Design and synthesis of electrocatalysts for efficient energy conversion and storage

Tan, Huang

2018

Tan, H. (2018). Design and synthesis of electrocatalysts for efficient energy conversion and storage. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/87808>

<https://doi.org/10.32657/10220/46868>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Design and Synthesis of Electrocatalysts for Efficient Energy
Conversion and Storage**

HUANG TAN

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

2018

DESIGN AND SYNTHESIS OF ELECTROCATALYSTS FOR EFFICIENT ENERGY CONVERSION AND STORAGE

HUANG TAN

INTERDISCIPLINARY GRADUATE SCHOOL

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

2018

Statement of Originality

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

July 2018

.....

Huang Tan

.....

Authorship Attribution Statement

Chapter 4 is published as Huang, Tan, Seung Ki Moon, and Jong-Min Lee. "Polymer-assisted formation of 3D Pd nanoassemblies: highly active catalysts for formic acid electrooxidation." *Sustainable Energy & Fuels* 1.3 (2017): 450-457.

The contributions of the co-authors are as follows:

- A/Prof Lee Jong-Min provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Prof. Moon Seung-Ki.
- I performed all the laboratory work and analyzed the data.

Chapter 5 is published as Huang, Tan, Yu Chen, and Jong-Min Lee. "Two-Dimensional Cobalt/N-Doped Carbon Hybrid Structure Derived from Metal–Organic Frameworks as Efficient Electrocatalysts for Hydrogen Evolution." *ACS Sustainable Chemistry & Engineering* 5.7 (2017): 5646-5650.

The contributions of the co-authors are as follows:

- Prof Lee Jong-Min suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Prof Chen Yu and Prof Lee Jong-Min.
- I performed all the materials synthesis, collected X-ray diffraction patterns and visible light spectra, carried transmission electron microscopy, and conducted data evaluation.

Chapter 6 is published as Huang, Tan, Yu Chen, and Jong-Min Lee. "A Microribbon Hybrid Structure of CoOx-MoC Encapsulated in N-Doped Carbon Nanowire Derived from MOF as Efficient Oxygen Evolution Electrocatalysts." *Small* 13.48 (2017).

The contributions of the co-authors are as follows:

- Prof Lee Jong-Min suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Prof Chen Yu and Prof Lee Jong-Min.

- I performed all the materials synthesis, collected X-ray diffraction patterns and visible light spectra, carried transmission electron microscopy, and conducted data evaluation.

July 2018

.....

Date

.....

Huang Tan

Abstract

Efficient energy conversion and storage applications (e.g. liquid fuel cell and water splitting) have been identified as promising solutions to future energy depletion. However, practical installation of energy conversion and storage applications is impeded by the low performance and high cost of electrocatalysts. Therefore, it is imperative to improve the electrocatalysts' performance so as to drive their corresponding applications. The objective of this thesis is to design and synthesize electrocatalysts for energy conversion and storage applications, through the scope as follows: (1) Designing 3D Palladium nanoarchitectures with abundant catalytic sites and open space for electrooxidation of formic acid; (2) Lowering the overpotential for hydrogen evolution by fabricating two dimensional Co/NC; (3) Introducing synergistic effect by hybridizing of molybdenum carbides and cobalt oxides for oxygen evolution; (4) Producing a heterostructure of layered double hydroxides for electrochemical oxygen evolution.

Firstly, three-dimensional Pd nanoassemblies were fabricated using a wet chemical reduction method. During the process, a polymer (polyallylamine hydrochloride) played the role of scaffold and cross-linking molecules, for the purpose of formation of three-dimensional nanoassemblies. The formation process and mechanism of the Pd nanoassemblies were investigated using temporal TEM images. Finally, the 3D Pd nanoassemblies were used as electrocatalysts towards electrooxidation of formic acid. Pd nanoassemblies exhibited superior electrochemical activity. This behavior is mainly contributed by their porous structure, high surface area which offers more catalytic sites, and their sufficient cavity space which enables facile charge transport of the electrochemical reaction.

Secondly, layered cobalt metal–organic frameworks were subjected to heat treatment to produce the hybrid of Co/N-Carbon. The derivative layered structure comprised of metallic cobalt and N-doped carbon was tested in the application of hydrogen evolution, which showed a superior electrocatalytic activity for electrochemical hydrogen evolution. More importantly, the hybrid materials displayed robust long-term stability. The hybrid of Co/N-

carbon possessed these excellent properties because of its two-dimensional configuration, which included metallic cobalt nanoparticles, the excellent conductivity of carbon and the carbon protection effect.

Thirdly, nitrogen-doped carbon supported CoOx-MoC heterostructures were reported as high-performance oxygen evolution electrocatalysts. The composition can be tuned by the addition of a Mo source to form a nanowire-assembled hierarchically porous microstructure, which can enlarge the specific surface area, facilitate mass transport and charge transfer. Moreover, it is demonstrated that the formation of CoOx-MoC heterostructures and the resulting synergistic effect between MoC and Co facilitate the reaction kinetics, leading to significantly improved OER activity. The well-constructed microarchitecture contributes to superior long-term stability electrochemical behaviors. This work provides a facile strategy which includes composition tuning and structure optimization for the development of next-generation non-precious metal based OER electrocatalysts.

Lastly, a strategy was reported for the synthesis of binary hybrid hydroxide microstructures which were wrapped by few-layer carbon with iridium doping. The results showed that NiCo-Ir hybrid microarchitecture with tunable compositions displayed excellent electrocatalytic behaviors towards the oxygen evolution in alkaline medium, due to their microstructural advantages with few-layer carbon and electronic interaction of iridium/hydroxides. This work develops a general paradigm of seed based growth of hierarchical layered double hydroxide heterostructures which display large surface area and distinct porous nature. These results validate the potential of the heterostructures in electrocatalysis after few-layer carbon coating and iridium doping via aqueous modification.

To conclude, the performances of the electrocatalysts could be improved by the design of their structure and control of the compositions. Thus, the overall cost of their respective energy conversion and storage devices could be lowered.

Lay Summary

Electrochemical energy conversion and storage is a sustainable and clean solution towards the worsening energy crisis worldwide. Electrochemical equipment consists of various components (MEA, electrolyte), usually electrocatalysts incur most of the overall cost. To fabricate high performance electrocatalysts, compositions and structures should be designed. The ultimate objective of this thesis is to design and synthesize electrocatalyst for efficient energy conversion and storage applications, including formic acid electrooxidation, hydrogen evolution and oxygen evolution. For electrooxidation of formic acid, palladium is an idea catalyst. However, more studies are required to improve its electrocatalytic activity and stability because of its high price; for electrochemical hydrogen evolution and oxygen evolution, microarchitectures should be well designed to cater for the need of gas evolving. Thus, the dissertation aims to address these issues through the scope as follows: (1) Fabrication of three-dimensional Palladium nanoarchitectures with abundant catalytic sites and open space for electrooxidation of formic acid; (2) Decreasing the overpotential for hydrogen evolution by fabricating the hybrid of Co/NC; (3) Introducing synergism by heteroatoms (Mo) into the MOFs for oxygen evolution; (4) Preparation of porous heterostructure of layered double hydroxides as a platform of electrocatalysts fabrication. All the as-synthesized electrocatalysts show outstanding electrocatalytic behaviors. The superior electrochemical behaviors of the catalysts should originate from their ordered exposure of active sites. More importantly, the growing process of the 3D Pd has been observed in a chronological way, some critical parameters of oxygen evolution catalysts have been measured and evaluated to investigate the factors that contribute to the enhancement electrocatalytic performances. This work develops several rational synthetic strategies for highly efficient catalyst design, observes the hybrid MOF's morphological evolution. Therefore, the work not only provides methodology enabling fabrication of efficient catalyst, but also sheds light on the growing process of the microarchitecture.

Acknowledgement

I would like to thank people who provide me with support during the PhD period. First, I should give thanks to my supervisors: my main supervisor, Prof. Lee Jong-min, who provides support both in academic and personal life; my co-supervisor, Prof. Moon Seung-ki, who encourages my coursework and research; and my mentor, Prof. Lau Wai-man, who helps me whenever I need.

Second, I should give thanks to my labmates: Anjali, Tai, Linlu, Dr. Wang Rong-hua, Dr. Dong Yu-cheng, Dr. Yao Lin, Dr. Chen Yu; and my batchmate and fellows: Zhai Shengli, Andy, Zhao Han, Cheng Zihao, Shao Hongxin, Zhang Chi, who accompany me in the leisure time and encourage me when faced with difficulties; and the technicians in SCBE, who always train me in terms of facility patiently; and the admin staff of IGS and ERI@N, including Lily, Angeline and Minying, who always give strong support to us PhD students.

Finally, I must give thanks to my family, my father and mother are permanent motivation of my upward mobility.

Table of Contents

Abstract	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions	xiii
Figure Captions	xv
Abbreviations	xxi
Chapter 1 Introduction.....	1
1.1 Problem statements/Hypothesis/Design and performance targets	2
1.2 Objectives and Scope	5
1.3 Dissertation Overview	5
1.4 Findings and Outcomes/Originality	6
References.....	7
Chapter 2 Literature Review	9
2.1 Overview	10
2.2 Literature review on the nanostructure palladium for electrocatalysis	12
2.2.1 Noble metals in electrocatalysts.....	12
2.2.2 Palladium in electrocatalysis.....	12

2.2.3	Direct fuel cells	13
2.2.4	Formic acid oxidation reaction (FAOR)	14
2.2.5	Electrocatalyst for FAOR	15
2.2.6	Synthesis method of electrocatalysts	15
2.2.7	Summary	16
2.3	Literature review on the cobalt based electrocatalytic hydrogen evolution	17
2.3.1	Electrochemical water splitting	17
2.3.2	Hydrogen evolution	18
2.3.3	Cobalt based electrocatalysts	20
2.3.4	MOF-derived cobalt electrocatalysts	22
2.3.5	Summary	22
2.4	Literature review on the cobalt based electrocatalysts for oxygen evolution	23
2.4.1	Oxygen evolution	23
2.4.2	Cobalt based electrocatalysts	25
2.4.3	Molybdenum carbides in electrocatalysis	26
2.4.4	MOF-derived cobalt materials for electrochemical oxygen evolution	26
2.4.5	Summary	27
2.5	Literature review on the layered double hydroxides in electrocatalysis	27
2.5.1	Layered double hydroxides	27
2.5.2	Layered double hydroxides as electrocatalysts	28
2.5.3	Summary	28

2.6	Questions to answer and PhD in context based on literature in section 2.2.....	29
2.7	Questions to answer and PhD in context based on literature in section 2.3.....	30
2.8	Questions to answer and PhD in context based on literature in section 2.4.....	30
2.9	Questions to answer and PhD in context based on literature in section 2.5.....	31
	References.....	32
 Chapter 3 Experimental Methodology		39
3.1	Rationale for Selection of Methods/Materials	40
3.2	Synthesis Method	42
3.2.1	Synthesis of palladium nanostructure	42
3.2.2	Synthesis of cobalt MOFs and fabrication of MOF-derived Co/N-Carbon	42
3.2.3	Synthesis of hybrid cobalt/molybdenum MOFs and fabrication of CoOx-MoC/N-Carbon	43
3.2.4	Synthesis of heterostructure of layered double hydroxides with carbon coating and iridium doping	43
3.3	Characterization Methods	44
3.3.1	UV-Vis Spectroscopy	44
3.3.2	Fourier Transform Infrared Spectroscopy	45
3.3.3	Energy-Dispersive X-ray Spectroscopy.....	45
3.3.4	X-ray Photoelectron Spectroscopy	46
3.3.5	Powder X-ray Diffraction	46
3.3.6	Raman Spectroscopy.....	47
3.3.7	Atomic Force Microscopy	47
3.3.8	Brunauer-Emmett-Teller.....	48
3.3.9	Scanning Electron Microscopy	48
3.3.10	Transmission Electron Microscopy	48

3.3.11 Cyclic Voltammetry and Linear Sweeping voltammetry	49
3.3.12 Chronoamperometry	49
3.3.13 Electrochemical Impedance Spectroscopy	49
References.....	50
 Chapter 4 Pd nanoassemblies for efficient electrooxidation of formic acid	53
4.1 Introduction	54
4.2 Principle Outcomes	55
4.2.1 Palladium morphology and growing mechanism	55
4.2.2 Physical characterization	61
4.2.3 Electrochemical performances.....	63
4.3 Conclusion.....	65
References.....	65
 Chapter 5 MOF derived cobalt based catalyst for hydrogen evolution.....	69
5.1 Introduction	70
5.2 Principle Outcomes	71
5.2.1 Structure information	71
5.2.2 Physical characterizations.....	75
5.2.3 Electrochemical performances.....	78
5.3 Conclusion.....	82
References.....	83
 Chapter 6 MOF derived cobalt/molybdenum based catalyst for oxygen evolution	85

6.1	Introduction	86
6.2	Principle Outcomes	88
6.2.1	Structure and growing Process.....	88
6.2.2	Physical characterization	92
6.2.3	Electrochemical measurements.....	95
6.3	Conclusion.....	100
	References	100
 Chapter 7 Hybrid of layered double hydroxide and carbon with iridium doping for oxygen evolution.....		105
7.1	Introduction	106
7.2	Principle Outcomes	108
7.2.1	Structure information	108
7.2.2	Physical characterization	112
7.2.3	Electrochemical characterization	118
7.3	Conclusion.....	124
	References	124
 Chapter 8 Implications/Impact/Outstanding Questions.....		127
8.1	General Discussion.....	128
8.1.1	Outcome reflected on hypothesis #1	129
8.1.2	Outcome reflected on hypothesis #2.....	129
8.1.3	Outcome reflected on hypothesis #3.....	130
8.1.4	Outcome reflected on hypothesis #4.....	131

8.2	Reconnaissance and Outstand Questions	131
8.2.1	Preparation of new metal nanostructures using the polymer-assisted method	132
8.2.2	Preparation of new hybrid materials based on metal organic frameworks for other applications	133
8.2.3	Preparation of metal/MOF composites for other applications	133
	References	134
	List of Publications	137

Table Captions

Table 6.1 Summary of Electrochemical Performances of CoO_x-MoC/NC and IrO₂/C.

Table 7.1 Electrochemical oxygen evolution behaviors of NiCo-Ir and IrO₂/C.

Figure Captions

Figure 2.1 Schematic drawing of Direct Ethanol Fuel Cell.

Figure 2.2 Dural pathway of electro-oxidation of formic acid.

Figure 2.3 Volcano plot of various electrocatalyst (exchange current density vs Gibbs free energy).

Figure 4.1 Procedure of fabrication of palladium nanoassemblies.

Figure 4.2 (a) Low resolution TEM image, (b) middle resolution and the inset shows SAED image of Pd nanoassemblies, (d) high resolution TEM image of a single Pd nanoassembly, (d) high resolution TEM image showing crystal lattice of Pd nanoassembly.

Figure 4.3 TEM images of the Pd nanoassemblies formed after the reaction time of 2.0 h, 2.5 h, 3.0 h, 3.5 h, 4.0 h, 4.5 h, 5.0 h. All the inset images are TEM images focusing on one nanoassembly at the corresponding reaction time.

Figure 4.4 Formation mechanism of Pd nanoassemblies.

Figure 4.5 (a) Pd bulk growing without PAH, (b) HRTEM image showing edge and corner atoms.

Figure 4.6 (a) Pd nanoassemblies size distribution histogram; (b) UV-Vis spectrum of solution of PdCl₂, PAH, PAH-Pd^{II} complex.

Figure 4.7 Comparison of dispersity of the three samples: Pd nanoassemblies, Pd bulk, Pd black.

Figure 4.8 (a) XRD pattern of Pd nanoassemblies, (b) Nitrogen adsorption-desorption

isotherm, (c) Pore size distribution.

Figure 4.9 XPS figure of Pd nanoassemblies in the area of N1s (a) and Pd3d (b), Pd nanoassemblies (d) and Pd bulk in the Pd 3d region (d).

Figure 4.10 (a) Superimposed Cyclic Voltammetric (CV) response of Pd nanoassemblies, Pd bulk and Pd black in the mixture of 0.5 M HCOOH and 0.5 M H₂SO₄ solution at sweep rate of 50 mV/s, (b) Superimposed I–t transients of HCOOH oxidation for Pd nanoassemblies, Pd bulk and Pd black at an applied potential (0.200 V) for 2000s, (c) Mass activity for Pd nanoassemblies, Pd bulk and Pd black, (d) Peak potential of electro-oxidation for Pd nanoassemblies, Pd bulk and Pd black.

Figure 5.1 Synthesis procedure of Co/N-carbon by pyrolysis of the mixture of the Co-MOF and hexamethylenetetramine.

Figure 5.2 FESEM images of (a) and (b) layered Cobalt MOFs; (c) and (d) Co-MOF pyrolysis under argon; (e) and (f) Co-MOF and hexamethylenetetramine pyrolysis under argon; (g) and (h) Co-MOF pyrolysis under air.

Figure 5.3 AFM of layered Co-MOF.

Figure 5.4 (a) XRD of Co-MOF; (b) Figure S1 Nanoparticles size distribution; (c) Crystal information frameworks of Co-MOF.

Figure 5.5 (a) TEM image of Co/N-carbon, (b) TEM image showing homogeneously embedded cobalt nanoparticles on carbon matrix, (c) TEM image showing densely dotted cobalt nanoparticles, (d) high resolution TEM image showing the lattice fringe of metallic cobalt.

Figure 5.6 (a) XRD patterns of Co-Carbon, Co/N-carbon and Co oxides derived from MOFs, (b) Raman spectra recorded at 532 nm laser excitation, (c) XPS data showing N 1s

spectrum of Co/N-carbon, (d) XPS data showing Co 2p spectrum of Co/N-carbon.

Figure 5.7 (a) nitrogen adsorption–desorption isotherm, and (b) pore size distribution.

Figure 5.8 EDX elemental mapping of Co/N-Carbon.

Figure 5.9 (a) LSV of different electrocatalysts with rotation disk electrode at 1600 rpm, (b) EIS of different electrocatalysts, (c) Cycling durability test of Pt/C (20%wt) and Co/N-carbon for 2000 cycles, (d) Current-time curve of Pt/C (20%wt) and Co/N-carbon.

Figure 5.10 The hydrogen is evolving during 0 s, 30 s, 1 min, 2 min as CV is performing.

Figure 5.11 LSV of catalysts with various doping degree.

Figure 6.1 Design strategy of hybrid MOF and the pyrolysis of the hybrid MOF.

Figure 6.2 (a, b, c) FESEM images of the hybrid Co-Mo-MOF; (d, e, f) FESEM images of the product derived from the hybrid Co-Mo-MOF after pyrolysis under argon.

Figure 6.3 (a) and (b) TEM image of CoOx-MoC/NC-2, (c) TEM image showing cobalt and MoC densely encapsulated in carbon matrix, (d) high resolution TEM image showing the lattice fringe of few layer graphene, which encapsulates cobalt and MoC nanoparticles.

Figure 6.4 Temporal FESEM image of the hybrid MOF formed after the reaction time of 2 h, 3 h, 5 h, 8 h, 10 h, 15 h. All the inset images are FESEM images focusing on one MOF microstructure at the corresponding reaction time.

Figure 6.5 HRTEM of CoOx-MoC/NC-2 displaying the lattice fringe of MoC and Co₃O₄.

Figure 6.6 FESEM images of the hybrid MOF produced without PVP (a) and with PVP (b).

