solution. The HER performance of tungsten carbides should be further improved.

(2) Metal nitrides

Metal nitrides are another group of promising noble metal free HER catalysts. Nitrogen atoms could modify the electronic structure of metal, which leads to an electronic structure similar to noble metals. Molybdenum nitride (MoN_x) and NiMoN_x with nanosheet morphology were prepared using Ni-Mo alloy as precursor. NiMoN_x showed a small Tafel slope of 35 mV/Dec and good stability in acid.¹¹¹ Similarly, Co_{0.6}Mo_{1.4}N₂ bimetallic nitride was synthesized and exhibited a good activity for HER in both acidic

and alkaline solution ($\eta=200$ mV @ $j=10$ mA/cm²).¹¹² Molybdenum carbonitride (MoCN) nanomaterial was synthesized in one-pot.¹¹³ The overpotential needed for 10 mA/cm² current density (140 mV) is among the lowest for Mo- and W- based HER catalysts.

(3) Metal sulfides

Inspired by the structure/composition of nitrogenase and hydrogenase, researchers have exploited a series of metal sulfides as efficient HER electrocatalysts. This is a profound achievement in the field of noble metal free HER electrocatalysts.

Hinnemann *et al.* found that the (1010) Mo-edge structure in MoS₂ had a close resemblance to the active site of nitrogenase.¹¹⁴ And they verified the HER activity of nanoscale MoS₂ by depositing MoS₂ on graphite. Jaramillo *et al.* prepared MoS₂ nanoparticles with the predominance of Mo-edges.¹¹⁵ Electrocatalytic activity measurements showed that the catalytic performance of MoS₂ nanoparticles was related to the edge state length, rather than the area coverage, directly establishing the relationship between MoS₂'s edges and the catalytic active sites. Bulk MoS₂ can be exfoliated into nanosheets by lithium intercalation,¹¹⁶ ball-milling¹¹⁷ and sonication¹¹⁸. Chemically exfoliated MoS₂ nanosheet exhibits a partial transformation from 2H phase to metastable 1T phase. Jin's group demonstrated that 1T polymorph of MoS₂ had higher metallic characteristic and better HER activity than 2H phase due to its better electrical conductivity.¹¹⁹ Chhowalla's group further found that the active sites of 1T MoS₂ were mainly located in the basal plane.¹²⁰ So the enhanced catalytic activity of 1T MoS₂ could be attributed to both the increase of active sites and the improvement of conductivity. Defect-rich MoS₂ nanosheets can be prepared by hydrothermal method.¹²¹ Catalytic activity was enhanced compared to defect-free MoS₂ sheets. A highly ordered double-gyroid MoS₂ bi-continuous network with nanopores has been prepared using SiO₂ as template, which showed superior HER activity due to the enhanced surface area.¹²² In addition, introduction of Co, Ni into MoS₂ could promote HER activity by increasing active sites.¹²³ Nanocomposites of MoS₂ and carbon materials exhibit enhanced electronic conductivity and HER activity. For example, Dai *et al.* synthesized MoS₂ nanosheets on reduced graphene oxide (rGO).¹²⁴ The

resulting MoS₂/graphene nanocomposite exhibited high HER activity and durability. Graphene could facilitate the charge transfer and inhibit agglomeration of MoS₂. Amorphous MoS_x is also active for HER. Amorphous MoS_x films with efficient HER activity can be prepared by electrochemical deposition.¹²⁵ This synthetic method is fast, mild and scalable, which opens a new way to achieve economical H₂ evolution.

In addition, Ni, Co and Fe sulfides are active for HER. NiS₂ and FeS₂ were found to be active for HER in acidic solution even though the performance is inferior to MoS₂.¹²⁶ Crystalline CoS₂ with various morphologies (thin film, microwire, nanowire) were synthesized by Jin's group.¹²⁷ CoS₂ nanowires exhibited a performance comparable to the best non-noble metal containing HER catalysts. Amorphous cobalt sulfide was prepared by electrochemical deposition and exhibited high activity and stability in neutral media.¹²⁸

(4) Metal phosphides

Metal phosphides have emerged as the most promising noble metal free HER catalysts during last several years. Numerous research studies are ongoing. From the crystal structure aspect, metal phosphides mimic the active site in hydrogenase. The negatively charged P atoms and isolated metal atoms behave as proton-acceptor and hydride-acceptor in the structure. This so-called "ensemble effect" would facilitate the HER.¹²⁹ Besides, metal phosphides tend to have many isotropic crystal structures, which might result in the formation of a large number of coordinatively unsaturated surface atoms. Thus, metal phosphides might have higher intrinsic HER activity than other noble metal free catalysts.

Ni₂P is the first experimental proof that shows the superior HER activity of metal phosphides. Popczun *et al.* synthesized Ni₂P nanoparticles in oleylamine (OA) using organic phosphine (trioctylphosphine, TOP) as P source.¹³⁰ The resulting Ni₂P NPs were hollow with preferential exposure of (001) plane. As-prepared Ni₂P/Ti electrode exhibited a good HER activity while the stability was moderate. After that, Hu's group developed a simple method for the preparation of Ni₂P nanoparticles using NiCl₂ and NaH₂PO₂ as Ni and P source.⁸³ Preparation was conducted at 250 °C in an inert atmosphere. Resulting Ni₂P showed enhanced stability in acid. Metal phosphides with

various morphologies could be prepared by this method using metal (hydro)oxides with certain morphologies as precursors. Besides Ni_2P , nickel phosphides with other crystal phases like NiP_2 and Ni_5P_4 have also been investigated as HER catalysts. For example, Liu's group prepared nickel phosphides nanosheet array on carbon fiber paper which composed of Ni_2P , NiP_2 and Ni_5P_4 . As-prepared CP@Ni-P electrode is able to drive overall water splitting in alkaline solution.¹³¹

Cobalt phosphides have been studied as HER catalysts. Popczun *et al.* synthesized CoP nanoparticles in OA using TOP as P source. CoP/Ti electrode exhibited a superior HER activity as a current density of 20 mA/cm^2 can be achieved at an overpotential of 85 mV.⁸⁴ It was quite stable in acidic solution for 24h. Sun's group has conducted a series of pioneering work in this field. They firstly synthesized CoP decorated CNT by phosphidation of $\text{Co}_3\text{O}_4/\text{CNT}$ into CoP/CNT, which is active for HER ($\eta=122 \text{ mV}$ @ $j=10 \text{ mA/cm}^2$).¹³² Then they prepared nanoporous CoP nanowire arrays on carbon cloth (CC) and found it to be active and stable for HER under all pH (0-14).¹³³ Furthermore, they prepared CoP nanoparticles, nanosheet arrays and nanowire arrays on CC or Ti plate as binder-free electrodes with high HER activities.¹³⁴⁻¹³⁶ In addition, amorphous cobalt phosphide can be prepared by electrochemical deposition from solution containing Co^{2+} and H_2PO_2^- .¹³⁷ As-deposited film was consisted of metallic Co, cobalt phosphate and cobalt oxide but reduced to cobalt phosphide after cathodic current is applied. This *in situ* formed Co-P film showed a current density of 10 mA/cm^2 at a overpotential of 85 mV.

FeP nanomaterials are also efficient HER catalysts. Zhang *et al.* firstly synthesized nanoporous FeP nanosheets by anion exchange of $\text{Fe}_{18}\text{S}_{25}$ -TETAH nanosheets. As-prepared FeP porous nanosheets were active for HER in acid media.¹³⁸ Callejas prepared hollow FeP nanoparticles in OA using TOP as P source which required an overpotential of as low as 50 mV to achieve a current density of 10 mA/cm^2 .⁸⁵ This performance is close to that of Pt. In addition, FeP nanowire arrays on CC or Ti substrate were prepared by NaH_2PO_2 phosphidation. These binder free electrodes exhibited good HER activity.^{139, 140} FeP/rGO and FeP/CNT were also synthesized with excellent performance for HER due to the enhanced electrical property and good dispersion of

FeP nanoparticles on carbon materials.^{141, 142}

MoP and WP were prepared using a temperature programmed reduction method and their HER activities were confirmed both experimentally and theoretically. Wang's group prepared bulk MoP and compared the HER performance with Mo and Mo₃P.⁸⁶ The result showed that the degree of phosphidation has an important effect on HER performance. Sun's group prepared a closely interconnected network of MoP nanoparticles with high surface area which showed good activity and stability in acid media.¹⁴³ The high activity was attributed to the enhanced electrical property within interconnected network. Jaramillo's group developed a surface sulfidation method to further improve the HER performance of MoP. As-prepared MoP|S was confirmed with superb HER activity and stability in acidic solution.¹⁴⁴ Amorphous MoP with a diameter of 4 nm was prepared in OA using TOP as P source.¹⁴⁵ Similarly, WP nanoparticles (3 nm) were prepared.¹⁴⁶ These materials exhibited moderate HER activities.

An activity comparison among recently reported noble metal free HER catalysts is listed in Table 2-2.

Table 2-2 Comparison of non-noble metal based HER catalysts in 0.5 M H₂SO₄.

Catalyst	Substrate	Loading mass (mg/cm ²)	η_{10} (mV) ^a	Tafel slope (mV/Dec)	Ref
CoP/CNT	GC	0.285	122	54	132
CoP nanowire arrays	CC ^c	0.92	67	51	133
CoP nanoparticles	Ti foil	0.9	88	48	147
CoP@NC	GC	0.306	78	49	148
Ni ₂ P/CNT	GC	0.184	124	41	149
Ni ₂ P hollow NPs	Ti foil	1.0	116	46	130
Fe ₂ P/NGr	GC	1.71	138	-	150
FeP nanotube	CC	1.6	88	36	151
Hollow FeP NPs	Ti foil	1	50	37	85
FeP nanosheet array	Ti foil	3.2	55	38	152
MoP	GC	0.36	125	54	143
MoP S	Ti foil	0.19	117	50	144
CoS P/CNT	GC	0.4	67	49	153
Mo ₂ C@NPC/NPRGO	GC	0.14	34	33.6	154
P-WN/rGO	GC	0.337	85	54	155
Co-NG ^d	GC	0.285	147	82	156
Co-G	GC	0.285	380	144	156
A-Ni-C ^d	GC	0.283	34	41	157
CoNi@N-doped carbon	GC	0.32	142	105	158
Co-embedded NCNT	CC	17	78	74	159
Co@N-doped carbon/NG	GC	0.285	200	79.3	160
Co@N-doped Graphene film	Graphene film	-	125	94	161
Co@N-doped carbon	Ti mesh	-	106	78.2	162
Co-C-N/carbon	CC	-	138	55	163
CoN _x /C	GC	2	133	57	164
Co@BCN	GC	0.43	96	63.7	165

a: the overpotential required to achieve a current density of 10 mA/cm²; b: glassy carbon; c: carbon cloth; d: single atom catalyst.

2.2.3 Non-noble metal containing electrocatalysts for O₂ evolution

OER proceeds through a four-electron transfer pathway, which is kinetically sluggish. The relatively low efficiency of OER is the bottleneck of the overall efficiency of water splitting. Therefore, efficient catalysts like RuO₂ and IrO_x are required. However, the

high price and scarcity of noble metal catalysts limit the practical application of water splitting. The development of efficient noble metal free OER catalysts is the main task in this area.

(1) Cobalt based OER catalysts

Co-based OER catalysts have been known for years as promising candidates to replace noble metal catalysts. Spinel-type oxides like Co_3O_4 and NiCo_2O_4 have been studied and confirmed to be active OER catalysts in alkaline solution.¹⁶⁶ Besides, amorphous Co-Pi exhibits good activity and excellent stability in both neutral and alkaline media.¹⁰⁰ Further improvement of the OER activity of cobalt based spinel-type oxides can be achieved by hybridization of cobalt oxides with carbon materials. For example, Dai's group prepared $\text{Co}_3\text{O}_4/\text{mRGO}$ which was an efficient catalyst for both oxygen evolution and reduction (ORR).¹⁶⁷ Carbon materials, as a support, could facilitate the charge transfer in the composite and inhibit agglomeration of catalysts during synthesis. In addition, $\text{Co}_3\text{O}_4/\text{carbon nanowire array on Cu foil}$ was prepared by the pyrolysis of a metal-organic framework (MOF) precursor.¹⁶⁸ As-prepared electrode exhibited excellent activity ($\eta=290 \text{ mV @ } j=10 \text{ mA/cm}^2$) with good stability. Cobalt based perovskite oxides like $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) has been prepared by solid state reaction and was confirmed to be a promising OER catalyst.¹⁶⁹ The good activity was attributed to the near-unity occupancy of the e_g orbital of Co, the fast oxygen exchange kinetics and the ionic conductivity of BSCF.

(2) Nickel based OER catalysts

Ni-based OER catalysts are another group of noble metal free OER catalysts. NiO has been investigated as OER catalyst due to its low cost and good activity. The activity of NiO depends on the particle size and surface state. For example, ultra-small, dispersible and crystalline NiO nanoparticles were prepared via a solvothermal method.¹⁷⁰ The decrease in particle size led to the formation of surface Ni^{3+} state with enhanced OER activity. Fe-doped NiO exhibited enhanced OER activity compared to NiO due to the *in situ* formed layered NiFe oxyhydroxide.¹⁷¹ Carbon materials could be used as supports to improve the performance of Ni based oxides. For example, a Ni based perovskite oxide, LaNiO_3 , exhibits strong activity for OER and ORR when coupled

with N doped carbon.¹⁷² Ni@C nanoparticle prepared by the pyrolysis of a MOF precursor exhibited good activities for both OER and overall water splitting in alkaline media.¹⁷³ Nickel hydroxides are another important group of noble metal free OER catalysts. α -Ni(OH)₂ and β -Ni(OH)₂ were prepared by solvothermal method and α -Ni(OH)₂ was found to exhibit better OER activity.¹⁷⁴ Ni-Fe layered double hydroxide (LDH) has emerged as the most promising candidates for noble metal free OER catalyst during recent years. The origin of the high activity was explained by Fe induced partial-charge-transfer activation of Ni during anodic conditioning. Combining electrochemical and spectroscopic studies, it was revealed that the incorporation of Fe suppressed the oxidation of Ni²⁺, leading to Ni^{3+/4+} with more oxidizing power and thus faster OER kinetics. Therefore, the composition of NiFe-LDH could be tuned to optimize its OER activity.^{175, 176} NiFe-LDH/carbon composites have also been extensively studied to enhance the OER activity. The introduction of carbon materials not only improves the charge transport, the strong interaction between metal and carbon can induce local electronic structure change of the metal centers and thus the redox behavior, leading to more active catalysts. For example, a recent research showed NiFe-LDH/carbon black exhibited higher OER activity with increased number of surface active sites.¹⁷⁷ An efficient OER catalyst was prepared by confined growth of NiFe-LDH nanoparticles of around 5 nm in N-doped mesoporous graphene framework.¹⁷⁸ Direct growth of NiFe-LDH nanoplates on functionalized CNTs afforded significant enhancement of OER activity due to strong association of LDH on CNTs.¹⁷⁹ NiFe-LDH/rGO nanocomposite was prepared by self-assembly of exfoliated single-layer LDH nanosheets and reduced graphene oxide (rGO) nanosheets via electrostatic interaction.¹⁸⁰ Strongly coupled NiFe-LDH/rGO hybrid was also obtained through an anion exchange process to intercalate negatively charged GO in the interlayer space of LDH followed by post-reduction of GO to rGO.¹⁸¹ The enhanced ECSA and molecular scale contact between LDH and carbon materials leads to synergistic effect for OER process in these works.

A comparison of Ni based OER electrocatalysts activity from recent publications is listed in Table 2-3.

Table 2-3 Comparison of Ni based OER electrocatalysts from recent publications.

Catalyst	Electrode	Synthesis method	[KOH] (M)	Catalyst loading (mg/cm ²)	η_{10} (mV) ^a	Stability	Ref .
NiFe-LDH/CNT	CFP	Multi-step ST	1.0	0.2	247 ^d	60 min at 5 mA/cm ² (98%)	179
Amorphous NiFe	NF ^e	ED ^f	1.0	-		10 h at 100 mA/cm ² (98%)	182
3D NiFe-LDH	NF	HT ^g (urea)	1.0	-	250	10 h at 1.5 V (RHE) (97.8%)	183
NiFe-LDH/CQD	GC	Multi-step ST	1.0	0.2	235	3000 s at 2.5 mA/cm ² (95%)	184
NiFeO _x film	Au/Ti	SD ^h	0.1	-	325	-	185
NiFe-LDH/rGO	GC	HP + Exf + LBL + Red ⁱ	1.0	0.25	210	10 h at 10 mA/cm ² (95%)	181
NiFe-rGO LDH	NF	HP + Red	1.0	0.25	206	80 min at 10 mA/cm ² (100%)	180
NiFe-LDH	HOPG	Pulsed laser ablation	1.0	0.36	280	5 h at 0.654 V (NHE) (98%)	186
NiFe-NS	GC	HP + Exf	1.0	0.07	300	13 h at 10 mA/cm ² (97%)	187
CoFeNiO _x	NF	ED	1.0	0.07	240	-	188
NiFe-LDH/NGF	GC	Co-precipitation	0.1	0.25	337	200 min at $\eta=350$ mV (100%)	178
NiCo-UMOF nanosheet	GC	Ultrasonication ^k	1.0	0.2	250	10000 s at 1.50 V and 1.52 V (RHE) (100%)	189
NiFeOOH	GC	ED + aging	1.0	-	280 ^j	-	190
G-CoFeW	GC	Sol-gel	1.0	0.21	223	500 h at 30 mA/cm ² (100%)	191
NiFeOOH	GC	ST	0.1	0.1	310	-	176
NiFeOOH/C	GC	ST	0.1	0.1	295	-	177

a: overpotential needed to achieve a current density of 10 mA/cm²; b: overpotential needed to achieve a current density of 100 mA/cm²; c: solvothermal method; d: measured from Tafel slope; e: Nickel foam; f: electrodeposition; g: hydrothermal; h: sputtered deposition; i: homogenous precipitation, exfoliation, layer by layer assembly, reduction; j: obtained at 2 mA/cm²; k: ultrasonication of metal ions and organic ligand (benzenedicarboxylic acid) in DMF.

2.3 Summary of literature review

Based on the literature study, it is still a great challenge to develop low-cost, noble metal free photocatalytic systems for H₂ evolution. The work presented in Chapter 3 and 4 was dedicated to meet this challenge by using CdS QDs as light absorber and MoP nanoparticles or ZnO supported Co_xP nanoparticles as co-catalysts.

The efficiency of electrocatalytic water splitting still needs to be further improved for both HER and OER catalyst. The work presented in Chapter 5 gives an example of CoP anchored on N, P co-doped CNT as an efficient and stable HER catalyst. The work present in Chapter 6 shows that it is possible to harness the OER activity of NiFe-LDH by constructing a closely interconnected framework of amorphous NiFe-LDH nanocrystals with N doped carbon nanodomains, both of which have a size of less than 5 nm.

CHAPTER 3 HIGHLY EFFICIENT NOBLE METAL FREE PHOTOCATALYTIC HYDROGEN EVOLUTION SYSTEM CONTAINING MoP AND CdS QUANTUM DOTS

(This Chapter is adapted from “Yin, S. M.; Han, J. Y.; Zou, Y. J.; Zhou, T. H.; Xu, R. A highly efficient noble metal free photocatalytic hydrogen evolution system containing MoP and CdS quantum dots, *Nanoscale*, **2016**, 8, 14438-14447.” Reproduced with permission from the Royal Society of Chemistry)¹⁹²

3.1 Introduction

As discussed in Chapter 2, photocatalytic water splitting which utilizes solar energy to reduce water to H₂ is considered to be a promising technology to produce H₂ at low price without burdening the environment.

Among various semiconductors used for photocatalytic water splitting, CdS QDs have received a great number of research interest due to its desirable CB and VB positions which are thermodynamic favorable for water splitting. Furthermore, the good stability and water dispersity of monodispersed CdS QDs could enhance the absorption of visible light. Lastly, the nanosized dimension of CdS QDs leads to shorter charge transportation length and lower possibility for charge recombination.

A suitable co-catalyst is key to improving the activity of a photocatalytic system. Noble metal free co-catalysts like NiS, MoS₂ have been utilized for the construction of efficient H₂ production system. Metal phosphides such as Ni₂P, CoP, FeP, and MoP have shown better HER activity compared to metal sulfides but only limited studies have been conducted using metal phosphides as co-catalysts in photocatalytic H₂ evolution, especially for nanosized MoP. As mentioned in Chapter 2, MoP/CdS NRs prepared by post calcination of MoP with large particle size and CdS nanorods exhibited moderate H₂ evolution activity. It is supposed that MoP with large particle size has a relatively low surface area and the charge transfer and transportation in the interface between MoP and CdS NRs is moderate.

In this Chapter, we constructed a highly efficient photocatalytic H₂ evolution system with CdS QDs as the light absorber and nanosized MoP as the co-catalyst for the first time. MoP particulates are prepared using conventional temperature programmed reduction (TPR) method. Then a probe sonicator is used to disperse the bulk MoP into small sized particles. Both electrocatalytic and photocatalytic activity of the nanosized MoP are investigated. The highest H₂ production rate of 1100 $\mu\text{mol/h}$ can be achieved by the optimized system under visible light irradiation. In addition, the photocatalytic system is rather stable after three runs for a total 36 h without decrease in its activity. The highest quantum efficiency of 45.1% is obtained at 460 nm irradiation. The activity of this system is even higher than that with Pt nanoparticles as the co-catalyst. This system represents a good example of highly efficient photocatalytic H₂ evolution system that contains only earth-abundant elements.

3.2 Experimental

3.2.1 Materials and reagents

Cadmium oxide (CdO, Sigma-Aldrich, purity: 99.5%), 1-octadecene (ODE, Sigma-Aldrich, purity: 90%), oleic acid (OA, Alfa-Aesar, purity: 90%), elemental sulfur (S, Alfa-Aesar, purity: 99.5%), trioctylphosphine (TOP, Sigma-Aldrich, purity: 90%), hexane (C₆H₁₄, Sigma-Aldrich, purity: 98.5%), methanol (CH₃OH, Sigma-Aldrich, purity: 99.8%), mercaptopropionic acid (MPA, Alfa-Aesar, purity: 99%), sodium hydroxide (NaOH, Sigma-Aldrich, purity: 98%), ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Acros, purity: 99%), diammonium hydrogen phosphate ((NH₄)₂HPO₄, Sigma-Aldrich, purity: 98%), citrate acid (CA, C₆H₈O₇, Acros, purity: 99.5%), L-ascorbic acid (Alfa-Aesar, purity: 99%), H₂PtCl₆·6H₂O (Sigma-Aldrich, purity: 37.5% Pt basis), trisodium citrate (Alfa-Aesar, purity: 99%), L-(+)-lactic acid (LA, Sigma-Aldrich, purity: 88-92% acid basis), 2-propanol (IPA, Sigma-Aldrich, purity: 99.5%), Nafion solution (5 wt% solution in lower aliphatic alcohols/H₂O mixture) were obtained and used without further purification.

3.2.2 Materials synthesis

CdS QDs were synthesized using a hot-injection procedure.⁴⁶ Typically, a mixture of 4

mmol of CdO, 5 mL of OA and 15 mL of ODE in a 50 mL 3-neck flask was heated to 300 °C under a nitrogen atmosphere until the solution turned optically clear and colorless. At this point, 2 mL of TOP containing 4 mmol of sulfur was quickly injected, and the temperature was stabilized at 260 °C for 5 minutes for growth. The reaction mixture was allowed to cool to 60 °C and 10.0 mL of hexane–CH₃OH (1:1 v/v) was used as the extraction solvent to separate the nanocrystals from byproducts and unreacted precursors. The as-prepared CdS QDs were purified by repeated precipitation with acetone and centrifugation to remove impurities. The hydrophilic CdS QDs were obtained by capping ligand exchange from TOP to MPA. MPA (5 mmol) was dissolved in 5.0 mL of methanol, and the pH of the solution was adjusted to 10.0 using NaOH. Such solution was then added into the hydrophobic QD n-hexane solution (0.2 M, 20 mL) and stirred for 2 h. Afterwards, 20 mL water was added into the mixture and stirred for 10 min. Eventually, the mixture was separated into two phases and the CdS QDs were transferred into the bottom aqueous phase from hexane. MPA capped CdS QDs was repeatedly washed and re-dispersed in water for further use. The concentration of CdS QDs dispersion was determined as following: an aliquot (2 mL) of CdS QDs solution was taken and CdS QDs were precipitated by adding methanol into the solution and centrifuged at high speed (12000 RPM) to isolate CdS QDs from the solvent; then the obtained CdS QDs were dried under vacuum and weighted to determine the concentration of CdS QDs solution (12 mg/mL).

MoP was prepared by TPR method.¹⁹² Ammonium heptamolybdate tetrahydrate (0.1 mmol), diammonium hydrogen phosphate (0.7 mmol) and citric acid (CA) were first dissolved in deionized water (20 mL) with a molar Mo:P:CA ratio of 1:1:*x* (*x* = 0, 1, 2, 3, 4). After evaporation of water at 120 °C, the obtained brown solid was ground into fine powder and calcined at 500 °C for 5 h. Then the calcined powder was reduced in H₂ (SOXAL, H₂O < 3 ppm, O₂ < 2 ppm) flow with the temperature ramping from room temperature to 350 °C within around 0.5 h and 350 °C to a desired temperature (550 °C, 600 °C, 650 °C, 700 °C, 750 °C) with a heating rate of 2 °C/min. The sample was held at the desired temperature for 2 h, followed by cooling to room temperature. After the tube furnace was cooled down to room temperature, the H₂ flow was changed to Ar

flow (SOXAL, $\text{H}_2\text{O} < 3$ vpm, $\text{O}_2 < 2$ vpm) and Ar flow (20 sccm) was kept for 1 h to make inert atmosphere. Then the downstream end of the tube furnace was opened to expose the sample in an air/Ar mixture to passivate its surface for another 1h. This passivation process is commonly applied in the preparation of metal phosphides to avoid bulk oxidation when exposed directly to air. The as-obtained samples are named as MoP- x CA with x as the ratio of CA to Mo.

Next, MoP was dispersed into nanosized particles. Typically, 5 mg MoP was dispersed in 50 mL deionized water and sonicated using a probe sonicator (Fig. 3-1, model VCX 750, Sonics & Materials, Inc., USA) at 90% amplitude for 30 min. Before sonication, the suspension was purged with Ar (SOXAL, $\text{H}_2\text{O} < 3$ vpm, $\text{O}_2 < 2$ vpm) for 30 min to remove dissolved O_2 to protect MoP from possible oxidation during sonication. The dispersion was used immediately for electrochemical or photocatalytic measurements to avoid further oxidation.

Figure 3-1 Photograph of probe sonicator.

3.2.3 Materials characterization

Powder X-ray diffraction (XRD) patterns were acquired on an X-ray diffractometer (Bruker AXS D8) with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 kV and 20 mA. Field emission scanning electron microscopy (FESEM) measurements were carried out on a JEOL JSM 6700F microscopy coupled with Energy Dispersive X-ray spectroscopy (EDS). The morphology, particle size and lattice fringe were analyzed on a transmission electron microscopy (TEM, JEOL 3010). The UV-visible absorption spectra were

obtained on a UV-2450 spectrophotometer (Shimadzu). Photoluminescence (PL) spectra were collected on a Fluoromax-3 spectrometer (Horiba Scientific) at 77 K with the sample tube immersed in a Quartz liquid nitrogen Dewar. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an AXIS-HSi spectroscopy (Kratos Analytical) using a monochromatic Al K α X-ray source (1486.7 eV) and the binding energy was calibrated using the C 1s peak at 285 eV. The Raman spectra were recorded on a Renishaw instrument, using a He/Ne laser with a wavelength of 633 nm.

3.2.4 Photocatalytic activity measurement

Visible light driven H₂ production measurements were conducted in a closed gas circulation-evacuation system fitted with a top window Pyrexcell. A 300 W Xenon lamp equipped with a cut-off filter ($\lambda \geq 420$ nm) was used as the light source. 10 mg CdS QDs were added into nanosized MoP dispersion (5 mg) and magnetically stirred for 10 min. Ar was purged into the mixture during the addition of CdS QDs and the subsequent stir. Then, a certain amount of LA solution was added to adjust the final solution to 100 mL containing 20 vol% LA. The pH of LA solution was pre-adjusted using NaOH pellets and the final pH of the reaction solution was measured using a pH meter (Sartorius, Docu-pH meter). The reaction solution was immediately sealed and connected to the photocatalytic system. The system was evacuated and refilled with Ar several times to remove the air trapped inside and finally refilled with 30 torr of Ar before photoreaction. The temperature of the photoreaction cell was kept at approximately 20 °C by jacketed cooling water. The H₂ evolved was analyzed by an online gas chromatography (GC, Agilent 6890N, thermal conductivity detector). The apparent quantum efficiency (AQE) was measured under the same reaction condition with band pass interference filters (Newport, center wavelength at 420, 440, 460, 480, 500 and 520 nm with a band width of 10 nm). The irradiation intensity (power per unit area) was measured using a silicon photodiode (13 DAS 005, MELLES GRIOT) connected to broad-band power/energy meter (13 PEM 001, MELLES GRIOT). The number of incident photons in one-hour irradiation can be obtained since the energy of one photon can be calculated by the wavelength of the photon and Planck constant. Eq.

(1) was used to calculate the QE.

$$QE = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\% \quad (1)$$

3.2.5 Electrochemical measurement

Briefly, 15 mg MoP was dispersed in 5 mL isopropanol (IPA) using probe sonicator (50% power, 30 min). Then, 20 μL of Nafion solution (5%) was added into the mixture which was sonicated in a water bath for another 1 h to prepare the catalyst ink. Subsequently, 5 μL of the catalyst ink was dropped onto the glassy carbon electrode (0.07 cm^2) and left to dry. This process was repeated several times to reach a loading of approximately 0.8 mg/cm^2 . Polarization curves were collected using linear sweep voltammetry (LSV) with a scan rate of 5 mV/s on a CHI 660D (CH Instrument, China) in 0.5 M aqueous H_2SO_4 solution at room temperature. The MoP modified glassy carbon (GC) electrode was used as the working electrode. A saturated calomel electrode (SCE) was used as reference electrode and a Pt plate was used as the counter electrode for all electrochemical tests. The current density was normalized to the geometrical area of the working electrode. The potential of SCE reference electrode was calibrated to reversible hydrogen electrode (RHE) by a reported method (0.276 V vs. RHE in 0.5 M H_2SO_4 at 20°C).¹⁶⁷ All the potentials were recorded with respect to RHE. Prior to the measurement, a resistance test was done and 95% iR compensation was applied using CHI software.

3.3 Results and discussion

3.3.1 Properties of MoP catalyst

Fig. 3-2 presents the typical XRD pattern of MoP-2CA prepared by the TPR method with the temperature kept at 650°C at the second stage. The main characteristic peaks can be assigned to (001), (100), (101), (110), (111), (102) and (201) facets of MoP (JCPDS, 24-0771) which is in a hexagonal crystal structure ($P\bar{6}m2$) with Mo 6-coordinated by P atoms.⁸⁶ No peaks of other phases can be observed indicating the as-prepared sample has a high purity.

Figure 3-2 XRD pattern of as-prepared MoP-2CA-650 sample before sonication.

The morphology of bulk MoP-2CA-650 before sonication is shown in Fig. 3-3 a and b at different magnifications. It can be found that MoP is in a form of dense aggregates due to high-temperature treatment. Similar morphological observations have been reported for MoP^{86, 193} and WP¹⁹⁴ prepared with the same method by other groups. Furthermore, EDS analysis reveals that the atomic ratio of Mo to P is 1.008:1, very close to the stoichiometric ratio (Fig. 3-3c).

Figure 3-3 (a, b) SEM images of as-prepared MoP-2CA-650 sample before sonication; (c) EDS spectrum of as-prepared MoP-2CA-650 sample before sonication.

Such aggregated clusters are not ideal to be used as co-catalysts for photocatalytic

and electrocatalytic reactions as exposed active sites and interface between MoP and CdS are limited. A high-power probe sonication process is applied the first time to disperse these large aggregates into smaller clusters. SEM image of the sample after sonication (Fig. 3-4a) shows that probe sonication is efficient in dispersing the dense aggregates into smaller and loose clusters. Both individual nanoparticles within the clusters and isolated nanoparticles can be easily observed. A closer observation of the particle size and morphology of MoP after sonication is provided by TEM and HRTEM images in Fig. 3-4. It can be clearly seen that the sample is composed of small clusters of nanoparticles and isolated nanoparticles with a size of 10-30 nm. This result is in accordance to that observed from SEM. HRTEM image in Fig. 3-4d shows the lattice fringes with a d-spacing of 3.2 Å, corresponding to the distance of (001) plane of MoP, which is related to the peak at 28° in the XRD pattern.

Figure 3-4 (a) SEM; (b, c) TEM and (d) HRTEM images of MoP-2CA-650 sample after probe sonication.

The valence states of individual elements and chemical composition on the surface of the sample are elucidated using XPS. The XPS survey spectrum of MoP-2CA-650

sample shows the existence of Mo, P and O elements (Fig. 3-5a), which is consistent with the EDS result. The oxygen element is originated from the surface oxidation of MoP. Fig. 3-5b and c present the high resolution XPS spectra of Mo 3d and P 2p of MoP sample. The main doublet of Mo 3d is located at 228.0 eV and 231.1 eV, which can be assigned to Mo 3d_{3/2} and Mo 3d_{5/2} of MoP.¹⁹⁵ In addition, other two doublets at 235.5 eV/232.3 eV (Mo⁶⁺ 3d_{3/2}/3d_{5/2}) and 232 eV/229.0 eV (Mo⁴⁺ 3d_{3/2}/3d_{5/2}) are observed. These doublets can be assigned to the high oxidation states of Mo (MoO₃ and MoO₂).¹⁹⁶ It is expected that surface oxidation takes place during the passivation process. This step is necessary to prevent pyrophoric oxidation of MoP upon exposure to air.^{86, 92, 145} The absence of diffraction peaks of MoO₃ and MoO₂ in the XRD pattern indicates that oxidation only takes place at the surface of MoP. The spectrum of P 2p displays the doublet at 130.0 eV/129.2 eV which is attributed to the low valence P in MoP, and a peak with high binding energy of 134 eV due to the presence of surface PO₃⁴⁻ or P₂O₅.⁸⁶

Figure 3-5 (a) XPS survey spectrum of MoP-2CA-650 sample; high resolution XPS spectrum of (b) Mo 3d and (c) P 2p in the as-prepared MoP-2CA-650 sample.

3.3.2 Effect of reaction conditions on phase structure and morphology of MoP

A series of MoP samples were prepared under different reaction conditions like reduction temperature and CA:Mo ratio. The effect of reaction conditions on phase structure and morphology of MoP is analyzed.

The XRD patterns and TEM images of MoP samples prepared at different temperatures are shown in Fig. 3-6. MoP-2CA-550 °C consists of amorphous MoO₂ and poorly crystallized MoP nanoparticles. As the reaction temperature is increased to

600 °C, the impurity phase of MoO₂ disappears and pure MoP can be obtained although the crystallinity is not high. At higher reduction temperatures of 650 °C and 700 °C, well crystallized MoP is formed. The size of nanoparticles increases along with the reaction temperature. Nanoparticles in MoP-2CA-700 show the largest particle size which is around 30-50 nm while other samples are typically composed of nanoparticles with their size of around 10 nm. The BET surface areas of these samples are listed in Table 3-1. The result shows samples prepared with CA:Mo ratio of 2:1 at different temperatures have similar surface area while the surface areas of MoP-2CA-550 and MoP-2CA-700 are slightly smaller than other samples.

Figure 3-6 (a) XRD patterns of MoP samples prepared at different temperatures. TEM images of MoP samples prepared at (b) 550 °C, (c) 600 °C, (d) 650 °C and (e) 700 °C.

The effect of CA:Mo ratio on crystalline structure and morphology of MoP was also studied with the thermal reduction temperature kept at 650 °C. CA plays a role as chelating agent during the preparation of the precursor for MoP which is beneficial for the formation of small particles with high surface area. The XRD patterns and TEM images of MoP prepared at 650 °C with different CA:Mo ratios are shown in Fig. 3-7. The diffraction peaks of MoP become broader with lower intensity at higher CA:Mo ratio, indicating that the particle size decreases. This can also be directly observed in TEM images. Without CA, large MoP nanoparticles around 50 nm are present in the

sample. After adding CA with a ratio of CA:Mo at 2:1, the particle size drops to around 20 nm. MoP-650 samples prepared with CA:Mo ratio at 3:1 or 4:1 show even smaller nanoparticles and larger surface areas (Table 3-1). However, such nanoparticles with larger BET surface area are more sensitive to surface oxidation which is clearly shown by the Raman spectra in Fig. 3-8. Raman spectra of freshly prepared MoP-2CA and MoP-3CA and MoP-2CA stored in a capped vial under ambient condition for half a year are compared with that of commercial MoO_3 . Both MoP-2CA-aged and freshly prepared MoP-3CA exhibit a broad peak at around 800 cm^{-1} , which is more significant than that in the spectrum of fresh MoP-2CA. Compared to the spectrum of commercial MoO_3 , this peak could be assigned to MoO_3 . Such observations indicate that MoP samples consisting of smaller particles are more prone to surface oxidation.

Figure 3-7 (a) XRD patterns of MoP samples prepared at 650 °C with CA:Mo ratio from 0 to 4. TEM images of MoP prepared at 650 °C with (b) 0CA, (c) 1CA, (d) 2CA, (e) 3CA and (f) 4CA.

Table 3-1 Brunaur-Emmett-Teller (BET) surface areas of different MoP samples.

Sample	Specific surface area (m ² /g)
2CA-550	6.6
2CA-600	18.2
2CA-650	19.8
2CA-700	15.1
0CA-650	8.8
1CA-650	7.3
3CA-650	32.5
4CA-650	43.5

Figure 3-8 Raman spectra of different samples recorded at 633 nm (MoP-2CA-aged refers to MoP-2CA stored at ambient condition for 0.5 year).

3.3.3 Electrocatalytic hydrogen evolution reaction (HER) activity

Electrocatalytic HER activity of MoP was investigated in 0.5 M H₂SO₄ solution in a standard three-electrode configuration. The effect of thermal reduction temperature and CA:Mo ratio during the sample preparation on the HER activity was investigated and correlated to their phase structure and morphology. The polarization curves of samples prepared at different reduction temperatures are shown in Fig. 3-9a. The best HER activity is achieved over MoP-2CA reduced at 650 °C. The current density reaches 30 mA/cm² at a potential of 172 mV vs RHE. This performance is slightly better than that reported previously with a similar loading where a potential of 180 mV was required to reach the same current density.⁸⁶ The superior electrocatalytic HER activity can be attributed to the smaller MoP nanoparticles (10-30 nm) with more exposed active sites

obtained after probe sonication process. For comparison, the size of MoP nanoparticles reported by Xiao *et al.* is much larger than 50 nm.⁸⁶ MoP-2CA samples prepared at other temperatures exhibit inferior activities, particularly MoP-2CA-550. As discussed before, MoP-2CA-550 is composed of MoO₂ and poorly crystallized MoP. A previous study of Mo₂C by Hu *et al.* revealed that MoO₂ itself is not an efficient HER catalyst.¹⁰³ In addition, the low crystallinity of the MoP phase in this sample does not benefit the HER activity. The HER activity of MoP-2CA-600 is substantially improved compared to that of MoP-2CA-550 due to the fully conversion of molybdenum oxide into MoP though the crystallinity is still low. The potential to reach 30 mA/cm² is 190 mV vs RHE. MoP-2CA-700, which composes of MoP with larger size and smaller surface area, exhibits a lower activity. Based on such observations, a balance between the crystallinity and particle size is needed to achieve the optimum activity.

The effect of CA:Mo ratio on HER activity was also studied. HER activities of the samples with CA:Mo ratio ranging from 0:1 to 4:1 are shown in Fig. 3-9b. Clearly, MoP-2CA exhibits superior activity among the three samples. Similar result has been reported previously indicating that the addition of CA is of key importance to achieve high HER activity.¹⁴³ As can be concluded from TEM result, MoP samples prepared with low CA:Mo ratio (MoP-0CA and MoP-1CA) contain large particles with small surface area, which lack active sites for HER. The surface metal oxides layer in MoP-3CA and MoP-4CA leads to a decreased HER activity.

Figure 3-9 The polarization curves of (a) MoP-2CA prepared at different temperatures and (b) MoP-650 prepared with different CA:Mo ratios.

3.3.4 Photocatalytic hydrogen evolution activity

The MoP nanoparticles were further investigated as co-catalysts for photocatalytic H₂ evolution using CdS QDs as the light absorber. Fig. 3-10 shows the XRD pattern of CdS QDs prepared by the hot injection method. Four main diffraction peaks are observed and can be attributed to the (111), (200), (220) and (311) facets of cubic CdS (JPCDS, 80-0019). TEM image shows the monodispersed nanoparticles with a size of around 3.5 nm (Fig. 3-10b). In the normalized UV-vis and fluorescence spectra with CdS QDs dispersed in hexane (Fig. 3-10c), a strong band-edge emission at 480 nm with a narrow full width at half maximum (FWHM) of 26 nm and the edge absorption at 465 nm (band gap = 2.68 eV) are observed. This result suggests a good crystallinity and narrow size distribution of the QDs. After the QDs were surface exchanged with hydrophilic ligand and transferred into the aqueous solution, the PL signal is completely quenched. These results are similar with those previously reported by our group.^{45, 46}

Figure 3-10 (a) XRD patterns, (b) TEM image and (c) UV-vis and PL spectra of as-prepared CdS QDs.

CdS/MoP composite is obtained by adding CdS QDs dispersion solution into the homogeneous suspension of MoP prepared by probe sonication. Based on zeta potential measurement, CdS is negatively charged (−48 mV) and MoP is nearly not charged (+2 mV). The fact that the zeta potential of CdS/MoP samples becomes close to zero (within ± 10 mV) indicates that CdS QDs are successfully deposited on MoP. An aliquot was also taken from the suspension before light irradiation and observed under TEM. Typical TEM and HRTEM images of CdS/MoP with a molar ratio for CdS:MoP at 1.75:1 are shown in Fig. 3-11. Different from the good dispersion of the pristine

nanoparticles, agglomeration is formed. CdS QDs with a diameter of around 4 nm can be seen attached on the surface of larger MoP nanoparticles with a size of around 20 nm. The red circle in Fig. 3-11b indicates the size, shape and location of a CdS QD. The d-spacing of 3.3 Å is attributed to the (111) crystal planes of CdS. Fig. 3-11c shows the enlarged portion indicated by the blue circle in Fig. 3-11b. The d-spacing of 2.2 Å can be assigned to the (101) crystal planes of MoP. CdS QDs and MoP nanoparticles form intimate interface as revealed by TEM observation which is beneficial for the charge transfer for H₂ evolution process. The nanocomposite is formed possibly due to that CdS QDs are homogeneously dispersed and could be entrapped in the loose cluster of MoP nanoparticles. CdS QDs are expected to lead to the efficient transport of photogenerated charges and quick injection of photoelectrons to MoP, which is similar to that reported in Pt/CdS system.⁴⁶ Recently, Du and coworkers reported the preparation of MoP/CdS nanorod composite and calculated the band structure and density of state (DOS) of MoP. Their results confirmed the metallic behavior of MoP by non-zero DOS crossing the Fermi energy level.⁹² When CdS QDs are used as the light absorber, the higher CB position due to quantum size effect provides larger driving force for excited electrons than the nanorods, which will benefit the H₂ evolution activity.

Figure 3-11 (a) TEM and (b, c) HRTEM images of MoP/CdS QDs composite with a molar ratio of 1.75:1 for CdS:MoP.

The photocatalytic H₂ evolution over MoP/CdS QDs composite was investigated under visible light irradiation (≥ 420 nm) in the aqueous solution containing 20 vol% LA as sacrificial reagent. Control experiments were conducted using MoP-2CA-650

and CdS QDs individually. It was found that very low H₂ production rate can be obtained (1.0 μmol/h for MoP-2CA-650 alone and 31 μmol/h CdS QDs alone). MoP samples prepared at 650 °C with different CA:Mo ratio were investigated under the same photoreaction conditions. As shown in Fig. 3-12a, MoP-650-2CA exhibits the highest H₂ evolution activity. The activity of MoP-2CA samples prepared at different thermal reduction temperatures was studied. Fig. 3-12b shows that the best H₂ evolution performance is achieved over MoP-2CA-600 with an average H₂ evolution rate of 1100 μmol/h calculated from the amount of H₂ evolved in the first 6 h, followed by samples prepared at 700, 650 and 550 °C which all display similar activities (around 800 μmol/h). The sample prepared at 750 °C gives the lowest H₂ evolution rate of 500 μmol/h. It is worth noting that there is some discrepancy in the trends of electrocatalytic and photocatalytic HER activity among these samples. Further, photocatalytic activity of the samples does not exhibit a linear dependence to the surface area due to the complexity introduced by other factors during photoreaction. Compared to the electrocatalytic process, the photocatalytic HER is a more complicated process involving light absorption by CdS QDs, charge generation and separation, and charge migration to the surface of CdS QDs and transfer to MoP co-catalyst for water reduction. As shown in Fig. 3-12b, MoP-0CA with the largest particle size and low surface area gives the lowest H₂ evolution rate of around 500 μmol/h while the H₂ evolution rates over other MoP samples are very close. The photoluminescence (PL) quenching measurement was conducted at 77 K to compare the charge transfer efficiency. As shown in Fig.3-12c, the main excitation peak of CdS alone is located at around 475 nm, which is close to that measured in non-aqueous solution and characteristic of the radiative recombination of charge carriers in CdS QDs. MoP alone does not exhibit any PL peaks at room temperature and 77 K. The PL spectra of CdS/MoP indicate that the emission of CdS is effectively quenched by all MoP samples obtained at different temperatures, suggesting that electron transfer between CdS and MoP samples is very efficient and is not the differentiating factor. The activity difference among the samples should be mainly derived from many other factors such as the particle size, surface area and surface oxidation state, etc.

Figure 3-12 (a) Time course of H₂ evolution using MoP-2CA samples prepared at different temperatures as co-catalysts; (b) Time course of H₂ evolution using MoP-xCA samples prepared at 650 °C as co-catalysts; (c) PL emission spectra of various samples at an excitation wavelength of 360 nm at 77 K.

Other parameters including the temperature ramping rate and calcination duration for preparation of MoP, the concentration of MoP and CdS QDs in the reaction solution and the pH of the solution have also been optimized (Figs. 3-13). It is worth noting that the fastest H₂ evolution rate was obtained at a pH around 3-3.5. It is proposed that the MoP co-catalyst in our photocatalytic system plays a significant role in the electrochemical adsorption and desorption kinetics for H₂ evolution which is similar to the mechanism in cathodic H₂ evolution reactions. Such behavior has also been reported on other transition metal containing co-catalysts like NiS.⁷⁵ The evolution of H₂ on the surface of MoP might proceed via a Volmer-Tafel route.⁸⁶

As shown in Fig. 3-13e, when the photocatalytic reaction was conducted at high pH values, the insufficient amount of H⁺ in the solution may limit the Volmer step which leads to a significantly decreased H₂ evolution rate. At lower pH values, the activity does not change substantially.

The activity of the optimized photocatalyst was compared with that Pt/CdS QDs. When 1 mg of Pt NPs reduced by L-ascorbic acid and stabilized by citrate acid was used as the co-catalyst, the H₂ evolution rate of 1000 μmol/h is obtained with CdS QDs (10 mg) used as light absorber. The ratio of 10:1 wt/wt for CdS:Pt has been previously reported to evolve H₂ at the highest evolution rate in our photoreactor system.⁴⁶ Hence,

the activity of MoP prepared in this work is comparable to that of precious Pt co-catalyst, while the cost of the former is much lower.

Figure 3-13 Time course of H₂ evolution using MoP-2CA-650 samples prepared with (a) different ramping rate; (b) different calcination duration; (c) different amount of MoP while the amount of CdS QDs was fixed at 50 μmol; (d) different amount of CdS QDs while the amount of MoP was fixed at 60 μmol; (e) H₂ evolution rate of CdS/MoP-650 at different pH values of the reaction solution.

The stability and AQE of the optimized MoP/CdS QDs system were investigated. As shown in Fig. 3-14a, the H₂ evolution rate remains nearly unchanged during three cycles for an overall reaction time of 36 h, indicating this system is stable under visible light irradiation. The photo corrosion of CdS QDs is suppressed due to the fast hole consumption by LA at the QDs/electrolyte interface.⁴⁶ A slight decrease in the H₂ evolution rate was observed at the end of the third run. A control experiment was carried out using less amount of MoP catalyst (2 mg vs. 5 mg in a normal run) while keeping other photoreaction conditions the same. As shown in Fig. 3-14b, after 50 h continuous irradiation, the H₂ evolution rate remains the same. Hence the slight decrease in H₂ evolution rate after three runs shown in Fig. 3-14a should be due to the LA concentration decrease. AQE was measured with band pass filter. The relative percentage error in AQE measurement was found to be less than 5% in our experiment.

The highest AQE of 45% is obtained at 460 nm light irradiation. At 480 nm, a reasonable high QE of 32% can still be obtained. When the wavelength is further increased to 500 nm which is at the edge of absorption of CdS QDs, the AQE is decreased to less than 5%. The H₂ evolution activity and the quantum efficiency of our system are among the non-noble metal containing systems as discussed in Chapter 2. This high efficiency can be attributed to that CdS QDs are used as the light harvester which provides a large driving force for proton reduction and MoP nanoparticles are activated via high energy probe sonication. The good dispersion and optical property of CdS QDs also account for the improved activity. In conclusion, this system represents for the efficient noble metal free photocatalytic H₂ evolution system.