Figure 6.7 (a) XRD patterns of CoOx-MoC/NC-1, CoOx-MoC/NC-2, CoOx-MoC/NC-3 derived from the hybrid MOF, (b) Raman spectra recorded at 532 nm laser excitation, (c) XPS data showing Co 2p spectrum of CoOx-MoC/NC-2, (d) XPS data showing Mo 3d spectrum of CoOx-MoC/NC-2.

Figure 6.8 XPS data of O 1s.

Figure 6.9 (a) LSV of different electrocatalysts with rotation disk electrode at 1600 rpm, (b) Tafel plot of different electrocatalysts, (c) Plot of current density (at 1.14 V vs RHE) vs scan rate, (d) Chronoamperometric responses of CoOx-MoC/NC-2 (at 1.56 V vs RHE) and IrO₂ (at 1.63 V vs RHE) in 1 M KOH at rotating disk electrodes (1600 rpm) for 36 000 s.

Figure 6.10 CVs of (a) CoOx-MoC/NC-1, (b) CoOx-MoC/NC-2, (c) CoOx-MoC-3 and IrO₂/C in the range of 1.095~1.155 V vs. RHE, measured in 1.0 M KOH solution, respectively.

Figure 6.11 (a) nitrogen adsorption–desorption isotherm, and (b) pore size distribution.

Figure 7.1 Design and synthesis of NiCo-Ir microarchitecture for efficient oxygen evolution.

Figure 7.2 (a,b) FESEM images of Ni hydroxides; (c,d) FESEM images of NiCo hydroxides; (e,f) FESEM images of NiCo-Ir hydroxides.

Figure 7.3 (a,b) TEM images of NiCo hydroxides; (c) TEM images of NiCo-Ir; (d) HRTEM images of NiCo-Ir showing the few-layer carbon and iridium doping.

Figure 7.4 HRTEM of NiCo-Ir showing the crystal plane of (003).

Figure 7.5 Elemental mapping of NiCo hydroxide after calcination in argon atmosphere.

Figure 7.6 (a) UV-Vis spectra of some precursors; (b) FT-IR spectra of Ni, NiCo, NiCo-Ir; (c) XRD patterns of Ni, NiCo, NiCo-Ir; (d) Nitrogen adsorption-desorption isotherm and pore size distribution of Ni, NiCo, NiCo-Ir; inset is the pore size distribution.

Figure 7.7 High-resolution XPS spectra of (a) Ni 2p, (b) Co 2p (c) Ir 4f and (d) C 1s core levels in NiCo-Ir-5 products.

Figure 7.8 Pore size distribution of nickel hydroxides, nickel cobalt hydroxides and NiCo-Ir.

Figure 7.9 XPS of NiCo-Ir-5 survey scan showing the existence of Ni, Co, Ir, C, N and O.

Figure 7.10 XPS of NiCo-Ir-5 for (a) N 1s, (b) O 1s.

Figure 7.11 (a) LSV of NiCo-Ir-3, NiCo-Ir-5, NiCo-Ir-7 and IrO₂/C with rotation disk electrode at 1600 rpm; (b) Tafel plot of NiCo-Ir-3, NiCo-Ir-5, NiCo-Ir-7 and IrO₂/C; (c) Plot of current density (at 1.14 V vs RHE) versus scan rate; (d) Current density - time curve of NiCo-Ir-5 (at 1.47 V vs RHE) and IrO₂/C (at 1.63 V vs RHE) in 1 M KOH, the duration is 36 000 s.

Figure 7.12 LSV of NiCo hydroxide, NiCo-Ir produced with glucose, NiCo-Ir produced with 2-methylimidazole, in 1.0 M KOH solution.

Figure 7.13 CVs of (a) NiCo-Ir-3, (b) NiCo-Ir-5, (c) NiCo-Ir-7 and (d) IrO₂/C in the range of 1.095 - 1.155 V vs. RHE, measured in 1.0 M KOH solution, respectively.

Figure 7.14 Compositional advantages and structural benefits of NiCo-Ir microarchitecture as an oxygen evolving electrocatalyst.

Abbreviations

AFM	Atomic Force Microscopy
BET	Brunauer-Emmett-Teller
BE	Binding Energy
C.E	Counter Electrode
CV	Cyclic Voltammetry
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
EASA	Electrochemical Active Surface Area
FESEM	Field Emission Scanning Electron Microscopy
FAOR	Formic Acid Oxidation Reaction
FTIR	Fourier Transform Infrared
HER	Hydrogen Evolution Reaction
LDH	Layered Double Hydroxide
LSV	Linear Sweeping Voltammetry
MOF	Metal-Organic Framework
OER	Oxygen Evolution Reaction
R.E	Reference Electrode
RHE	Reversible Hydrogen Electrode
SAED	Selected Area Electron Diffraction
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UV-Vis	Ultraviolet-Visible
W.E	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
2D	Two-Dimensional
3D	Three-Dimensional

Chapter 1

Introduction

Chapter 1 briefly introduces the content of the thesis. The hypotheses and design rationales of the thesis are stated. Then the scope and objectives of the thesis are described. A dissertation overview of each chapter of the thesis is included. Last, the outcomes and findings of the thesis are described.

1.1 Problem statements/Hypothesis/Design and performance targets

In recent years, the environmental pollution and fossil energy depletion have been the serious problems.^[1-3] Sustainable energy conversion and storage applications (e.g. liquid fuel cell and electrocatalytic water splitting) have been intensively investigated by researchers due to their renewable energy sources (biomass derived liquid fuel, solar energy).^[4-9] This dissertation focuses on three electrochemical reaction: formic acid electrooxidation, hydrogen evolution and oxygen evolution. For the electrooxidation of formic acid, it is the half reaction of direct formic acid fuel cell. This kind of direct fuel cell has a series of advantages such as high theoretical open circuit potential and utilization of recyclable resources. For hydrogen evolution and oxygen evolution, they make up the overall water splitting reaction. Coupled with solar energy, electrochemical hydrogen evolution and oxygen evolution could be a promising and reliable energy conversion and storage route. However, considering they are gas-evolving processes, surface area and pores of the electrocatalysts should be enhanced to drive efficient and durable electrochemical water splitting. Moreover, these electrochemical devices still encounter one major challenge, which is the slow reaction kinetics that cause large overpotential and in turn lead to low performances in these energy conversion and storage applications.^[10-12] Therefore, rational-design of electrocatalysts becomes vital for the improvement of the electrocatalytic performance for cost-effective energy storage and conversion applications.^[13-15] In this research, focus is on the enhancement of electrocatalytic ability of the electrode materials by tuning the composition and optimizing the structure such as: (1) Constructing the Pd nanoassemblies by using PAH-assisted hydrothermal method, the Pd nanoassemblies possess large surface area and abundant pore and cavities, which is beneficial to the electrooxidation of formic acid; (2) Fabrication of 2D hybrid of Co/N-carbon for hydrogen evolution, the hybrid materials integrate the advantageous properties of the cobalt nanoparticles and N-carbon; (3) Inducing synergistic effect by addition of Mo atoms into cobalt based MOF in order to improve their electrocatalytic performance for oxygen evolution; (4) Synthesis of hierarchical heterostructure of layered double hydroxides with plethora of open pores and well-displayed catalytic sites, which significantly improved oxygen-evolving behaviors.

Problem statement:

Problem statement #1

(1) How does the hierarchical nanoassembly structure influence their performance in electrooxidation of formic acid?

Hypothesis (1) Hierarchical nanoassembly structure has abundant pores, which contribute to more surface area as compared to nonporous material. As a result, the former promotes the electrochemical reaction kinetics for gas involving reaction. This pore and cavity space provides a short electron transport pathway, and thus improves the electrocatalysts' activity as well as stability.

Design/Performance Target #1:

In Chapter 4, Pd precursor complexed with cross-linking agents, after one-step hydrothermal reaction, the three-dimensional Pd nanoassemblies were formed. The well-designed nanostructures have an excellent electrocatalytic activity which is 3 times that of commercial Pd black.

Problem statement #2:

How does the nitrogen-doping have an improving effect on the carbon supported cobalt materials in the HER?

Hypothesis #2:

Nitrogen-doping can improve electronic conductivity in HER, which significantly increase the HER kinetics, leading to a lower HER overpotential.

Design/Performance Target #2:

In Chapter 5, composites of cobalt/N-carbon for HER were produced. For example, two-dimensional hybrid displays a 103 mV operating HER overpotential, which is below the operation HER overpotential of non-doped one as defined at a practical current density of 10 mA cm^{-2} .

Problem statement #3:

How does a proper hybridization of molybdenum carbides with cobalt/carbon improve the catalysts' electrochemical performances for efficient OER?

Hypothesis #3:

Chemical hybridization of molybdenum carbides with cobalt oxides could alter the electronic structure of catalyst species and changes the interaction between the catalyst and oxygen intermediates. An ideal catalyst consists of a moderate catalyst-intermediates interaction. The catalytic active sites will be blocked if excessive heteroatoms area used, whereas the catalytic behaviors will not be improved if insufficient heteroatoms are employed.

Design/Performance Target #3:

In Chapter 6, hybrid of cobalt oxides and molybdenum carbides was prepared, the MoC-cobalt oxide electrocatalyst shows the potential of 1.56 V (vs RHE) at 10 mA cm^{-2} , which is lesser than the other electrocatalysts. For example, the overpotentials (@ 10 mA cm^{-2}) for CoOx-MoC-1 and CoOx-MoC-3 samples are 1.60 V (vs RHE) and 1.62 V (vs RHE), respectively.

Problem statement #4

(1) What is the advantageous properties of heterostructure of layered double hydroxides in electrocatalysis?

Hypothesis #4:

Seed based synthesis of microstructure would produce various heterostructure. Layered double hydroxides have been extensively used in electrocatalysis, while seed based synthesis of layered double hydroxides was not reported yet. As such, using seed based method to fabricate heterostructure of layered double hydroxides may display novel and superior properties in electrocatalysis.

Design/Performance Target #4:

In Chapter 7, binary hybrid hydroxide microstructures were prepared as a platform for electrocatalyst fabrication. Moreover, the NiCo layered double hydroxides were coated by few-layer carbon with iridium doping. The final products showed excellent electrochemical behaviors of oxygen evolution.

1.2 Objectives and Scope

This dissertation's objective is to improve the performances of electrocatalysts for energy conversion and storage applications, such objective has been achieved by carrying out the following investigations: (1) Synthesis of self-supported palladium nanoassemblies via polymer-assisted method; (2) Preparation of two dimensional Co/NC by using the 2D cobalt based MOF as the template; (3) Reconstruction of cobalt based MOF by simultaneously using polymers and molybdate; (4) Fabrication of heterostructure of layered double hydroxides using seed based procedure.

1.3 Dissertation Overview

The thesis addresses the development of various strategies for fabricating novel micro-

/nanostructures together with their intrinsic properties (e.g. composition, porosity and structure) in order to obtain a great energy efficacy for high energy storage devices (fuel cell, water splitting). In total, 8 chapters are discussed and arranged in a manner as follows:

Chapter 1 defines the problem statements, proposes the hypotheses and performance targets for this study; summarizes the objective and scope for this research; presents the findings and outcomes/originality of this work.

Chapter 2 reviews the literatures, which address the importance, mechanisms and challenges for high energy storage devices (e.g. liquid fuel cell and water splitting); discusses the kinetics limitations for electrocatalysis. It also provides the readers with knowledge on the topics (e.g. composition, porosity, and metal-intermediates electronic structure) that are related to this research. Lastly, it raises a short question to discuss and answer the PhD in the context based on the literature findings.

Chapter 3 discusses the rationale for selection of materials/methods and elaborates the principles of synthesis/characterization techniques used in this context. Also, it discusses the limitations of the characterization techniques.

Chapter 4 develops three-dimensional Pd nanoassemblies for formic acid electrooxidation.

Chapter 5 designs and synthesizes hybrid of cobalt and carbon structure for hydrogen evolution.

Chapter 6 improves performances of electrocatalysts for oxygen evolution by structure optimization and composition tuning of the cobalt MOFs.

Chapter 7 designs and synthesizes a heterostructure of layered double hydroxides with carbon coating and iridium doping.

Chapter 8 discusses the threads, implications and impacts of the thesis. It addresses whether

the hypothesis of each study has been proven, or the design target has been met. Lastly, it includes the reconnaissance studies and outstanding questions raised relating to the future work.

1.4 Findings and Outcomes/Originality

This thesis leads to several original outcomes, which are listed as following:

(1) Construction of Pd nanoassemblies could well display the catalytic sites and modify the electronic structure by adopting a PAH-assisted hydrothermal method.

(2) For the first time, a hybrid of Co/N-Carbon has been fabricated for electrochemical hydrogen evolution. Metallic cobalt nanoparticles have low H binding energy, and N-carbon facilitates charge transfer. More importantly, the metallic cobalt nanoparticles are wrapped in the N-doped carbon matrix. Therefore, such configuration displays highly efficient electrochemical hydrogen evolution.

(3) The MOF structure was reconstructed by using PVP and modified compositionally by adding molybdenum source. The optimized CoOx-MoC/NC shows an excellent oxygen evolution performance due to high surface area and compositional advantages.

(4) A novel heterostructure of LDH was fabricated by using seed based method. Moreover, the carbon coating and iridium doping of the heterostructure endow the electrocatalysts with excellent oxygen evolution performances.

References

- [1] M. Hoel and S. Kverndokk, *Resour Energy Econ*, **1996**, 18, 115-136.
- [2] J. A. I. do Sul and M. F. Costa, *Environ Pollut*, **2014**, 185, 352-364.
- [3] C. McGlade and P. Ekins, *Nature*, **2015**, 517, 187-U143.

- [4] N. Mahato, A. Banerjee, A. Gupta, S. Omar and K. Balani, *Prog Mater Sci*, **2015**, 72, 141-337.
- [5] J. J. More, P. F. Puleston, C. Kunusch and M. A. Fantova, *Ieee T Energy Conver*, **2015**, 30, 218-225.
- [6] O. Z. Sharaf and M. F. Orhan, *Renew Sust Energ Rev*, **2014**, 32, 810-853.
- [7] I. Roger, M. A. Shipman and M. D. Symes, *Nat Rev Chem*, **2017**, 1.
- [8] K. Sivula, F. Le Formal and M. Gratzel, *Chemsuschem*, **2011**, 4, 432-449.
- [9] L. A. Stern, L. G. Feng, F. Song and X. L. Hu, *Energ Environ Sci*, **2015**, 8, 2347-2351.
- [10]. C. Lamy, E. M. Belgsir and J. M. Leger, *J Appl Electrochem*, **2001**, 31, 799-809.
- [11] I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Norskov and J. Rossmeisl, *Chemcatchem*, **2011**, 3, 1159-1165.
- [12] W. J. Zhou, B. Zhou, W. Z. Li, Z. H. Zhou, S. Q. Song, G. Q. Sun, Q. Xin, S. Douvartzides, A. Goula and P. Tsiakaras, *J Power Sources*, **2004**, 126, 16-22.
- [13] Y. Y. Wang, C. Xie, D. D. Liu, X. B. Huang, J. Huo and S. Y. Wang, *Acs Appl Mater Inter*, **2016**, 8, 18652-18657.
- [14] L. H. Wu, Q. Li, C. H. Wu, H. Y. Zhu, A. Mendoza-Garcia, B. Shen, J. H. Guo and S. H. Sun, *J Am Chem Soc*, **2015**, 137, 7071-7074.
- [15] B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. Lou and X. Wang, *Nat Energy*, **2016**, 1.

Chapter 2

Literature Review

Chapter 2 collects and summarizes the recent advancements of electrocatalysts investigations. The palladium based nanostructures for electrocatalysis are first introduced. Secondly, the cobalt based electrocatalysts for electrochemical water splitting was introduced and discussed in detail. Thirdly, layered double hydroxides in electrocatalysis are discussed.

2.1 Overview

Nowadays, the depletion of fossilized energy sources and environmental pollution have triggered the intensive development of clean and efficient energy conversion and storage. In this thesis, several methods/hypotheses were developed to drive the applications of energy conversion and storage devices (e.g. Liquid fuel cell, water splitting) by design and fabrication of the electrocatalysts. The major challenge of these high energy storage devices that involve electrocatalytic processes is that low electrocatalytic performances caused by slow reaction kinetics that results in poor energy efficiency. In this dissertation, the electrocatalysts were designed to resolve the above-mentioned issues and they fall into four parts/hypotheses: (1) Palladium hierarchical nanoassembly structure has abundant pores, which contribute to more surface area with well-displayed electroactive sites, thereafter improving the electrocatalysts' activity as well as stability; (2) Nitrogen-doping can improve electronic conductivity in HER, which significantly increases the HER kinetics, leading to a lower HER overpotential; (3) Chemical hybridization of heteroatoms with cobalt oxides could modify the electronic structure of catalyst-adsorbate species, which substantially improve the oxygen evolution performances; (4) By using the nickel hydroxides as seeds, a heterostructure of layered double hydroxides is fabricated, which shows significantly enlarged specific surface area. The heterostructure is used as a platform for electrocatalysts synthesis, which show superior electrochemical oxygen evolution.

Pd-based catalysts have great advantage in electrocatalytic oxidation of formic acid, such as their low overpotential. More importantly, it has been reported that utilizing Pd catalysts electro-oxidation of formic acid mainly goes along the “direct pathway” of electrooxidation of formic acid, which avoids the formation of carbon monoxide. Therefore, Pd-based catalysts tend to have high performances for formic acid electrooxidation, because of avoiding the CO poisoning effect, which is proved highly detrimental to the performance of catalysts. While the morphology of nanocatalysts primarily decides their catalytic performance, the controllable synthesis for desirable nanostructure is urgently sought. Currently, various preparation method including solvothermal synthesis, chemical vapor deposition and hydrothermal method have been reported to produce Pd nanoparticle

catalyst. Notably, Pd-based nanocrystals whose nanoarchitecture possess larger surface area and sufficient catalytic sites attract intensive attention in electrocatalyst fabrication, owing to their excellent catalytic property.

Transitional metal based electrocatalysts provides a great platform for tuning their intrinsic properties towards desired functions, which further draws tremendous attention and offers a lot of opportunities for various applications. Especially the earlier works on cobalt based metal-organic frameworks provide valuable instruction for structure tuning of transitional metal materials. On one hand, metal-organic frameworks have plenty of nanopores, which are necessary properties for gas evolving electrochemical reaction; on the other hand, the inorganic center can be replaced which lead to vast compatibility of MOFs. Therefore, products derived from cobalt based electrocatalysts have been intensively studied because of their earth abundance and theoretical high catalytic activity. In particular, direct carbonization of MOFs is an efficient route for electrocatalyst preparation, the carbon matrix derived from the organic molecules can be a good support for catalytic sites, the literature review on MOF-derived electrocatalysts is discussed in the part of 2.3.

Transitional metal oxides derived from MOFs have also been used in electrocatalysis of oxygen evolution, due to the similar characteristic advantages derived from the porous nature of MOF. Moreover, molybdenum carbides have also been used in design and synthesis of transitional metal based electrocatalysts, considering their synergism with each other as reported by previous works, electrocatalytic aspects of molybdenum carbides are included and discussed in the part of 2.4.

Recently, layered double hydroxides have been intensively investigated in electrochemical applications, including supercapacitors, oxygen evolution and hydrogen evolution. In particular, plenty of studies reported that nickel hydroxides were grown on nickel foam, which could be directly used as an electrode material for supercapacitor. A hybrid layered double hydroxides containing cobalt and nickel for oxygen evolution is the focus of the thesis. Therefore, electrocatalytic aspects of nickel/cobalt layered double hydroxides are included and discussed in the part of 2.5.