Figure 3-14 (a) stability test (b) long duration irradiation test and (c) AQE of the optimized MoP/CdS QDs system.

Based on the results obtained, the mechanism for the photocatalytic H₂ evolution over MoP/CdS QDs system is proposed in Scheme 3-1. Photons are first absorbed by CdS QDs to generate the free charge carriers (electrons and holes). The minimum of CB of CdS QDs is located at -0.8 V and the maximum of VB is at 1.6 V vs NHE as measured by Mott-Schottky plots in our previous work.⁴⁵ The photoexcited electrons are thermodynamically favorable for H₂ evolution from water. Due to the small size of QDs, the charge carriers can quickly migrate to the surface of CdS where the holes can be consumed by LA sacrificial agent in the solution. The electrons in the CB of CdS QDs can be transferred to MoP co-catalyst due to the intimate interface between the two components and the metallic characteristics of MoP makes it possible to accept electrons efficiently to attain the high activity.⁹² In addition, the metallic feature of MoP allows a good electron mobility which leads to efficient evolution of H₂ on the surface

of MoP co-catalyst.

Scheme 3-1 Schematic illustration of photocatalytic H₂ evolution over MoP/CdS QDs system.

3.3.5 Characterization of photocatalyst after reaction

The MoP/CdS QDs after photoreaction is characterized in order to probe the compositional and structural stability. MoP/CdS nanocomposite was recovered from the reaction mixture of 60 μmol of MoP and 75 μmol of CdS (the red curve in Fig. 3-13d) after 36 h of photocatalytic reaction. The XRD pattern of MoP/CdS QDs after reaction together with the patterns of CdS and MoP are shown in Fig. 3-15a. The diffraction peaks of MoP are clearly observed after photoreaction, indicating that the bulk remains as MoP. Raman spectra taken under 633 nm excitation are shown in Fig. 3-15b and c. Typical Raman spectra of exfoliated MoS₂ and amorphous MoS₃ are used for comparison to check if MoP was transformed to molybdenum sulfides. Raman spectrum of the MoP/CdS QDs composite after reaction contains the same peaks observed in the pure CdS QDs and MoP. Furthermore, the characteristic Raman peaks of MoS₂ and MoS₃ are not found in this spectrum, confirming that the catalyst remains to be MoP. The local structure analysis by HRTEM shows that the interface between CdS QDs and MoP is maintained and no other crystal lattices or amorphous layers can be found (Fig. 3-15d). The individual MoP nanoparticle displays coherent lattice fringes throughout the bulk and surface (Fig. 3-15e), indicating the surface structure is in

accordance to the bulk. XPS was also applied to investigate the catalyst after reaction. Fig. 3-16a shows the Mo 3d spectrum. The doublet located at around 232 eV and 235 eV can be attributed to MoO₃ (Mo⁶⁺ oxidation state) which formed by the surface oxidation. A small doublet observed at 227.5 eV and 230.7 eV is assigned to MoP. Since this sample is stored in air for several weeks before XPS measurement, the XPS peak intensity for MoP becomes much smaller. This is similar to that reported previously.⁸⁶ The Mo 3d spectrum of MoS₂ and amorphous MoS₃ is mainly composed of a 229 eV/232 eV doublet which is attributed to the Mo⁴⁺ oxidation state which is not observed in the XPS spectrum of our sample.^{197, 198} The XPS peak at 226.2 eV is assigned to S 2s in CdS. The XPS spectrum of P 2p shown in Fig. 3-16b is similar to that obtained in MoP before reaction. The doublet at 130.0 eV/129.2 eV is assigned to the low valence P in MoP. The peak at high binding energy is assigned to PO₄³⁻ or P₂O₅ in which P is at high valence state. In addition, the S 2p spectrum is composed of a doublet with binding energy of 161.8 eV/162.8 eV, originated from the inner and surface S in CdS QDs, respectively.¹⁹⁹ A higher binding energy for S in commercial MoS₂ was reported with a doublet located at 162.3 eV and 163.5 eV.¹⁹⁸ The XPS spectrum of amorphous MoS₃ prepared by Hu *et al.* shows that the peaks of S₂²⁻ are located at even higher binding energy than those in MoS₂, which are absent in our result (Fig. 3-16c).^{197, 198} This indicates that the S signal in the XPS spectrum of our sample comes mainly from CdS QDs, ruling out the possibility that MoS_x species are formed *in situ* during photoreaction and act as the real co-catalyst. The results confirm that MoP is stable during photoreaction and is indeed the co-catalyst for H₂ evolution.

Figure 3-15 (a) XRD patterns, (b, c) Raman spectrum and (d, e) HRTEM images of MoP/CdS QDs after photoreaction.

Figure 3-16 High resolution XPS spectra of (a) Mo, (b) P and (c) S in the MoP/CdS QDs after photoreaction.

3.4 Conclusion

In summary, a photocatalytic H₂ evolution system has been constructed using CdS QDs as the light absorber and MoP as the co-catalyst. This noble metal free system is highly efficient and stable during the photocatalytic reaction for more than 36 h. The preparation conditions of MoP affect its electrocatalytic and photocatalytic H₂ evolution activity. The highest H₂ evolution rate of 1100 μmol/h and AQE of 45% at 460 nm can be achieved over the optimized system. The metallic characteristics of MoP and the efficient charge transfer from CdS to MoP lead to the highly efficient H₂ evolution activity.

CHAPTER 4 $\text{Co}_x\text{P-ZnO/CdS}$ QUANTUM DOTS NANOCOMPOSITE AS AN ARTIFICIAL PHOTOCATALYST FOR EFFICIENT HYDROGEN EVOLUTION

4.1 Introduction

In Chapter 3, we used a probe sonicator to disperse large MoP particles into nanosized particles or clusters. Such nanosized MoP particles afford better HER activity than large MoP particles when used as an electrocatalyst in acidic solution due to the decrease of particle size with enhanced number of surface active sites. Furthermore, these nanoparticles can be used as co-catalysts while CdS QDs were used as the light absorber. The MoP/CdS QDs composite with an intimate interface is formed possibly due to that CdS QDs are homogeneously dispersed in the solution and could be entrapped by the loose cluster of MoP nanoparticles. However, as metal phosphides are prone to surface oxidation during surface passivation process as well as probe sonication treatment, it is difficult to further decrease the particle size of metal phosphides to increase its activity.

It has been well established that support materials could be used to disperse the nanosized catalysts on their surface and stabilize the catalyst through catalyst-support interaction.²⁰⁰ Metal oxides with large surface area are typically used as support materials. In our previous research, we used different metal oxides like In_2O_3 and TiO_2 as the support for Pt nanoparticles and the hybrid materials were used for H_2 evolution with CdS QDs as light absorber.⁴⁵ We found that the photogenerated electrons could be transferred from the CB of CdS QDs to metal oxides due to the alignment of electronic structures or through surface defect sites which could trap electrons. The photogenerated electrons could be further transferred to Pt nanoparticles and reduce water to H_2 .

In this Chapter, the effect of metal oxide support on the photocatalytic H_2 evolution activity of metal phosphide was investigated using CdS QDs as light absorber. A novel composite, $\text{Co}_x\text{P-ZnO}$, through a versatile one step reaction at relatively low temperature was fabricated. Co_xP is used as the co-catalyst instead of MoP. Co_xP could be prepared at a relatively low temperature which prevents the agglomeration or

formation of large-sized particles. Besides, cobalt phosphides have been reported to exhibit better HER activity than MoP. By using ZnO supported Co_xP as co-catalyst, we may further improve the H₂ production performance of the photocatalytic system. The hybrid material was further combined with CdS QDs to construct the Co_xP-ZnO/CdS QDs composite, which is a highly efficient and stable photocatalyst for H₂ evolution.

4.2 Experimental

4.2.1 Materials and reagents

Cadmium oxide (CdO, Sigma-Aldrich, purity: 99.5%), 1-octadecene (ODE, Sigma-Aldrich, purity: 90%), oleic acid (OA, Alfa-Aesar, purity: 90%), elemental sulfur (S, Alfa-Aesar, purity: 99.5%), trioctylphosphine (TOP, Sigma-Aldrich, purity: 90%), hexane (C₆H₁₄, Sigma-Aldrich, purity: 98.5%), methanol (CH₃OH, Sigma-Aldrich, purity: 99.8%), mercaptopropionic acid (MPA, Alfa-Aesar, purity: 99%), sodium hydroxide (NaOH, Sigma-Aldrich, purity: 98%), Zinc oxide (ZnO, Kanto Chemical, purity: 99.0%), Cobalt chloride (CoCl₂·6H₂O, VWR, purity: 101%), Sodium hypophosphite hydrate (NaH₂PO₂·xH₂O, Sigma-Aldrich, purity: 98-101%), L-(+)-lactic acid (LA, Sigma-Aldrich, purity: 88-92% acid basis) were obtained and used without further purification.

4.2.2 Materials synthesis

CdS QDs were synthesized using the same hot injection method as described in Chapter 3. Co_xP-ZnO was prepared by one-pot and one-step phosphidation method.⁸³ CoCl₂·6H₂O, NaH₂PO₂ and ZnO were mixed and ground into fine powders in a mortar. The weight ratio of CoCl₂·6H₂O to NaH₂PO₂ were kept 1:5. The amount of ZnO was varied to obtained different loading percentage (0.3%, 1% and 3%). Then the mixture was transferred into a crucible with a lid on it and calcined in N₂ (SOXAL, gas purity: 99.9995%, H₂O < 3 ppm, O₂ < 2 ppm) flow at 350 °C for 4h (ramping rate: 2 °C/min), followed by cooling to room temperature naturally. After heating, NaH₂PO₂ decomposes to generate PH₃ and Na₂HPO₄ (2NaH₂PO₂→Na₂HPO₄+PH₃). PH₃ is a highly reducing gas and reacts with CoCl₂·6H₂O to form cobalt phosphides. The as-obtained samples were taken out, washed with copious DI water and dried in vacuum

oven at 60 °C.

4.2.3 Materials characterization

Powder X-ray diffraction (XRD) patterns were acquired on an X-ray diffractometer (Bruker AXS D8) with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 kV and 20 mA. The morphology, particle size and lattice fringe were analyzed on a transmission electron microscopy (TEM, JEOL 3010). The UV-visible absorption spectra were obtained on a UV-2450 spectrophotometer (Shimadzu). X-ray photoelectron spectroscopy (XPS) analysis was conducted on an AXIS-HSi spectroscopy (Kratos Analytical) using a monochromatic Al K α X-ray source (1486.7 eV) and the binding energy was calibrated using the C 1s peak at 285 eV. Quantitative study of metal elements (Cobalt) in the bulk catalysts was conducted using a Prodigy Inductively coupled plasma-optical emission spectrometry (ICP-OES). X-ray absorption near edge spectrum (XANES) was recorded at the XAFCA beamline in Singapore Synchrotron Light Source (SSLS) using the transmission mode.⁴⁹ The electron storage ring of SSLS was operated at the energy of 700 MeV with a current of 100-200 mA. Si (111) double crystal monochromator was used for varying the X-ray energy in the desired range.

4.2.4 Photocatalytic activity measurement

Photocatalytic reactions were carried out under the same conditions as those stated in Chapter 3 except Co_xP-ZnO was used as the co-catalyst. The light source, H₂ analysis method and apparent quantum efficiency measurement are the same as those used in Chapter 3.

4.3 Results and discussion

4.3.1 Structure and morphology of Co_xP-ZnO

The as-prepared Co_xP-ZnO composite was first characterized using XRD to study the structure. The result is shown in Fig. 4-1. The standard XRD patterns of ZnO, CoP and Co₂P are also shown for comparison. The XRD pattern of 3% Co_xP-ZnO shows clearly the diffraction peaks of ZnO and small peaks at 28°, 31° and 33° that can be assigned to Co₂P (JSPDS: 32-0306). A small peak at around 45° might be attributed to CoP. No

peaks at around 40° is seen in the spectrum, ruling out the existence of metallic Co in the product. Besides, XRD pattern of Co_xP prepared using the same procedure as $\text{Co}_x\text{P}/\text{ZnO}$ without addition of ZnO is also recorded in Fig. 4-1b. Co_xP is a mixture of CoP and Co_2P revealed by the XRD pattern. In summary, XRD results indicates that, Co_2P is formed while a small portion of CoP may be present in $\text{Co}_x\text{P}-\text{ZnO}$ prepared under such reaction conditions.

Figure 4-1 (a) XRD patterns of ZnO, 3% $\text{Co}_x\text{P}-\text{ZnO}$, CoP and Co_2P ; (b) XRD patterns of Co_xP prepared without ZnO.

The morphology and structure of 3% $\text{Co}_x\text{P}-\text{ZnO}$ was further observed using TEM and HRTEM. As shown in Fig. 4-2, irregular shaped particles with a large particle size of several hundred nanometers are observed, which could be attributed to ZnO. Commercial ZnO was used directly during the synthesis without further treatment. Besides, nanoparticles are seen on the surface of ZnO with a size of around 10 nm. Clear lattice fringes can be seen in the HRTEM image. Inter-planar spacing of 0.27 nm can be attributed to the CoP (002) plane with orthorhombic phase. 0.21 nm inter-planar spacing could be assigned to the (211) plane of orthorhombic Co_2P . This result indicates the nanoparticles on the surface of ZnO are Co_2P , which matches well with XRD result.

Figure 4-2 TEM and HRTEM images of 3% Co_xP-ZnO.

The chemical states of Co, Zn and P in Co_xP-ZnO were further studied by XPS and XANES. All XPS spectra are referenced to aliphatic carbon at binding energy of 284.5 eV. The XPS survey spectrum clearly shows the existence of Co, P, Zn in this sample (Fig. 4-3a). Two main peaks located at binding energy of 779.3 eV and 794.1 eV are recorded in high resolution Co 2p spectrum. XPS result indicates the existence of Co with low oxidation state in this sample, which is close to metallic Co. This result matches well with previously reported XRD binding energy for cobalt phosphide. An overlay peak at higher binding energy (~782 eV) is attributed to the surface oxidation of cobalt phosphide. As shown in the XPS spectrum of P 2p (Fig. 4-3c), two peaks at 128.5 eV and 133.1 eV are observed, which could be attributed to the P in cobalt phosphides and oxidized P species. The presence of oxidized P species results from the doping of P in ZnO structure. In addition, it was found that the binding energy of Co 2p is slightly shifted to a higher value compared to that of metallic Co (778.2 eV) whereas the binding energy of P 2p is slightly shifted to a lower value compared to that of elemental P (130.2 eV). Such results suggest that P in Co_xP is negatively charged (δ^-) while Co in Co_xP is positively charged (δ^+) due to a charge transfer of electron density from Co to P.⁸⁴ The surface of Co_xP-ZnO features pendant base P (δ^-) moieties in close proximity to the metal center Co (δ^+), so the Co_xP-ZnO is active for HER. In addition, the Zn 3s spectrum displays one peak located at 139.8 eV, which is assigned to Zn²⁺ chemical state of ZnO.

Figure 4-3 (a) XPS survey spectrum of 3% Co_xP-ZnO; (b) high resolution Co 2p spectrum of 3% Co_xP-ZnO; (c) high resolution Zn 3s and P 2p spectra of 3% Co_xP-ZnO.

The valence state of Co is further confirmed by Co *K*-edge XANES. A Co⁰ foil was used as the reference material. As can be seen from Fig. 4-4, Co_xP-ZnO and Co foil show similar XANES spectra, both exhibiting a pre-edge peak at around 7710 eV due to the 1s→3d electron transition. The absorption edge of Co_xP-ZnO is close to that of Co foil, indicating the low valence state of Co in Co_xP-ZnO. Such Co_xP exhibits metallic characteristics, which can facilitate charge transfer from semiconductor to Co_xP, improving its photocatalytic activity.

Figure 4-4 Co K-edge X-ray absorption near edge spectrum (XANES) of 3% Co_xP-ZnO.

The UV-vis spectra of 0.3% Co_xP-ZnO and 3% Co_xP-ZnO are compared with that of ZnO. As shown in Fig. 4-5, the absorption edge of 0.3% Co_xP-ZnO, 3% Co_xP-ZnO and ZnO are similar at around 390 nm, indicating that the electronic structure of ZnO remain unchanged after hybridization with Co_xP. Such results clearly evidence that Co and P

are not doped into the crystal structure of ZnO. However, the absorption of 3% Co_xP-ZnO is extended to the visible light range up to 800 nm. Comparably, 0.3% Co_xP-ZnO exhibits similar visible light absorption behavior. This is due to the intimate interface of metallic-like black Co_xP on the surface of ZnO. In addition, the UV-vis spectrum of CdS QDs is also shown in Fig. 4-5.

Figure 4-5 UV-vis spectra of 0.3% Co_xP-ZnO, 3% Co_xP-ZnO, ZnO and CdS.

4.3.2 Photocatalytic hydrogen evolution activity of Co_xP-ZnO

Co_xP-ZnO is used as a co-catalyst for photocatalytic H₂ production with CdS QDs used as the light absorber. In Chapter 2, it has been concluded from literature review that the interface between co-catalyst and semiconductor is crucial for the efficient charge transfer as well as the photocatalytic activity.

Our experiment results show that metal oxide, ZnO, can be successfully hybridized with Co₂P and an intimate interface is formed between the two components. CdS QDs were further added into the dispersion of Co_xP-ZnO in LA solution (pH=1.5). Zeta potential measurement shows that CdS QDs are negatively charged (-35 mV) whereas Co_xP-ZnO is positively charged (40 mV). This result is consistent with what we have obtained for other metal oxides (In₂O₃ and Ga₂O₃) in previous report.⁴⁵ Thus, a good interface can be formed between CdS QDs and Co_xP-ZnO driven by electrostatic interaction. The TEM image of Co_xP-ZnO/CdS QDs in Fig. 4-6 shows that the surface of Co_xP-ZnO is coated with uniformly sized and shaped spherical nanoparticles. HRTEM image further confirms these nanoparticles are CdS QDs, as the lattice fringes

with a d-spacing of 0.33 nm correspond to the (111) planes of cubic phase CdS.

Figure 4-6 TEM and HRTEM image of $\text{Co}_x\text{P-ZnO/CdS}$ QDs.

The photocatalytic H_2 production activity of $\text{Co}_x\text{P-ZnO/CdS}$ QDs was evaluated using LA as sacrificial reagent under visible light irradiation (≥ 420 nm). Firstly, the role of ZnO support on the photocatalytic activity was investigated by forming composite between Co_xP and a series of metal oxides. The results are shown in Fig. 4-7. As can be seen, $\text{Co}_x\text{P-ZnO/CdS}$ QDs has the highest activity while $\text{Co}_x\text{P-Ta}_2\text{O}_5/\text{CdS}$ QDs exhibits the lowest activity. $\text{Co}_x\text{P-ZnO/CdS}$ QDs exhibits a H_2 evolution rate of $1405 \mu\text{mol/h}$, which is nearly 2 times higher than other samples. $\text{Co}_x\text{P-WO}_3$ also shows a relatively high activity. All metal oxide supports are commercially available, and no further treatment was applied. The intrinsic property or surface state of these metal oxides should contribute to the difference in H_2 evolution activity. For example, the band alignment may not favor charge transfer from CdS QDs to metal oxide; the interface between Co_xP and some metal oxides may not be well constructed for the synthesis of stabilized Co_xP nanoparticles. On-going work is carried out to reveal the catalyst-support interaction in this system. The H_2 production rate was determined from the time course result by linear curve fitting. The results are listed in Fig. 4-7b. Besides, two control samples were involved for comparison. The first control sample is unsupported Co_2P which is prepared using the same phosphidation method without the addition of ZnO. Another control sample was prepared without adding $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (labeled as P/ZnO). In comparison, the unsupported Co_2P only exhibits a H_2 evolution rate of $237 \mu\text{mol/h}$, which is inferior to all supported samples. Besides, the amount of Co_2P used is

1 mg, which is much larger than the amount of Co_xP in Co_xP -ZnO composite (0.15 mg for 3% Co_xP -ZnO). This result clearly shows the important role of support material for the efficient photocatalytic H_2 production. H_2 production rate over P/ZnO/CdS QDs (83 $\mu\text{mol/h}$) is closed to that obtained using CdS QDs alone without adding any catalyst (119 $\mu\text{mol/h}$), indicating P/ZnO is not an active catalyst for H_2 production. It can be inferred that Co is vital for the formation of active species in Co_xP -ZnO.

Figure 4-7 (a) Time course of photocatalytic H_2 evolution of Co_xP hybridized with different metal oxides; (b) H_2 evolution rate of Co_xP hybridized with different metal oxides. Reaction conditions: 5 mg Co_xP -ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).

The effect of the loading of Co_xP on ZnO was studied and the catalyst with the optimized loading was obtained. As shown in Fig. 4-8, pure ZnO shows negligible activity. H_2 production rate increases from 503 $\mu\text{mol/h}$ for 0.3% Co_xP -ZnO to 1418 $\mu\text{mol/h}$ for 3% Co_xP -ZnO. The photocatalytic activity is positively related with the percentage of Co_xP in Co_xP -ZnO. After more Co_xP is loaded on ZnO (5% Co_xP -ZnO), the activity remains almost the same, indicating the number of active sites has reached maximum in 3% Co_xP -ZnO.

Figure 4-8 H₂ evolution rate over Co_xP-ZnO with different loading percentage. Reaction conditions: 5 mg Co_xP-ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).

Next, 3% Co_xP-ZnO was used as the co-catalyst to optimize the photocatalytic conditions including the amount of catalyst, amount of CdS QDs and concentration of LA to obtain the highest H₂ production activity. As can be seen from Fig. 4-9a, CdS QDs alone exhibit the lowest activity due to the lack of co-catalyst to efficiently reduce water. After Co_xP-ZnO is added, the H₂ evolution performance is dramatically enhanced. The photocatalytic system containing 1 mg catalyst could afford a H₂ production rate of 854 μmol/h, which is 8 times higher than CdS alone. Further increasing the amount of catalyst in the system up to 5 mg, photocatalytic performance could be improved continuously. The photocatalytic systems containing 5 mg, 7 mg and 9 mg exhibit similar performance, indicating the photogenerated charge carriers in these systems have been optimally used. Subsequently, the amount of catalyst was fixed at 5 mg and the amount of CdS was varied. The results are shown in Fig. 4-9b. Co_xP-ZnO without CdS QDs is unable to evolve H₂ under visible light irradiation, which clearly shows the importance of photoexcited electrons for H₂ evolution in this system. Photocatalytic activity reaches the highest value with 20 mg CdS QDs (1418 μmol/h). The concentration of LA might also affect the performance of this system. If LA is not sufficient, the consumption of photoexcited holes is limited which would become rate-limiting step for the overall process. At high concentration of LA, the solution pH becomes very low, which is not ideal for the water reduction process on the surface of

the catalyst.⁷⁵ The optimal concentration is found to be 30 v/v% for this system. After optimization, it was found that the best photocatalytic H₂ production performance could be achieved under following conditions: 20 mg CdS QDs, 7 mg 3% Co_xP-ZnO and LA solution concentration of 30 v/v%.

Figure 4-9 (a) Photocatalytic H₂ evolution activity with different amount of 3% Co_xP-ZnO (20 mg CdS QDs; 20 v/v% LA solution); (b) photocatalytic H₂ evolution activity with different amount of CdS QDs (5 mg 3% Co_xP-ZnO; 20 v/v% LA solution); (c) photocatalytic H₂ evolution activity with different LA concentration (20 mg CdS QDs and 5 mg 3% Co_xP-ZnO); (d) photocatalytic H₂ evolution activity with different amount of 3% Co_xP-ZnO (20 mg CdS QDs; 30 v/v% LA solution).

Apparent quantum efficiency (AQE) was determined using the optimized reaction conditions. AQE was measured with band pass filter. The relative percentage error in AQE measurement was found to be less than 5% in our experiment. The highest AQE of 66% was obtained at 420 nm light irradiation. At 480 nm, a reasonable high QE of 48% can still be obtained. When the wavelength is further increased to 500 nm which is at the edge of absorption of CdS QDs, the AQE is decreased to less than 5%. The activity and AQE are higher than those of the unsupported nanosized MoP reported in

Chapter 3, which indicates the photocatalytic activity of metal phosphides can be further improved upon introduction of suitable support materials. This activity is among the best reported values for non-noble metal containing photocatalytic water splitting systems.

Figure 4-10 AQE of the optimized Co_xP-ZnO/CdS QDs system. Reaction conditions: 5 mg 3% Co_xP-ZnO, 20 mg CdS QDs, 100 mL LA solution (30 v/v%).

Besides high activity, the stability of this system was studied using 0.3% Co_xP-ZnO/CdS. Three cycled runs were conducted. After 48 h, the light was turned off and the evolved H₂ in the reactor was evacuated. Then the light was turned on again for the next run. As can be seen in Fig. 4-11, the photocatalytic activity during the second run is even higher than that in the initial run, which could be attributed to the activation of photocatalyst under light irradiation. After the end of third run (144 h), the evolved H₂ amount from this system is slightly higher than the initial run. No decrease in activity can be observed, indicating the excellent stability of the system.

Figure 4-11 Stability test of Co_xP-ZnO/CdS QDs system. Reaction conditions: 5 mg 0.3% Co_xP-ZnO, 20 mg CdS QDs, 100 mL LA solution (20 v/v%).

This high efficiency and excellent stability can be attributed to several factors, **i.** CdS QDs are used as the light harvester which provides a large driving force for water reduction; **ii.** Co_xP nanoparticles exhibit a superior activity for water reduction as the noble metal free catalyst; **iii.** the effective loading of CdS QDs on the surface of ZnO and **iv.** good interface between CdS QDs and ZnO which facilitates the charge transfer of photoexcited electrons from CdS QDs to ZnO. As can be seen from the PL emission spectrum, Co_xP-ZnO effectively quenches the emission of CdS QDs, indicating the efficient charge transfer.

Figure 4-12 PL emission spectra of CdS QDs and 3% Co_xP-ZnO/CdS QDs at an excitation wavelength of 360 nm at 77 K.

Based on the above discussion, the mechanism for the photocatalytic H_2 evolution over Co_xP -ZnO/CdS QDs system is proposed in Scheme 4-1. Photons are first absorbed by CdS QDs to generate the excited electrons and holes. The photoexcited electrons are thermodynamically favorable for H_2 evolution from water. Due to the small size of QDs, the charge carriers can quickly migrate to the CdS/ZnO interface whereas the holes can be consumed by LA at the surface of CdS QDs. The electrons in the CB of CdS QDs can be transferred to Co_xP -ZnO due to the intimate contact between the two components and the alignment of band structure between CdS QDs and ZnO as shown in Schematic 4-1b.²⁰¹ The metallic characteristics of Co_xP makes it possible to accept electrons efficiently which leads to efficient evolution of H_2 on the surface of Co_xP co-catalyst.

Schematic 4-1 (a) Schematic illustration of photocatalytic H_2 evolution over Co_xP -ZnO/CdS QDs system; (b) band structure of Co_xP -ZnO/CdS QDs system.

4.4 Conclusion

In summary, ZnO supported cobalt phosphide (Co_xP) can be prepared using a one step and one pot phosphidation method. In combination with CdS QDs as the light absorber, the composite photocatalysts are highly active for H_2 evolution. By screening different metal oxides such as WO_3 , TiO_2 , Ta_2O_5 , *etc.*, it was found that Co_xP -ZnO exhibits the best photoactivity. The intimate interface between ZnO and CdS QDs is constructed via electrostatic interaction and the alignment between the band structure of ZnO and CdS QDs facilitates charge transfer under light irradiation. Co_xP , in this system shows metallic-like properties which efficiently accepts electrons and reduces water to H_2 on its surface. This noble metal free system is highly efficient and stable during photocatalytic reaction for more than 144 h. The highest H_2 evolution rate of 1713 $\mu\text{mol/h}$ and AQE of 66% at 420 nm can be achieved over the optimized system.

CHAPTER 5 CoP ON MESOPOROUS CARBON NANOTUBE FOR EFFICIENT HYDROGEN EVOLUTION

5.1 Introduction

In Chapter 3 and 4, research efforts are mainly focused on the construction of nanocomposite between the semiconductor and the co-catalyst with engineered interface for photocatalytic H₂ production. Besides photocatalytic H₂ production which converts solar energy into chemical fuel, it is of equal importance to develop efficient and low-cost electrocatalysts for electrochemical water splitting to utilize electricity from clean energy.

The findings from Chapter 4 indicate that CoP nanoparticle is highly promising catalyst for H₂ evolution reaction (HER). However, the poor electrical conductivity of metal oxide limits the charge transportation from electrode to catalyst in electrolysis. Therefore, carbon materials like carbon nanotube (CNT) and graphene are utilized as a conductive support to disperse and stabilize CoP nanoparticles and improve the electrical conductivity.^{132, 202} Recently, carbon materials derived from metal-organic frameworks (MOFs) or porous coordination polymers with embedded metal phosphide nanoparticles have been developed as excellent HER electrocatalysts.^{203, 204} For example, polydopamine (PDA) has been used to fabricate heteroatom-doped carbon materials. The direct pyrolysis of PDA leads to the formation of N doped carbon.²⁰⁵ N, S co-doped carbon materials can be synthesized by pyrolysis of thiol grafted PDA.^{206, 207} However, there are only limited reports on the fabrication of P doped carbon using PDA precursor.

In this Chapter, we developed a method for the preparation of CoP nanoparticles (NPs) embedded N, P co-doped CNT using CoNA (NA: nitrilotriacetic acid) coordination polymer nanowires as template and PDA as carbon source. NA is reported to coordinately bonded to Co through the carboxyl (OCO-Co) or amino (N-Co) groups for the synthesis of nanowires. CNT stabilizes the nanosized catalysts via surface bond and enhances the electrical property. The acid-leached catalyst exhibits an excellent HER activity and stability in acidic media. The overpotential to achieve a current

density of 10 mA/cm² is only 44 mV and 95% of activity could be maintained after 15h chronopotentiometry test. A relatively small Tafel slope of 55 mV/Dec was obtained.

5.2 Experimental

5.2.1 Materials and reagents

Cobalt chloride (CoCl₂·6H₂O, Sigma-Aldrich, purity: 97%), nitrilotriacetic acid (NA, 99%, ACS reagent, Sigma-Aldrich), Sodium hypophosphite hydrate (NaH₂PO₂·xH₂O, Sigma-Aldrich, purity: 98-101%), 2-propanol (99%, VWR), tris-buffer (pH: 8.5, 99.8%, ACS reagent, Sigma-Aldrich), dopamine (dopamine hydrochloride, 98%, Aldrich), Nafion (5% in a mixture of lower aliphatic alcohols and water, Aldrich) were obtained and used without further purification.

5.2.2 Preparation of Co@P-NCNTs

Cobalt ion based coordination polymer nanowires (CoNA NWs) was prepared using a modified method reported by Li et al.²⁰⁸ In a typical procedure, 3 mmol of NA and 9 mmol of CoCl₂·6H₂O was dissolved in DI-water separately in ultrasonic water bath. Then, CoCl₂ solution was added dropwise into NA suspension under vigorous stirring. The total volume of the mixture solution was 35 mL. Finally, 5 mL 2-propanol was added into the mixture solution and stirred vigorously for another 30 min. The mixture solution (40 mL) was then transferred into a Teflon-lined autoclave, which was heated in an electric oven at 180 °C for 6h. The pink product was centrifuged and washed using water and ethanol for several times. After washing, the CoNA NWs were re-dispersed in DI-water. Then 5 mL of CoNA dispersion was added into 150 mL tris-buffer solution under stirring, followed by adding 60 mg dopamine. The mixture was stirred mildly for 16 h. The brown product was purified by centrifugation, washed using water and ethanol for several times and subsequently lyophilized to obtained CoNA/PDA core/shell NWs.

Next, 20 mg CoNA/PDA and 200 mg NaH₂PO₂ were placed separately in a crucible with a lid on it. The crucible was heated in a tube furnace at 350 °C for 5h under N₂ flow for phosphidation. Subsequently, the solid sample was dispersed in a crucible and preheated at 350 °C for 2h with a ramp rate of 1 °C/min. Then the temperature in tube

furnace was raised to a desired temperature with a ramp rate of 5 °C/min and maintained for another 2h for carbonization. After cooling down to room temperature, the black loose powder was taken out, stirred and ultrasonicated in 0.1 M KOH solution. Subsequently, the product was ultrasonicated in 0.5 M H₂SO₄ for 1h to remove exposed Co species. The acid leaching step was repeated twice, followed by washing with copious water. The final product was obtained by lyophilization.

5.2.3 Materials characterization

The morphologies and structures are characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM 6700F) coupled with Energy Dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL 3010). High angle annular dark field image (HAADF) and elemental mapping was obtained on JEOL 2100F equipped with a field emission gun. Powder XRD patterns were acquired on an X-ray diffractometer (Bruker AXS D8) with Cu K α (λ = 1.5406 Å) radiation at 40 kV and 20 mA. XPS analysis was conducted on an AXIS-HSi spectroscopy (Kratos Analytical) using a monochromatic Al K α X-ray source (1486.7 eV) and the binding energy was calibrated using the C 1s peak at 284.5 eV. Brunauer-Emmett-Teller (BET) surface area measurements were conducted by N₂ adsorption and desorption at 77K using a Quantachrome Autosorb-6 sorption system. Samples were degassed offline at 150 °C for 16 h under vacuum before analysis. Raman spectra were recorded with a He/Ne laser wavelength of 514 nm in a Micro-Raman spectrometer system (inVia, Renishaw, UK).

5.2.4 Electrochemical measurements

The catalyst ink was prepared by dispersing 3 mg of catalyst in 1 mL solution containing 0.68 mL 2-propanol, 0.3 mL DI-water and 20 μ L Nafion under ultrasonication for 10 min. Then 15 μ L catalyst ink was dropped on the surface of a glassy carbon (GC) electrode (diameter: 5 mm, area: 0.196 cm²) and dried in air to evaporate solvent. The final catalyst loading was ~0.21 mg/cm². The GC electrode was polished using aqueous alumina suspension on felt polishing pads before use.

All electrocatalytic measurements were carried out in a standard three-electrode cell

system controlled by a CHI 660E electrochemistry workstation using a rotating disk electrode (RDE, PINE Research Instrument) at ambient temperature. Catalyst powders cast on the RDE was used as the working electrode. A Platinum plate and Ag/AgCl (filled with Saturated KCl) were used as the counter electrode and reference electrode, respectively. 0.5 M H₂SO₄ solution was used as the electrolyte. The counter electrode (CE, Pt plate) was separated from working electrode (WE) and reference electrode (RE) by a proton exchange membrane (Nafion® 117, Sigma-Aldrich) to prevent any possible Pt deposition on working electrode. The set-up for electrochemical measurements is shown in Fig. 5-1. All potentials in this study were referred to reversible hydrogen electrode (RHE), $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.197$. For electrochemical data collection, linear sweep voltammetry (LSV) was carried out at 5 mV/s for the polarization curves and 0.1 mV/s for Tafel slope plots. Before measuring polarization curves, the catalyst was cycled 3 times by CV at 20 mV/s to develop a stable CV curve. All polarization curves were corrected with 95% iR-compensation. The series resistance was determined by the high frequency intercept from the Nyquist plot obtained by the electrochemical impedance spectroscopy (EIS) technique. In 0.5 M H₂SO₄ electrolyte, the value of R typically ranges from 5 to 8 Ω . During all electrocatalytic measurements, the RDE was continuously rotating at 1600 rpm to get rid of the gas bubble. For the stability test, chronopotentiometry was carried out at $j=40$ mA/cm².

Figure 5-1 Electrochemical system with three-electrode configuration and proton exchange membrane.

5.3 Results and discussion

5.3.1 Characterization of Co-P/NCNT

The preparation process is depicted in Schematic 5-1. PDA was firstly coated on the surface of CoNA NWs to construct a core/shell structure. Then CoNA/PDA NWs were phosphidized using NaH_2PO_2 as P source. After pyrolysis in N_2 flow under elevated temperature, PDA shell converted to N, P co-doped carbon while CoNA NWs decomposed and derived Co and CoP nanoparticles were embedded in carbon nanotube. After being electrochemically activated, the less stable Co nanoparticles are removed by acid and CoP NPs stabilized by the unique P–Co–N bonding on the surface of CNT are exposed which exhibit superior HER activity in acidic electrolyte.

Schematic 5-1 Illustration of fabrication procedure of the Co NPs embedded N, P co-doped CNT.

The morphology of as-prepared CoNA NWs was observed using SEM (Fig. 5-2). CoNA NWs shows 1D nanostructure with a high aspect ratio. The diameter of as-prepared nanowire is around 50 nm while its length is more than 20 μm . CoNA NWs decompose after being annealed in N_2 at 700 $^\circ\text{C}$. The resultant is mainly consisted of metallic Co and dissolved in H_2SO_4 solution. Subsequently, CoNA NWs were coated with PDA, the sample color changes from white for dopamine monomer to brown for PDA after polymerization. Typical SEM and TEM images of CoNA/PDA are shown in Fig. 5-2 c and d. CoNA/PDA shows 1D nanostructure similar to that observed for CoNA

NWs. Besides, core/shell structure is clearly seen in TEM image. The shell thickness was measured to be ~20 nm from TEM observation.

Figure 5-2 (a, b) SEM images of CoNA MWs at different magnifications, inset: photograph of CoNA MWs; (c, d) SEM and TEM image of CoNA/DPA NWs; inset: photograph of CoNA/DPA NWs.

Co embedded P, N co-doped carbon nanotube (Co-P/NCNT) was obtained after pyrolysis of CoNA/PDA NWs. Crystalline structure of Co-P/NCNT was characterized using XRD (Fig. 5-3a). A weak and broad peak at around 25° is attributed to carbon (002) while two peaks at 44° and 51° can be assigned to metallic Co. The nanowire morphology with uniform size and shape is present in the product after pyrolysis as shown in SEM images (Fig. 5-3 b and c).

Figure 5-3 (a) XRD pattern of Co-P/NCNT; (b, c) SEM image of Co-P/NCNT under different magnifications; inset: photograph of Co-P/NCNT.

The nanotube structure can be clearly seen in TEM image in Fig. 5-4a and nanoparticles are homogeneously distributed on the inner surface of the nanotube. From HRTEM image, we can see that Co nanoparticles is encapsulated in a graphitic shell, evidenced by the clear difference between their lattice fringes. The HRTEM image of carbon tube shows lattice fringe corresponding to carbon (002) facet, indicating the high crystallinity of PDA-derived carbon (Fig. 5-4c). HAADF-STEM is utilized to distinguish Co and carbon nanotubes by showing atomic contrast in the sample. As can be seen in Fig. 5-4d, Co NPs are mainly located on the inner surface of the carbon wall. And the thickness of the carbon nanotube is around 15 nm, which is consistent with TEM result. Elemental mapping result is also shown in Fig. 5-4e. It is found that Co signal is mainly seen inside the carbon nanotube, which matches well with TEM and HAADF-STEM result. N and P are uniformly dispersed throughout the sample, indicating a homogeneous doping of N and P in carbon nanotube.

Figure 5-4 (a) TEM image of Co-P/NCNT; (b, c) HRTEM images of Co-P/NCNT; (d) HAADF-STEM image and (e) elemental mapping of Co-P/NCNT.

Besides, BET surface area of Co-P/NCNT was obtained by nitrogen adsorption measurement (Fig. 5-5). Co-P/NCNT exhibits a mesoporous structure with a large

surface area ($407.1 \text{ m}^2/\text{g}$). The pore size distribution curve shows clearly the presence of mesopores at 2-5 nm and large pores at 10-30 nm, corresponding to the inner cavity of CNT and the voids in the cross-stacking CNT network, respectively.²⁰⁹ This mesoporous structure is conducive to electrocatalytic process through the exposure of catalytic sites and enhanced diffusion.

Figure 5-5 N_2 absorption and desorption isotherms of Co-P/NCNT. Inset: pore size distribution curve of Co-P/NCNT.

The chemical states of each elements in Co-P/NCNT were investigated by XPS. The C 1s spectrum mainly contains graphitic C–C bond at 284.5 eV and C=N bond at 285.6 eV (Fig. 5-6a). The C–O bond is very weak. N 1s spectrum reveals that the doping N in the carbon structure is in three forms: pyridinic N (398.3 eV), pyrrolic N (400.7 eV) and graphitic N (403.8 eV). Pyrrolic N and pyridinic N dominate the N 1s spectrum. This result is the same as reported for other PDA-derived carbon materials.²⁰⁵ Besides, Co–N bonding state is observed in a binding energy of 399.7 eV. $2p_{3/2}$ peak in Co 2p spectrum can be deconvoluted into three peaks with their shakeup satellite peaks (Fig. 5-6c). The peaks at 778.3 eV and 781.2 eV can be assigned to metallic Co and surface oxidized Co species, respectively. Another peak at a binding energy of 779.9 eV may be related to the surface N–Co–P site, which was reported by our group to be active for photocatalytic H_2 evolution when constructed on the surface of $\text{g-C}_3\text{N}_4$.²¹⁰ The charge transfer from Co to N and P via the N–Co–P bond results in positively charged Co (δ^+) and negatively charged N and P (δ^-), which is confirmed by Co $2p_{3/2}$ spectrum

shifting to higher binding energy position compared to elemental Co. Four peaks are found in P 2p spectrum. Those at low binding energy (129.5 eV and 130.3 eV) are corresponded to the N–Co–P bond and CoP, indicating CoP is also formed in this sample during high-temperature pyrolysis. The negative shift of P 2p spectrum relative to elemental P matches well with the conclusion that negatively charge P (δ^-) is formed due to the charge transfer from Co to P via N–Co–P bond. Surface oxidized P like PO_4^{3-} is observed at a binding energy of 138 eV. The peak at around 133 eV matches well with the reported value in P doped carbon.²¹¹ Additionally, a quantity analysis from XPS shows the content of Co, N and P in the sample is 8.4 at%, 3.7 at% (1.3 at% for pyridinic N; 2.4 at% for pyrrolic N) and 2.3 at%, respectively.

Figure 5-6 (a) C 1s; (d) N 1s; (c) Co 2p and (d) P 2p high resolution XPS spectra of Co-P/NCNT.

Raman spectroscopy was used to characterize the structure of Co-P/NCNT. Raman spectrum of Co-P/NCNT is shown in Fig. 5-7a. The two bands located at 1340 cm^{-1} and 1580 cm^{-1} , characteristic of D band and G band in carbon materials, are observed with $I_D/I_G = 1.7$. Besides, 2D and D+G peaks are also observed. This result indicates that defect-rich graphitic carbon is formed from pyrolysis of PDA. The defect-rich nature

originated from the heteroatom doping.²¹² Previous report reveals that doping of heteroatoms into the graphite structure is favorable for accelerating the charge transfer and accordingly improving the electrocatalytic activity.²¹³

The Co content in Co-P/NCNT is measured using Thermogravimetric analysis (TGA) since the carbon-encapsulated Co NPs cannot be dissolved even by *Aqua Regia*. TGA result is shown in Fig. 5-7b. TGA was conducted under air flow, so the solid product after TGA analysis corresponds to Co₃O₄. The weight percent of Co in the sample is measured from the weight of Co₃O₄ (39 wt%). Since the content of N and P is low in the sample, their contribution can be ignored for simplification. So, the molar percent of Co is measured as: $(39\%/58.9) / (39\%/58.9 + 61\%/12) = 11.7\%$, which shows 11.7 at% Co are present in Co-P/NCNT.

Figure 5-7 (a) Raman spectrum and (b) TGA result of Co-P/NCNT.

5.3.2 Acid leaching of Co-P/NCNT

The above characterization results reveal that Co/CoP nanoparticles are encapsulated by graphite shell in the inner wall of carbon nanotube. As-prepared sample was then acid leached to remove the unstable metallic Co particles with a large particle size. Co-P/NCNT was pretreated in 0.1 M KOH under stirring and transferred to 0.5 M H₂SO₄ acid solution to remove unstable Co nanoparticles via ultrasonication. After leaching, the product was washed thoroughly using DI-water and lyophilized to obtain the acid leached sample, A-Co-P/NCNT. KOH-treated Co-P/NCNT can react with H₂SO₄ to evolve bubbles while untreated Co-P/NCNT cannot. It is presumed that, after being treated in KOH, more defects appeared in the graphitic structure of CNT and the

intercalation of K ions results in the enlarged interlayer distance. These changes in graphitic structure lead to the exposure of the less stable Co nanoparticles.

The crystalline structure of A-Co-P/NCNT was characterized by XRD. As can be seen in Fig. 5-8a, only the broad diffraction peak assigned to carbon is observed in the pattern. The Co content in A-Co-P/NCNT was further determined using TGA as described before. The molar percentage of Co in A-Co-P/NCNT is 6.7 at%, indicating a portion of Co NPs in Co-P/NCNT were dissolved during leaching.

Figure 5-8 (a) XRD pattern of A-Co-P/NCNT; (b) TGA result of A-Co-P/NCNT.

The chemical states of individual elements in A-Co-P/NCNT were investigated by XPS (Fig. 5-9). C 1s spectrum contains mainly one peak at 284.5 eV which is attributed to graphitic C–C bond and small peaks of C=N, C=O bonds are located at higher binding energy position. K 1s spectrum at around 292.5 eV is also recorded due to the pretreatment in KOH. N 1s spectrum is observed in the sample and the atomic percentage of N is 3.6 at% measured from XPS, which is similar to that in pristine sample. The content of pyridinic N and pyrrolic N is 0.5 % and 3.1 % in A-Co-P/NCNT, showing an obvious decrease in pyridinic N. Besides, N–Co bond is still observed at the binding energy of 399.9 eV. N–Co–P bond and oxidized Co species are observed in Co 2p spectrum while metallic Co is absent in the spectrum, indicating the dissolution of unstable metallic Co in acidic electrolyte (Fig. 5-9c). P 2p spectrum shows the N–Co–P bond and C–P bond at the binding energies of 129.5 eV and 133.2 eV, respectively. Besides, Pt is not observed, indicating the HER activity of A-Co-P/NCNT is not from Pt nanoparticles (Fig. 5-9e). In conclusion, after activation process, less stable Co NPs is dissolved in H₂SO₄ and CoP stabilized by N–Co–P bond is exposed.

Raman spectroscopy was also conducted on A-Co-P/NCNT. Shown in Fig. 5-9f, the presence of D band and G band confirms the graphitic structure maintains. The increased I_D/I_G ratio (1.7 to 2.3) reveals that CNT become more defective after activation.

Figure 5-9 (a-e) C 1s, N 1s, Co 2p, P 2p and Pt 4f high resolution XPS spectra of A-Co-P/NCNT; (f) Raman spectrum of A-Co-P/NCNT.

Typical SEM and TEM images of A-Co-P/NCNT are shown in Fig. 5-10a and b. The results are similar to those of Co-P/NCNT, showing typical nanotube morphology. HAADF-STEM image of A-Co-P/NCNT was also obtained. The amount of Co NPs with a size of 6-10 nm clearly decreases after activation. Besides, CoP nanoparticles with a size of 1-2 nm are observed on both inner and outer surface of the nanotube. Voids on the nanotube can be observed, which might come from the removal of unstable metallic Co particles. Elemental mapping result confirms a homogeneous dispersion of C and N in the sample whereas Co and P are detected where nanoparticles are observed, indicating these nanoparticles are related to cobalt phosphide (CoP). These results reveal that CoP nanoparticles stabilized by N-Co-P bond on the surface of CNT lead to the improved HER activity.

Figure 5-10 (a, b) SEM image and TEM image of A-Co-P/NCNT; (c) HAADF-STEM image of A-Co-P/NCNT; (d) elemental mapping result for A-Co-P/NCNT.

5.3.3 Electrocatalytic activity of A-Co-P/NCNT

The electrocatalytic HER performance of A-Co-P/NCNT was evaluated in 0.5 M H_2SO_4 . A-Co-P/NCNT prepared at 800 °C and A-Co/NCNT (without phosphidation process) were studied as control samples. Pt/C was used as a reference. CV curve was recorded at a scan rate of 100 mV/s (Fig. 5-11a). A small oxidation peak can be seen at ~ 0 V vs RHE. Such oxidation peak has been reported for A-Ni-C catalyst and its intensity was enhanced during activation process. Such enhancement of the oxidation peak is indicative of the valence change of active sites in the catalyst.¹⁵⁷ The same trend is found for A-Co-P/NCNT that the oxidation peak is enhanced after activation. Polarization curves of various catalysts are shown in Fig. 5-11b. Only 44 mV overpotential was needed to achieve a HER current density of 10 mA/cm² over A-Co-P/NCNT, which is close to that for Pt/C (27 mV). Such HER performance in acidic solution is among the best noble metal free electrocatalysts we have discussed in Chapter 2. A-Co-P/NCNT prepared at 800 °C with the same activation process shows medium HER activity and A-Co/NCNT catalyst exhibits the lowest activity (130 mV in overpotential). This result shows the excellent HER activity of A-Co-P/NCNT as a

noble metal free catalyst. The electrochemical active surface area (ECSA) of various catalysts are shown in Fig. 5-11c. A-Co-P/NCNT exhibits the highest ECSA among all catalysts, which is in accordance with its superior HER activity. ECSA of A-Co-P/NCNT-800 dramatically decreased to 2.2 mF/cm². To study the effect of pyrolysis temperature on the structure and HER activity of A-Co-P/NCNT. A-Co-P/NCNT-800 was characterized using XRD, Raman and N₂ absorption. The results are shown in Fig. 5-12. It is found that highly crystalized Co and graphitic carbon are formed in A-Co-P/NCNT-800. And the high-temperature treatment results in the shrinkage of the CNT inner cavity so that A-Co-P/NCNT-800 shows a medium BET surface area (122.6 m²/g as well as a decreased ECSA. EIS spectra of various catalysts exhibit similar depressed semicircle with a rapid charge transfer feature in the high frequency region, indicating the good electrical property of these catalysts due to the incorporation of carbon nanotube. The charge transfer resistances derived from the low frequency part in EIS exhibit a trend of Pt/C>A-Co-P/NCNT-700>A-Co-P/NCNT-800>A-Co/NCNT. The small charge transfer resistance of Pt/C and A-Co-P/NCNT indicates the fast water reduction kinetics. Tafel slope of A-Co-P/NCNT was also obtained and compared with that of Pt/C (Fig. 5-11e). A-Co-P/NCNT exhibits a Tafel slope of 55 mV/Dec which is higher than that of Pt/C (34 mV/Dec), implying the hydrogen evolution on this catalyst undergoes a Heyrovsky mechanism.¹⁰¹

Figure 5-11 (a) CV scan of A-Co-P/NCNT in H₂SO₄; (b) polarization curves of various electrocatalysts; (c, d) ECSA plot and EIS spectra of various electrocatalysts; and (e) Tafel slope of A-Co-P/NCNT and Pt/C.