2.2 Literature review on the nanostructured palladium for electrocatalysis

2.2.1 Noble metals in electrocatalysis

Nobel metals (Pt, Pd, Rh etc.) has long been used in the area of electrocatalysis.^[1-3] Various studies find that precious metal catalyst possess excellent electrocatalytic performance in the oxidation of an array of organic molecules, including methanol, ethanol, formaldehyde and formic acid,^[4-6] which makes it ideal candidate materials as the anode in fuel cell such as DFAFC, DMFC and DEFC.

Previously, Pt is thought to be the best catalyst for electro-oxidation, because of its high intrinsic activity. However, the high price of Pt has triggered intensive research in using other less expensive metals, meanwhile improving the activity and stability of the less expensive metals.^[7] Among these efforts, alloying Pt with other metals shows to enhance the performance.^[8-10] In particular, the alloyed Pt-Pd showed prominent electrocatalytic behaviors in formic acid electrooxidation of formic acid. The improved behaviors are usually explained by the combination of the advantageous properties of platinum and palladium.

2.2.2 Palladium in electrocatalysis

Pd-based catalysts have great advantage over Pt-based catalyst, which used to be thought as having the best property in electrocatalytic reaction, such as their low overpotential.^[11] More importantly, it has been reported that utilizing Pd catalysts electro-oxidation of formic acid mainly goes along the “direct pathway”, while for Pt catalyst, electro-oxidation of formic acid adopts a dual pathway mechanism,^[12] including “direct pathway” and a “CO pathway”. Therefore, Pd-based catalysts tend to have high performances for electro-oxidation of formic acid, because of avoiding the CO poisoning effect, which is proved highly detrimental to the performance of catalyst.

The morphology of nanocatalysts primarily decides their catalytic performance. Therefore, the controllable synthesis for desirable nanostructure is urgently sought. Currently, various preparation method including solvothermal synthesis, chemical vapor deposition and hydrothermal method ^[13-15] have been reported to produce Pd nanoparticle catalyst. Notably, Pd-based nanocrystals whose morphology possess larger surface area and high-index facets attract close attention in electrocatalysts synthesis, owing to their excellent catalytic property and dense kinks and atomic steps.^[16, 17]

2.2.3 Direct Fuel cells

Fuel cells are highly efficient energy converter, with conversion of chemical energy to electrical energy. It is expected to be the ideal candidate as future mobility provider, because of its high utilization efficiency of energy.^[18, 19] However, a lot of difficulties need to be overcome before popularizing the use of fuel cell technology. The fuel cell is composed of an electrolyte medium, a cathode and an anode. The anode facilitates the electro-oxidation of the fuel, while the cathode promotes the electro-reduction of the oxidant (usually O_2). The electrolyte serves not only as a path of charge transport, but also as a barrier between the anode and cathode. Electrons generated during the electrochemical process travel along the circuit and thereafter produce electricity.^[20]

Figure 2.1 Schematic drawing of Direct Ethanol Fuel Cell.

2.2.4 Formic acid oxidation reaction (FAOR)

Plenty of investigations have been made on the electrooxidation of formic acid, since the Direct Formic Acid Fuel Cell has some advantages. Advantages are as following: (1) Formic acid is benign and non-explosive, and the property of easily being dissolved in water makes it can be easily distributed; (2) Formic acid can be produced from biomass, therefore it is a type of recyclable sources; (3) Direct formic acid fuel cells have a high theoretical open circuit potential (1.45V).^[12]

It is usually reported that formic acid is oxidized to CO₂ via a dual path mechanism. (26-28) The dehydrogenation pathway (1) involves a reactive intermediate, while the dehydration pathway (2) forms the adsorbed CO as a poisoning species, as shown on figure 2.2.

Figure 2.2 Dual pathway of electrooxidation of formic acid.

2.2.5 Electrocatalyst for FAOR

The central part of fuel cell is the membrane electrode assembly, which is composed of a proton exchange membrane, electrocatalyst and gas diffusion layers. Most of the cost lies on the electrocatalyst, because the most active catalysts are noble metals which is of high

price. For this reason, it is critically important to improve the catalysts' activity to commercialize PEMFC. Typically, the electrooxidation of formic acid was studied on noble metals such as Pt,^[21] palladium.^[22] For example, extensive investigations reported the improvement of catalytic behaviors of formic acid on platinum by coating various surface adatoms. Modifier elements such as Ru,^[23] Cu,^[24] Pb,^[25] have been used for boost of catalytic performance. In particular, the Pt-Pd alloy^[26] has produced an increased reactivity. The enhancement of the electrocatalytic activity induced by the adatoms has been explained by bifunctional mechanism, which prevents surface poison.

2.2.6 Synthesis method of electrocatalysts

(1) Wet chemical reduction method

The method usually involves water or organic chemicals as the media for reaction and uses protective agents as a stabilizer while the reducing agents reduce the metal precursor into the metal nanoparticles. Common protective ligands are PVP.^[27] Although this method can produce nanoparticles with a controlled size, the presence of protective agents can hinder the metal's catalytic active sites and hence lower the rate of catalysis. Also, the process may generate toxic compound that is not benign towards the environment.

(2) Ultrasonic-assisted method

This method uses a small amount of liquid mixed with the precursor and surrounded by surfactants, forming a micro-emulsion. The micro-emulsion is dispersed in liquid phase and the reducing agent is introduced into the solution by stirring and the reaction is finished within minutes.^[28]

(3) Electrochemical deposition

Many studies have reported the synthesis of Pt nanoparticles using electrochemical methods. Generally, the cycled potential would be applied on electrode to produce various

nanoparticles. For example, Wang et al have developed a methodology for synthesis of high-indexed platinum nanocrystals through a pulsed potential, by electrodepositing platinum nanospheres on glassy carbon electrode firstly.^[29]

2.2.7 Summary

Among all the methods, the hydrothermal chemical reduction method proved to be a suitable technique for growing nanoparticles, because of its simplicity, low cost and environmentally benign. Previously many chemical methods adopting organic solvent systems have been put forward for Pd nanostructures synthesis, albeit utilizing expensive organometallic precursors and involving complicated protocols.^[30, 31] Currently scientific community is increasingly seeking for low cost reactants and environmentally friendly reaction protocols in nanomaterial synthesis. Also in nanoparticle production, usually the monodispersity and uniformity of the products are not satisfactory. In this work, the focus is using wet chemical reduction method to fabricate Pd nanoassemblies for electrooxidation of formic acid, with environmentally benign materials.

2.3 Literature review on the cobalt based electrocatalytic hydrogen evolution

2.3.1 Electrochemical water splitting

Nowadays, the energy crisis and environmental issue are the emerging topics faced by the society, which greatly motivate scientists' enthusiasm to devote to the development of sustainable energy applications, one viable way is generation of electricity from reproducible source (solar energy), such electricity energy can be converted to chemical form (hydrogen and oxygen).^[32] Driven by these concerns, it is believed electrochemical water splitting can be a promising solution towards sustainable energy production.^[33] The water splitting is an energy-conversion technology which produces hydrogen (H₂) on the cathode and oxygen (O₂) on the anode.^[34] Electrolysis is an important technology for the production of hydrogen and oxygen with several advantages including high energy conversion efficiency and highly pure gas production.^[35] More importantly, H₂ with high

energy density can be used as an alternative for electricity storage for fuel cells because chemicals can be stored in a portable and safe way.^[36] Therefore, electrochemical water splitting is a promising alternative when coupled with renewable energy sources.

Van Trostwijk and Deiman reported the first water splitting in 1789, this technology has been intensively studied and applied for real applications.^[37] For example, it was used for providing the necessary oxygen gas for the human daily use at the submarines.^[38] Though this technology possesses a lot of advantages, the technology still needs improvement to increase efficiency and long-term durability during practical applications and commercially viable production. Generally, the electrochemical water splitting can be sorted out into two different systems based on the nature of electrolyte: alkaline water electrolyzers and polymer electrolyte membrane electrolysis in acidic media.^[39] Notably, this thesis address issues with the overall water splitting at the alkaline media, and the reaction can be described by the following equations:

2.3.2 Hydrogen evolution

The water splitting coupled with solar energy would be a promising and sustainable way for resolving the energy depletion, the overall water splitting is composed by two reactions: hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Hydrogen evolution is the reduction reaction at cathode, which requires a low-cost catalyst with high catalytic behaviors so as to enhance the efficiency of the overall water splitting.^[40] Currently, the most active catalyst for HER under alkaline media is Pt with nearly zero overpotential to drive the onset of hydrogen evolution.^[41] However, the high price of Pt hinders its commercial and large-scale applications. As such, it is urgent to design and synthesize highly excellent hydrogen evolution electrocatalysts using high abundance materials. Recent studies in the scientific community have shown that transition metal based electrocatalysts, would be the suitable and inexpensive candidates for the

electrochemical hydrogen evolution reaction.^[42] The hydrogen evolution process at alkaline media is as following:

- (1) Volmer: $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$
- (2) Heyrovsky: $\text{H}_2\text{O} + \text{e}^- + \text{H}^* \rightarrow \text{H}_2 + \text{OH}^-$
- (3) Tafel: $2\text{H}^* \rightarrow \text{H}_2$

During the overall hydrogen evolution reaction, in the first step, i.e. Volmer step, the bonding of hydrogen with the surface of the electrocatalysts; the second step is the molecular H_2 formation, either by Heyrovsky step or by Tafel step.^[43] The hydrogen evolution performances of various electrocatalysts can be summarized in the volcano plot as shown in Figure 2.3.^[44] An excellent electrocatalyst would offer catalytic sites which show a nearly zero Gibbs free energy change towards adsorbed hydrogen. Therefore, a suitable electrocatalyst should neither bind the intermediate M-H_{ads} too weakly nor too strongly.^[45] Notably, in the volcano plot of exchange current density vs Gibbs free energy of adsorbed hydrogen, the value for cobalt sits closely with those of the platinum metals, indicating the advantages of cobalt-based electrocatalysts as an alternative to Pt for hydrogen evolution electrocatalysis. There are several important parameters to describe the electrochemical performances of hydrogen evolution catalysts, this part will make discussion on them.

Figure 2.3 Volcano plot of various electrocatalyst (exchange current density vs Gibbs free energy), reproduced with permission.^[44]

Butler-Volmer equation is used to relate current density and overpotential,^[46] the equation is given by:

$$j = j_0[e^{(1-\alpha)\eta f} - e^{-\alpha\eta f}]$$

j : current density,

j_0 : exchange current density,

η : overpotential (overpotential is defined as the difference between the applied potential and the reversible potential),

α : transfer coefficient,

$f = F/RT$ (F : Faraday constant, R : gas constant, T : temperature in Kelvin).

The onset potential is the smallest potential required for the electrocatalyst to initiate and drive the hydrogen evolution process, therefore, this value is important when evaluating a electrocatalyst.^[47] On the other hand, overpotential at a designated current density is a commonly accepted value to study an electrocatalyst in the operating media, usually the designated current density is 10 mA cm^{-2} , which is the standard current density of solar fuel synthesis.^[48]

In particular, Tafel equation can be derived from the Butler–Volmer equation when overpotential is large,^[49] it is as following:

$$\eta = a + b \log j$$

The electrochemical evaluations of hydrogen evolution electrocatalysts are described by the Tafel slope (b) of Tafel equation. Generally, Tafel slope can be related to the catalyst's reaction kinetics. The value of b depends on the reaction steps and the adsorption surface of the electrocatalysts.^[50] In case of cobalt-based electrocatalysts, the Tafel slope usually vary in a wide range. For example, previous studies have shown the Tafel slope of cobalt electrocatalysts displayed a range of (50 mV dec^{-1} , 231 mV dec^{-1}).^[51]

During characterization of an efficient electrocatalyst for hydrogen evolution, long term stability is a vital parameter, the evaluation of electrocatalytic stability for electrocatalysts

is conducted by the test of current density-time for the hydrogen evolution, which is known as chronoamperometric analyses and is a critical parameter describing the electrochemical reaction stability at a constant potential.^[52] Stability under constant potential is tested for several hours. Nowadays, the widely accepted setting is applying a constant potential (the potential is selected when the current density is 10 mA cm^{-2}) by using chronoamperometry, which is used to test the high-performance electrocatalyst towards hydrogen evolution. Additionally, an electrocatalyst may be subject to CV cycling test for the purpose of investigation of its stability,^[53] such test is also named as accelerated degradation test (ADT). For hydrogen evolution, the ADT is conducted for several thousands of cycles. All of the above-mentioned parameters are of importance to optimize the performances of cathode materials for HER.

2.3.3 Cobalt based electrocatalysts

(1) Overall introduction

In general, cobalt based electrocatalysts have several advantageous properties in terms of electrochemical reaction. For example, metallic cobalt has a low hydrogen binding energy.^[54] As a result, cobalt could be used as good starting materials for hydrogen evolution electrocatalysts. Due to their earth abundance and high activity for hydrogen evolution, cobalt based electrocatalysts are expected to replace Pt in electrochemical hydrogen production.^[55] Recently, intensive investigations for the synthesis of cobalt based catalysts have been conducted, particularly speaking, those studies include carbon encapsulated cobalt nanoparticles dispersed on graphene sheets, molecular cobalt complexes and Co-doped iron pyrite.^[56-58]

(2) Cobalt based electrocatalysts

Over the past decades, extensive investigations have demonstrated that transitional metal (Fe, Co, Ni) products are excellent starting materials for electrocatalytic applications such as hydrogen evolution, oxygen evolution and electrochemical capacitors.^[59-61] Notably,

cobalt nanocrystallites have been frequently employed as an electrochemical hydrogen evolution electrocatalyst, due to its propitious hydrogen atom binding energy.^[54] Zhou et al designed and prepared the carbon-wrapped cobalt nanoparticles which were deposited on graphene, the fabrication process is as following: solvothermal method followed by calcination procedure. The products showed a small overpotential of -49 mV.^[62] This work provides a novel route of fabrication of outstanding electrocatalysts for electrochemical hydrogen evolution. Subsequently, the authors prepared carbon-wrapped cobalt nanorod which were supported on a titanium mesh, which displayed remarkable hydrogen evolution behaviors.^[63] Experimentally, the authors prepared Co_3O_4 nanorod on the support of a titanium mesh, which were reduced to metallic cobalt by thermal decomposition of dicyanodiamine. However, controlled fabrication of micro-/nanostructured metals with desirable compositions for superior electrochemical performances remains a great challenge, such difficulty mainly originates from the inevitable aggregation of nanoparticles at high reaction temperature during synthesis and usage, which leads to lower electrochemical performance.^[64]

2.3.4 MOF-derived cobalt electrocatalysts

Metal-organic frameworks (MOFs) are crystalline porous architectures which are made up metal ions and organic ligands, have been identified as promising templates electrochemical catalysis. MOFs have many promising properties such as ordered pores and large surface area which are required for highly efficient hydrogen evolution process.^[65] The porous structure of MOFs serves as a good platform for electrocatalyst synthesis due to their unique structural advantage for synthesizing metal-carbon hybrid materials. Wu et al reported a MOFs-assisted route for synthesizing molybdenum carbide nanoparticles as electrocatalysts for electrochemical hydrogen evolution reaction.^[66] The as-obtained products showed an onset potential of 80 mV (vs RHE), had the current density of 10 mA cm^{-2} at overpotential of 151 mV. The authors believed that such metal-organic framework assisted methodology is beneficial for a variety of electrocatalysts development. While You et al showed a metal-organic framework-derived method to produce the hybrid of Co-P/NC for hydrogen evolution.^[67] Notably, the products showed high specific surface area,

such property is beneficial for gas-evolving reaction. The fabrication of Co-P/NC followed the two-step synthesis route: for the first step, ZIF-67 is carbonization in argon; for the second step, the carbonized products underwent phosphidation by using sodium hypophosphite. As a result, the optimal products displayed abundant mesopores and high specific surface area, which induced efficient exposure of electroactive sites, facile charge transport and gas release. Therefore, the resulting products exhibited superior electrocatalytic behaviors: they required a small overpotential of 154 mV at 10 mA cm⁻² for electrochemical hydrogen evolution.

2.3.5 Summary

In conclusion, cobalt based electrocatalysts derived from MOF have shown strong catalytic performances for hydrogen evolution. Recently, intensive attention has been put on controlling the morphology at the nanoscale and hybridizing MOF with other doping molecules. Therefore, it is foreseeable that there is still sufficient potential to utilize MOF for design and synthesis of efficient electrocatalysts, by manipulating micro-/nanostructure and optimizing composition.

2.4 Literature review on the cobalt based catalyst for oxygen evolution

2.4.1 Oxygen evolution

(1) Overall introduction

In general, the oxygen evolution reaction is composed by some elementary reactions, the metal catalytic site (M) adsorb the proton followed by the electron transfer, secondly the metal surface form an O-O bond,^[68] which can be described as four individual reaction steps: where M refers to the adsorption metal site on the surface of catalyst.

Due to the sluggish kinetics of bond formation, some important aspects should be considered when designing and producing excellent electrocatalysts for oxygen evolution reaction. First, the catalysts need to keep contact with electrolytes during the electrochemical reaction, as such, the electrocatalysts should have large electrochemical active surface area.^[69] Second, the oxygen evolution process would produce gaseous bubbles inside and outside the electrocatalysts, which may be addressed by developing porous materials.^[70] Third, the current commercial catalysts are susceptible to corrosion at alkaline media under operating potentials.^[71] To sum up, the superior electrocatalysts for oxygen evolution would have low free energy for each reaction step, higher surface area and be corrosion resistant.

(2) Parameters of evaluating electrochemical oxygen evolution

In this part, discussion on the parameters for evaluating and comparing the catalytic performances of the electrocatalysts. During measurements of electrochemical oxygen evolution reaction, testing is conducted with a reference electrode (in this work, Ag/AgCl reference electrode is used). Moreover, the overpotential (η) is the result of the subtraction value between the applied potentials and the standard reduction potential of oxygen. Therefore, overpotential (η) = $V_{\text{RHE}} - 1.23 \text{ V}$, where 1.23 V (vs RHE) is the standard thermodynamic potential for water splitting.^[72] Herein, the applied potential (V_{RHE}) is converted in the scale versus the reversible hydrogen electrode (RHE) (e.g., $V_{0(\text{Ag}/\text{AgCl})} = 0.197 \text{ V vs. RHE}$). Under this circumstance, the applied potential can be converted into the RHE scale using this equation: $V_{\text{RHE}} = V_{(\text{Ag}/\text{AgCl})} + V_{0(\text{Ag}/\text{AgCl})} + 0.059 \cdot \text{pH}$. The most direct evaluation of describing the performances of the catalyst towards electrochemical oxygen evolution is the current density under a specific applied potential.^[73] In this case, the applied potential on the electrode materials can be directly determined as the driving force to initiate the electrochemical oxygen evolution reaction.