Figure 5-12 (a) XRD patterns of A-Co-P/NCNT prepared at 700 °C and 800 °C; (b) Raman spectrum of A-Co-P/NCNT-800; (c) N₂ absorption-desorption isotherms of A-Co-P/NCNT-800.

5.3.4 Stability of A-Co-P/NCNT

Except for the high activity, the durability of A-Co-P/NCNT is also confirmed by the chronopotentiometry test which was conducted on GC electrode with a current density of 40 mA/cm². The overpotential increased only 13 mV after 15 h. The polarization curve is almost unchanged after durability test. Only a slight decrease in current density is observed in high current density region.

Figure 5-13 (a) chronopotentiometry of A-Co-P/NCNT on GC electrode; (b) polarization curves of A-Co-P/NCNT before and after stability test.

A-Co-P/NCNT after HER durability test was characterized to study the stability of its structure. The chemical states of C, N, P in A-Co-P/NCNT after durability test are almost the same with that in A-Co-P/NCNT whereas the N–Co–P bond become pronounced in Co 2p spectrum (Fig. 5-14a). The peak intensity of oxidized Co species decreases due to the cathodic conditioning. The Raman spectrum of A-Co-P/NCNT after durability test is shown in Fig. 5-14e. D band and G bands are seen in the spectrum with a slightly larger I_D/I_G ratio (2.5), indicating the graphitic structure of CNT remains stable during HER test. Furthermore, the nanostructure of A-Co-P/NCNT keeps almost the same before and after HER durability test, as can be seen in both TEM and HAADF-STEM images (Fig. 5-15). Elemental mapping result shows the dispersion of C, N, Co and P is consistent with that of A-Co-P/NCNT before HER durability test. The above characterization results indicate the high stability of the structure of A-Co-P/NCNT during HER durability test.

Figure 5-14 (a-d) Co 2p, C 1s, N 1s and P 2p high resolution XPS spectra of A-Co-P/NCNT after stability test; Raman spectrum of A-Co-P/NCNT after stability test.

Figure 5-15 (a) TEM image, (b) HAADF-STEM image and (c) elemental mapping result of A-Co-P/NCNT after stability test.

5.4 Conclusion

In summary, we developed a facile method to fabricate Co encapsulated N, P co-doped carbon nanotube using PDA as carbon precursor. CoNA nanowires are used as the template for the growth of CNT. After acid leached, the less stable Co nanoparticles are dissolved by acidic solution and the CoP nanoparticles stabilized by N–Co–P surface bonding state on CNT are exposed which exhibit a high HER activity ($\eta=44$ mV @ 10 mA/cm²) and good stability. The superior activity is attributed to the enhanced ECSA due to the mesoporous structure, improved electrical conductivity of hetero-atom doped CNT and good HER activity of CoP. As such, this material shows potential to be used as an alternative to replace noble metal based electrocatalysts for water splitting.

CHAPTER 6 HIGHLY EFFICIENT OXYGEN EVOLUTION CATALYST CONSISTING OF INTERCONNECTED AMORPHOUS Ni-Fe LAYERED DOUBLE HYDROXIDE AND CARBON NANODOMAIN

6.1 Introduction

In previous Chapters, nanocomposites are prepared and applied in photocatalytic and electrocatalytic hydrogen evolution process. However, the overall efficiency of water splitting is constrained by the sluggish kinetics of oxygen evolution reaction (OER) at the anode. Developing efficient, robust and low-cost OER catalyst remains a key task to the production of renewable fuels. As discussed in Chapter 2, intensive research efforts have been spent searching for earth-abundant OER catalysts that are potentially more active than the state-of-the-art noble metal based catalysts such as IrO_2 and RuO_2 . Among these noble metal free OER catalysts, Ni-Fe layered double hydroxides (LDHs) or Ni-Fe(OOH) have been reported with the fastest intrinsic electrocatalytic activity under basic conditions.¹⁷⁶⁻¹⁸⁸ Among previous researches, NiFe-LDH/carbon composite materials show superior OER activities. The introduction of carbon materials like CNT and graphene could improve charge transport. The strong interaction between metal and carbon can induce local electronic structure change of the metal centers and thus the redox behavior, leading to more active catalysts. Some examples showing strongly couple NiFe-LDH/carbon composite as efficient OER catalysts have been discussed in Chapter 2.¹⁷⁸⁻¹⁸¹ However, NiFe-LDH/carbon composites are mainly prepared by deposition of NiFe-LDH on pre-synthesized carbon material or self-assembly of exfoliated NiFe-LDH single layer and graphene. These preparation approaches result in the formation of large LDH crystals.

In this Chapter, highly efficient NiFe-LDH/carbon OER catalyst was prepared by a one-pot synthesis using molecularly mixed precursors of both metal and carbon sources. Different from previously reported methods using pre-synthesized LDHs and carbon materials, both Ni-Fe LDH and carbon nanodomains are *in situ* formed together in a single reaction pot. This results in the fabrication of nanosheets consisting of amorphous LDH domains of less than 5 nm interconnected by highly disordered N-

doped nanocarbon of similar domain sizes (Scheme 1). The unique amorphous feature and small domain sizes of the as-formed NiFe-LDH/C afford greatly enhanced number of active sites compared to the bulk crystalline LDHs. The ultrafine blending of LDH and nanocarbon domains allows fast electron transfer within the nanosheets which overcomes the limitation of low conductivity of pure LDH nanosheets. NiFe-LDH/C after being activated by CV cycling and aging in alkaline electrolyte solution affords high catalytic OER activity. OER current density of 10 mA/cm² and 100 mA/cm² can be achieved at an overpotential of 210 mV and 260 mV, respectively. The Tafel slope was determined to be as low as 35 mV/Dec and turnover frequency (TOF) reaches as high as 0.3 s⁻¹ at 300 mV over the optimized catalyst on glassy carbon (GC) electrode in 1.0 M KOH solution. Superior stability of NiFe-LDH/C on both GC and carbon fiber paper (CFP) electrodes were obtained. The superior performance is attributed to the high intrinsic activity of Ni-Fe LDH, enhanced ECSA, highly integrated LDH and N-doped carbon domains in this unique structure obtained from one-pot synthesis. This work demonstrates a simple but novel synthetic route to obtain the hybrid of metal based nanocatalyst and nanocarbon to harness the high activity of Ni-Fe LDH. In addition, this method should be easily extendable to other systems for synthesis of metal-carbon functional materials.

6.2 Experimental

6.2.1 Materials and reagents

Ni(NO₃)₂·6H₂O (99%, ACS reagent, Acros Organics), Fe(NO₃)₃·9H₂O (98%, ACS reagent, Acros Organics), N, N-dimethylformamide (DMF, HPLC grade, Fluka), 2-mercapto-5-nitrobenzimidazole (MNBI, 97%, Sigma-Aldrich), Nafion (5% in a mixture of lower aliphatic alcohols and water, Aldrich) and carbon fiber paper (CFP, 0.5 cm×0.5 cm, from Fuel Cell Store) are obtained and used without further purification.

6.2.2 Preparation of Ni_xFe_{1-x}/C

A one-step and one-pot solvothermal method was applied to synthesize the Ni_xFe_{1-x}/C samples. The metal solution was prepared by dissolving appropriate amounts of Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O with different molar ratio in 5 mL of DMF. The

molar ratio of Ni:Fe was varied at 1:0, 3:1, 2:1, 1:1 for the synthesis of Ni/C, Ni_{0.75}Fe_{0.25}/C, Ni_{0.67}Fe_{0.33}/C, Ni_{0.5}Fe_{0.5}/C, respectively. The total amount of metal cations (Ni²⁺+Fe³⁺) was kept at 2 mmol. A solution of 25 mL DMF containing 0.5 mmol of MNBI was stirred vigorously. Then, Ni-Fe metal solution was added into MNBI solution dropwise while stirring to obtain a mixture. The mixture solution was then transferred into a stainless-steel Teflon-lined autoclave and heated in an electrical oven at 160 °C for 12 h. After reaction, the autoclave was cooled down to room temperature naturally. The product was rinsed in ethanol thoroughly to remove DMF and unreacted species. After washing, the yellowish product was re-dispersed in ethanol for storage and used directly for Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and electrochemical characterization. For other measurements, the samples were lyophilized to dry powders. NiFe-LDH with the Ni/Fe ratio of 2:1 was prepared by a conventional urea hydrolysis method with trisodium citrate as the morphology directing agent.²¹⁴

6.2.3 Physical characterization

FESEM specimen was prepared by dropping the catalyst suspension on a silicon substrate followed by drying under atmospheric condition. The measurements were carried out on a JEOL JSM 6700F microscopy coupled with Energy Dispersive X-ray spectroscopy (EDS). The morphology, particle size and lattice fringe were analyzed on a TEM (JEOL 3010). Elemental mapping and high angle annular dark field (HAADF-STEM) images were obtained on a field emission TEM in scanning mode (JEOL 2100F). AFM was used to measure the thickness of nanosheets with a MFP-3D classic AFM (Asylum Research) in the tapping mode. The specimen was prepared by dropping the catalyst suspension onto a silicon substrate followed by drying. Powder X-ray diffraction (XRD) patterns were acquired on an X-ray diffractometer (Bruker AXS D8) with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an AXIS-HSi spectroscopy (Kratos Analytical) using a monochromatic Al K α X-ray source (1486.7 eV). The binding

energy was calibrated using the C 1s peak at 284.5 eV. Brunauer-Emmett-Teller (BET) surface area measurements were conducted by N₂ adsorption and desorption at 77 K using a Quantachrome Autosorb-6 sorption system. Samples were degassed offline at 150 °C for 16 h under vacuum before analysis. Raman spectra were recorded with a He/Ne laser wavelength of 514 nm in a Micro-Raman spectrometer system (in Via, Renishaw, UK). Raman spectrum was fitted using Lorentzian band profile. Quantitative study of metal elements (Ni, Fe) and non-metal elements (C, H, N, S) in the bulk catalysts were conducted using a Prodigy Inductively coupled plasma-Optical emission spectrometry (ICP-OES) spectrometer and a Vario EL III Element analyzer, respectively. Extended X-ray absorption fine structure (EXAFS) was recorded at the XAFCA beamline in Singapore Synchrotron Light Source (SSLS) using the transmission mode.⁴⁹ The electron storage ring of SSLS was operated at the energy of 700 MeV with a current of 100-200 mA. Si (111) double crystal monochromator was used for varying the X-ray energy in the desired range. Energy calibration was performed with Ni and Fe foil.

6.2.4 Electrode preparation

The concentration of catalyst suspension was determined by drying a portion of suspension and weighing the dry powder. To obtain the catalyst ink, 10 μ L 0.5 wt% Nafion solution was added into 990 μ L diluted catalyst suspension by ultrasonication in a water bath for less than 5 min. Then a certain volume (10-20 μ L) of catalyst ink was dropped on the surface of a glassy carbon (GC) electrode (diameter: 5 mm, area: 0.196 cm²) which was dried in air to evaporate solvent. The final catalyst loading was about 0.28 mg/cm². The GC electrode was polished using aqueous alumina suspension on felt polishing pads before the use. Before electrochemical measurements, the activity of bare GC electrode is tested by a cycle voltammetry scan to confirm no contaminants on GC surface. For stability test, a certain amount of catalyst was also loaded on CFP to reach a catalyst loading of around 0.3 mg/cm². To characterize the catalyst after OER test, the catalyst was loaded on an ITO glass slide by drop-casting and used for OER test. After test, the catalyst was scratched off and collected after washing with deionized

water for characterization.

6.2.5 Electrochemical measurements

All electrocatalytic measurements were carried out in a standard three-electrode cell system controlled by a CHI 660E electrochemistry workstation using a rotating disk electrode (RDE, PINE Research Instrument) at ambient temperature. Catalyst powder cast on the RDE was used as the working electrode. A platinum plate and Ag/AgCl (filled with saturated KCl) were used as the counter electrode and reference electrode, respectively. The electrolyte was 1.0 M KOH (85%, ACS reagent, Sigma-Aldrich) solution. All reported potentials were referred to reversible hydrogen electrode (RHE), $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.197$. The pH value of the electrolyte was determined to be 13.6. In addition, the Ag/AgCl reference electrode was calibrated to RHE in H₂ saturated 1.0 M KOH electrolyte with a Pt wire as the working electrode. For electrochemical data collection, linear sweep voltammetry (LSV) was carried out at 5 mV/s for the polarization curves. Tafel slope is derived from polarization curve at a scan rate of 0.1 mV/s to reduce the capacitance effect. Before measuring polarization curves, the catalyst was cycled 3 times by cyclic voltammetry (CV) at 20 mV/s to develop a stable CV curve. All polarization curves were corrected with 95% iR-compensation. The series resistance (R) was determined by the high frequency intercept from the Nyquist plot obtained by the electrochemical impedance spectroscopy (EIS) technique. In 1.0 M KOH electrolyte, the value of R typically ranges from 5 to 8 Ω . During all electrocatalytic measurements, the RDE continuously rotated at 1600 rpm to get rid of the oxygen bubbles. For the stability test, chronopotentiometry was carried out under a constant current density of 40 mA/cm² with the catalyst loaded CFP as the working electrode. The electrochemical active surface area (ECSA) was determined by CV on tested samples in 1M KOH electrolyte. Data was recorded between 0 and 0.1 V vs Ag/AgCl at 20 mV/s to 100 mV/s in 20 mV/s steps. The current density difference between positive and negative sweep was taken at 0.05 V vs Ag/AgCl and a linear fit was carried out, the slope of which corresponds to two times double layer capacitance ($2C_{dl}$).

6.2.6 Turnover frequency (TOF) calculation

The TOF value is calculated from the following equation:

$$TOF = \frac{J \times A}{4 \times F \times m}$$

Where J is the current density at a given overpotential in A/cm^2 , A is the area of working electrode, F is the faraday constant (a value of 96485 C/mol) and m is the number of moles of the active materials deposited on the working electrode. The current density was obtained from polarization curve with a scan rate of 1 mV/s and iR correction was conducted before TOFs estimation. All the Ni and Fe atoms are regarded as the active sites to give a conservative estimation of TOF.

6.3 Results and discussion

6.3.1 Electrocatalyst characterization

The crystalline structure of the catalysts was studied by XRD. As shown in Fig. 6-1a, the sample $Ni_{0.67}Fe_{0.33}/C$ exhibits an almost featureless pattern, indicating its amorphous nature. Alternatively, the sample might consist of nanocrystals smaller than the coherence length of X-ray. Samples with other Ni/Fe ratios display some weak diffraction peaks. The patterns of Ni/C and $Ni_{0.75}Fe_{0.25}/C$ indicate the formation of poorly crystallized α -Ni(OH)₂ phase when Ni^{2+} is dominant. When the portion of Fe^{3+} is higher, spinel $NiFe_2O_4$ of low crystallinity can be observed in $Ni_{0.5}Fe_{0.5}/C$. These observations indicate that at the optimum Ni/Fe ratio (2:1 in this case), the most amorphous material is obtained. The SEM images of samples with other Ni/Fe ratios present that LDH or α -Ni(OH)₂ dominant samples appear flower-like (Ni/Fe at 1:0, 2:1 and 3:1) and the oxide sample (Ni/Fe at 1:1) consists of spherical particles.

Figure 6-1 (a) XRD patterns of $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ samples prepared with different Ni/Fe ratio; SEM images of (b) Ni/C, (c) $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$, (d) $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ and (e) $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$.

The morphological observation of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ using TEM shows that the sample predominantly consists of irregularly shaped nanosheets (Fig. 6-2c). The presence of weak and broad ring-like patterns (Fig. 6-2c inset) in selected area electron diffraction (SAED) reveal the poor crystallinity of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$, which is in good agreement with XRD result. Three ring patterns can be observed. Two of them with lattice fringes of 2.56 Å and 1.5 Å are assigned to the (012) and (110) lattices of LDH structure, respectively. Another ring at about 2.0 Å could be assigned to (101) lattice of amorphous carbon.²¹⁵ Such observations provide the evidence that amorphous NiFe-LDH and carbon co-exist in the sample. It should be noted that the (00 l) diffractions of LDH are not seen in both XRD and SAED. This is possibly because the growth of LDH along c -axis is suppressed. The TEM observation of the morphology of $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ samples with other Ni/Fe ratios is consistent with SEM results. Nanoflowers assembled by nanosheets are seen in Ni/C and $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$. Spherical nanoparticles with a particles size of about 10 nm are observed in $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$.

Figure 6-2 TEM images of (a) Ni/C, (b) Ni_{0.75}Fe_{0.25}/C, (c) Ni_{0.67}Fe_{0.33}/C and (d) Ni_{0.5}Fe_{0.5}/C.

A closer observation of the nanosheet was provided by HRTEM. As shown in Fig. 6-3a, the nanosheet is comprised of numerous nanocrystals of less than 5 nm dispersed with random orientations in the amorphous matrix. The nanocrystals appear to be interconnected by amorphous regions which could be the disordered carbon material. The enlarged HRTEM image of one portion of the nanosheet is shown in Fig. 6-3b. NiFe-LDH nanocrystal with lattice fringes of (012) planes (2.6 Å) and amorphous region can be clearly seen in the enlarged HRTEM image. The lattice distance of 3.4 Å corresponding to the interlayer distance of graphite is not found throughout the sample, indicating the as-synthesized carbon has a highly amorphous or defective nature. The HRTEM image of Ni_{0.5}Fe_{0.5}/C is shown in Fig. 6-3c. Three sets of lattice fringes are seen in the image which could be assigned to NiFe₂O₄ phase. This result is consistent with that from XRD analysis.

Figure 6-3 (a) HRTEM image of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$; (b) enlarged image of red circled area in (a); (c) HRTEM image of $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$.

High-angle annular dark field (HAADF) image was obtained using STEM to show the atomic contrast in the sample. As shown in Fig. 6-4a, bright and dark regions in HAADF-STEM image of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ are evenly dispersed throughout the whole nanosheet, indicating uniformly blended NiFe-LDH and amorphous carbon domains. Furthermore, elemental mapping was conducted using energy-dispersive X-ray spectroscopy (EDX). Ni, Fe, O and C are homogeneously distributed in the sample and no compositional segregation was found. Such results indicate that a fine blending of NiFe-LDH and carbon nanodomains is formed in this sample.

Figure 6-4 (a) HAADF-STEM image of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$, (b) Ni, Fe, O, C elemental mapping results of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$.

The ultrathin feature of the nanosheets was further confirmed by AFM measurement. As shown in Fig. 6-5a, the as-prepared nanosheet has a lateral size of 5-10 μm and a thickness of 3-4 nm. The nanosheet thickness corresponds to 4-6 NiFe-LDH layers. The photograph of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ dispersed in deionized water under laser irradiation is

shown in Fig. 6-5b. Tyndall effect is clearly observed, confirming the colloidal nature of the solution, which is also an indication of the formation of ultrathin nanosheets.

Figure 6-5 (a) AFM image and height profile of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$; (b) Photographs of colloidal solution of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ dispersed in deionized water with laser irradiation.

Furthermore, the effect of reaction conditions on the phase structure and morphology of resultant sample was studied. The samples were prepared with a Ni/Fe of 3:1 at different temperatures. As shown in Fig. 6-6a, only weak diffraction peaks from LDH structure were observed in $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -160 and $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -180. At higher temperature, metallic Ni or NiFe alloy was formed in the sample ($\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -200). During the solvothermal reaction, MNBI would decompose and release NH_3 which reduces NiFe-LDH into NiFe alloy. All these samples contain sheet-like particles.

Figure 6-6 (a) XRD patterns of $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ prepared at different temperatures; (b-d) TEM images of $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -160, $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -180 and $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -200.

The role of MNBI was also studied by preparing control samples with different ligands or without ligand (Ni:Fe=3:1). As can be seen from Fig. 6-7a, the XRD patterns of samples prepared with different ligands are similar. All patterns exhibit weak and broad diffraction peaks, indicating poorly crystallized LDH structure are formed in these samples. The morphology of these samples was revealed by SEM observation. $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MNBI is composed of irregular shaped sheet-like particles, which has been well discussed before. $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MIM was prepared using 2-methyl imidazole and the sample contains mainly spherical nanoparticles. $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -BIM was prepared using benzimidazole which consists of nanosheet assemblies but the size is much larger than that obtained in $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MNBI. Another control sample was prepared without addition of any ligand. XRD pattern and SEM image show clearly the existence of metal Ni and NiFe_2O_4 nanoparticles in this sample. Such results indicate the addition of MNBI in the preparation process is important for the formation of the unique structure that NiFe-LDH and carbon nanodomains are well blended in one nanosheet.

Figure 6-7 (a) XRD patterns of samples prepared with Ni/Fe ratio of 3:1 using different ligands; (b-d) SEM images of $\text{Ni}_{0.75}\text{Fe}_{0.25}$ /C-MNBI, $\text{Ni}_{0.75}\text{Fe}_{0.25}$ /C-BIM and $\text{Ni}_{0.75}\text{Fe}_{0.25}$ /C-MIM; (e, f) XRD pattern and SEM image of sample prepared without ligand.

6.3.2 *In situ* growth of nanocarbon and metal-carbon interaction

The above observations corroborate an interesting *in situ* growth of inter-weaved LDH and carbon nanodomains confined in the same material. As shown in Scheme 1, the synthesis process starts from molecular precursors of metal cations and organic ligand, 2-mercapto-5-nitrobenzimidazole (MNBI). Fig. 6-8a presents the UV-vis spectra of metal ions, metal/MNBI mixture and MNBI dissolved in DMF. The absorption band at around 380 nm in MNBI spectrum is attributed to the n to π^* transition in the chromophores, which shifts slightly to shorter wavelength in metal/MNBI mixture. Besides, the absorption bands in metal ion solution disappear after adding MNBI. These results are indicative of the influence of the formation of metal-ligand complex.²¹⁶ A similar ligand, 2-Mercapto-benzimidazole, was reported to form complexes with Ni^{2+} and other metal cations.^{217, 218} As shown in Scheme 6-1, both N and S groups in the ligand can coordinate with metal cations although the exact structure is to be determined. As such, the formation of complex ensures that the precursors are molecularly mixed. After being stored in atmospheric condition for 48 h, the UV-vis spectrum of the solution mixture remains the same. The absence of Tyndall effect indicates that the complex is stable and no colloidal nanoparticles were formed before solvothermal treatment (Fig. 6-8b). The conversion of such molecularly assembled precursor under solvothermal condition is presumed to result in self-confined growth of LDH and carbon nanodomains. As discussed in previous section, the addition of MBNI is important for the formation of this structure. On the other hand, in the absence of metal cations, no carbon product is formed after solvothermal treatment of the MNBI itself. In this section, we will further discuss the role of metal cations in conversion of MNBI to carbon by combining the elemental analysis and Raman results.

Schematic 6-1 Schematic representation of the synthesis for the preparation of amorphous NiFe-LDH interconnected by highly disordered N-doped nanocarbon.

Figure 6-8 (a) UV-vis spectra of NiFe, MNBI and NiFe-MNBI in DMF; (b) optical images of NiFe-MNBI solution before and after stored in ambient atmosphere irradiated with a laser beam.

The elemental analysis results are shown in Table 6-1. The Ni/Fe ratios in the solid samples are the same or almost the same as those in the precursor solution, indicating that all metal cations can be precipitated from the metal-ligand complex after solvothermal reaction. However, the C content decreases along with the increase of the Fe content, from 9.5 wt% in Fe-free Ni/C to 2.7 wt% in $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$. Correspondingly, the N content also decreases from 4.7 wt% to 1.7 wt%. The conversion of biomass or organic precursors to carbon materials under hydro-/solvothermal condition via condensation and carbonization has been well reported.^{219, 220} In the present study, metal species might catalyze the conversion of carbon precursor to form N-doped graphitic-like carbon which is more conductive than the amorphous carbon. The Raman spectra of samples with various Ni/Fe ratios are shown in Fig. 6-9a. The Raman spectra of all samples can be fitted by four bands. Those at 1580 cm^{-1} and 1320 cm^{-1} are attributed to the G band and D band from graphitic carbon. The ν_1 and ν_3 vibrations at 1150 cm^{-1} and 1450 cm^{-1} originate from trans-polyacetylene in amorphous carbon.²²¹ The I_D/I_G ratio reduces from 1.7 (Ni/C) to 1.1 ($\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$) with the increase of Fe content in the samples. Based on the three-stage model of variation of the Raman G position and $I(\text{D})/I(\text{G})$ ratio with increasing disorder in carbon, it can be concluded that amorphous carbon with graphitic domain is formed in $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ and $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{C}$.^{221, 222} It is speculated that Fe species catalyzes the conversion of carbon precursor to graphitic carbon. The graphitization occurs only in a short range around the surface of NiFe

crystallites as the migration of catalytic site is difficult under low reaction temperature. As such, *in situ* grown inter-connected LDH and carbon nanodomains are formed. The degree of graphitization increases with the Fe content. In samples with higher Fe contents like $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$, Raman spectra indicate the presence of conductive graphitic carbon domain although not found in HRTEM images, which should be advantageous to construct an efficient electrocatalyst. Similarly, the Raman spectra of $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ prepared at different temperatures are fitted with these four bands (Fig. 6-9b). The calculated ID/IG ratio clearly decreases from 1.5 ($\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -160) to 1 ($\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -200), showing an increase in graphitic degree of the carbon in these samples. As discussed above, metallic Ni or NiFe alloy was formed in $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{C}$ -200, which could be favorable for the synthesis of graphitic carbon. Besides, the Raman spectra of $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MNBI, $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -BIM and $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MIM are shown in Fig. 6-9c. The result shows that graphitic carbon domains are only present in $\text{Ni}_{0.75}\text{Fe}_{0.25}$ -MNBI, indicating the thiol functional group in MNBI might contribute to the formation of catalytic site with Fe for graphitization of carbon.

XPS analysis further confirms that N doped carbon is formed in $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ (Fig. 6-9). The C 1s spectrum contains mainly one peak at 284.5 eV which is attributed to graphitic C-C bond. Interestingly, a small peak at lower binding energy of 283.9 eV is observed which is typically found in metal carbides like Fe_3C and Ni_3C .²²³ Although the presence of metal carbides in $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ is not supported by other analysis results, this observation implies a strong interaction between NiFe-LDH and nanocarbon. Pyridinic-N (398.5 eV), pyrrolic-N (400.0 eV) and quaternary-N (401.8 eV) are observed in N 1s spectrum while the pyrrolic-N is slightly dominant. Sulfur in MBNI is mostly oxidized to SO_4^{2-} and might not be doped in carbon structure based on the binding energy of S 2p.

Table 6-1 Bulk and surface elemental composition and BET surface area of various samples.

	Ni/C	Ni _{0.75} Fe _{0.25} /C	Ni _{0.67} Fe _{0.33} /C	Ni _{0.5} Fe _{0.5} /C
Ni/Fe in precursor	1:0	3:1	2:1	1:1
Bulk Ni/Fe (wt%) ^a	- (40%)	3:1 (42%)	2:1 (40%)	0.99:1 (51%)
Bulk C (wt%) ^b	9.5%	7.5%	6.7%	2.7%
Bulk N (wt%) ^b	4.7%	4.3%	3.8%	1.7%
Bulk S (wt%) ^b	6.0%	5.3%	4.5%	4.2%
Surface Ni/Fe ^c	-	3.3:1	2.1:1	1.4:1
BET surface area (m ² /g)	244	180	133	139

a: mole ratio and total weight percentage of metal from ICP-AES analysis; b: weight percentage of C, N and S from elemental analysis; c: mole ratio from XPS analysis.

Figure 6-9 (a) Raman spectra of Ni/C, Ni_{0.75}Fe_{0.25}/C, Ni_{0.67}Fe_{0.33}/C and Ni_{0.5}Fe_{0.5}/C prepared at 160 °C; (b) Raman spectra of Ni_{0.75}Fe_{0.25}/C-160, Ni_{0.75}Fe_{0.25}/C-180 and Ni_{0.75}Fe_{0.25}/C-200; (c) Raman spectra of Ni_{0.75}Fe_{0.25}/C-BMNI, Ni_{0.75}Fe_{0.25}/C-BIM and Ni_{0.75}Fe_{0.25}/C-MIM; (d-f) C 1s, N 1s and S 2p high resolution XPS spectra of Ni_{0.67}Fe_{0.33}/C.

The chemical states of metal elements and oxygen in Ni_{0.67}Fe_{0.33}/C were further studied by XPS (Fig. 6-10). The Ni 2p spectrum can be fitted into two spin-orbit peaks, namely Ni 2p_{3/2} at 856 eV and Ni 2p_{1/2} at 874 eV, with their shakeup satellite peaks, indicating the presence of Ni²⁺ oxidation state. Similarly, the Fe 2p spectrum can be

fitted into Fe 2p_{3/2} at 711 eV and Fe 2p_{1/2} at 726 eV with shakeup satellite peaks of Fe³⁺ oxidation state. Besides Ni²⁺ and Fe³⁺, very small portions of partially reduced nickel and iron species are also observed at lower binding energies. During solvothermal reaction, MNBI may decompose and release NH₃. Ni and Fe ions in the precursor solution could be partially reduced in such an atmosphere. At higher solvothermal temperature of 200 °C, NiFe alloy is formed with the same Ni-Fe/MNBI precursor solution (shown in previous section). Compared to NiFe-LDH prepared from urea hydrolysis, the binding energies of Ni 2p and Fe 2p in Ni_{0.67}Fe_{0.33}/C are shifted to higher values, which should be caused by the interaction between NiFe-LDH and carbon with a possible formation of Ni/Fe–O–C bond in the sample.^{178, 179} In O 1s spectrum (Fig. 6-10c), three peaks at 531 eV, 532.3 eV and 534 eV can be assigned to OH⁻, SO₄²⁻ and C=O bond, respectively. No lattice oxygen from metal oxide is observed.

Figure 6-10 (a-c) Ni 2p, Fe 2p and O 1s high resolution XPS spectra of Ni_{0.67}Fe_{0.33}/C; (d) comparison of Ni 2p and Fe 2p high resolution XPS spectra between Ni_{0.67}Fe_{0.33}/C and NiFe-LDH.

X-ray absorption spectroscopy (XAS) was used to confirm the local structure around Ni and Fe in the sample. The Ni and Fe *K*-edge X-ray absorption near edge structure (XANES) spectra of Ni_{0.67}Fe_{0.33}/C are compared with those of NiFe-LDH (Fig. 6-11). The peak intensities of both spectra are reduced. More significantly, the absorption edge

of Fe *K*-edge XANES spectrum in Ni_{0.67}Fe_{0.33}/C shifts to lower energy position. The change in Fe absorption edge can be clearly seen in the enlarged spectrum in Fig. 6-11c. The transfer of electron density from C to Fe is formed in this composite. A similar absorption edge shift of Co *K*-edge in Co₃O₄ and rGO composite was attributed to the charge transfer from Co to C and the formation of Co–O–C bond in the composite.²²⁴ A similar type of Ni(Fe)–O–C bond was also found in NiFe-LDH/CNT composite based on carbon *K*-edge absorption.¹⁷⁹ Corresponding Fourier transformed (FT) $k^3\chi(k)$ function of Ni and Fe extended X-ray absorption fine structure (EXAFS) spectra are shown in Fig. 6-11 d and e. The reduction in oscillation amplitude compared to NiFe-LDH and absence of high coordination shells confirms the structural change around Ni and Fe. The local structure parameters derived from curve fitting show that Ni_{0.67}Fe_{0.33}/C exhibits higher Debye-Waller factor around both Ni and Fe centers, indicating highly amorphous NiFe-LDH nanocrystals are formed in Ni_{0.67}Fe_{0.33}/C (Table 6-2). The amorphous nature of Ni_{0.67}Fe_{0.33}/C revealed by XAS analysis is consistent with XRD and Raman results. In a recent study, researchers found a similar trend in the EXAFS result of the exfoliated LDH by plasma etching which possesses multiple vacancies and dangling bonds.²²⁵ In this study, the formation of LDH nanocrystals is possibly resulted from the confined growth of NiFe-LDH surrounded by nanocarbon. Such amorphous structure leads to defective lattice and possibly coordinatively unsaturated metal centers which improve the intrinsic OER activity of NiFe-LDH.

Figure 6-11 (a, b) Ni and Fe K-edge X-ray absorption near edge structure (XANES) spectra of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ and NiFe-LDH as a reference; (c) enlarged Fe K-edge XANES spectrum; (d, e) Magnitude of k^3 -weighted Fourier transform of Ni and Fe edge of extended X-ray absorption fine structure (EXAFS) of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ and NiFe-LDH.

Table 6-2 Local structure parameters around Ni and Fe estimated by EXAFS analysis.

Sample	Shell	N^a	R (Å) ^b	σ^2 (10^{-3} Å ²) ^c
NiFe-LDH	Ni–O _{OH}	6	2.05 (± 0.02)	4.8 (± 0.5)
$\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$	Ni–O _{OH}	6	2.04(± 0.02)	6.2 (± 0.6)
NiFe-LDH	Fe–O _{OH}	6	2.03 (± 0.02)	1.7 (± 0.2)
$\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$	Fe–O _{OH}	6	1.99 (± 0.02)	5.8 (± 0.6)

a: N = coordination number; coordination number was fixed to 6 during EXAFS curve fitting in order to study the Debye-Waller factor difference between NiFe-LDH and $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$; b: R = distance between absorber and backscatter atoms; c: σ^2 = Debye-Waller factor.

6.3.3 Electrocatalytic activity and stability

The OER activity of the catalysts was measured in 1.0 M KOH electrolyte solution. Bare GC electrode was tested by cyclic voltammetry (CV) scan to confirm its clean surface. Before OER activity measurement, the catalyst was cycled for 5 runs in 0.1 – 0.7 V (vs Ag/AgCl) and aged in 1.0 M KOH solution for 6 h. CV scan was recorded at

20 mV/s after aging. The activity of Ni_{0.75}Fe_{0.25}/C is close but inferior to that of Ni_{0.67}Fe_{0.33}/C. To avoid overcrowding of the curves in the same figure, results for Ni_{0.75}Fe_{0.25}/C are not included. The emphasis is to compare the performances of Ni/C, Ni_{0.67}Fe_{0.33}/C and Ni_{0.5}Fe_{0.5}/C with distinct composition and activity. As shown in Fig. 6-12a, OER activity of Ni/C decreases after aging. The CV curve of Ni/C after aging is similar with that of β -Ni(OH)₂. Several recent studies have shown that the aging of α -Ni(OH)₂ in impure KOH solution results in the incorporation of Fe³⁺ cation into Ni(OH)₂ lattice to form NiFe-LDH with an improved OER activity.^{175, 185, 190} Our result shows that Fe³⁺ cation is not introduced into Ni/C catalyst to form NiFe-LDH during aging, which is probably due to restricted space or cation exchange flexibility in α -Ni(OH)₂ nanodomains which are weaved in the carbon matrix. Both Ni_{0.67}Fe_{0.33}/C and Ni_{0.5}Fe_{0.5}/C exhibit improved OER activities after activation. A drastic OER activity improvement is achieved over Ni_{0.67}Fe_{0.33}/C and a large redox couple due to oxidation/reduction of Ni(OH)₂/NiOOH is observed in the CV curve. It is worth noting that the peak area of the redox couple is larger than previously reported mixed Ni-Fe OER catalysts.¹⁷⁵⁻¹⁸³ This should be due to more abundantly exposed Ni atoms in our catalyst due to the fine blending of NiFe-LDH and carbon nanodomains.¹⁷⁷ LSV curves were obtained to compare the OER activity among different catalysts. Commercial Ir/C and NiFe-LDH prepared by urea hydrolysis was used as a comparison. As seen in Fig. 6-12b, the best activity is achieved over Ni_{0.67}Fe_{0.33}/C with a large Ni²⁺/Ni³⁺ oxidation peak. Ni/C exhibits the lowest activity which is in accordance with the CV analysis result. Ni_{0.5}Fe_{0.5}/C shows medium OER activity and the oxidation peak is not obvious. This result is consistent with previous report that excessive Fe in the structure can mute the redox activity of Ni.^{175, 190} Both Ni_{0.67}Fe_{0.33}/C and Ni_{0.5}Fe_{0.5}/C show superior OER activity than NiFe-LDH. The overpotentials required to achieve a current density of 10 mA/cm² and turnover frequencies (TOFs) at overpotential of 300 mV for different catalysts are compared in Fig. 6-12c. For Ni_{0.67}Fe_{0.33}/C, only 210 mV and 260 mV overpotential are required to drive OER at a current density of 10 mA/cm² and 100 mA/cm², respectively. Ni_{0.67}Fe_{0.33}/C even shows better OER activity than commercial Ir/C (280 mV @ 10 mA/cm²), confirming its potential to be used as an alternative to

Ir/C for OER. This activity is among the best of non-noble metal containing OER catalysts, as we discussed in Chapter 2. The OER activity of Ni_{0.5}Fe_{0.5}/C is close to that of Ir/C in small current density region and surpass Ir/C in large current density region. The TOF of Ni_{0.67}Fe_{0.33}/C can achieve as high as 0.3 s⁻¹ which is about 3 times of that of Ir/C (0.1 s⁻¹). To make a safe estimation, the TOF was calculated based on total metal content in the catalyst (Ni + Fe). It is challenging to directly compare this value with those in other works due to the variation in reaction condition, catalyst loading, and the quantification method of the active sites. But this value is among the best TOFs ever reported for mixed Ni-Fe based catalysts. Tafel slope is calculated from polarization curves recorded with a scan rate of 0.1 mV/s to reduce the capacitance effect. The results are listed in Fig. 6-12d. The lowest Tafel slope of 35.1 mV/Dec for Ni_{0.67}Fe_{0.33}/C indicates a fast OER dynamics. It is generally believed that the increase in ECSA contributes the most to enhanced electrochemical activity for nanostructured catalysts, especially nanosheets.^{226, 227} The ECSA values of various catalysts are shown in Fig. 6-12e. Indeed, Ni_{0.67}Fe_{0.33}/C with the optimal structural properties exhibits the highest ECSA (0.76 mF/cm²), which is several times higher than that of NiFe-LDH (0.21 mF/cm²). This confirms that ultrafine blending of NiFe-LDH and nanocarbon domains favors the exposure of active sites and thus leads to much enhanced activity. The electrochemical impedance spectra (EIS) were recorded at the overpotential of 250 mV (Fig. 6-12f). All ohmic resistances are similar and the absence of a 45° feature in the high frequency region indicates a fast charge transportation at the interface between GC electrode and catalyst film. The charge transfer resistances (R_{ct}) derived from the low frequency region in EIS follows the similar trend of OER activity for different catalyst. As R_{ct} is related to the electrocatalytic reaction kinetics at constant reactant concentration, the sharply decreased R_{ct} of Ni_{0.67}Fe_{0.33}/C shows a fast kinetics at the interface between catalyst film and electrolyte.⁵⁵

Figure 6-12 (a) CV curves of the electrocatalysts before (dotted line) and after (solid line) activation, scan rate: 20 mV/s; (b) polarization curves of the $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ electrocatalysts, Ir/C and NiFe-LDH, scan rate: 5 mV/s; (c) calculated TOFs from current density at η of 300 mV and overpotential at j of $10 \text{ mA}/\text{cm}^2$; (d) Tafel slopes of $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ electrocatalysts and Ir/C; (e) ECSA of $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ electrocatalysts and NiFe-LDH; (f) EIS of $\text{Ni}_x\text{Fe}_{1-x}/\text{C}$ electrocatalysts.

Besides high OER activity, $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ catalyst exhibits a good stability. The stability test was conducted with $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ coated on both GC and carbon fiber paper (CFP) electrodes. The loading of the catalyst on CFP reduces the mass loss during the stability test. A chronopotentiometry test was used to check the stability of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ on CFP electrode. To maintain a current density of $40 \text{ mA}/\text{cm}^2$, only 10 mV overpotential increase was encountered over 28 h, corresponding to an activity loss of less than 5%. The polarization curve was recorded before and after stability test. As shown in Fig. 6-13b, the polarization curves are almost the same at low overpotential region while a slight activity loss can be seen at the high overpotential region. Stability test on GC electrode was conducted using CV cycling method to reduce the mass loss as much as possible. The current density at 0.6 V vs Ag/AgCl for each cycle was used to determine the catalyst stability. After 2000 cycles, the current density is found nearly unchanged with a slight decrease from $100 \text{ mA}/\text{cm}^2$ to $95 \text{ mA}/\text{cm}^2$. The polarization curves are similar before and after CV cycling. Only a slight decrease of OER current

in the high overpotential region is observed. The $\text{Ni}^{2+}/\text{Ni}^{3+}$ oxidation peak even increases after cycling, indicating more redox sites are exposed after CV cycling. In summary, durability tests on both CPF and GC electrodes confirm the good stability of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ catalyst.

Figure 6-13 (a) Chronopotentiometry test for $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ on CPF electrode; (b) polarization curves of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ on CPF before and after test in (a); (c) CV cycling test for $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ on GC electrode; and (d) polarization curves of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ before and after test in (c).

6.3.4 Characterization of catalyst after OER durability test

The $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ catalyst after OER stability test was examined. The TEM image shows the nanosheet morphology is retained after OER test (Fig. 6-14a). The ring-like patterns in SAED dim while bright dots appear, indicating that the crystallinity of NiFe-LDH is improved after OER test. Lattice fringes with distances of 2.4 Å and 2.6 Å corresponding to (015) and (012) facets of NiFe-LDH are observed in HRTEM image. The amorphous components are still present in the catalyst (Fig. 6-14b). Ni, Fe, O and C remains homogeneously distributed as evidenced in elemental mapping.

Figure 6-14 (a) TEM image of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER, inset: SAED; (b) HRTEM image of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER; (c) elemental mapping result for $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER.

The XRD pattern of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER test (Fig. 6-15a) shows that the sample is still quite amorphous except some broad peaks around 62° for (110) and (113) lattice appeared. This result is consistent with HRTEM observation. Raman spectrum in the range of $1000\text{--}2000\text{ cm}^{-1}$ becomes nearly featureless after OER durability test. However, the elemental analysis shows that the weight percentage of carbon is only slightly reduced from 6.7% to 5.0% after OER test (Table 6-1). Ferrari reported that Raman spectrum of polymeric amorphous hydrogenated carbon can only be obtained with UV excitation.²²² During OER in highly alkaline electrolyte, N-doped graphitic carbon may be converted to such hydrogenated carbon. Besides, FTIR spectrum was obtained and shown in Fig. 6-15c. Two peaks at 2850 and 2924 cm^{-1} due to the stretching vibration of the $-\text{CH}$ group and one peak at 1385 cm^{-1} originated from symmetric deformation of $-\text{CH}_3$ group become prominent after OER, supporting the

formation of more defective hydrogenated carbon. The strong peaks in the range of 1100-1150 cm^{-1} disappear after OER test, indicating the removal of SO_4^{2-} . The peak at 2200 cm^{-1} observed in $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ before reaction could be assigned to the stretching vibration of $\text{C}\equiv\text{N}$ triple bond (nitrile).²²⁸ Such a bond is unstable in oxidation current under OER condition and it is not observed in the sample after OER test. ICP analysis also confirms that Ni/Fe ratio in the catalyst remains the same after OER test (Table 6-1). No significant mass loss was found after OER test.

Figure 6-15 (a) XRD pattern and (b) Raman spectrum of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER; (c) comparison of FTIR spectra between $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ before and after OER; (d) C 1s high resolution XPS spectrum of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER.

Chemical structure of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER was further studied using Raman spectroscopy, XPS and XAS techniques. Two bands at 470 and 545 cm^{-1} are clearly seen in the Raman spectrum (Fig. 6-16a). These bands match well with previously reported Ni-O vibration in NiOOH , indicating that Ni redox center undergoes $\text{Ni}^{2+}/\text{Ni}^{3+}$ transformation during OER test.^{175, 183} A new peak assigned to NiOOH in Ni 2p spectrum is observed at a slightly higher binding energy. Fe 2p spectrum is almost the same with that obtained before OER test. Lattice oxygen is found in O 1s spectrum,

corresponding to the formation of oxyhydroxide. In addition, the shift of absorption edge of Ni *K*-edge XANES to higher energy position indicates that Ni centers are partially oxidized while Fe *K*-edge XANES remains almost unchanged. The energy shift of 0.8 eV is slightly smaller than previously reported 1.5 eV for Ni atom changing from oxidation state +2 to +3, indicating a mixture of Ni^{2+} and Ni^{3+} in the sample after OER. Despite some controversial conclusions about the oxidation states of Ni and Fe and the origin of active sites in the literature,^{176, 177, 183, 229} our study confirms that Ni^{2+} , Ni^{3+} and Fe^{3+} are present in the catalyst after OER test, which is similar with those observed in NiFe/C catalyst.²² In addition, more pronounced metal-carbon interaction is evidenced from the spectrum of C 1s where the relative intensity of the peak at 283.2 eV after OER test becomes obviously larger, as shown in Fig. 6-15c. These results suggest that $\text{Ni}^{2+/3+}\text{Fe}^{3+}$ -LDH and oxyhydroxide acts as the catalytic center while the surrounding nanocarbon facilitates charge transfer and promotes the activity by altering the electronic structure of metal centers.

Figure 6-16 (a) Raman spectrum in the range of 200-1000 cm^{-1} ; (b, c, d) Ni 2p, Fe 2p and O 1s high resolution XPS spectra; (e) Ni K-edge XANES; and (f) Fe K-edge XANES of $\text{Ni}_{0.67}\text{Fe}_{0.33}/\text{C}$ after OER durability test.

6.4 Conclusions

In this work, we have developed a new synthetic method to prepare amorphous and nanosized NiFe-LDH interconnected with carbon nanodomains in an ultrathin nanosheet as a highly efficient OER electrocatalyst. Different from the solid-state annealing process, the interconnected NiFe-LDH and carbon nanodomains are *in situ* formed in solution starting from the metal-ligand molecular precursor. During the nucleation of NiFe-LDH, the ligand (MNBI) decomposes and transforms to amorphous carbon with graphitic nanodomains. Amorphous carbon binds NiFe-LDH and constructs the nanosheet morphology. The incorporation of carbon nanodomain not only improves the electronic property of this composite but also enhances the exposure of surface redox sites. These factors together contribute to the harnessing of the high intrinsic activity of NiFe-LDH towards a much improved OER activity with good durability. The combined material characterization results reveal the presence of $\text{Ni}^{2+/3+}\text{Fe}^{3+}$ -LDH and oxyhydroxide as the active species under OER condition. The use of metal-ligand molecular precursor for one-pot synthesis of strongly coupled metal-carbon hybrid under mild condition is believed a promising strategy for preparation of high-performance catalysts.

CHAPTER 7 CONCLUSIONS AND OUTLOOK

7.1 Conclusions

Water splitting towards H_2 evolution is considered to be an economical and environmentally friendly approach to convert clean energy like solar energy and wind energy to chemical fuels. During recent years, extensive researches have been conducted for the development of low-cost and efficient catalysts for water splitting which contains earth abundant elements only. The improvement in this area would lead to practical application of water splitting. The research work present in this thesis contributes to this project and focused on the development of novel synthetic approach to engineer the interface between catalysts and semiconductor/carbon material for the construction of efficient H_2 evolution systems.

First, MoP particulates were synthesized and dispersed into nanosized particles using probe sonicator. Nanosized MoP particles exhibit improved HER activity compared to its bulk form due to the small particle size with increased surface area and surface active sites. The good dispersion of CdS QDs in solution allows them to be trapped in the cluster of MoP nanoparticles, leading to the formation of an intimate interface between CdS QDs and MoP. Efficient charge transfer from CdS QDs to MoP and metallic property of MoP with good HER activity contributes to the efficient and stable H_2 evolution.

Next, ZnO was used as a support material to disperse and stabilize Co_xP nanoparticles on its surface. The interface between the oppositely charged metal oxide and CdS QDs is formed via electrostatic interaction. CdS QDs is adsorbed on the surface of ZnO and a thin layer is formed such that light absorption is not affected by the Co_xP/ZnO . Besides, the band structure alignment between ZnO and CdS QDs facilitates the charge transfer from CdS QDs to ZnO. Apparent quantum efficiency of this system can reach as high as 66% at 420 nm and no activity loss is observed for this system after 144 h photocatalytic reaction.