As discussed in the previous part, the Butler–Volmer equation can be put in the simplified form at large overpotential, it is as following:

$$\eta = a + b \log j$$

Tafel slope (b) is a useful parameter, which is extensively used as the evaluation parameter for the catalytic kinetics towards electrochemical oxygen evolution, considering that it is effective to quantitatively make evaluation of the behaviors of the electrocatalysts.^[74]

Long term stability towards electrochemical oxygen evolution is of critical importance when characterizing the electrocatalysts, chronoamperometry is usually conducted to measure this stability. Specifically, a constant potential is set for the electrocatalysts for several hours. Currently the widely accepted setting is applying a constant potential for about 10 h by using chronoamperometry, which is sufficient to evaluate the excellent electrocatalysts for the electrochemical oxygen evolution.^[75]

As mentioned in the introduction, the catalysts need to keep contact with electrolytes during the electrochemical reaction, hence the designed catalyst should have a high electrochemical active surface area (EASA), the electrochemical active surface area is studies by using CV with different scan rates. In practice, the EASAs of the electrocatalysts were represented by using double-layer capacitance(C_{dl}), which is directly used to represent EASA. By comparing the EASA of various samples, it is possible to design and synthesize effective oxygen evolution electrocatalysts with high performance.^[76]

2.4.2 Cobalt based materials for oxygen evolution

(1) Cobalt based electrocatalysts

To develop commercially viable water splitting equipment, development of cost-effective electrocatalysts for oxygen evolution is essential. In recent years, because of their earth abundance rich redox activity, 3d transition-metal-based electrocatalysts (for example, cobalt oxides) have been considered as promising OER electrocatalyst candidates.^[77]

Notably, cobalt oxide based electrocatalysts have shown promising catalytic performance towards oxygen evolution reaction. For example, Bell et al investigated how metals enhance the activity of cobalt oxides for electrochemical oxygen evolution.^[78] In particular, they reported cobalt oxide electrocatalyst which were supported on the surface of gold. Notably, experimental results showed that CoOx/Au displayed an activity which was much higher than that of Ir and that of bulk cobalt oxides; While Sun et al reported a convenient heating route for synthesizing Co₃O₄ with non-layered structures by using CoO as starting materials.^[79] Ultimately, the atomically-thick Co₃O₄ nanostructure delivered a high current density of 341.7 mA cm⁻² (at 1.0 V vs. Ag/AgCl), such current density is thirty times larger than that of the commercial electrocatalysts of Pt/C. However, cobalt oxide nanoparticle based electrocatalysts still have many disadvantages such as aggregation issues during long-time usage.^[80] As such, it is necessary to design electrocatalysts' microarchitecture and composition to address such drawbacks.

2.4.3 Molybdenum carbides in electrocatalysis

Recently, molybdenum carbides have been extensively used as composition tuning agents and are found to promote electrocatalytic activity and stability, possibly because of their high electronic conductivity and multiple valence states.^[81] For example, Zhang et al reported that the formation of MoC@Ni heterostructures and the resulting synergistic effect between MoC and Ni can improve the reaction kinetics, contributing to significantly improved oxygen evolution activity with a low overpotential of 310 mV to reach 10 mA cm⁻².^[82] This electrocatalyst was synthesized by a heating treatment of homogeneously mixed melamine, molybdate tetrahydrate and nickel chloride hexahydrate. Jiang et al fabricated a microarchitecture comprised of carbon wrapped cobalt and molybdenum carbide, such products showed superior behaviors for electrochemical oxygen evolution catalysis in alkaline medium, which exhibited the current density of 10 mA cm⁻² at an overpotentials of 0.33 V.^[83] Therefore, by using cobalt MOF hybridized with molybdenum carbide, the as-prepared composite materials of CoOx-MoC/N-doped carbon may be a superior electrocatalyst for electrochemical oxygen evolution.

2.4.4 MOF-derived cobalt materials for electrochemical oxygen evolution

Metal-organic frameworks (MOFs) have attracted much interest for electrocatalysis as they are highly porous. The porous structure of MOFs offers a unique structural advantage for synthesizing metal oxide-carbon hybrid material.^[84] Ma et al produced MOF-derived cobalt oxide-carbon nanowire arrays for oxygen evolution reaction.^[85] The detailed synthesis process is as following: firstly a layered cobalt MOF was grown on copper foil via an aqueous procedure; next, the cobalt MOFs were carbonized into the hybrid of Co_3O_4 and carbon, in which the inorganic component was converted to cobalt oxide and the organic component was converted carbon matrix. Moreover, the as-prepared hybrid materials possessed abundant pores. This novel oxygen evolution electrode made from the products showed excellent electrochemical oxygen evolution performances. In particular, it delivered an onset potential of 1.47 V (vs RHE) and maintained a robust current density at 1.52 V during the long-term stability tests. While Liu et al used cobalt MOFs to produce a novel hollow structure of cobalt phosphides.^[86] The as-obtained cobalt phosphides possessed large surface area and abundant pores, which would offer electroactive sites. Notably, the as-obtained structure showed outstanding electrocatalytic behaviors for oxygen evolution reaction, which displayed an overpotential of 400 mV at 10 mA cm^{-2} . Furthermore, the results are better than those of particulate cobalt phosphides. Therefore, this porous nature of MOF-derived electrocatalysts contribute to low overpotentials and excellent electrochemical performances for oxygen evolution reaction.

2.4.5 Summary

To conclude, MOF-derived cobalt based electrocatalysts possess strong catalytic electrocatalytic capability for oxygen evolution, molybdenum carbides are further used to modify the composition and improve their performances. Nowadays, plenty of bimetallic MOFs have been fabricated as electrocatalyst precursors, based on the knowledge that the metal node of MOFs can be easily replaced by other similar metals. Inspired by this strategy, the porous nature of MOFs can be utilized to host other distinct metal ions, to produce homogeneously mixed bimetal hybridized MOFs. The newly introduced heteroatoms

might play beneficial roles in tuning the electronic structure of the host materials for superior electrocatalyst synthesis.

2.5 Literature review on the layered double hydroxides in electrocatalysis

2.5.1 Layered double hydroxides

Layered double hydroxide comprises of metal cations (Fe, Co, Ni), hydroxyl groups (OH^-) and intercalated anions (NO_3^-) in a repetitive manner. Layered double hydroxides have extensive applications such as drug controlled release, electrochemical sensing and supercapacitors,^[87-89] because of LDH's unique structural repetitive layered characteristics and ease of replacement of the anions. In particular, Li et al reported the intercalation of an anti-inflammatory molecule into LDH, this drug could be released when the interlayer distance was expanded resulted from the pH increase.^[90] This example showed that LDH can be developed as a platform for drug delivery system. Moreover, Vialat et al produced cobalt layered double hydroxides by using cobalt hydroxides as precursors via an oxidation route.^[91] The LDH was used to fabricate electrochemical capacitors, which displayed high energy storage performances due to their layered characteristics and electronic conductivity afforded by cobalt cations. More recently, layered double hydroxides have been utilized in the development of electrocatalysts, such hydrogen evolution and oxygen evolution, such discussion will be included in the following part.

2.5.2 Layered double hydroxides as electrocatalysts

Layered double hydroxides have been intensively studied in electrocatalysis because of their earth abundance and intrinsic activity.^[92] For example, Chen et al produced ruthenium-doped nickel-iron layered double hydroxides, the products displayed better electrochemical hydrogen evolution performances than that of the state-of-the-art electrocatalysts (Pt/C).^[93] Recently, various studies reported that the transformation of hydroxides to (oxo)hydroxides would be beneficial for improving electrochemical oxygen evolution behaviors. While Li et al synthesized high-performance oxygen evolution

electrocatalysts by tuning the electronic structure of nickel-iron LDH via vanadium-doping.^[94] Additionally, Yang et al directly grew nickel-iron-chromium layered double hydroxides on carbon paper for electrochemical oxygen evolving reaction.^[95]

2.5.3 Summary

To conclude, layered double hydroxide based electrocatalysts have shown unprecedentedly high catalytic activity for oxygen evolution, some doping atoms such as ruthenium and vanadium can be used to further improve the oxygen evolution capabilities. At present, most of the monometallic, bimetallic and trimetallic layered double hydroxides are grown on hard templates such as nickel foam, carbon paper, the layered double hydroxides are produced in a macroscale way. However, in order to fundamentally improve the electrochemical catalytic behaviors of layered double hydroxides, it is necessary to manipulate their micro-/nanostructure and optimize the compositions. However, such controlled fabrication of layered double hydroxides has been little reported. Based on this knowledge, the electrocatalytic performances of layered double hydroxides may be significantly improved via structure engineering and composition optimization.

2.6 Question to answer and PhD in context based on literature in section 2.2

(1) Question: How can the electrocatalytic behaviors of palladium towards the electrooxidation of formic acid be improved? What is a suitable method to fabricate the palladium electrocatalyst for electrooxidation of formic acid?

Answer: As discussed in the first part the literature review, the nanostructure of electrocatalysts has strong influence on their catalytic performances. In particular, Pd-based nanocrystals which possess larger surface and porous properties have attracted intensive attention in electrocatalysts synthesis. Therefore, the controllable synthesis of three-dimensional nanostructure is urgently researched. Among various preparation method including wet chemical synthesis, chemical vapor deposition, ultrasonic assisted

method, wet chemical synthesis has been reported to be an ideal way to produce Pd nanoparticle catalyst, due to their simplicity and scalability.

(2) PhD in context:

In this work, two different Pd materials have been produced, Pd bulk and Pd nanoassemblies. The results show that by careful design of 3D nanoarchitecture of palladium with the assistance of polymers, the nanoarchitecture has abundant pores and high surface area. Moreover, it is tested that the 3D Pd nanoassemblies were used as catalysts for formic acid electrooxidation. Compared to Pd bulk produced without using polymers and the commercial Pd black, the Pd nanoassemblies exhibited higher electrochemical activity. It is speculated that the pores of nanostructure provide a shorter charge transport pathway, which accelerates the reaction kinetics and improves the efficiency of fuel cell. Such facile hydrothermal process for fabrication of palladium nanostructure might serve as an example for other electrocatalyst synthesis.

2.7 Question to answer and PhD in context based on literature in section 2.3

(1) Question: What are the advantages of using cobalt MOF to fabricate electrocatalysts for hydrogen evolution?

Answer: As discussed in the second part of literature review, metal-organic frameworks (MOFs) are crystalline porous architectures composed by metal ions and organic ligands. MOFs have outstanding properties such as ordered pores and large surface area. Therefore, MOFs have been regarded as promising platform in electrocatalysis. Moreover, the cobalt has low hydrogen binding energy and rich redox chemistry. Thus, it is very likely that excellent hydrogen evolution electrocatalysts can be produced by using cobalt MOFs as precursors.

(2) PhD in context:

In this thesis, various electrocatalysts were derived (cobalt oxides, Co/Carbon, Co/N-Carbon) from the layered cobalt MOFs. The hybrid of Co/N-Carbon show enhanced activity, and better cycled durability when compared to a commercial Pt/C electrocatalyst under the alkaline media for hydrogen evolution. The advantages of Co/N-Carbon electrocatalysts originate from the integration of cobalt nanoparticles, N-doped carbon matrix, which are inherited from their precursors, cobalt MOFs. This work well displays the potential of using cobalt MOFs to fabricate various electrocatalysts for applications of energy conversion and storage.

2.8 Question to answer and PhD in context based on literature in section 2.4

(1) Question: How can the advantageous properties of MOFs be utilized for electrochemical oxygen evolution?

Answer: Considering the ordered pores of MOFs, various molecules and atoms could be introduced into the cobalt MOFs to tune the derivatives' properties for oxygen evolution. Therefore, in this work, by chemically hybridizing cobalt and molybdenum in cobalt MOFs, the derived electrocatalysts of CoO_x-MoC showed significantly enhancement of the electrocatalytic performances of oxygen evolution. The results indicated that the introduction of molybdenum could improve the formation of more electroactive sites for oxygen evolution, which ultimately improving the electrochemical performances. As such, more effective electrocatalysts for energy and storage devices could be fabricated, by making good use of MOFs' vast compatibility.

(2) PhD in context:

In this research, cobalt oxides are used as the catalytic materials, MoC material is chosen to tune the properties of cobalt oxides, due to its intrinsic properties as mentioned in section 2.5. More importantly, experimental results show that the hybridized CoO_x-MoC products exhibits the low onset overpotential and the overpotential at the current density of 10 mA

cm⁻². These results demonstrate the feasibility of producing effective electrocatalysts by using cobalt MOFs hybridized with other molecules.

2.9 Question to answer and PhD in context based on literature in section 2.5

(1) Question: What are the advantageous properties of the heterostructure of layered double hydroxides towards electrochemical oxygen evolution reaction?

Answer: Layered double hydroxides have been frequently employed in electrocatalysis, while seed based synthesis of layered double hydroxides was not reported yet. As such, using seed based method to fabricate heterostructure of layered double hydroxides may display novel microstructure with attractive properties such as porous and large surface area. All these properties are beneficial for oxygen evolving reaction.

(2) PhD in context:

Heterostructure of layered double hydroxide microstructures was prepared as a platform for electrocatalyst synthesis. Moreover, the NiCo layered double hydroxides were coated by few-layer carbon with iridium doping. The final products showed excellent electrochemical behaviors of oxygen evolution. This work demonstrates an example of producing intricate microstructure as a versatile platform for electrochemical applications.

References

- [1] G. T. Fu, W. Han, L. F. Yao, J. Lin, S. H. Wei, Y. Chen, Y. W. Tang, Y. M. Zhou, T. H. Lu and X. H. Xia, *J Mater Chem*, **2012**, 22, 17604-17611.
- [2] B. R. Sathe, B. K. Balan and V. K. Pillai, *Energ Environ Sci*, **2011**, 4, 1029-1036.
- [3] J. F. Xu, G. T. Fu, Y. W. Tang, Y. M. Zhou, Y. Chen and T. H. Lu, *J Mater Chem*, **2012**, 22, 13585-13590.
- [4] M. Arenz, V. Stamenkovic, T. J. Schmidt, K. Wandelt, P. N. Ross and N. M. Markovic, *Phys Chem Chem Phys*, **2003**, 5, 4242-4251.

- [5] A. Safavi, N. Maleki, F. Farjami and E. Farjami, *J Electroanal Chem*, **2009**, 626, 75-79.
- [6] C. W. Xu, L. Q. Cheng, P. K. Shen and Y. L. Liu, *Electrochem Commun*, **2007**, 9, 997-1001.
- [7] M. S. Wilson, J. A. Valerio and S. Gottesfeld, *Electrochim Acta*, **1995**, 40, 355-363.
- [8] D. S. Wang and Y. D. Li, *Adv Mater*, **2011**, 23, 1044-1060.
- [9] H. Z. Yang, J. Zhang, K. Sun, S. Z. Zou and J. Y. Fang, *Angew Chem Int Edit*, **2010**, 49, 6848-6851.
- [10] X. Zhao, M. Yin, L. Ma, L. Liang, C. P. Liu, J. H. Liao, T. H. Lu and W. Xing, *Energ Environ Sci*, **2011**, 4, 2736-2753.
- [11] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J Phys Chem B*, **2004**, 108, 17886-17892.
- [12] C. Rice, R. I. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski and T. Barnard, *J Power Sources*, **2002**, 111, 83-89.
- [13] A. Rabenau, *Angew Chem Int Edit*, **1985**, 24, 1026-1040.
- [14] T. Ramulifho, K. I. Ozoemena, R. M. Modibedi, C. J. Jafta and M. K. Mathe, *Electrochim Acta*, **2012**, 59, 310-320.
- [15] G. Xomeritakis and Y. S. Lin, *J Membrane Sci*, **1996**, 120, 261-272.
- [16] J. W. Hong, M. Kim, Y. Kim and S. W. Han, *Chem-Eur J*, **2012**, 18, 16626-16630.
- [17] Y. J. Deng, N. Tian, Z. Y. Zhou, R. Huang, Z. L. Liu, J. Xiao and S. G. Sun, *Chem Sci*, **2012**, 3, 1157-1161.
- [18] C. K. Dyer, *J Power Sources*, **2002**, 106, 31-34.
- [19] B. C. H. Steele and A. Heinzl, *Nature*, **2001**, 414, 345-352.
- [20] T. E. Springer, T. A. Zawodzinski and S. Gottesfeld, *J Electrochem Soc*, **1991**, 138, 2334-2342.
- [21] T. Iwasita, X. H. Xia, E. Herrero and H. D. Liess, *Langmuir*, **1996**, 12, 4260-4265.
- [22] A. Capon and R. Parsons, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **1973**, 44, 239-254.
- [23] H. A. Gasteiger, N. Marković, P. N. Ross Jr and E. J. Cairns, *Electrochim Acta*, **1994**, 39, 1825-1832.

- [24] A. Taylor, S. Kirkland and S. Brummer, *Transactions of the Faraday Society*, **1971**, 67, 819-827.
- [25] M. Watanabe, M. Horiuchi and S. Motoo, *Journal of electroanalytical chemistry and interfacial electrochemistry*, **1988**, 250, 117-125.
- [26] A. Capon and R. Parsons, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **1975**, 65, 285-305.
- [27] S. E. Skrabalak, L. Au, X. D. Li and Y. N. Xia, *Nat Protoc*, **2007**, 2, 2182-2190.
- [28] S. C. Tang, S. Vongehr, Z. Zheng, H. Ren and X. K. Meng, *Nanotechnology*, **2012**, 23.
- [29] Y. Yu, Q. Zhang, B. Liu and J. Y. Lee, *J Am Chem Soc*, **2010**, 132, 18258-18265.
- [30] C. Wang, H. Daimon, Y. Lee, J. Kim and S. Sun, *J Am Chem Soc*, **2007**, 129, 6974-+.
- [31] Y. J. Xiong, B. Wiley, J. Y. Chen, Z. Y. Li, Y. D. Yin and Y. N. Xia, *Angew Chem Int Edit*, **2005**, 44, 7913-7917.
- [32] E. L. Miller, *Energ Environ Sci*, **2015**, 8, 2809-2810.
- [33] X. M. Li, X. G. Hao, A. Abudula and G. Q. Guan, *J Mater Chem A*, **2016**, 4, 11973-12000.
- [34] M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renew Sust Energ Rev*, **2007**, 11, 401-425.
- [35] K. Zeng and D. K. Zhang, *Prog Energ Combust*, **2010**, 36, 307-326.
- [36] S. Sharma and S. K. Ghoshal, *Renew Sust Energ Rev*, **2015**, 43, 1151-1158.
- [37] Y. Matsumoto and E. Sato, *Materials chemistry and physics*, **1986**, 14, 397-426.
- [38] P. Millet, F. Andolfatto and R. Durand, *Int J Hydrogen Energ*, **1996**, 21, 87-93.
- [39] L. R. Ma, S. Sui and Y. C. Zhai, *Int J Hydrogen Energ*, **2009**, 34, 678-684.
- [40] P. Jiang, Q. Liu, Y. H. Liang, J. Q. Tian, A. M. Asiri and X. P. Sun, *Angew Chem Int Edit*, **2014**, 53, 12855-12859.
- [41] C. G. Morales-Guio, L. A. Stern and X. L. Hu, *Chem Soc Rev*, **2014**, 43, 6555-6569.
- [42] D. S. Kong, J. J. Cha, H. T. Wang, H. R. Lee and Y. Cui, *Energ Environ Sci*, **2013**, 6, 3553-3558.
- [43] S. Trasatti, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **1972**, 39, 163-184.

- [44] T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science*, **2007**, 317, 100-102.
- [45] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jorgensen, J. H. Nielsen, S. Horch, I. Chorkendorff and J. K. Nørskov, *J Am Chem Soc*, **2005**, 127, 5308-5309.
- [46] D. A. Noren and M. A. Hoffman, *J Power Sources*, **2005**, 152, 175-181.
- [47] N. Fujiwara, K. A. Friedrich and U. Stimming, *J Electroanal Chem*, **1999**, 472, 120-125.
- [48] C. C. L. McCrory, S. H. Jung, J. C. Peters and T. F. Jaramillo, *J Am Chem Soc*, **2013**, 135, 16977-16987.
- [49] E. Gileadi and E. Kirowa-Eisner, *Corros Sci*, **2005**, 47, 3068-3085.
- [50] B. E. Conway and B. V. Tilak, *Electrochim Acta*, **2002**, 47, 3571-3594.
- [51] Z. P. Huang, Z. Z. Chen, Z. B. Chen, C. C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, **2014**, 9, 373-382.
- [52] P. Xiao, M. A. Sk, L. Thia, X. M. Ge, R. J. Lim, J. Y. Wang, K. H. Lim and X. Wang, *Energ Environ Sci*, **2014**, 7, 2624-2629.
- [53] J. F. Xie, H. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. Lou and Y. Xie, *Adv Mater*, **2013**, 25, 5807.
- [54] H. Y. Jin, J. Wang, D. F. Su, Z. Z. Wei, Z. F. Pang and Y. Wang, *J Am Chem Soc*, **2015**, 137, 2688-2694.
- [55] M. S. Faber, K. Park, M. Caban-Acevedo, P. K. Santra and S. Jin, *J Phys Chem Lett*, **2013**, 4, 1843-1849.
- [56] H. L. Fei, Y. Yang, Z. W. Peng, G. D. Ruan, Q. F. Zhong, L. Li, E. L. G. Samuel and J. M. Tour, *Acs Appl Mater Inter*, **2015**, 7, 8083-8087.
- [57] C. C. L. McCrory, C. Uyeda and J. C. Peters, *J Am Chem Soc*, **2012**, 134, 3164-3170.
- [58] D. Y. Wang, M. Gong, H. L. Chou, C. J. Pan, H. A. Chen, Y. P. Wu, M. C. Lin, M. Y. Guan, J. Yang, C. W. Chen, Y. L. Wang, B. J. Hwang, C. C. Chen and H. J. Dai, *J Am Chem Soc*, **2015**, 137, 1587-1592.
- [59] M. S. Burke, M. G. Kast, L. Trotochaud, A. M. Smith and S. W. Boettcher, *J Am Chem Soc*, **2015**, 137, 3638-3648.
- [60] C. Lupi, A. Dell'Era and M. Pasquali, *Int J Hydrogen Energ*, **2009**, 34, 2101-2106.

- [61] T. Y. Wei, C. H. Chen, H. C. Chien, S. Y. Lu and C. C. Hu, *Adv Mater*, **2010**, 22, 347.
- [62] W. J. Zhou, J. Zhou, Y. C. Zhou, J. Lu, K. Zhou, L. J. Yang, Z. H. Tang, L. G. Li and S. W. Chen, *Chem Mater*, **2015**, 27, 2026-2032.
- [63] W. J. Zhou, Y. C. Zhou, L. J. Yang, J. L. Huang, Y. T. Ke, K. Zhou, L. G. Li and S. W. Chen, *J Mater Chem A*, **2015**, 3, 1915-1919.
- [64] N. H. Chou, P. N. Ross, A. T. Bell and T. D. Tilley, *Chemsuschem*, **2011**, 4, 1566-1569.
- [65] T. Wang, Q. Y. Zhou, X. J. Wang, J. Zheng and X. G. Li, *J Mater Chem A*, **2015**, 3, 16435-16439.
- [66] H. B. Wu, B. Y. Xia, L. Yu, X. Y. Yu and X. W. Lou, *Nat Commun*, **2015**, 6.
- [67] B. You, N. Jiang, M. L. Sheng, S. Gul, J. Yano and Y. J. Sun, *Chem Mater*, **2015**, 27, 7636-7642.
- [68] M. Gong and H. J. Dai, *Nano Res*, **2015**, 8, 23-39.
- [69] Y. Q. Zhang, B. Ouyang, J. Xu, G. C. Jia, S. Chen, R. S. Rawat and H. J. Fan, *Angew Chem Int Edit*, **2016**, 55, 8670-8674.
- [70] P. Z. Chen, K. Xu, Z. W. Fang, Y. Tong, J. C. Wu, X. L. Lu, X. Peng, H. Ding, C. Z. Wu and Y. Xie, *Angew Chem Int Edit*, **2015**, 54, 14710-14714.
- [71] S. D. Song, H. M. Zhang, X. P. Ma, Z. G. Shao, R. T. Baker and B. L. Yi, *Int J Hydrogen Energ*, **2008**, 33, 4955-4961.
- [72] R. D. L. Smith, M. S. Prevot, R. D. Fagan, Z. P. Zhang, P. A. Sedach, M. K. J. Siu, S. Trudel and C. P. Berlinguette, *Science*, **2013**, 340, 60-63.
- [73] A. T. Swesi, J. Masud and M. Nath, *Energ Environ Sci*, **2016**, 9, 1771-1782.
- [74] Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier and H. J. Dai, *Nat Mater*, **2011**, 10, 780-786.
- [75] T. Maiyalagan, K. A. Jarvis, S. Therese, P. J. Ferreira and A. Manthiram, *Nat Commun*, **2014**, 5.
- [76] Z. Lu, W. W. Xu, W. Zhu, Q. Yang, X. D. Lei, J. F. Liu, Y. P. Li, X. M. Sun and X. Duan, *Chem Commun*, **2014**, 50, 6479-6482.
- [77] W. J. Zhou, X. J. Wu, X. H. Cao, X. Huang, C. L. Tan, J. Tian, H. Liu, J. Y. Wang and H. Zhang, *Energ Environ Sci*, **2013**, 6, 2921-2924.

- [78] B. S. Yeo and A. T. Bell, *J Am Chem Soc*, **2011**, 133, 5587-5593.
- [79] Y. F. Sun, S. Gao, F. C. Lei, J. W. Liu, L. Liang and Y. Xie, *Chem Sci*, **2014**, 5, 3976-3982.
- [80] X. Wang, W. S. Liu, X. H. Lu and P. S. Lee, *J Mater Chem*, **2012**, 22, 23114-23119.
- [81] C. Wan, Y. N. Regmi and B. M. Leonard, *Angew Chem Int Edit*, **2014**, 53, 6407-6410.
- [82] X. P. Zhang, L. Huang, Y. J. Han, M. Xu and S. J. Dong, *Nanoscale*, **2017**, 9, 5583-5588.
- [83] J. Jiang, Q. X. Liu, C. M. Zeng and L. H. Ai, *J Mater Chem A*, **2017**, 5, 16929-16935.
- [84] J. J. Mao, L. F. Yang, P. Yu, X. W. Wei and L. Q. Mao, *Electrochem Commun*, **2012**, 19, 29-31.
- [85] T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *J Am Chem Soc*, **2014**, 136, 13925-13931.
- [86] M. J. Liu and J. H. Li, *Acs Appl Mater Inter*, **2016**, 8, 2158-2165.
- [87] D. K. Pan, H. Zhang, T. Fan, J. G. Chen and X. Duan, *Chem Commun*, **2011**, 47, 908-910.
- [88] J. Yang, C. Yu, X. M. Fan and J. S. Qiu, *Adv Energy Mater*, **2014**, 4.
- [89] Z. H. Zhu, L. N. Qu, Y. Q. Guo, Y. Zeng, W. Sun and X. T. Huang, *Sensor Actuat B-Chem*, **2010**, 151, 146-152.
- [90] B. X. Li, J. He, D. G. Evans and X. Duan, *Appl Clay Sci*, **2004**, 27, 199-207.
- [91] P. Vialat, C. Mousty, C. Taviot-Gueho, G. Renaudin, H. Martinez, J. C. Dupin, E. Elkaim and F. Leroux, *Adv Funct Mater*, **2014**, 24, 4831-4842.
- [92] X. Long, S. Xiao, Z. L. Wang, X. L. Zheng and S. H. Yang, *Chem Commun*, **2015**, 51, 1120-1123.
- [93] G. B. Chen, T. Wang, J. Zhang, P. Liu, H. J. Sun, X. D. Zhuang, M. W. Chen and X. L. Feng, *Adv Mater*, **2018**, 30.
- [94] P. S. Li, X. X. Duan, Y. Kuang, Y. P. Li, G. X. Zhang, W. Liu and X. M. Sun, *Adv Energy Mater*, **2018**, 8.
- [95] Y. Yang, L. N. Dang, M. J. Shearer, H. Y. Sheng, W. J. Li, J. Chen, P. Xiao, Y. H. Zhang, R. J. Hamers and S. Jin, *Adv Energy Mater*, **2018**, 8.

Chapter 3

Experimental Methodology

Chapter 3 elaborates on the rationale for selection of methods and materials. Then the experimental procedures are presented. Subsequently, the descriptions of the physical characterization techniques and equipment are described. Lastly, the electrochemical characterization is described with the introductions of the data interpretation.

3.1 Rationale for selection of materials and methods

In the first part of the thesis, the noble metal, i.e., palladium nanomaterials, were selected as the materials, and the polymers (PAH) was utilized to tune the composition and structure of the palladium nanostructures. From the materials point of view, the palladium, especially those processed in solution, are particularly attractive because of the inherently active performances for formic acid electrooxidation and favorably direct electrooxidation path, anti-poisoning ability. Currently, commercial palladium based catalysts have been synthesized and characterized on the support of some carbon materials, the Pd nanoparticles on the carbon supports would be aggregated easily due to their high surface energy. One promising strategy is to generate three-dimensional palladium nanoassemblies with the assistance of polymers, which can also be applied to other metal nanostructures. From the method point of view, it has been known from Chapter 2 that electrochemical deposition, ultrasonic-assisted method, wet chemical method can be used to fabricate palladium nanostructure. The wet chemical synthesis of palladium nanomaterials in solution phase is one of the facile and straightforward processes to produce nanostructures with various morphology and composition, with tailorable functions.

In the second part of the thesis, layered MOFs were selected as the starting materials, which was produced by low temperature hydrothermal method, to produce electrocatalysts of cobalt/N-carbon, and calcination process in inert gas atmosphere was used to fabricate well-ordered nanoparticles on carbon matrix. From materials point of view, MOF materials are a particularly attractive candidate due to their diversified compositions and abundant nanopores with high compatibility. From the method point of view, hydrothermal method is one of the most facile and straightforward processes to synthesize and manipulate metal-organic frameworks at micro-/nanoscale. Due to the simplicity and scalability of hydrothermal synthesis, the optimized parameter and procedures for MOF synthesis would contribute to the industrial applications of electrocatalysts. Moreover, the calcination process, which in situ convert inorganic ions into metallic cobalt nanoparticles, which act as the catalytic site; and convert organic linkers into carbon matrix, which act as charge transport path. Thus, the calcination process can well retain the structural characteristics

and advantages of MOF, and lead to the formation of well-presented metallic catalytically active sites. From the application point of view, the vast compatibility of MOFs, provide a rich platform for investigation of their applications not only in hydrogen evolution, but also in oxygen evolution.

In the third part of the thesis, cobalt MOF, polymers (PVP), sodium molybdate was selected as the precursor material, with similar method including hydrothermal process and calcination. While during hydrothermal process, PVP was used to tune the microstructure of layered cobalt MOF, sodium molybdate was loaded into the cobalt MOF on the basis of their nanopore; in the calcination process, the precursors were in situ converted into cobalt oxides, molybdenum carbide and carbon matrix. From the material point of view, cobalt oxide is intensively used in electrocatalysis of oxygen evolution, which has shown promising properties due to its unique crystal structures. While molybdenum carbide is also used for electrocatalysis because that they formed synergism with catalytic site. From the method point of view, the polymer-assisted hydrothermal method was used to produce cobalt MOF with novel microstructure, polymer-assisted hydrothermal method has been proven to be effective in synthesizing metal nanostructures, and this work managed to control the microstructure of MOF by using polymers. Considering the excellent electrocatalytic behaviors and long-term stability of the products derived from the structural characteristics, it is reasonable to extend this method to produce other intricate MOF architectures.

In the last part of the thesis, nickel nitrate and cobalt nitrate were selected as the precursors for binary layered double hydroxides synthesis, the synthetic procedure is conducted at room temperature via an aqueous method. After that, carbon layers and iridium were simultaneously grown on the hybrid layered double hydroxides. From the material point of view, nickel nitrate and cobalt nitrate are both common and cheap chemicals in the lab, while nickel and cobalt are regarded as ideal precursors for electrocatalysts fabrication due to their rich redox chemistry; glucose, which is a safe and common chemical, is used as a source of carbon layers. From the method point of view, a room temperature aqueous procedure was adopted for hybrid layered double hydroxides preparation, the only solvent

is ethanol. This work has contributed a simple and scalable protocol to the industry for efficient electrocatalysts development.

3.2 Synthesis Method

The part of Materials and Synthesis Method consists of three sections: (1) Synthesis of palladium nanostructures; (2) Synthesis of cobalt MOFs and fabrication of MOF-derived Co/N-Carbon; (3) Synthesis of hybrid cobalt/molybdenum MOFs and fabrication of CoOx-MoC/N-Carbon; (4) Synthesis of heterostructure of layered double hydroxides with carbon coating and iridium doping.

3.2.1 Synthesis of palladium nanostructures

Experimentally, 0.025 M PdCl₂ (2 mL) was mixed with water (7 mL). 0.50 M PAH (1 mL) was added into the above-mentioned PdCl₂ aqueous solution, generating a light brown flocculent precipitate (*i.e.* PAH-Pd^{II} complex solution). After sonication for 10 min, the precipitate flocculent completely dissolved and a clear PAH-Pd^{II} complex solution was obtained. 0.01 mol reducing agent (CH₃OH) was added into the above-mentioned mixture, the as-obtained solution was heated at 150 °C for 5 h. Finally, the products were subject to centrifugation for collection of the samples. All the samples were washed by using water before characterization.

3.2.2 Synthesis of cobalt MOFs and fabrication of MOF-derived Co/N-Carbon

For preparation of the layered cobalt MOF, 320 mg H₂NDC and 400 mg Co(acac)₂ were mixed in 180 ml water, and the solution was subject to stirring. The mixed solution was heated at 70 °C for 20 h. The products were subject to centrifugation for collection of the samples. After that, the samples were dried at 60 °C for overnight.

While the preparation of Co/carbon, Co/N-carbon, Co oxide derived from Co-MOF is as following: the as-prepared layered Cobalt MOF (30 mg) were mixed with

hexamethylenetetramine (30 mg) on a mortar, the mixture was subject to heating treatment in a furnace under Argon flow. The samples were first heated to 400 °C at a ramping rate of 1°C/min, 400 °C was held for 2 hours, subsequently, the heating temperature was increased to 650 °C at a ramping rate of 5°C/min, afterwards 650 °C was held for 4 hours. After heating treatment, the resulting black powders were designated as Co/N-carbon and directly used for further characterization and measurements. For Co/carbon, the aforementioned protocol was followed without hexamethylenetetramine. For Co oxide derived from Co-MOF, the as-prepared layered Cobalt MOF (30 mg) was calcined at 500 °C for 5 hours in a box furnace.

3.2.3 Synthesis of hybrid cobalt/molybdenum MOFs and fabrication of CoOx-MoC/N-Carbon

Experimentally, 30 mg H₂NDC and 30 mg Co(acac)₂ and 20mg sodium molybdate dehydrate were dissolved in 10 ml water under vigorous stirring for half an hour. The mixed solution was heated at 70 °C for 20 h. The products were subject to centrifugation for collection of the samples, the samples were dried at 60 °C for overnight. The as-prepared hybrid Co-Mo-MOF (30 mg) were subject to heating treatment in a furnace under Argon flow. The samples were first heated to 400 °C at a ramping rate of 1°C/min, and 400 °C was held for 2 hours, subsequently, the temperature was increased to 650 °C at a ramping rate of 5°C/min, afterwards 650 °C was held for 4 hours. After heating treatment, the resulting black powders were designated as CoOx-MoC/NC and directly used for further characterization and measurements.

3.2.4 Synthesis of heterostructure of layered double hydroxides with carbon coating and iridium doping

Experimentally, 10 mg Nickel(II) nitrate hexahydrate and 20 mg 2-methylimidazole were dissolved in 10 ml ethanol under vigorous stirring until all the chemicals were dissolved at room temperature. The as-obtained solution was kept still at room temperature for 20 h and the light green nickel hydroxides were formed. The products were subject to centrifugation

for collection of the samples, the samples were dried at 60 °C after that. For NiCo hydroxides, 2 mg nickel hydroxides and 100 mg Cobalt(II) nitrate hexahydrate and 20 mg 2-methylimidazole were dissolved in 10 ml ethanol under vigorous stirring until all the chemicals were dissolved at room temperature. The as-obtained solution was kept still at room temperature for 2 days and the pink NiCo hydroxides were formed. The products were subject to centrifugation for collection of the samples, the samples were dried at 60 °C after that. For Ir-doped/Carbon-coated NiCo hydroxides, 2 mg NiCo hydroxides and 2 mg 2-methylimidazole, 0.40 mg glucose and 3 mg Iridium(III) chloride hydrate were mixed fully in 10 ml D.I water by stirring until all the chemicals were dissolved at room temperature. The mixed solution was kept at 160 °C for 10 h and the black Ir-NiCo hydroxides were formed. The products were subject to centrifugation for collection of the samples, the samples were dried at 60 °C after that.

3.3 Characterization Methods

In order to investigate the nature of the electrocatalysts so that the origin of the enhancement of the activity can be explained clearly, various physical characterization and electrochemical experiments will be used. After design and synthesis of these micro-/nanomaterials, proper techniques are required to characterize their structure features, such as the composition, morphology, crystal phase, electrochemical properties. Notably, each technique has its own purpose, needs specific operating requirement and possesses different advantages and weakness. Thus, in this section, each characterization techniques used to characterize the materials will be described and discussed.

3.3.1 UV-Vis Spectroscopy

Different molecules absorb radiation at different wavelengths with different absorption intensity. Usually, an absorption spectrum will show a few absorption bands corresponding to the functional groups within the molecule, thus UV-Vis spectroscopy can be used to study the interactions in the synthesis reaction system, and to shed some light upon formation mechanism of the nanoparticles.^[1] To prepare the samples for UV-Vis

characterization, the products and/or precursors were dissolved in the water solution with a proper concentration, either excessive concentration or insufficient concentration will cause inaccuracy of the absorption spectra, usually keeping the absorbance in the range of 1 to 2 is suitable. A UV-1800 (Shimadzu) was used to obtain the UV-vis absorption spectra of samples in water solution at room temperature.

3.3.2 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a non-destructive tool to study the samples' optical spectrum of absorption and emission, which can be used to reveal their bonding environment.^[2] The working principle of the FTIR is as following: The technique irradiates a beam including many frequencies ($0 - 4000 \text{ cm}^{-1}$) of light upon the samples, after which the beam absorbance resulted from the sample is recorded by the equipment. Subsequently, the beam is changed to contain a different group of optical frequencies, generating a set of different data point. Such process is repeated several times so that accurate information can be obtained at each wavelength point. This endows FTIR major advantages such as generating result with higher signal-to-noise ratio. For preparation of the samples, the powder form of products will be dried in the vacuum oven for overnight before testing, the commercial FTIR-grade KBr powder will also be dried in the same condition. After that, the products and KBr would be mixed in a very homogeneous way, and be pressed in a form of round tablet, this round tablet would be placed on the FTIR for irradiation measurement.

3.3.3 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) is a technique coupled with SEM and/or TEM to investigate the products' elemental composition.^[3] During the testing period, X-ray excitation would interact with the products. Each element has a characteristic atomic structure which produces corresponding set of peaks with various intensity upon X-ray emission. By plotting the energy and peak intensity of the X-rays emitted from the products, one can easily acquire the elemental composition of the products, based on their atomic

structures. EDX is usually applicable to elements with high atomic number such as metals. Therefore, in this thesis, EDX coupled with SEM is used to measure the composition of cobalt, molybdenum.