Catalyst/carbon composites are believed to afford higher electrocatalytic activity as large surface area can be achieved from mesoporous carbon materials. As an example,

CoP is supported on N, P co-doped carbon nanotube which is exposed to electrolyte after removal of less stable Co nanoparticles during acid leaching. Catalysts exhibit a high HER activity close to that of Pt and a relatively low Tafel slope of 55 mV/Dec. This study is a clear evidence that the chemical binding state at the interface between catalysts and carbon material could be efficient active sites for water splitting.

Lastly, we developed a novel synthetic approach to prepare an ultrafine blending of amorphous NiFe-LDH nanocrystals (< 5 nm) and N doped carbon nanodomains as an efficient and stable OER electrocatalyst. The strong interaction between metal centers and carbon leads to the local electronic structure modification, which results in the increased active sites and enhanced electrochemical active surface area. Such improvements and enhanced electrical property contribute to the improved OER activity with a good stability. This study provides evidence that, besides design catalyst composition to optimize the activity of a catalyst, we are able to harness the intrinsic high activity of the catalyst by optimizing the synthetic procedure to prepare a desired composite.

7.2 Outlook

Although significant progress has been made from the work in this thesis, there are still significant challenges to be solved before practical application of water splitting can be widely utilized. Firstly, development of low-cost and efficient catalysts is still unsatisfactory. Secondly, the work in this thesis is mainly focused on half reactions while the practical usage calls for overall water splitting to evolve H₂ and O₂ simultaneously with a ratio of 2:1. Thirdly, although H₂ is considered a promising energy carrier, the storage of H₂ remains a challenge. It is more desirable to store clean energy in liquid forms like methanol and ethanol. Thus, the development of catalysts for CO₂ reduction would be pursued. Several research directions are suggested and elaborated in the following section.

(1) Preparation of catalyst/carbon nanocomposite thin film

As stated earlier, electrocatalysts can be deposited directly on the surface of PV module to construct the wireless photoelectrochemical water splitting cell. As catalyst/carbon

nanocomposite exhibits better electrocatalytic performance than pristine catalyst, we need to develop novel synthetic method to deposit catalyst/carbon nanocomposite using solution based method while the optical property of PV shall not be affected by the thin film. To our knowledge, there lacks such kind of research. We believe the breakthrough in this area would open new possibilities for practical application of photoelectrochemical water splitting. Besides, even though great efforts and progress have been made to develop high-performance robust nanocomposites for HER and OER, the detailed mechanism for improved activity is unraveled. The mechanism study using advanced characterization techniques and theoretical calculations could be conducted in the future and would be helpful for us to develop efficient electrocatalysts.

(2) Application of MOF materials in water splitting

Taking NiFe-LDH as an example, the introduction of Fe in Ni(OH)₂ crystal structure leads to the cathodic shift of Ni^{2+/3+} redox peak. The peak disappears after the addition of excess Fe and a large onset potential is observed. These results indicate there is limitation on modification of elemental composition for improved OER activity. Alternatively, we may use MOF materials as electrocatalyst to overcome these disadvantages. The chemical state and coordination environment around metal ions could be tuned by modification of the ligand molecule. Therefore, we may be able to obtain a desired redox potential as what has been done on homogeneous catalysts. Besides, the highly porous structure and atomic dispersion of catalytic sties could result in highly improved ECSA. An enhanced electrocatalytic activity might be expected. Another main disadvantage of using MOFs as electrocatalysts is that most MOFs are not conductive. Recent researches show that conductive MOFs with electrical conductivity greater than 5000 S/m can be synthesized using suitable organic ligand (2,3,6,7,10,11-hexaiminotriphenylene) and used as active electrode in electrochemical double layer capacitor.²³⁰ This kind of conductive and highly porous materials might be developed as efficient electrocatalysts in water splitting.

(3) Overall water splitting

To achieve overall water splitting, highly efficient HER and OER catalysts are required and they need to be efficient and stable in the same electrolyte. Some metal phosphides

have been reported as bifunctional catalyst that can drive overall water splitting when used as both the cathode and the anode. For photocatalytic overall water splitting, Z-scheme system may be promising. The noble metal free catalysts can be used as co-catalysts in the Z scheme process to construct low cost overall water splitting system.

(4) CO₂ reduction

As discussed before, it would be more promising if we can convert clean energy to liquid fuels like methanol and ethanol. The research on photocatalytic CO₂ reduction toward solar fuel production is still at its early stage. The selectivity of product is an important issue in CO₂ reduction. By adopting the synthetic method developed in this thesis, we may develop efficient catalysts for CO₂ reduction with high selectivity for desired products.

LIST OF PUBLICATION

1. Yin, S. M.; Tu, W. G.; Sheng, Y.; Du, Y.; Kraft, M.; Borgna, A.; Xu, R. Highly efficient oxygen evolution catalyst consisting of interconnected nickel-iron layered double hydroxide and carbon nanodomains, *Adv. Mater.*, **2017**, in press.
2. Yin, S. M.; Han, J. Y.; Zou, Y. J.; Zhou, T. H.; Xu, R. A highly efficient noble metal free photocatalytic hydrogen evolution system containing MoP and CdS quantum dots, *Nanoscale*, **2016**, 8, 14438-14447.
3. Yin, S. M.; Han, J. Y.; Zhou, T. H.; Xu, R. Recent progress in g-C₃N₄ based low cost photocatalytic system: activity enhancement and emerging applications, *Cat. Sci. Technol.*, **2015**, 5, 5048 – 5061.
4. Nie, L. N.; Xiong, W. W.; Li, P. Z.; Han, J. Y.; Zhang, G. D.; Yin, S. M.; Zhao, Y. L.; Xu, R.; Zhang, Q. C. Surfactant-thermal method to prepare two novel two-dimensional Mn-Sb-S compounds for photocatalytic applications, *J. Solid. State. Chem.*, **2014**, 220, 118-123.
5. Hong, J. D.; Yin, S. M.; Pan, Y. X.; Han, J. Y.; Zhou, T. H.; Xu, R. Porous carbon nitride nanosheets for enhanced photocatalytic activities, *Nanoscale*, **2014**, 6, 14984-14990.
6. Han, J. Y.; Wang, D. P.; Du, Y. H.; Xi, S. B.; Hong, J. D.; Yin, S. M.; Chen, Z.; Zhou, T. H.; Xu, R. Metal-organic framework immobilized cobalt oxide nanoparticles for efficient photocatalytic water oxidation, *J. Mater. Chem. A*, **2015**, 3, 20607 – 20613.
7. Dou, J.; Zhang, B. W.; Liu, H.; Hong, J. D.; Yin, S. M.; Huang, Y. Z.; Xu, R. Carbon supported Pt₉Sn₁ nanoparticles as an efficient nanocatalyst for glycerol oxidation, *Appl. Cat. B-Env.*, **2016**, 180, 78-85.
8. Han, J. Y.; Wang, D. P.; Du, Y. H.; Xi, S. B.; Chen, Z.; Yin, S. M.; Zhou, T. H.; Xu, R. Polyoxometalate immobilized in MIL-101(Cr) as an efficient catalyst for water oxidation, *Appl. Cat. A-Gen.*, **2016**, 521, 83-89.
9. Dou, J.; Yin, S. M.; Chong, J. Y.; Zhang, B. W.; Han, J. Y.; Huang, Y. Z.; Xu, R. Carbon spheres anchored Co₃O₄ nanoclusters as an efficient catalyst for dye degradation, *Appl. Cat. A-Gen.*, **2016**, 513, 106-115.

10. Zhou, T. H.; Du, Y. H.; Yin, S. M.; Tian, X. Z.; Yang, H. B.; Wang, X.; Liu, B.; Zheng, H. M.; Qiao, S. Z.; Xu, R. Nitrogen-doped cobalt phosphate @ nanocarbon hybrids for efficient electrocatalytic oxygen reduction, *Energy Environ. Sci.*, **2016**, 9, 2563-2570.
11. Wang, Y. B.; Xie, Y.; Yin, S. M.; Xu, R.; Lau, R. Municipal solid waste incineration bottom ash supported cobalt oxide catalysts for dye degradation using sulfate radical, *J. Taiwan. Inst. Chem. E.*, 2016, **68**, 246-253.
12. Li, X.; Wang, Y. B.; Xie, Y.; Yin, S. M.; Lau, R.; Xu, R. CdS nanoparticles loaded on porous poly-melamine-formaldehyde polymer for photocatalytic dye degradation, *Res. Chem. Intermed.*, **2017**, accepted.
13. Wan, D. Y.; Zhao, Y. L.; Cai, Y.; Asmara, T. C.; Huang, Z.; Chen, J. Q.; Hong, J.; Yin, S. M.; Nelson, C. T.; Motapothula, M. R.; Yan, B. X.; Xiang, D.; Chi, X.; Zheng, H.; Chen, W.; Xu, R.; Ariando; Rusydi, A.; Monor, A. M.; Breese, B. H.; Sherburne, M.; Asta, M.; Xu, Q. H.; Venkatesan, T. Electron transport and visible light absorption in a plasmonic photocatalyst based on strontium niobate. *Nature Commun.*, **2017**, 8, 15070.
14. Xu, Y.; Tu, W. G.; Yin, S. M.; Kraft, M.; Zhang, Q. C.; Xu, R. Self-template synthesis of CdS/NiS_x heterostructured nanohybrids for efficient Photocatalytic Hydrogen Evolution, *Dalton Trans.*, **2017**, doi:10.1039/C7DT00842B.
15. Li, C. M.; Du, Y. H.; Wang, D. P.; Yin, S. M.; Tu, W. G.; Chen, Z.; Kraft, M.; Chen, G.; Xu, R. Unique P–Co–N surface bonding states constructed on g-C₃N₄ nanosheets for drastically enhanced photocatalytic activity of H₂ evolution, *Adv. Funct. Mater.*, **2017**, 27, 1604328.
16. Xu, Y.; Tu, W. G.; Zhang, B. W.; Yin, S. M.; Huang, Y. Z.; Kraft, M.; Xu, R. Nickel nanoparticles encapsulated in few-layer nitrogen-doped graphene derived from metal-organic frameworks as efficient bifunctional electrocatalysts for overall water splitting, *Adv. Mater.*, **2017**, 29, 1605957.
17. Tu, W. G.; Xu, Y.; Wang, J. J.; Zhang, B. W.; Zhou, T. H.; Yin, S. M.; Wu, S. Y.; Li, C. M.; Huang, Y. Z.; Zhou, Y.; Zou, Z. G.; Robertson, J.; Kraft, M.; Xu, R. Investigating the role of tunable nitrogen vacancies in graphitic carbon nitride nanosheets for efficient

visible-light-driven H₂ evolution and CO₂ reduction, *ACS Sus. Chem. Eng.*, **2017**, doi: 10.1021/acssuschemeng.7b01477.

18. Zhou, T. H.; Du, Y. H.; Wang, D. P.; Yin, S. M.; Tu, W. G.; Chen, Z.; Borgna, A.; Xu, R. Phosphonate-based metal-organic framework derived Co–P–C hybrid as an efficient electrocatalyst for oxygen evolution reaction, *ACS Catal.*, **2017**, doi: 10.1021/acscatal.7b00937.

REFERENCE

- (1) Hammarström, L.; Hammes-Schiffer, S. *Acc. Chem. Res.* **2009**, 42, 1859.
- (2) Turner, J. A. *Science* **2004**, 305, 972.
- (3) Norton, B. In *Harnessing Solar Heat*; Springer, 2014; Vol. 18.
- (4) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. *Prog. Photovolt: Res. Appl.* **2016**, 24, 905.
- (5) Phutuangrat, A.; Ham, D. J.; Thongtem, S.; Lee, J. S. *Electrochem. Commun.* **2009**, 11, 1740.
- (6) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. *Chem. Rev.* **2010**, 110, 6446.
- (7) Moniz, S. J. A.; Shevlin, S. A.; Martin, D. J.; Guo, Z.; Tang, J. *Energy Environ. Sci.* **2015**, 8, 731.
- (8) Yang, J.; Wang, D.; Han, H.; Li, C. *Acc. Chem. Res.* **2013**, 46, 1900.
- (9) Wang, H.; Dai, H. *Chem. Soc. Rev.* **2013**, 42, 3088.
- (10) Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, 38, 253.
- (11) Fujishima, A.; Honda, K. *Nature* **1972**, 238, 37.
- (12) Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, 103, 4685.
- (13) Li, R.; Weng, Y.; Zhou, X.; Wang, X.; Mi, Y.; Chong, R.; Han, H.; Li, C. *Energy Environ. Sci.* **2015**, 8, 2377.
- (14) Domen, K.; Naito, S.; Onishi T.; Tamaru, K. *J. Phys. Chem.* **1982**, 86, 3657.
- (15) Yamashita, Y.; Yoshida, K.; Kakihana, M.; Uchida, S.; Sato, T. *Chem. Mater.* **1999**, 11, 61.
- (16) Kim, J.; Hwang, D. W.; Kim, H. G.; Bae, S. W.; Ji, S. M.; Lee, J. S. *Chem. Commun.* **2002**, 21, 2488.
- (17) Zou, J.; Liu, C.; Zhang, Y. *Langmuir* **2006**, 22, 2334.
- (18) Wang, X.; Xu, Q.; Li, M.; Shen, S.; Wang, X.; Wang, Y.; Feng, Z.; Shi, J.; Han, H.; Li, C. *Angew. Chem. Int. Ed.* **2012**, 51, 13089.
- (19) Chen, X.; Yu, T.; Fan, X.; Zhang, H.; Li, Z.; Ye, J. Zou, Z. *Appl. Surf. Sci.* **2007**, 253, 8500.

- (20) Takahara, Y.; Kondo, J.; Takata, T.; Lu, D.; Domen, K. *Chem. Mater.* **2001**, 13, 1194.
- (21) Yuan, Y.; Zhang, X.; Liu, L.; Jiang, X.; Lv, J.; Li, Z.; Zou, Z. *Int. J. Hydrogen Energy* **2008**, 33, 5941.
- (22) Uno, M.; Kosuga, A.; Okui, M.; Horisaka, K.; Muta, H.; Kurosaki, K.; Yamanaka, S. *J. Alloys Compd.* **2006**, 420, 291.
- (23) Domen, K.; Kudo, A.; Shibata, M.; Tanaka, A.; Maruya, K.; Onishi, T. *J. Chem. Soc. Chem. Commun.* **1986**, 23, 1706.
- (24) Chen, D.; Ye, J. *Chem. Mater.* **2009**, 21, 2327.
- (25) Kato, H.; Kudo, A. *J. Phys. Chem. B* **2001**, 105, 4285.
- (26) Kato, H.; Kudo, A. *Catal. Today*, **2003**, 78, 561.
- (27) Kato, H.; Asakura, k.; Kudo, A. *J. Am. Chem. Soc.* **2003**, 125, 3082.
- (28) Kōta, R.; Ishii, T.; Kato, H.; Kudo, A.; *J. Phys. Chem. B* **2004**, 108, 8992.
- (29) Liu, G.; Hua, G.; Wang, X.; Cheng, L.; Pan, J.; Gao, Q.; Cheng, H. *J. Am. Chem. Soc.* **2009**, 131, 12868.
- (30) Wang, Y.; Wang, Y.; Meng, Y.; Ding, H.; Shan, Y.; Zhao, X.; Tang, X. *J. Phys. Chem. C* **2008**, 112, 6620.
- (31) He, Z.; Xu, X.; Song, S.; Xie, L.; Tu, J.; Chen, J.; Yan, B. *J. Phys. Chem. C* **2008**, 112, 16431.
- (32) Long, R.; English, N. *J. Chem. Phys. Lett.* **2009**, 478, 175.
- (33) Li, J.; Xu, J.; Dai, W.; Li, H.; Fan, K. *Appl. Catal. B* **2008**, 82, 233.
- (34) Hara, M.; Kondo, T.; Komoda, M.; Ikeda, S.; Shinobara, K.; Tanaka, A.; Kondo, J.; Domen, K. *Chem. Commun.* **1998**, 357.
- (35) Sivula, K.; Le Formal, F.; Grätzel, M.; *ChemSusChem* **2011**, 4, 432.
- (36) Wang, G.; Ling, Y.; Wang, H.; Yang, X.; Wang, C.; Zhang, J.; Li, Y. *Energy Environ. Sci.* **2012**, 5, 6180.
- (37) Kim, T. W.; Choi, K. S. *Science*, **2014**, 343, 990.
- (38) Yi, Z.; Ye, J.; Kikugawa, N.; Kako, T.; Ouyang, S.; Stuart-Williams, H.; Yang, H.; Cao, J.; Luo, W.; Li, Z.; Liu, Y.; Withers, R. L. *Nature Mater.* **2010**, 9, 559.
- (39) Böhler, N.; Meier, K.; Reber, J. F. *J. Phys. Chem.* **1984**, 88, 3261.

- (40) Youn, H.; Baral, S.; Fendler, J. H. *J. Phys. Chem.* **1988**, 92, 6320.
- (41) Yang, J.; Yan, H.; Wang, X.; Wen, F.; Wang, Z.; Fan, D.; Shi, J.; Li, C. *J. Catal.* **2012**, 290, 151.
- (42) Liu, M.; Chen, Y.; Su, J.; Shi, J.; Wang, X.; Guo, L. *Nature Energy* **2016**, 1, 16151.
- (43) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. *Science* **2012**, 338, 1321.
- (44) Wu, L.; Chen, B.; Li, Z.; Tung, C. *Acc. Chem. Res.* **2014**, 47, 2177.
- (45) Pan, Y.; Zhuang, H.; Hong, J.; Fang, Z.; Liu, H.; Liu, B.; Huang, Y.; Xu, R. *ChemSusChem* **2014**, 7, 2537.
- (46) Fang, Z.; Wang, Y.; Song, J.; Sun, Y.; Zhou, J.; Xu, R.; Duan, H. *Nanoscale* **2013**, 5, 9830.
- (47) Wang, J.; Li, Z.; Li, X.; Fan, X.; Meng, Q.; Yu, S.; Li, C.; Li, J.; Tung, C.; Wu, L. *ChemSusChem* **2014**, 7, 1468.
- (48) Li, Y.; Takata, T.; Cha, D.; Takanabe, K.; Minegishi, T.; Kubota, J.; Domen, K. *Adv. Mater.* **2013**, 25, 125.
- (49) Ma, S. S. K.; Hisatomi, T.; Maeda, K.; Moriya, Y.; Domen, K. *J. Am. Chem. Soc.* **2012**, 134, 19993.
- (50) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. *Nat. Mater.* **2009**, 8, 76.
- (51) Wang, X.; Maeda, K.; Chen, X.; Takanabe, K.; Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. *J. Am. Chem. Soc.* **2009**, 131, 1680.
- (52) Sun, J.; Zhang, J.; Zhang, M.; Antonietti, M.; Fu, X.; Wang, X. *Nat. Commun.* **2012**, 3, 1139.
- (53) Zhang, M.; Wang, X. *Energy Environ. Sci.* **2014**, 7, 1902.
- (54) Niu, P.; Zhang, L.; Liu, G.; Cheng, H. *Adv. Funct. Mater.* **2012**, 22, 4763.
- (55) Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *Nature* **2006**, 440, 295.
- (56) Maeda, K.; Teramura, K.; Domen, K. *J. Catal.* **2008**, 254, 198.
- (57) Maeda, K.; Domen, K. *Chem. Mater.* **2010**, 22, 612.
- (58) Abe, R.; Sayama, K.; Domen, K.; Arakawa, H. *Chem. Phys. Lett.* **2001**, 344, 339.

- (59) Maeda, K.; Higashi, M.; Lu, D.; Abe, R.; Domen, K. *J. Am. Chem. Soc.* **2010**, 132, 5858.
- (60) Iwashina, K.; Iwase, A.; Ng, Y. H.; Amal, R.; Kudo, A. *J. Am. Chem. Soc.* **2015**, 137, 604.
- (61) Ran, J.; Zhang, J.; Yu, J.; Jaroniec, M.; Qiao, S. *Chem. Soc. Rev.* **2014**, 43, 7787.
- (62) Tran, R. D.; Xi, L.; Batabyal, S. K.; Wong, L. H.; Barber, J.; Loo, J. S. C. *Phys. Chem. Chem. Phys.* **2012**, 14, 11596.
- (63) Huang, L.; Wang, X.; Yang, J.; Liu, G.; Han, J.; Li, C. *J. Phys. Chem. C* **2013**, 117, 11584.
- (64) Lin, H.; Yang, H.; Wang, W. *Catal. Today* **2011**, 174, 106.
- (65) Agegnehu, A. K.; Pan, C.; Rick, J.; Lee, J. F.; Su, W. N.; Hwang, B. J. *J. Mater. Chem.* **2012**, 22, 13849.
- (66) Foo, W. J.; Zhang, C.; Ho, G. W.; *Nanoscale* **2013**, 5, 759.
- (67) Sreethawong, T.; Suzuki, Y.; Yoshikawa, S. *Int. J. Hydrogen Energy* **2005**, 30, 1053.
- (68) Choi, J.; Ryu, S. Y.; Balcerski, W.; Lee, T. K.; Hoffmann, M. R. *J. Mater. Chem.* **2008**, 18, 2371.
- (69) Kumar, D. P.; Shankar, M. V.; Kumari, M. M.; Sadanandam, G.; Srinivas, B.; Durgakumari, V. *Chem. Commun.* **2013**, 49, 9443.
- (70) Wender, H.; Gonçalves, R. V.; Dias, C. S. B.; Zapata, M. J. M.; Zagonel, L. F.; Mendonça, E. C.; Teixeira, S. R.; Garcia, F. *Nanoscale* **2013**, 5, 9310.
- (71) Yu, J.; Wang, S.; Cheng, B.; Lin, Z.; Huang, F. *Catal. Sci. Technol.* **2013**, 3, 1782.
- (72) Yu, J.; Ran, J. R. *Energy Environ. Sci.* **2011**, 4, 1364.
- (73) Tabata, M.; Maeda, K.; Ishihara, T.; Minegishi, T.; Takata, T.; Domen, K. *J. Phys. Chem. C* **2010**, 114, 11215.
- (74) Wang, J.; Li, B.; Chen, J.; Li, N.; Zheng, J.; Zhao, J.; Zhu, Z. *Appl. Surf. Sci.* **2012**, 259, 118.
- (75) Zhang, W.; Wang, Y.; Wang, Z.; Zhong, Z.; Xu, R. *Chem. Commun.* **2010**, 46, 7631.
- (76) Zhang, J.; Xu, Q.; Qiao, S.; Yu, J. *ChemSusChem* **2013**, 6, 2009.
- (77) Zong, X.; Yan, H.; Wu, G.; Ma, G.; Wen, F.; Wang, L.; Li, C. *J. Am. Chem. Soc.* **2008**, 130, 7176.

- (78) Tang, M. L.; Grauer, D. C.; Lassalle-Kaiser, B.; Yachandra, V. K.; Amirav, L.; Yano, J.; Long, J. R.; Alivisatos, A. P. *Angew. Chem. Int. Ed.* **2011**, 50, 10203.
- (79) Zong, X. Han, J.; Ma, G.; Yan, H.; Wu, G.; Li, C. *J. Phys. Chem. C* **2011**, 115, 12202.
- (80) Nguyen, M.; Tran, P. D.; Pramana, S. S.; Lee, R. L.; Batabyal, S. K.; Mathews, N.; Wong, L. H.; Grätzel, M. *Nanoscale* **2013**, 5, 1479.
- (81) Jang, J. S.; Ham, D. J.; Lakshminarasimhan, N.; Choi, W. Y.; Lee, J. S. *Appl. Catal. A* **2008**, 346, 149.
- (82) Garcia-Esparza, A. T.; Cha, D.; Qu, Y.; Kubota, J.; Domen, K.; Takanabe, T. *ChemSusChem* **2013**, 6, 168.
- (83) Stern, L.; Feng, L.; Song, F.; Hu, X. *Energy. Environ. Sci.* **2015**, 8, 2347.
- (84) Popczun, E. J.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E. *Angew. Chem. Int. Ed.* **2014**, 53, 5427.
- (85) Callejas, J. F.; McEnaney, J. M.; Read, C. G.; Crompton, J. C.; Biacchi, A. J.; Popczun, E. J.; Gordon, T. R.; Lewis, N. S.; Schaak, R. E. *ACS Nano* **2014**, 8, 11101.
- (86) Xiao, P.; Alam Sk, M.; Thia, L.; Ge, X.; Lim, R. J.; Wang, J.; Lim, K. H.; Wang, X. *Energy Environ. Sci.* **2014**, 7, 2624.
- (87) Tian, J.; Cheng, N.; Liu, Q.; Xing, W.; Sun, X.; *Angew. Chem. Int. Ed.* **2015**, 54, 5493.
- (88) Cao, S.; Chen, Y.; Wang, C.; He, P.; Fu, W. *Chem. Commun.* **2014**, 50, 10427.
- (89) Cao, S.; Chen, Y.; Hou, C.; Lv, X.; Fu, W. *J. Mater. Chem. A* **2015**, 3, 6096.
- (90) Cao, S.; Chen, Y.; Wang, C.; Lv, X.; Fu, W. *Chem. Commun.* **2015**, 51, 8708.
- (91) Sun, Z.; Zheng, H.; Li, J.; Du, P. *Energy Environ. Sci.* **2015**, 8, 2668.
- (92) Sun, Z.; Yue, Q.; Li, J.; Xu, J.; Zheng, H.; Du, P. *J. Mater. Chem. A* **2015**, 3, 10243.
- (93) Chang, K.; Mei, Z.; Wang, T.; Kang, Q.; Ouyang, S.; Ye, J. *ACS Nano* **2014**, 8, 7078.
- (94) Chen, G.; Li, D.; Li, F.; Fan, Y.; Zhao, H.; Luo, Y.; Yu, R.; Meng, Q. *Appl. Catal. A* **2012**, 443, 138.
- (95) Li, R.; Chen, Z.; Zhao, W.; Zhang, F.; Maeda, K.; Huang, B.; Shen, S.; Domen, K.; Li, C. *J. Phys. Chem. C* **2013**, 117, 376.