3.3.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface composition analysis technique, it is employed to quantify the surface (top 0 - 10 nm) elemental composition and even the distribution of various valence states of one element of the tested samples.^[4]

Preparation of the samples is as following: about 10 mg powder form of samples is dried in a vacuum oven for overnight firstly, when necessary, the powder samples are grinded in a mortar. A cleaned aluminum foil with size 1 cm * 1 cm is prepared and washed by using acetone to remove any residuals and contaminants. After that, a piece of dual adhesive tape is pasted on the aluminum foil, and the samples are spread evenly on the adhesive tape, a second aluminum foil is used to cover the samples. Thus, the sandwich-like samples and aluminum foil is subject to pressing. After pressing, one aluminum foil is uncovered and the other one aluminum foil with samples can be subjected to testing. The working procedure of XPS is as following: one sample containing the tested materials is irradiated with a beam of X-rays, after that, the spectrometer collects the data of the kinetic energy and number of electrons (intensity) that emit from the tested samples. By plotting the kinetic energy and intensity of the electrons emitted from the products, one can easily obtain the surface elemental composition of the products, by the similar working principles of EDX. In this thesis, XPS is used to study the composition of palladium, the interaction of palladium and polymers; Secondly, XPS is used to confirm the surface existence of cobalt, nitrogen and carbon; Thirdly, XPS is used to investigate the surface composition of cobalt and molybdenum. To sum up, XPS is a strong composition analysis technique, which serves in a non-destructive way.

3.3.5 Powder X-ray Diffraction

X-ray diffraction is a characterization method which is used to determine the sample's crystal phase and structure.^[5] In particular, X-ray diffraction can be used for the characterization of the crystalline materials and the determination of their structure, the basis is that each crystalline solid possesses its unique X-ray Diffraction pattern, and thus X-Ray crystallography may be used to determine the crystalline state and the interatomic distance of the specific nanomaterial. For this work, the X-ray diffraction pattern can give information about the formation of metallic crystal structure and facet. The preparation of the samples is as following: about 10 mg powder sample is grinded into a very fine substance, after that it is placed on the silicon holder for X-ray irradiation. The diffraction angle can vary from 0 to 90 degree.

3.3.6 Raman spectroscopy

Raman microspectrometer (Renishaw inVia) is configured and used to collect Raman spectra of the samples under ambient conditions. The sample preparation for Raman spectroscopy is as following: the powder form of samples was dried at vacuum oven for overnight, after that, the samples were placed on a piece of glass slides for Raman characterization. As such Raman spectroscopy is a facile spectroscopic method which enables characterization of sample's structural and electronic features based on the vibration, rotation and other low-frequency modes of molecules. In particular, the Raman spectroscopy was employed to obtain the composition and crystal phase information of carbon materials, i.e. it is used to measure and evaluate the graphitic degree of the carbon matrix in Co/N-Carbon and the products of CoOx-MoC/NC.^[6]

3.3.7 Atomic Force Microscopy

Before dropping samples, the silicon wafer should be clean enough. The cleaning process of silicon support is as following: the silicon wafer was first cut into small pieces. Then they were sequentially sonicated in ethanol and water for 30 min. Finally, the wafers were washed with DI water for three times and then dried at vacuum oven. The layered cobalt MOFs solution were dropped on silicon wafer and dried at room temperature for atomic

force microscopy (AFM) characterization. AFM was operated in tapping mode. AFM is a surface topographical imaging technique with high resolution up to atomic scale, where a small probe with a sharp tip is scanned across a sample in a controlled manner. Currently, AFM has been widely used in materials science as a surface analytical technique to conduct measurement of the thickness of two-dimensional nanomaterials. In this thesis, AFM were used to unravel the thickness of layered cobalt MOFs by analyzing the height profiles.^[7]

3.3.8 Brunauer-Emmett-Teller

Brunauer-Emmett-Teller (BET) theory is based on the knowledge of the physical adsorption of gas molecules on a solid surface. The theory has been extensively used to measure the surface area of a sample. As such, the BET characterization adopts probing gases which are not reactive with the tested materials. Nitrogen is the commonly used gas molecule for probing. In practical tests, the BET analysis is essentially conducted at 77 K, which is the boiling temperature of N₂. In this work, N₂ physisorption measurements were conducted to study the porous structure, surface area and pore size distribution of the samples.^[8]

3.3.9 Scanning Electron Microscopy

The scanning electron microscope (SEM) scans surface of samples with an electron beam. The electron beams interact with atoms of the products, generating signals which are transformed into the information of the sample's surface structure. SEM can achieve resolution about one nanometer and is suitable for acquire the surface structure information of nanomaterials. In this thesis, the micro-/nanostructures were drop-cast on well-cleaned Si wafer for scanning electron microscopy (SEM) characterization. A field emission scanning electron microscope (FESEM, JEOL JSM-7600F) was used to acquire the SEM images, at the accelerating voltage of 5 keV with a working distance of 8 cm and probe current of 10 μ A.^[9]

3.3.10 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) uses electrons to observe the structure information of micro-/nanostructures, with a similar working principle to that of optical microscopy. However, TEM with electron beam of lower wavelength makes it possible to get a resolution better than with a light microscope. The nanomaterials can be seen at the order of few angstroms, so that atomic level picture of the nanoparticles can be acquired. For this work, TEM will be used to acquire the morphological information.^[10]

3.3.11 Cyclic Voltammetry and Linear Sweeping voltammetry

The CHI Electrochemical Workstation will be used to control the applied current and/or potential, and the three-electrode configuration is for characterizing the detailed catalytic activity, which will be recorded by some typical methods:

Cyclic Voltammetry and Linear Sweeping Voltammetry: For CV, the working electrode potential is scanned linearly with time in a reversible way, throughout a potential window of interest where the current response is recorded; For LSV, the working electrode potential is scanned linearly with time from one potential point to another different potential point, LSV is a useful technique to characterize electrocatalysts' activity by measuring their current density at a designated potential.^[11]

3.3.12 Chronoamperometry

Chronoamperometry is also named as current-time plotting, a constant potential is applied on the samples via the working electrode, the resulting current response (usually normalized to current density) is plotted against time. As the working principle indicates, chronoamperometry generates charging current at first, which usually decay with time. As such, the long-term stability of the electrocatalysts might be demonstrated by judging from the rate of current response decays.^[12]

3.3.13 Electrochemical Impedance Spectroscopy

During the impedance spectroscopy testing, an alternating current (AC) potential is applied across the electrode materials, the output current from the cell is produced as a result in the form of Nyquist plot. A simplified Randles circuit model can be acquired with the output value of R_s , C_{dl} , and R_{ct} . R_s represents the resistance of solution, C_{dl} denotes the capacitance of double-layer, R_{ct} represents the resistance of charge transfer across the electrode materials and electrolytes. Therefore, a lot of information can be extrapolated from the Nyquist plot for guiding the preparation of electrocatalysts.^[13]

References

- [1] W. Haiss, N. T. K. Thanh, J. Aveyard and D. G. Fernig, *Anal Chem*, **2007**, 79, 4215-4221.
- [2] H. S. Mansur, C. M. Sadahira, A. N. Souza and A. A. P. Mansur, *Mat Sci Eng C-Bio S*, **2008**, 28, 539-548.
- [3] D. Shindō and T. Oikawa, *Analytical electron microscopy for materials science*, Springer, Tokyo ; Berlin, **2002**.
- [4] P. Van der Heide, *X-ray photoelectron spectroscopy : an introduction to principles and practices*, Wiley, Hoboken, N.J., **2012**.
- [5] J. P. Zhang, P. Q. Liao, H. L. Zhou, R. B. Lin and X. M. Chen, *Chem Soc Rev*, **2014**, 43, 5789-5814.
- [6] C. Castiglioni, F. Negri, M. Tommasini, E. Di Donato and G. Zerbi, *Top Appl Phys*, **2006**, 100, 381-402.
- [7] P. Cubillas, K. Etherington, M. W. Anderson and M. P. Attfield, *Crystengcomm*, **2014**, 16, 9834-9841.
- [8] W. Chaikittisilp, K. Ariga and Y. Yamauchi, *J Mater Chem A*, **2013**, 1, 14-19.
- [9] Z. J. Wang, G. Weinberg, Q. Zhang, T. Lunkenbein, A. Klein-Hoffmann, M. Kurnatowska, M. Plodinec, Q. Li, L. F. Chi, R. Schloegl and M. G. Willinger, *Acs Nano*, **2015**, 9, 1506-1519.
- [10] J. B. Wu, W. P. Gao, J. G. Wen, D. J. Miller, P. Lu, J. M. Zuo and H. Yang, *Nano Lett*, **2015**, 15, 2711-2715.

- [11] H. Bi, G. T. Burstein, B. B. Rodriguez and G. Kawaley, *Corros Sci*, **2016**, 102, 510-516.
- [12] S. Hosseini, M. Shaterian, M. Vahedpour and M. A. Rezvani, *Int J Hydrogen Energ*, **2018**, 43, 4961-4966.
- [13] R. K. Shervedani and A. R. Madram, *Int J Hydrogen Energ*, **2008**, 33, 2468-2476.

Chapter 4*

Pd nanoassemblies for efficient electrooxidation of formic acid

Three-dimensional palladium nanoassemblies were prepared via an aqueous route, during the process the polymers were used and played a role of scaffold and crosslinking molecules. The formation process and mechanism of the Pd nanoassemblies were investigated using temporal TEM images. XRD was used to probe their crystal structure, which showed a clear appearance of metallic nanocrystallites with high index crystal facet. XPS was conducted to study surface element composition, which confirmed the physical and chemical integration of Pd and PAH. Finally, the 3D Pd nanoassemblies were used as catalysts for formic acid electro-oxidation. Compared with Pd bulk produced without PAH and the commercial Pd black, the Pd nanostructure assemblies towards the electro-oxidation of formic acid exhibited higher electrochemical activity. This behavior is mainly due to their porous structure, high specific surface area which offers more catalytic sites, and their sufficient cavity space which enables facile charge transport of the electrochemical reaction.

*This section published as T. Huang, S. K. Moon and J.-M. Lee, Sustainable Energy & Fuels, 2017, 1, 450-457.

4.1 Introduction

Low-temperature polymer electrolyte membrane fuel cells, have been intensively studied for transportation and portable electronics.^[1,2] However, their commercialization is impeded by the low electrocatalytic activity of electrocatalysts.^[3] As important catalytic electrode materials, Pd catalysts possess high intrinsic electrocatalytic properties for the eletro-oxidation of an array of organic molecules, including methanol, formic acid and dimethyl ether,^[3, 4] which make them ideal candidate material as the anode in fuel cells. However, current superior electrocatalysts have been composed by Pd nanoparticles and carbon materials, the Pd nanoparticles on the carbon supports would be aggregated easily due to their high surface energy,^[5] which would cause low electrocatalytic activity.

Constructing three-dimensional (3D) Pd nanoassemblies could improve the electrocatalytic activity of Pd electrode materials, because 3D nanoassemblies have many superior structural properties such as high porosity, and interconnected cavity space, which contribute to enhanced electrocatalytic performance.^[6, 7] For example, Park et al reported the synthesis of chestnut-bur-like Pd nanoassemblies, which show higher catalytic activity for electro-oxidation of ethanol, compared to cubic and octahedral Pd nanostructures;^[8] Han et al fabricated Pd-Au alloy nanodendrites with improved electrocatalytic activity towards ethanol oxidation.^[9] Previously many studies adopted complicated protocols for constructing 3D nanoassemblies, which usually require multi-step reactions and sophisticated experimental skill.^[8, 9] Thus, it is necessary to develop a simple method towards 3D nanoassemblies.

Herein, PAH was used acting as macromolecular cross-linking agents for the purpose of creating the uniform 3D Pd nanoassemblies through a simple and green method (Figure 4.1). Currently, the observations of the growing process of 3D Pd nanoassemblies have rarely been reported. In this work, the growing process of the nanoassemblies was oberved during 0-5 hours by temporal TEM in order to study their formation mechanism, such knowledge could be beneficial for more intricate nanoassemblies design. As proof of concept, the as-prepared products were subject to electrochemical characterization, which

demonstrated that Pd nanoassemblies had great catalytic activity for formic acid electro-oxidation, because of their advantageous properties originating from the interconnected 3D nanostructures.

4.2 Principle Outcomes

4.2.1 The Pd nanoassemblies morphology and their growing mechanism

Figure 4.1 Procedure of fabrication of palladium nanoassemblies.

To investigate the morphology and nanoassembly size distribution of the electrocatalysts, electron microscopy TEM was employed to observe morphological changes, Figure 4.2 shows representative TEM images of as-fabricated catalysts. In this image, the catalysts are relatively monodispersed nanoassemblies with a mean diameter of 56.12 nm (Figure

4.6a), and their surfaces are rough with a high porosity. Figure 4.2c shows that one Pd nanoassembly is a three-dimensional nanostructure, which is composed by a group of building unit of Pd nanoparticles whose diameter are about 10 nm. In addition, at different Pd building units the lattice fringes spread across in a consistent way, which was demonstrated by the arrow in Figure 4.2d. This could show that the Pd building units grow along the direction of crystal facet of (111).^[10-12] Thus, it is assumed that the Pd seeds were formed firstly, then the Pd nanoassemblies grow through a homoepitaxial way on the preformed Pd seeds. (Figure 4.4). Previous studies show amine groups contribute to the formation of abundant Pd (111) facets in the Pd nanoassemblies^[13]. Therefore, in the present work it was the coordination of amine that helped to stabilize the facet of (111), leading to the homoepitaxial growth along (111) crystal facet.

Figure 4.2 (a) Low resolution TEM image, (b) middle resolution and the inset shows SAED image of Pd nanoassemblies, (c) high resolution TEM image of a single Pd nanoassembly, (d) high resolution TEM image showing crystal lattice of Pd nanoassembly.

Figure 4.3 TEM images of the Pd nanoassemblies formed after the reaction time of 2.0h, 2.5h, 3.0h, 3.5h, 4.0h, 4.5h, 5.0h. All the inset images are TEM images focusing on one nanoassembly at the corresponding reaction time.

Figure 4.4 Formation mechanism of Pd nanoassemblies.

To elucidate the growing process of the Pd nanoassemblies, the products at different reaction times were collected and observed by TEM (Figure 4.3). Correspondingly, the initiate Pd nanocrystals (ca.20 nm) were formed at 2.5-3.0 h. At $t = 3.5$ h, the nanocrystals were transformed into complete Pd nanoassemblies with ca. 50 nm size. From 4.0 h- 4.5 h, the nanoparticles diameter increased to ca.60 nm. From 4.5-5.0 h, no obvious variation was observed regarding to size and shape, indicating the formation of fully mature Pd nanoassemblies. Based on these observations, the formation mechanism was proposed as shown by Figure 4.4. Specifically, at the beginning, some polyhedron nanoparticles were formed and subsequently they acted as a nucleus; secondly Pd was reduced and deposited on the nucleus Pd surface to gain a three dimensional shape and finally Pd nanoassemblies grew larger at the end of 5 hours of reaction time.

Figure 4.5 (a) Pd bulk growing without PAH, (b) HRTEM image showing edge and corner atoms.

To study the effect of PAH in the formation of Pd nanoassemblies, the synthesis reaction without PAH was conducted as a control. As demonstrated by Figure 4.5a, the Pd product had irregular shapes and displayed the severe aggregation. This demonstrated that PAH, as cross-linking and scaffold molecules, was essential for synthesizing Pd nanoparticles with well-controlled morphology.^[14] The molecular basis could be that the PAH's nature of hydrophilicity and bulky molecular size make it as a good linker and scaffold molecules.^[15] Therefore, in terms of the process of polyallylamine hydrochloride as cross-linking units. due to the unique physical and chemical properties of PAH, the formation process of Pd nanoassemblies can be described as following: First, the complex of Pd^{II}-PAH was well dispersed in the water solution (Figure 4.6b); second, the reaction solution was heated at 150 °C, the Pd was reduced to Pd⁰, subsequently the Pd atoms nucleated to the seeds; finally, the preformed seeds acted as the core to recruit the building blocks assisted by PAH to form the well-defined Pd nanoassemblies due to the aforementioned physical and chemical properties of PAH. Therefore, the Pd nanoassemblies were monodispersed in a water solution, while Pd bulk and Pd black were precipitated (Figure 4.7). Furthermore, compared with that of Pd bulk obtained produced without PAH, the binding energy of Pd 3d in the Pd nanoassemblies negatively shift ca. 0.3 eV, which should prove the interaction between Pd and PAH (Figure 4.9c and Figure 4.9d).^[16]

Figure 4.6 (a) Pd nanoassemblies size distribution histogram; (b) UV-Vis spectrum of solution of PdCl₂, PAH, PAH-Pd^{II} complex.

Figure 4.7 Comparison of dispersity of the three samples: Pd nanoassemblies, Pd bulk, Pd black.

4.2.2 Physical characterization of Pd nanoassemblies

Figure 4.8 (a) XRD pattern of Pd nanoassemblies, (b) Nitrogen adsorption-desorption isotherm, (c) Pore size distribution.

Powder X-ray diffraction was conducted to probe Pd nanoassemblies' crystal structure. The Pd nanoassembly crystal structure was identified by comparing the XRD results of the as-fabricated products with the reference database. According to Figure 4.8a, the XRD spectra of Pd nanoassemblies displayed the four typical characteristic peaks (JCPDS standard 5-681): Pd(111), Pd(200), Pd(220) and Pd(311).^[10, 12] Thus, Pd nanoassembly is a classic face centered cubic structure with Pd (111) being the

dominant face. In order to study surface area and pore size distribution, nitrogen adsorption and desorption isotherm tests were conducted. Figure 4.8b and Figure 4.8c show the Brunauer–Emmett–Teller results of the Pd nanoassemblies. The hysteresis loop of Figure 4.8b showed the adsorption–desorption features of porous materials. Figure 4.8c demonstrated that the Pd nanoassemblies were dominated by pores with sizes c.a 5~10 nm. The Brunauer–Emmett–Teller surface area of the Pd nanoassemblies was $68.5 \text{ m}^2 \text{ g}^{-1}$, which is 7.7 times of the value of $8.9 \text{ m}^2 \text{ g}^{-1}$, which was the value of the surface area of Pd dense spheres. To sum up, the results of XRD (Figure 4.8a) and HRTEM (Figure 4.5b) show Pd nanoassemblies are abundant with high index crystal facet, edge and corner atoms. The nitrogen adsorption–desorption isotherm is consistent with the TEM images, showing their porous nanostructure. All these results demonstrate the structural basis of high electrocatalytic activity of Pd nanoassemblies.

Figure 4.9 XPS figure of Pd nanoassemblies in the area of N1s (a) and Pd3d (b), Pd nanoassemblies (c) and Pd bulk in the Pd 3d region (d).

To analyze the surface chemical composition of the Pd nanoassemblies, XPS tests were performed (Figure 4.9). The Pd 3d spectrum of the Pd nanoassemblies corresponds to two pairs of peaks: Pd 3d_{3/2} (340.74 eV), Pd 3d_{5/2} (335.47 eV) and Pd 3d_{3/2} (342.89 eV), Pd 3d_{5/2} (337.88 eV), which can be attributed to the presence of Pd⁰ and Pd^{II}O species, respectively (Figure 4.9b).^[16] Moreover, by calculating and comparing the respective peak area, the atomic ratio of Pd⁰ and Pd^{II} in the Pd nanoassemblies could be confirmed as 8.4:1, which can prove that most of the Pd^{II} precursor had already been reduced to metallic Pd in the synthesis reaction. More notably, the presence of N 1s peak also confirms the interaction of PAH with the Pd (Figure 4.9a).^[17] Specifically, the N 1s spectrum is composed of two peaks (Figure 4.9A). The peak at 400.17 eV is assigned to N 1s peak of –NH₂ groups, the peak at 398.74 eV corresponds to the N atom integrated with the Pd. On the other hand, the binding energy values of Pd⁰ and Pd^{II}-O species in the Pd nanoassemblies negatively shift 0.3 eV compared to that of Pd bulk produced without PAH (Figure 4.9c and Figure 4.9d), which proves the chemical interaction of Pd and N.^[16]

4.2.3 Electrocatalytic activity of Pd catalysts

Figure 4.10 (a) Superimposed Cyclic Voltammetric (CV) response of Pd nanoassemblies, Pd bulk and Pd black in the mixture of 0.5 M HCOOH and 0.5 M H₂SO₄ solution at sweep rate of 50 mV/s, (b) Superimposed I–t transients of HCOOH oxidation for Pd nanoassemblies, Pd bulk and Pd black at an applied potential (0.200 V) for 2000s, (c) Mass activity for Pd nanoassemblies, Pd bulk and Pd black, (d) Peak potential of electro-oxidation for Pd nanoassemblies, Pd bulk and Pd black.

Subsequently, the Pd nanostructure electrodes were studied in the presence of HCOOH at room temperature. All the electrodes used were put in the mixed HCOOH and H₂SO₄ solution for 10 min to let the 3-electrode configuration achieve a stable state prior to electrochemical measurement.^[18] Figure 4.10a shows the cyclic voltammograms of 3 different Pd catalysts under 0.5M HCOOH + 0.5M H₂SO₄ solution. For Pd nanoassemblies, the two sharp peaks in the anodic direction at 0.028 V and 0.200 V corresponding to the hydrogen desorption and direct oxidation of formic acid.^[19-21] During the anodic scan, the oxidative peaks are located at 0.200 V for Pd nanoassemblies, 0.225 V for Pd bulk, 0.350 V for commercial black (Figure 4.10b).^[22] More importantly, the formic acid oxidation mass activity peaks at the direct oxidation pathway for Pd nanoassemblies, Pd bulk and Pd black are 158 A g⁻¹, 42 A g⁻¹ and 35 A g⁻¹ (Figure 4.10c), respectively. The results show

that the as-constructed Pd nanoassembly catalysts displayed the lowest peak potential (0.200 V vs SCE) and possessed the highest electrocatalytic activity (158 A g^{-1}) among the three catalysts. The I-t tests were used to study the electrocatalytic stability of the Pd catalysts. Accordingly, Figure 4.10b shows the i-t curves of the three catalysts at a constant potential (0.200 V vs SCE). During the whole testing period, the mass activity of Pd nanoassembly catalysts always outperformed the mass activity of Pd bulk and Pd black. In the end, the formic acid oxidation mass activity of the Pd nanoassembly, Pd bulk and Pd black at 2,000 s are 7.41 A g^{-1} , 0.218 A g^{-1} and 2.95 A g^{-1} , proving that the Pd nanoassembly catalysts have the best electrocatalytic long term electrocatalytic performance. More notably, the Pd bulk's mass activity nearly decreased to zero, which in turn demonstrates the superiority of the Pd nanoassemblies constructed by PAH; while the commercial Pd black's mass activity showed the severe serrated curve in the I-t test, which tells its unstable long term electrocatalytic performance and unsuitability for formic acid oxidation applications.

The aforementioned superior electrochemical performance should arise from the three dimensional porous structure of Pd nanoassemblies.^[23] On one hand, the Pd nanoassemblies possess a three-dimensionally interconnected nanostructure which has more corner and edge sites, which is evidenced by Figure 4.5b. The increase of these atoms exhibits more open coordination sites which leads to boosting catalytic activity of the electrocatalysts.^[24] On the other hand, the three-dimensionally interconnected nanoassembly configuration has sufficient cavity space which facilitates charge transfer, thus enhancing catalytic reaction kinetics.^[25] Moreover, the lone pair electrons of N ($-\text{NH}_2$) of PAH donate electrons to Pd, which is demonstrated by the negative shift of the Pd binding energy from its XPS results, such charge transfer would contribute to a decrease in the activation energy of the formic acid molecules.^[26]

4.3 Conclusion

In summary, a facile hydrothermal synthesis of Pd nanoassemblies is reported, utilizing PAH as a cross-linking and scaffold molecules. The growing process of the Pd

nanoassemblies was observed using temporal TEM, proposed their formation mechanism based on the observing results and the synthesis protocol. The Pd nanoassemblies possess abundant cavity space, corner and edge atoms revealed by HRTEM, and have high specific surface area exemplified by nitrogen adsorption–desorption isotherm. Therefore, it is safe to deduce that the 3D porous nanostructure of Pd nanoassemblies leads to significantly enhanced catalytic activity for eletro-oxidation of formic acid compared to commercial Pd black. This work developed a polymer-assisted method to construct 3D Pd nanoassemblies, the work proposed their formation mechanism, such knowledge would be useful for constructing more intricate assemblies for energy conversion applications.

References

- [1] Song J M, Cha S Y, Lee W M. *Journal of Power Sources*, **2001**, 94, 78-84.
- [2] J.-H. Wee, *Renewable and Sustainable Energy Reviews*, **2007**, 11, 1720-1738.
- [3] J.-H. Choi, K.-J. Jeong, Y. Dong, J. Han, T.-H. Lim, J.-S. Lee and Y.-E. Sung, *Journal of Power Sources*, **2006**, 163, 71-75.
- [4] J.-H. Yu, H.-G. Choi and S. M. Cho, *Electrochemistry Communications*, **2005**, 7, 1385-1388.
- [5] Z. Jin, D. Nackashi, W. Lu, C. Kittrell and J. M. Tour, *Chemistry of Materials*, **2010**, 22, 5695-5699.
- [6] S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *Journal of the American Chemical Society*, **2002**, 124, 7642-7643.
- [7] Y. Piao, Y. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, *Small*, **2007**, 3, 255-260.
- [8] S. J. Ye, D. Y. Kim, S. W. Kang, K. W. Choi, S. W. Han and O. O. Park, *Nanoscale*, **2014**, 6, 4182-4187.
- [9] Y. W. Lee, M. Kim, Y. Kim, S. W. Kang, J.-H. Lee and S. W. Han, *The Journal of Physical Chemistry C*, **2010**, 114, 7689-7693.
- [10] S. Kim, D.-W. Lee and K.-Y. Lee, *Journal of Molecular Catalysis A: Chemical*, **2014**, 383-384, 64-69.
- [11] H. Yoon, S. Ko and J. Jang, *Chemical communications*, **2007**, DOI:

- 10.1039/b616660a, 1468-1470.
- [12] Kim S W, Park J, Jang Y, Chung Y, Hwang S, Hyeon T, *Nano Letters*, **2003**, 3, 1289-129.
- [13] X. Huang, Z. Zhao, J. Fan, Y. Tan and N. Zheng, *Journal of the American Chemical Society*, 2011, **133**, 4718-4721.
- [14] L. M. Rossi, I. M. Nangoi and N. J. Costa, *Inorganic chemistry*, **2009**, 48, 4640-4642.
- [15] T. Okubo, S. Kanayama, H. Ogawa, M. Hibino and K. Kimura, *Colloid & Polymer Science*, **2004**, 282, 230-235.
- [16] Drelinkiewicz A, Hasik M, Choczyński M, *Materials research bulletin*, **1998**, 33, 739-762.
- [17] J. R. Kitchin, J. K. Norskov, M. A. Barteau and J. G. Chen, *Physical review letters*, **2004**, 93, 156801.
- [18] Gu Y J, Wong W T, *Langmuir*, **2006**, 22, 11447-11452.
- [19] Y. Zhou, J. Liu, J. Ye, Z. Zou, J. Ye, J. Gu, T. Yu and A. Yang, *Electrochimica Acta*, **2010**, 55, 5024-5027.
- [20] Pan W, Zhang X, Ma H, Zhang J, *The Journal of Physical Chemistry C*, **2008**, 112, 2456-2461.
- [21] Zhang J, Qiu C, Ma H, Liu X, *The Journal of Physical Chemistry C*, **2008**, 112, 13970-13975.
- [22] R. Larsen, S. Ha, J. Zakzeski and R. I. Masel, *Journal of Power Sources*, **2006**, 157, 78-84.
- [23] T. Sun, Z. Zhang, J. Xiao, C. Chen, F. Xiao, S. Wang and Y. Liu, *Scientific reports*, **2013**, 3, 2527.
- [24] D. Kim, Y. W. Lee, S. B. Lee and S. W. Han, *Angewandte Chemie*, **2012**, 51, 159-163.
- [25] Y.-W. Lee and K.-W. Park, *Catalysis Communications*, **2014**, 55, 24-28.
- [26] Fu GT, Xia BY, Ma RG, Chen Y, Tang YW, Lee JM. *Nano Energy*, **2015**, 12, 824-832.

Chapter 5*

MOF derived cobalt based catalyst for hydrogen evolution

Layered cobalt metal–organic frameworks were subjected to heat treatment to produce the hybrid of Co/N-Carbon. The derivative layered structure comprised of metallic cobalt nanoparticles and carbon matrix was tested in the application of hydrogen evolution, which showed a low overpotential at 10mA/cm². More importantly, the hybrid materials displayed robust cycle durability and long-term stability. The hybrid of Co/N-carbon possessed these excellent properties because of its two-dimensional configuration, which included metallic cobalt nanoparticles, the superior conductivity of carbon and the stability of carbon protection effect.

*This section published as T. Huang, Y. Chen and J.-M. Lee, Acs Sustain Chem Eng, 2017, 5, 5646-5650.

5.1 Introduction

Water splitting coupled with solar energy has been considered as a promising and sustainable solution in terms of hydrogen and oxygen production.^[1, 2] Hydrogen evolution reaction (HER) using platinum remains among the most powerful catalyst, despite their high cost in order to reach high hydrogen production. Up to now, this catalyst still suffers from high cost, and low stability which presently limit their integration in real commercial applications.^[3] Therefore, replacement of this noble metal catalysts with low cost, highly active and stable catalysts, represent the bottleneck of the development of hydrogen evolution reaction. In this context, non-precious metal-based HER catalyst represents a serious alternative that have been intensively studied explored.^[4-6] Recently, transition metals such as cobalt (Co) based electrocatalysts have been intensively studies for HER with different forms such as carbon encapsulated cobalt NPs dispersed on graphene sheets,^[7] molecular cobalt complexes^[8] and Co-doped iron pyrite.^[9] Notably, cobalt nanocrystallites are reported to be superior electrocatalyst, ^[10,11] due to its propitious hydrogen atom binding energy.^[12] However, preparation of cobalt nanocrystallites and desirable compositions for superior electrocatalytic performance remains a difficult task, whose difficulty mainly arises from the inevitable aggregation of nanoparticles during synthesis and usage, which leads to lower electrochemical performance.^[12]

Recently, metal-organic frameworks (MOFs), which are crystalline porous architectures composed by metal ions/clusters and organic ligands, are reported to be suitable precursors in energy storage and catalysis.^[13, 14] MOFs have many promising properties such as ordered pores and large surface area which are required for high efficient hydrogen evolution process.^[15, 16] As such, cobalt based metal-organic frameworks could achieve uniform carburization and in situ formation of metallic cobalt nanoparticles, therefore they can be expected to be an ideal self-sacrificial template for fabrication of electrocatalysts for electrochemical hydrogen evolution. For example, Chen et al reported the preparation of nitrogen-doped graphene/cobalt embedded porous carbon polyhedron,^[17] which showed a stable current density of 10 mA cm^{-2} at -229 mV (vs RHE) in acid media; while Sun et al synthesized porous hybrid materials composed by Co-P/N-doped carbon, which

delivered excellent catalytic activity for HER with affording the current density of 10 mA cm^{-2} at low overpotentials of -154 mV (vs RHE).^[18] Despite the fact that many works have been conducted on Co-based MOF derived materials, development of functional catalyst derived from two-dimensional MOFs for hydrogen evolution have rarely been reported. Hybrid materials derived from 2D MOFs have the advantages of large surface area and facilitation of charge transport, which are necessary properties for excellent electrocatalysts. Thus 2D MOFs are expected to be the suitable precursors for HER catalysts.^[19]

This work reports the fabrication and characterization of a 2D hybrid structure of Co/N-Carbon (Figure 5.1). The catalysts showed excellent hydrogen evolution activity and stability. The as-prepared 2-D sheet structures retained the well-defined morphology of the initial Co-based MOFs, and cobalt nanoparticles (ca. 7.2 nm) were well embedded on the N-carbon. Thanks to the integration of the advantageous features of ultrafine cobalt nanoparticles and N-carbon, the resultant Co/N-Carbon show enhanced activity and durability under the alkaline media. More importantly, Co/N-carbon's electrocatalytic activities for hydrogen evolution have been more advantageous over other nanocarbon-based electrocatalysts reported previously.

Figure 5.1 Synthesis procedure of Co/N-carbon by pyrolysis of the mixture of the Co-MOF and hexamethylenetetramine.

5.2 Principle Outcomes

5.2.1 Structure information

Figure 5.2 FESEM images of (a) and (b) layered Cobalt MOFs; (c) and (d) Co-MOF pyrolysis under argon; (e) and (f) Co-MOF and hexamethylenetetramine pyrolysis under argon; (g) and (h) Co-MOF pyrolysis under air.

Figure 5.3 AFM of layered Co-MOF.

The synthesis of 2D layered cobalt based MOF with controlled thickness shown in Figure 5.1. FESEM images show that the parallelogram-like structure of the Co-MOF with lateral size of ca. 3 μm was presented (Figure 5.2a, Figure 5.2b). XRD experimental results (Figure 5.4a) show the typical XRD peaks of Co-MOF match well with those of previously reported MOF: $\text{Co}(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})_4$.^[20] Additionally, the crystal information frameworks

(Figure 5.4c) is presented. The Atomic Force Microscopy reveals the thickness of ultrathin layered Co-MOF is 2~3 nm (Figure 5.3). Importantly, the prepared 2D Co-MOF can be converted to 2D Co/N-Carbon hybrid structure through the calcination process (Figure 5.1). XRD was used to study the calcined products, which showed the existence of carbon and cobalt (Figure 5.6a).

Figure 5.4 (a) XRD of Co-MOF; (b) Figure S1 Nanoparticles size distribution; (c) Figure S4 Crystal information frameworks of Co-MOF.

Moreover, the layered Co-MOF with lateral size of ca. 3 μm were subject to heat treatment in argon atmosphere, the as-obtained hybrid materials well retained their precursors' structure (Figure 5.2). Furthermore, the 2D Co/N-carbon nanocomposite was characterized by TEM (Figure 5.5). Figure 5.5c displays the as-prepared materials of 2D Co/N-carbon possess cobalt nanoparticles (c.a. 7.2 nm) supported on the nitrogen-doped carbon matrix (Figure 5.4b). Figure 5.5d demonstrates a crystalline facet ($D_{\text{space}} = 0.205 \text{ nm}$), such D spacing is metallic cobalt's crystal plane of (111).^[21] Therefore, during the calcination process, the cobalt precursors of MOF was transformed into metallic cobalt nanoparticles.

While the nitrogen-containing hexamethylenetetramine molecules which contain sufficient nitrogen and carbon atoms, were calcined to form nitrogen-doped graphitic carbon. A uniform dispersion of metallic Co nanoparticles were wrapped in the nitrogen-doped carbon after the in situ calcination of the frameworks by thermal annealing. As a result, the configuration of Co/N-Carbon forms the structural basis of high performances of Co/N-carbon catalysts.

Figure 5.5 (a) TEM image of Co/N-carbon, (b) TEM image showing homogeneously embedded cobalt nanoparticles on carbon matrix, (c) TEM image showing densely dotted cobalt nanoparticles, (d) high resolution TEM image showing the lattice fringe of metallic cobalt.

5.2.2 Physical characterization

XRD was used to study the three products derived from different procedures in terms of crystal structure. For the hybrid structure of Co/N-Carbon, its dominant compositions were metallic Co (44.3° , 51.5°) and graphitic carbon (26.1°), with some minor Co_3O_4 which might be from the cobalt being oxidized by carboxyl of H_2NDC . (Figure 5.6a). Furthermore, the HRTEM image confirmed the existence of highly crystalline Co^0 . For the hybrid structure derived from Co-MOF without N-doping, it showed similar XRD spectrum to that of Co/N-carbon. While for Co oxides prepared by calcination of Co-MOF, they showed greater amount of Co_3O_4 (19.06° , 31.27° , 36.9° , 59.5° , 65.4°) and CoO (42.5° and 61.8°).^[17] Raman spectrum was conducted to investigate the appearance of graphitic carbon (Figure 5.6b). The Raman spectrum of 2D Co/N-carbon hybrid showed the intensive G band, proving the formation of graphitic carbon, which is highly conductive and can act as the current collector in the hybrid materials.^[22] Besides, nitrogen adsorption–desorption isotherm was conducted to study Co/N-Carbon's surface area and pore size, the experimental results showed a specific surface area of $36.85 \text{ m}^2/\text{g}$ and that the dominant pore size was 20 nm. (Figure 5.7) Therefore, the graphitic structured carbon and well-dispersed metallic cobalt nanoparticles together form a good configuration for electrochemical hydrogen evolution reaction.^[3]

Figure 5.6 (a) XRD patterns of Co-Carbon, Co/N-carbon and Co oxides derived from MOFs, (b) Raman spectra recorded at 532 nm laser excitation, (c) XPS data showing N 1s spectrum of Co/N-carbon, (d) XPS data showing Co 2p spectrum of Co/N-carbon.

Figure 5.7 (a) nitrogen adsorption–desorption isotherm, and (b) pore size distribution.

X-ray photoelectron spectroscopy (XPS) was conducted to study the composition of the as-prepared 2D Co/N-carbon hybrid materials (Figure 5.6c and Figure 5.6d). For N 1s spectrum, it had peaks which are corresponding to pyridinic N (397.2 eV), pyrrolic N (400.5 eV), graphitic nitrogen doped in the carbon matrix (402.3 eV) and the oxidized N atoms (404.5 eV) (Figure 5.6c).^[17] Apparently, nitrogen-doped carbon was formed because of the thermal conversion of the nitrogen atoms existing in the hexamethylenetetramine. For Co 2p spectrum, it showed two peaks: metallic Co (778.2 eV), Co^{2+} (782.0 eV), and the atomic ratio of Co and Co^{2+} was 2:1.^[23] In addition to XPS, the EDX elemental mapping was also used to study the composition of the products. From Figure 5.8, homogeneous distribution of element of C, Co and N have been demonstrated.

Figure 5.8 EDX elemental mapping of Co/N-Carbon.

5.2.3 Electrochemical characterization

Figure 5.9 (a) LSV of different electrocatalysts with rotation disk electrode at 1600 rpm, (b) EIS of different electrocatalysts, (c) Cycling durability test of Pt/C (20% wt) and Co/N-carbon for 2000 cycles, (d) Current-time curve of Pt/C (20% wt) and Co/N-carbon.