- (96) Zhang, J.; Grzelczak, M.; Hou, Y.; Maeda, K.; Domen, K.; Fu, X.; Antonietti, M.; Wang, X. *Chem. Sci.* **2012**, 3, 443.
- (97) Wang, Y.; Wang, Y.; Jiang, R.; Xu, R. *Ind. Eng. Chem. Res.* **2012**, 51, 9945.
- (98) Liu, L.; Li, Z.; Zou, W.; Gu, X.; Deng, Y.; Gao, F.; Tang, C.; Dong, L. *ACS Catal.* **2013**, 3, 2052.
- (99) Zhang, F.; Yamakata, A.; Maeda, K.; Moriya, Y.; Takata, T.; Kubota, J.; Teshima, K.; Oishi, S.; Domen, K. *J. Am. Chem. Soc.* **2012**, 134, 8348.
- (100) Kanan, M. W.; Nocera, D. G. *Science*, **2008**, 321, 1072.
- (101) Zou, X.; Zhang, Y. *Chem. Soc. Rev.* **2015**, 44, 5148.
- (102) Levy, R. B.; Boudart, M. *Science* **1973**, 181, 547.
- (103) Vrubel, H.; Hu, X. *Angew. Chem., Int. Ed.* **2012**, 51, 12703.
- (104) Wan, C.; Regmi, Y. N.; Leonard, B. M. *Angew. Chem., Int. Ed.* **2014**, 53, 6407.
- (105) Liao, L.; Wang, S.; Xiao, J.; Bian, X.; Zhang, Y.; Scanlon, M. D.; Hu, X.; Tang, Y.; Liu, B.; Girault, H. H. *Energy Environ. Sci.* **2014**, 7, 387.
- (106) Chen, W.; Wang, C.; Sasaki, K.; Marinkovic, N.; Xu, W.; Muckerman, J. T.; Zhu, Y.; Adzic, R. R. *Energy Environ. Sci.* **2013**, 6, 943.
- (107) Pan, L.; Li, Y.; Yang, S.; Liu, P.; Yu, M.; Yang, H. *Chem. Commun.* **2014**, 50, 13135.
- (108) Youn, D. H.; Han, S.; Kim, J. Y.; Kim, J. Y.; Park, H.; Choi, S. H.; Lee, J. S. *ACS Nano* **2014**, 8, 5164.
- (109) Wirth, S.; Harnisch, F.; Weinmann, M.; Schröder, U. *Appl. Catal. B* **2012**, 126, 225.
- (110) Hunt, S. T.; Nimmanwudipong, T.; Roman-Leshkov, Y. *Angew. Chem. Int. Ed.* **2014**, 53, 5131.
- (111) Chen, W.; Sasaki, k.; Ma, C.; Frenkel, A.I.; Marinkovic, N.; Muckerman, J. T.; Zhu, Y.; Adzic, R. R. *Angew. Chem. Int. Ed.* **2012**, 91, 6131.
- (112) Cao, B.; Veith, G. M.; Neuefeind, J. C.; Adzic, R. R.; Khalifah, P. G. *J. Am. Chem. Soc.* **2013**, 135, 19186.
- (113) Zhao, Y.; Kamiya, K.; Hashimoto K.; Nakanishi, S. *J. Am. Chem. Soc.* **2015**, 137, 110.

- (114) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jorgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Norskov, J. *J. Am. Chem. Soc.* **2005**, 127, 5308.
- (115) Jaramillo, T. F.; Jorgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. *Science* **2007**, 317, 100.
- (116) Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. *ACS Catal.* **2014**, 4, 3957.
- (117) Wu, Z.; Fang, B.; Wang, Z.; Wang, C.; Liu, Z.; Liu, F.; Wang, W.; Alfantazi, A.; Wang, D.; Wilkinson, D. P. *ACS Catal.* **2013**, 3, 2101.
- (118) Gopalakrishnan, D.; Damien, D.; Shaijumon, M. M. *ACS Nano* **2014**, 8, 5297.
- (119) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. *J. Am. Chem. Soc.* **2013**, 135, 10274.
- (120) Voiry, D.; Salehi, M.; Silva, R.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. *Nano Lett.* **2013**, 13, 6222.
- (121) Xie, J.; Zhang, H.; Li, S.; Wang, R.; Sun, X.; Zhou, M.; Zhou, J.; Lou, X.; Xie, Y. *Adv. Mater.* **2013**, 25, 5807.
- (122) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. *Nat. Mater.* **2012**, 11, 963.
- (123) Zhang, K.; Kim, H. J.; Lee, J. T.; Chang, G. W.; Shi, X.; Kim, W.; Ma, M.; Kong, K. J.; Choi, J. M.; Song, M. S.; Park, J. H. *ChemSusChem* **2014**, 7, 2489.
- (124) Li, Y.; Wang, H. Xie, L.; Liang, Y.; Hong, G.; Dai, H. *J. Am. Chem. Soc.* **2011**, 133, 7296.
- (125) Morales-Guio, C. G.; Hu, X. *Acc. Chem. Res.* **2014**, 47, 2671.
- (126) Kong, D.; Cha, J. J.; Wang, H.; Lee, H. R.; Cui, Y. *Energy Environ. Sci.* **2013**, 6, 3553.
- (127) Faber, M. S.; Dziedzic, R.; Lukowski, M. A.; Kaiser, N. S.; Ding, Q.; Jin, S. *J. Am. Chem. Soc.* **2014**, 136, 10053.
- (128) Sun, Y.; Liu, C.; Grauer, D. C.; Yano, J.; Long, J. R.; Yang, P.; Chang, C. J. *J. Am. Chem. Soc.* **2013**, 135, 17699.
- (129) Xiao, P.; Chen, W.; Wang, X. *Adv. Energy Mater.* **2015**, 5, 1500985.
- (130) Popczun, E. J.; McKone, J. R.; Read, C. G.; Biacchi, A. J.; Wilttrout, A. M.; Lewis,

- N. S.; Schaak, R. E. *J. Am. Chem. Soc.* **2013**, 135, 9267.
- (131) Wang, X.; Li, W.; Xiong, D.; Petrovykh, D. Y.; Liu, L. *Adv. Funct. Mater.* **2016**, 26, 4067.
- (132) Liu, Q.; Tian, J.; Cui, W.; Jiang, P.; Cheng, N.; Asiri, A. M.; Sun, X. *Angew. Chem. Int. Ed.* **2014**, 53, 6710.
- (133) Tian, J.; Liu, Q.; Asiri, A. M.; Sun, X. *J. Am. Chem. Soc.* **2014**, 136, 7587.
- (134) Li, Q.; Xing, Z.; Asiri, A. M.; Jiang, P.; Sun, X. *Int. J. Hydrogen Energy* **2014**, 39, 16806.
- (135) Pu, Z.; Li, Q.; Jiang, P.; Asiri, A. M.; Obaid, A. Y.; Sun, X. *Chem. Mater.* **2014**, 26, 4326.
- (136) Gu, S.; Du, H.; Asiri, A. M.; Sun, X.; Li, C. M. *Phys. Chem. Chem. Phys.* **2014**, 16, 16909.
- (137) Saadi, F. H.; Carim, A. I.; Verlage, E.; Hemminger, J. C.; Lewis, N. S.; Soriaga, M. P. *J. Phys. Chem. C* **2014**, 118, 29294.
- (138) Xu, Y.; Wu, R.; Zhang, J.; Shi, Y.; Zhang, B. *Chem. Commun.* **2013**, 49, 6656.
- (139) Jiang, P.; Liu, Q.; Liang, Y.; Tian, J.; Asiri, A. M.; Sun, X. *Angew. Chem., Int. Ed.* **2014**, 53, 1.
- (140) Liang, Y.; Liu, Q.; Asiri, A. M.; Sun, X.; Luo, Y. *ACS Catal.* **2014**, 4, 4065.
- (141) Zhang, Z.; Lu, B.; Hao, J.; Yang, W.; Tang, J. *Chem. Commun.* **2014**, 50, 11554.
- (142) Tian, J.; Liu, Q.; Liang, Y.; Xing, Z.; Asiri, A. M.; Sun, X. *ACS Appl. Mater. Interfaces* **2014**, 6, 20579.
- (143) Xing, Z.; Liu, Q.; Asiri, A. M.; Sun, X. *Adv. Mater.* **2014**, 26, 5702.
- (144) Kibsgaard, J.; Jaramillo, T. F. *Angew. Chem. Int. Ed.* **2014**, 53, 1.
- (145) McEnaney, J. M.; Crompton, J. C.; Callejas, J. F.; Popczun, E. J.; Biacchi, A. J.; Lewis, N. S.; Schaak, R. E. *Chem. Mater.* **2014**, 26, 4826.
- (146) McEnaney, J. M.; Crompton, J. C.; Callejas, J. F.; Popczun, E. J.; Read, C. G.; Lewis, N. S.; Schaak, R. E. *Chem. Commun.* **2014**, 50, 11026.
- (147) Ha, D.; Han, B.; Risch, M.; Giordano, L.; Yao, K.; Karayaylali, P.; Shao-Horn, Y. *Nano Energy* **2016**, 29, 37.
- (148) Yang, F.; Chen, Y.; Cheng, G.; Chen, S.; Luo, W. *ACS Catal.* **2017**, 7, 3824.

- (149) Pan, Y.; Hu, W.; Liu, D.; Liu, Y.; Liu, C. *J. Mater. Chem. A* **2015**, 3, 13087.
- (150) Huang, Z.; Lv, C.; Chen, Z.; Chen, Z.; Tian, F.; Zhang, C. *Nano Energy* **2015**, 12, 666.
- (151) Yan, Y.; Xia, B.; Ge, X.; Liu, Z.; Fisher, A.; Wang, X. *Chem. Eur. J.* **2015**, 21, 18062.
- (152) Jiang, P.; Liu, Q.; Liang, Y.; Tian, J.; Asiri, A. M.; Sun, X. *Angew. Chem. Int. Ed.* **2014**, 53, 12855.
- (153) Liu, W.; Hu, E.; Jiang, H.; Xiang, Y.; Weng, Z.; Li, M.; Fan, Q.; Yu, X.; Altman, E.; Wang, H. *Nat. Commun.* **2016**, 7, 10771.
- (154) Li, J.; Wang, Y.; Liu, C.; Li, S.; Wang, Y.; Dong, L.; Dai, Z.; Li, Y.; Lan, Y. *Nat. Commun.* **2016**, 7, 11204.
- (155) Yan, H.; Tian, C.; Wang, L.; Wu, A.; Meng, M.; Zhao, L.; Fu, H. *Angew. Chem. Int. Ed.* **2015**, 54, 6325.
- (156) Fei, H.; Dong, J.; Arellano-Jimenez, M.; Ye, G.; Kim, N.; Samuel, E.; Peng, Z.; Zhu, Z.; Qin, F.; Bao, J.; Yacaman, M.; Ajayan, P.; Chen, D.; Tour, J. *Nat. Commun.* **2015**, 6, 8668.
- (157) Fan, L.; Liu, P.; Yan, X.; Gu, L.; Yang, Z.; Yang, H.; Qiu, S.; Yao, X. *Nat. Commun.* **2016**, 7, 10667.
- (158) Deng, J.; Ren, P.; Deng, D.; Bao, X. *Angew. Chem. Int. Ed.* **2015**, 54, 2100.
- (159) Xing, Z.; Liu, Q.; Xing, W.; Asiri, A. M.; Sun, X. *ChemSusChem* **2015**, 8, 1850.
- (160) Zhou, W.; Zhou, J.; Zhou, Y.; Lu, J.; Zhou, K.; Yang, L.; Tang, Z.; Li, L.; Chen, S. *Chem. Mater.* **2015**, 27, 2026.
- (161) Hou, D.; Zhou, W.; Zhou, K.; Zhou, Y.; Zhong, J.; Yang, L.; Lu, J.; Li, G.; Chen, S. *J. Mater. Chem. A* **2015**, 3, 15962.
- (162) Zhou, W.; Zhou, Y.; Yang, L.; Huang, J.; Ke, Y.; Zhou, K.; Li, L.; Chen, S. *J. Mater. Chem. A* **2015**, 3, 1915.
- (163) Wang, Z.; Hao, X.; Jiang, Z.; Sun, X.; Xu, D.; Wang, J.; Zhong, H.; Meng, F.; Zhang, X. *J. Am. Chem. Soc.* **2015**, 137, 15070.
- (164) Liang, H.; Bruller, S.; Dong, R.; Zhang, J.; Feng, X.; Mullen, K. *Nat. Commun.* **2015**, 6, 7992.

- (165) Zhang, H.; Ma, Z.; Duan, J.; Liu, H.; Liu, G.; Wang, T.; Chang, K.; Li, M.; Shi, L.; Meng, X.; Wu, K.; Ye, J. *ACS Nano* **2016**, 10, 684.
- (166) Han, L.; Dong, S.; Wang, E. *Adv. Mater.* **2016**, 28, 9266.
- (167) Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. *Nature Mater.* **2011**, 10, 780.
- (168) Ma, T.; Dai, S.; Jaroniec, M.; Qiao, S. *J. Am. Chem. Soc.* **2014**, 136, 13925.
- (169) Suntivich, J.; May, K. J.; Gasteiger, H. A.; Goodenough, J. B.; Shao-Horn, Y. *Science* **2011**, 334, 1383.
- (170) Fominykh, K.; Feckl, J. M.; Sicklinger, J.; Döblinger, M.; Böcklein, S.; Ziegler, J.; Peter, L.; Rathousky, J.; Scheidt, E. W.; Bein, T.; Fattakhova-Rohlfing, D. *Adv. Funct. Mater.* **2014**, 24, 3123.
- (171) Fominykh, K.; Chernev, P.; Zaharieva, I.; Sicklinger, J.; Stefanic, G.; Döblinger, M.; Müller, A.; Pokharel, A.; Böcklein, S.; Scheu, C.; Bein, T.; Fattakhova-Rohlfing, D. *ACS Nano* **2015**, 9, 5180.
- (172) Hardin, W. G.; Slanac, D. A.; Wang, X.; Dai, S.; Johnston, K. P.; Stevenson, K. J.; *J. Phys. Chem. Lett.* **2013**, 4, 1254.
- (173) Xu, Y.; Tu, W.; Zhang, B.; Yin, S.; Huang, Y.; Kraft, M.; Xu, R. *Adv. Mater.* **2017**, 29, 1605957.
- (174) Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan, Y. *J. Am. Chem. Soc.* **2014**, 136, 7077.
- (175) Louie, M. W.; Bell, A. T. *J. Am. Chem. Soc.* **2013**, 135, 12329.
- (176) Görlin, M.; Chernev, P.; Araújo, J. F.; Reier, T.; Dresch, S.; Paul, B.; Krähnert, R.; Dau, H.; Strasser, P. *J. Am. Chem. Soc.* **2016**, 138, 5603.
- (177) Görlin, M.; Araújo, J.; Schmies, H.; Bernsmeier, D.; Dresch, S.; Gliech, M.; Jusys, Z.; Chernev, P.; Krähnert, R.; Dau, H.; Strasser, P. *J. Am. Chem. Soc.* **2017**, 139, 2070.
- (178) Tang, C.; Wang, H. S.; Wang, H. F.; Zhang, Q.; Tian, G. L.; Nie, J. Q.; Wei, F. *Adv. Mater.* **2015**, 27, 4516.
- (179) Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J. Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. *J. Am. Chem. Soc.* **2013**, 135, 8452.
- (180) Ma, W.; Ma, R.; Wang, C.; Liang, J.; Liu, X.; Zhou, K.; Sasaki, T. *ACS Nano*

2015, 9, 1977.

(181) Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chen, H.; Yang, S. *Angew. Chem. Int. Ed.* **2014**, 53, 7584.

(182) Lu, X.; Zhao, C. *Nat. Commun.* **2015**, 6, 6616.

(183) Lu, Z.; Xu, W.; Zhu, W.; Yang, Q.; Lei, X.; Liu, J.; Li, Y.; Sun, X.; Duan, X. *Chem. Comm.* **2014**, 50, 6479.

(184) Tang, D.; Liu, J.; Wu, X.; Liu, R.; Han, X.; Han, Y.; Huang, H.; Liu, Y.; Kang, Z. *ACS Appl. Mater. Interfaces* **2014**, 6, 7918.

(185) Klaus, S.; Louie, M. W.; Trotochaud, L.; Bell, A. T. *J. Phys. Chem. C* **2015**, 119, 18303.

(186) Hunter, B.; Blakemore, J.; Deimund, M.; Gray, H. B.; Winkler, J.; Müller, A. *J. Am. Chem. Soc.* **2014**, 136, 13118.

(187) Song, F.; Hu, X. *Nat. Commun.* **2014**, 4477.

(188) Morales-Guio, C.; Liardet, L.; Hu, X. *J. Am. Chem. Soc.* **2016**, 138, 8946.

(189) Zhao, S.; Wang, Y.; Dong, J.; He, C.; Yin, H.; An, P.; Zhao, K.; Zhang, X.; Gao, C.; Zhang, L.; Lv, J.; Wang, J.; Zhang, J.; Khattak, A.; Khan, N.; Wei, Z.; Zhang, J.; Liu, S.; Zhao, H.; Tang, Z. *Nature Energy* **2016**, 184.

(190) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher S. W. *J. Am. Chem. Soc.* **2014**, 136, 6744.

(191) Zhang, B.; Zheng, X.; Voznyy, O.; Comin, R.; Bajdich, M.; García-Melchor, M.; Han, L.; Xu, J.; Liu, M.; Zheng, L.; Pelayo García de Arquer, F.; Dinh, C. T.; Fan, F.; Yuan, M.; Yassitepe, E.; Chen, N.; Regier, T.; Liu, P.; Li, Y.; Luna, P. D.; Janmohamed, A.; Xin, H. L.; Yang, H.; Vojvodic, A.; Sargent, E. H. *Science* **2016**, 352, 333.

(192) Yin, S.; Han, J.; Zou, Y.; Zhou, T.; Xu, R. *Nanoscale*, **2016**, 8, 14438.

(193) Cheng, R.; Shu, Y.; Li, L.; Zheng, M.; Wang, X.; Wang, A.; Zhang, T. *Appl. Catal. A* **2007**, 316, 160.

(194) Ibeh, B.; Zhang, S.; Hill, J. M. *Appl. Catal. A* **2009**, 368, 127.

(195) Bai, J.; Li, X.; Wang, A.; Prins, R.; Wang, Y. *J. Catal.* **2012**, 287, 161.

(196) Marin Flores, O. G.; Ha, S. *Appl. Catal. A* **2009**, 352, 124.

(197) Vrubel, H.; Merki, D.; Hu, X. *Energy Environ. Sci.* **2012**, 5, 6136.

- (198) Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. *Chem. Sci.* **2011**, 2, 1262.
- (199) Peng, X.; Schlamp, M. C.; Kadavanich, A.V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, 119, 7019.
- (200) Munnik, P.; de Jongh, P. E.; de Jong, K. P. *Chem. Rev.* **2015**, 115, 6687.
- (201) Kamat, P. V. *Acc. Chem. Res.* **2012**, 45, 1906.
- (202) Zhang, G.; Wang, G.; Liu, Y.; Liu, H.; Qu, J.; Li, J. *J. Am. Chem. Soc.* **2016**, 138, 14686.
- (203) Han, S.; Feng, Y.; Zhang, F.; Yang, C.; Yao, Z.; Zhao, W.; Qiu, F.; Yang, L.; Yao, Y.; Zhuang, X.; Feng, X. *Adv. Funct. Mater.* **2015**, 25, 3899.
- (204) Jiao, L.; Zhou, Y.; Jiang, H. *Chem. Sci.* **2016**, 7, 1690.
- (205) Ai, K.; Liu, Y.; Ruan, C.; Lu, L.; Lu, G. *Adv. Mater.* **2013**, 25, 998.
- (206) Qu, K.; Zheng, Y.; Dai, S.; Qiao, S. *Nano Energy* **2016**, 19, 373.
- (207) Qu, K.; Zheng, Y.; Jiao, Y.; Zhang, X.; Dai, S.; Qiao, S. *Adv. Energy Mater.* **2017**, 1602068.
- (208) Li, C.; Yin, X.; Chen, L.; Li, Q.; Wang, T. *Chem. Eur. J.* **2010**, 16, 5215.
- (209) Chen, S.; Duan, J.; Jaroniec, M.; Qiao, S. *Adv. Mater.* **2014**, 26, 2925.
- (210) Li, C.; Du, Y.; Wang, D.; Yin, S.; Tu, W.; Chen, T.; Kraft, M.; Chen, G.; Xu, R. *Adv. Funct. Mater.* **2017**, 27, 1604328.
- (211) Patel, M.; Luo, F.; Khoshi, M.; Rabie, E.; Zhang, Q.; Flach, C.; Mendelsohn, R.; Garfunckel, E.; Szostak, M.; He, H. *ACS Nano* **2016**, 10, 2305.
- (212) Fantini, C.; Pimenta, A.; Strano, M. *J. Phys. Chem. C* **2008**, 112, 13150.
- (213) Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, 323, 760.
- (214) Long, X.; Li, G.; Wang, Z.; Zhu, H.; Zhang, T.; Xiao, S.; Guo, W.; Yang, S. *J. Am. Chem. Soc.* **2015**, 137, 11900.
- (215) Neidhardt, J.; Hultman, L.; Czigany, Zs. *Carbon* **2004**, 42, 2729.
- (216) Sudhesh, P.; Tamilarasan, K.; Arumugam, P.; Berchmans, S. *ACS Appl. Mater. Interfaces* **2013**, 5, 8263.
- (217) Cui, H.; Wang, J.; Hu, M.; Ma, C.; Wen, H.; Song, X.; Chen, C. *Dalton Trans.* **2013**, 42, 8684.
- (218) Han, S.; Miao, X.; Liu, S.; Bu, X. *Dalton Trans.* **2015**, 44, 560.

- (219) Sun, X.; Li, Y. *Angew. Chem. Int. Ed.* **2004**, 43, 597.
- (220) Titirici, M.; Antonietti, M. *Chem. Soc. Rev.* **2010**, 39, 103.
- (221) Ferrari, A.; Robertson, J. *Phil. Trans. R. Soc. A* **2004**, 362, 2477.
- (222) Ferrari, A.; Rodil, S.; Robertson, J. *Phys. Rev. B* **2003**, 67, 155306.
- (223) Grosvenor, A.; Biesinger, M.; Smart, R.; McIntyre, N. *Surf. Sci.* **2006**, 600, 1771.
- (224) Leng, M.; Huang, X.; Xiao, W.; Ding, J.; Liu, B.; Du, Y.; Xue, J. *Nano Energy* **2017**, 33, 445.
- (225) Wang, Y.; Zhang, Y.; Liu, Z.; Xie, C.; Feng, S.; Liu, D.; Shao, M.; Wang, S. *Angew. Chem. Int. Ed.* **2017**, 56, 5867.
- (226) Fan, K.; Chen, H.; Ji, Y.; Huang, H.; Claesson, P. M.; Daniel, Q.; Philippe, B.; Rensmo, H.; Li, F.; Luo, Y.; Sun, L. *Nature Commun.* **2016**, 7, 11981.
- (227) Liu, Y.; Xiao, C.; Lyu, M.; Lin, Y.; Cai, W.; Huang, P.; Tong, W.; Zou, Y.; Xie, Y. *Angew. Chem. Int. Ed.* **2015**, 54, 11231.
- (228) Wei, J. J. *Appl. Phys.* **2002**, 92, 6525.
- (229) Chen, J.; Dang, L.; Liang, H.; Bi, W.; Gerken, J.; Jin, S.; Alp, E.; Stahl, S. *J. Am. Chem. Soc.* **2015**, 137, 15090.
- (230) Sheberla, D.; Bachman, J.; Elias, J.; Sun, C.; Shao-Horn, Y.; Dincă, M. *Nat. Mater.* **2017**, 16, 220.