The electrocatalytic performances of the four different catalysts were studied towards electrochemical hydrogen evolution reaction. Firstly, linear sweeping voltammetry (LSV) was conducted to probe their electrocatalytic activities. The current density of 10.0 mA cm^{-2} is correlated with standard current density of solar fuel synthesis, as such, this work compared the overpotential at 10 mA cm^{-2} for the four electrocatalysts.^[24] In Figure 5.9a, Pt/C (20%wt) required an overpotential of 35 mV (vs RHE) to reach 10 mA cm^{-2} , Co/N-carbon needed the overpotential of 103 mV (vs RHE) to reach 10 mA cm^{-2} , whereas Co-Carbon demanded 460 mV overpotential to reach 10 mA cm^{-2} , and cobalt oxides required 450 mV overpotential to reach 10 mA cm^{-2} . The experimental results show that Co/N-carbon has high electrocatalytic activity. Figure 5.10 shows the hydrogen bubbles produced on the glassy carbon electrode which is modified by Co/N-carbon, which aids to confirm

the high electrocatalytic activity of Co/N-carbon towards HER. Furthermore, the amount of doping reagents has been varied from 20 mg, 30 mg, 40 mg to prepare different products, and the corresponding products have been tested for electrochemical hydrogen evolution. From the Figure 5.11, catalysts with 30 mg doping reagent show best catalytic activity. It is speculated that less doping reagent does not provide sufficient electron-rich N atoms; while excessive doping reagents may decrease graphitic carbon and conductivity of the catalyst, which is unfavorable for the HER. These results show that amount of nitrogen doping influences the HER performance.

Figure 5.10 The hydrogen is evolving during 0 s, 30 s, 1 min, 2 min as CV is performing.

To study how the charge transport inside the four electrocatalysts influence their catalytic activity towards hydrogen evolution, the electrochemical impedance spectroscopy (EIS) was conducted on Co/N-carbon, Co/Carbon, Co oxides derived from MOFs and the commercial Pt/C. The Nyquist plot is shown in Figure 5.9b, in the high-frequency area the semicircles was ascribed to the resistance of charge-transfer (R_{ct}), and a lower value of R_{ct} denotes a faster reaction rate.^[25] As such, similar R_{ct} of 45 Ohm is realized on Co/N-carbon

compared to Pt/C (43 Ohm), which is consistent with the results acquired from the polarization tests. The low charge transfer resistance helps to achieve greatly fast charge transport, which is mainly due to the two-dimensional configuration and highly conductive N-doped graphitic carbon of Co/N-carbon.^[14]

Figure 5.11 LSV of catalysts with various doping degree.

To study the durability of the samples, the cycling test of Co/N-carbon to hydrogen evolution reaction was also performed. For Co/N-carbon, its current density at 10 mA cm⁻² fluctuated from 103 mV to 101 mV, with variation being 2 mV (Figure 5.9c). While for Pt/C, its overpotential at 10 mA cm⁻² changed from 35 mV to 56 mV with the difference being 21 mV. Moreover, long-term stability is another significant concern for the excellent electrocatalyst. To study the stability of Co/N-carbon under alkaline solution, continuous hydrogen evolution reaction was conducted at constant overpotential using Pt/C and Co/N-carbon. As shown in Figure 5.9d, For Co/N-Carbon, the current density tended to increase at the preceding 5,000 s, and then underwent a minor decrease of current density until 36,000 s, its final current density is 109.3% of its initial value; for Pt/C, the current density dropped down continuously, the final current density retention rate is 45.2%. The well stability of Co/N-carbon is ascribed to the metallic cobalt nanoparticles which were firmly embedded in N-carbon matrix. Besides, the increase of activity should come from the activation effect of two-dimensional layered carbon structure.^[26] Specifically speaking, the

forming hydrogen inside the stacked layered carbon structure may continuously open and expose more catalytic sites for hydrogen evolution.^[27] Therefore, the current density continuously increased in the i-t curve.

The aforementioned superior electrochemical behaviors of the 2D Co/N-carbon hybrid materials may originate from two reasons. First, the layered 2D Co/N-carbon hybrid structure with lateral size of ca. 3 μm (Figure 5.2a, Figure 5.2b) provided facile diffusion path of electrolyte ions, presented homogeneously dispersed cobalt nanoparticles as active sites for the hydrogen evolution reaction. As previously reported, cobalt metal has a propitious binding energy towards hydrogen atoms.^[28] Second, the carbon matrix acted as a current reservoir for electron transport inside the hybrid of Co/N-carbon structures, which improved the electrochemical reaction kinetics. Notably, some previous works demonstrate that nitrogen-doping increases disorder and edge plane sites with a larger density of active sites, which is beneficial for electron transfer. As such, nitrogen-doping would benefit the electrochemical performances our products.^[29] Therefore, the two-dimensional hybrid materials of Co/N-carbon including ultrafine metallic cobalt nanoparticles and N-doped carbon led to their exceptional electrocatalytic performances towards hydrogen evolution reaction.

5.3 Conclusion

By using the layered 2D Co-MOF as a template, cobalt particles embedded on two-dimensional N-doped carbon structure were prepared. Similar to the noble metal platinum, the hybrid materials herein showed similar high hydrogen evolution activity. More importantly, the hybrid structure of Co/N-carbon exhibited much better cycle durability and long-term stability. During the pyrolysis synthesis, Co-MOFs not only provided the carbon source for growth of graphitic carbon which was catalyzed by the in situ formed metallic cobalt nanoparticles, but also served as the template for two-dimensional hybrid materials. The as-prepared Co/N-carbon exhibits remarkable electrocatalytic activity, and even has greater electrochemical behaviors in durability and stability tests. The outstanding electrocatalytic behaviors should arise from the beneficial properties of cobalt and N-

carbon. Moreover, the superior cycle stability and long term activity are due to their robust overall two-dimensional structure. Because of the sufficient variability of MOF compositions and the availability of cavity space for loading suitable doping molecules, this work provides the basis to create more two-dimensional nanocarbon based electrocatalysts as a replacement to precious metals for electrochemical applications.

References

- [1] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori and N. S. Lewis, *Chem Rev*, **2010**, 110, 6446-6473.
- [2] S. Licht, B. Wang, S. Mukerji, T. Soga, M. Umeno and H. Tributsch, *J Phys Chem B*, **2000**, 104, 8920-8924.
- [3] H. Y. Jin, J. Wang, D. F. Su, Z. Z. Wei, Z. F. Pang and Y. Wang, *J Am Chem Soc*, **2015**, 137, 2688-2694.
- [4] H. B. Wu, B. Y. Xia, L. Yu, X. Y. Yu and X. W. Lou, *Nat Commun*, **2015**, 6.
- [5] W. J. Zhou, J. Jia, J. Lu, L. J. Yang, D. M. Hou, G. Q. Li and S. W. Chen, *Nano Energy*, **2016**, 28, 29-43.
- [6] W. J. Zhou, J. Lu, K. Zhou, L. J. Yang, Y. T. Ke, Z. H. Tang and S. W. Chen, *Nano Energy*, **2016**, 28, 143-150.
- [7] H. L. Fei, Y. Yang, Z. W. Peng, G. D. Ruan, Q. F. Zhong, L. Li, E. L. G. Samuel and J. M. Tour, *Acs Appl Mater Inter*, **2015**, 7, 8083-8087.
- [8] C. C. L. McCrory, C. Uyeda and J. C. Peters, *J Am Chem Soc*, **2012**, 134, 3164-3170.
- [9] D. Y. Wang, M. Gong, H. L. Chou, C. J. Pan, H. A. Chen, Y. P. Wu, M. C. Lin, M. Y. Guan, J. Yang, C. W. Chen, Y. L. Wang, B. J. Hwang, C. C. Chen and H. J. Dai, *J Am Chem Soc*, **2015**, 137, 1587-1592.
- [10] W. J. Zhou, J. Zhou, Y. C. Zhou, J. Lu, K. Zhou, L. J. Yang, Z. H. Tang, L. G. Li and S. W. Chen, *Chem Mater*, **2015**, 27, 2026-2032.
- [11] W. J. Zhou, Y. C. Zhou, L. J. Yang, J. L. Huang, Y. T. Ke, K. Zhou, L. G. Li and S. W. Chen, *J Mater Chem A*, **2015**, 3, 1915-1919.
- [12] N. H. Chou, P. N. Ross, A. T. Bell and T. D. Tilley, *Chemsuschem*, **2011**, 4, 1566-1569.

- [13] B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. Lou and X. Wang, *Nat Energy*, **2016**, 1.
- [14] F. F. Cao, M. T. Zhao, Y. F. Yu, B. Chen, Y. Huang, J. Yang, X. H. Cao, Q. P. Lu, X. Zhang, Z. C. Zhang, C. L. Tan and H. Zhang, *J Am Chem Soc*, **2016**, 138, 6924-6927.
- [15] J. S. Qin, D. Y. Du, W. Guan, X. J. Bo, Y. F. Li, L. P. Guo, Z. M. Su, Y. Y. Wang, Y. Q. Lan and H. C. Zhou, *J Am Chem Soc*, **2015**, 137, 7169-7177.
- [16] J. Lu, W. J. Zhou, L. K. Wang, J. Jia, Y. T. Ke, L. J. Yang, K. Zhou, X. J. Liu, Z. H. Tang, L. G. Li and S. W. Chen, *Acs Catal*, **2016**, 6, 1045-1053.
- [17] Y. Hou, Z. H. Wen, S. M. Cui, S. Q. Ci, S. Mao and J. H. Chen, *Adv Funct Mater*, **2015**, 25, 872-882.
- [18] B. You, N. Jiang, M. L. Sheng, S. Gul, J. Yano and Y. J. Sun, *Chem Mater*, **2015**, 27, 7636-7642.
- [19] A. J. Clough, J. W. Yoo, M. H. Mecklenburg and S. C. Marinescu, *J Am Chem Soc*, **2015**, 137, 118-121.
- [20] J. A. Kaduk and J. A. Hanko, *J Appl Crystallogr*, **2001**, 34, 710-714.
- [21] Y. J. Oh, C. A. Ross, Y. S. Jung, Y. Wang and C. V. Thompson, *Small*, **2009**, 5, 860-865.
- [22] X. X. Zou, X. X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew Chem Int Edit*, **2014**, 53, 4372-4376.
- [23] Y. P. Zhu, T. Y. Ma, M. Jaroniec and S. Z. Qiao, *Angew Chem Int Edit*, **2017**, 56, 1324-1328.
- [24] C. C. L. McCrory, S. H. Jung, J. C. Peters and T. F. Jaramillo, *J Am Chem Soc*, **2013**, 135, 16977-16987.
- [25] D. T. Dam and J. M. Lee, *Acs Appl Mater Inter*, **2014**, 6, 20729-20737.
- [26] L. Yu, J. F. Yang and X. W. Lou, *Angew Chem Int Edit*, **2016**, 55, 13422-+.
- [27] J. F. Xie, X. D. Zhang, H. Zhang, J. J. Zhang, S. Li, R. X. Wang, B. C. Pan and Y. Xie, *Adv Mater*, **2017**, 29.
- [28] W. Chaikittisilp, N. L. Torad, C. L. Li, M. Imura, N. Suzuki, S. Ishihara, K. Ariga and Y. Yamauchi, *Chem-Eur J*, **2014**, 20, 4217-4221.
- [29] J. D. Wiggins-Camacho and K. J. Stevenson, *J Phys Chem C*, **2009**, 113, 19082-19090.

Chapter 6*

MOF derived cobalt/molybdenum based catalyst for oxygen evolution

It is reported that nitrogen-doped carbon supported CoOx-MoC heterostructures for the first time as high excellent electrochemical oxygen evolution electrocatalysts. The composition can be tuned by the addition of a Mo source to form a nanowire-assembled hierarchically porous microstructure, which can enlarge the specific surface area, thus exposing more active sites, facilitating charge transfer. Moreover, it is demonstrated that the formation of CoOx-MoC heterostructures and the resulting synergistic effect between MoC and Co facilitate the reaction kinetics, leading to significantly improved OER activity. The well-constructed micro-architecture contributes to long term stability electrochemical behaviors. This work provides a universal and facile strategy which includes composition tuning and structure optimization for the development of next-generation non-precious metal based OER electrocatalysts.

*This section published as T. Huang, Y. Chen and J. M. Lee, Small, 2017, 13, 1702753.

6.1 Introduction

The exhausted petroleum resources have triggered the development of alternative energy sources. The electrochemical water splitting coupled with solar energy has been considered as a reliable solution to the energy depletion problems ^[1-3]. Among the water splitting equipment components, electrocatalysts bear most of the cost. Therefore, engineering highly active and inexpensive catalysts has been an essential part of developing commercially viable electrochemical water splitting technology. In particular, development of oxygen evolution reaction (OER) catalysts is imperative, because the current electrocatalysts suffer sluggish kinetics and require large overpotential. ^[4-6]

Over the past decade, RuO₂ and IrO₂ have been proven as active electrocatalysts in enhancing the OER kinetics and decreasing the overpotential ^[7-9]. However, high cost of these materials seriously hinder their practical installations on a large scale. Therefore, it is urgent to design and synthesize cost-effective electrocatalysts towards electrochemical oxygen evolution. Nowadays, due to their earth abundance, theoretically high catalytic activity and rich redox activity, 3d transition-metal-based electrocatalysts (for example, cobalt oxides) have been considered as promising OER electrocatalyst candidates.^[10] Notably, cobalt oxide based electrocatalysts have shown promising catalytic performance towards oxygen evolution reaction. For example, Bell et al reported cobalt oxide catalyst supported on gold, which displayed an activity higher than that of Ir under the same condition;^[11] Xie et al fabricated an atomically-thick Co₃O₄ porous sheet which delivered a current of 341.7 mA cm⁻² at 1.0 V vs Ag/AgCl.^[12] However, cobalt oxide nanoparticles suffer several drawbacks, such as low conductivity and ease of aggregation in alkaline media, which make cobalt oxide based electrocatalysts not viable for commercial applications.^[13-14] Therefore, it is imperative to optimize catalysts' micro-architecture and tune their surrounding composition of cobalt oxides simultaneously for high performance oxygen evolution electrocatalysts.

Metal-organic framework (MOF) is extensively used as precursors/templates for developing highly efficient electrocatalysts in view of its favorable properties such as tunability of MOFs into various microstructure choice, good compatibility with various metal ions, as well as the uniform dispersion of derived carbon in MOFs, thus bringing along inherent conductivity.^[15-20] For example, Loh et al designed the hybrid of copper-centered MOF and graphene oxide which showed excellent performances in hydrogen evolution, oxygen evolution and oxygen reduction;^[21] Tang et al produced carbonized nanoparticles derived from nanoscale MIL-88B-NH₃, which exhibited superior oxygen reduction activity.^[22] Recently, several direct carbonization of MOFs have been reported to produce materials for electrochemical applications ^[23-25]. On the other hand, molybdenum carbides have been frequently used as composition tuning agents and are found to promote electrocatalytic activity and stability, because of their good electrical conductivity.^[26,27] For example, Chen et al demonstrated the Pt-Mo₂C with high hydrogen evolution activity while maintaining excellent stability.^[28] Therefore, by using cobalt MOF loaded with Mo source as precursors, the derivative structure of CoOx-MoC/N-carbon (CoOx-MoC/NC) will be a good candidate for oxygen evolution reaction.

To this end, this work intends to simultaneously realize the integration of the advantageous properties of Co oxide, Mo carbides, and the construction of the well-assembled structure with high electrochemical active surface area. Such well-designed hierarchical structure is deemed to have robust stability, facile charge and electrolyte transfer, well-arrayed catalyst sites. Herein, cobalt-based MOF was used as a template to fabricate micro-ribbon hybrid of CoOx-MoC encapsulated in N-doped carbon for electrochemical oxygen evolution, with an assistance of polyvinylpyrrolidone (PVP). Ultimately, a well-assembled composite derived from the hybrid metal organic frameworks shows superior electrochemical behaviors, compared to that of the IrO₂/C in an alkaline solution, which originate from ordered exposure of active sites, a 3D conductive carbon matrix, and apparent synergism among CoOx, MoC and N-doped carbon. More importantly, the growing process of the well-defined microstructure was observed by temporal FESEM, some critical descriptors (graphitic degree, EASA) of oxygen evolution catalysts have been measured and evaluated to unravel the factors that contribute to electrocatalytic performances. Such knowledge

along with the combinatorial synthetic strategy would be instructive for future non-precious metal based electrocatalyst design.

Figure 6.1 Design strategy of hybrid MOF and the pyrolysis of the hybrid MOF.

Figure 6.2 (a, b, c) FESEM images of the hybrid Co-Mo-MOF; (d, e, f) FESEM images of the product derived from the hybrid Co-Mo-MOF after pyrolysis under argon.

6.2 Principle Outcomes

6.2.1 Structure Information

The preparation process is illustrated in Figure 6.1, which involves a two-step route, in which the layered cobalt MOFs act as a template. The cobalt MOFs were studied in one previous work [29]. For the first time, PVP was used as the structure directing agent and N-dopant during MOF synthesis. Here, PVP was simultaneously utilized to lower the surface energy of ultrathin MOF and recruit the nanoplate-like MOF, which contribute to the formation of such combination and integration in 2-dimension and 3-dimension.^[30] FESEM images of Co-Mo-MOF are shown in Figure 6.2a-6.2c, which show the well-defined hierarchical microstructure of the hybrid MOF, composed by nanowires. The hybrid MOFs were subject to the heating treatment at 600 °C to fabricate the MOF-derived electrocatalysts.

Figure 6.3 (a) and (b) TEM image of CoO_x-MoC/NC-2, (c) TEM image showing cobalt and MoC densely encapsulated in carbon matrix, (d) high resolution TEM image showing the lattice fringe of few layer graphene, which encapsulates cobalt and MoC nanoparticles.

To study the role of PVP, the products were prepared without using PVP, while the aggregated and irregular nanostructures were obtained as shown in Figure 6.6, which demonstrates that the polymer was essential for the formation of the microarchitecture of Co-Mo-MOF. The pyrolysis temperature was set at 600 °C for the purpose of formation of graphitic carbon,^[31] and correspondingly Figure 6.2d-6.2f showed the microribbon structure with well-arrayed nanoparticles were fabricated. More importantly, the high-orderly microribbon hybrid structure of CoOx-MoC/NC can efficiently suppress the aggregation of micro-/nanostructure and facile diffusion of gas (O₂), which can avoid pulverization and therefore achieve robust long-term stability. To sum up, the superiority of the microstructure would be a critically important factor that account for its excellent electrochemical performances.

Figure 6.3 shows Transmission electron microscope image of the hybrid materials of CoOx-MoC/NC, which shows that the nanowire is made up nanoparticles and has porous nature, such as large electrochemical active surface area, interconnected void space which facilitates gas release.^[32,33] Consistent with the FESEM images, TEM images also demonstrate the densely and orderly arrayed catalytic sites. Higher-resolution transmission electron microscope (HRTEM) image of CoOx-MoC/NC is shown in Figure 6.3d, which shows that the crystal CoOx-MoC/NC are covered by highly crystalline atomically thin graphitic carbon layers. The carbon matrix could improve the overall conductivity of catalysts, as well as maintain the structure of CoOx-MoC/NC. HRTEM image of a typical CoOx-MoC/NC is shown in Figure 6.5 and the plane of (101) of MoC is observed;^[34] while the plane of (220) of Co₃O₄ is also observed.^[35] Three samples with different Co/Mo ratios were prepared in order to obtain compositionally favorable electrocatalyst, CoOx-MoC/NC-1's atomic ratio of Co/Mo is 35.8, and for CoOx-MoC/NC-2 and CoOx-MoC/NC-3, the ratio is 21 and 10.3, respectively.

Figure 6.4 Temporal FESEM image of the hybrid MOF formed after the reaction time of 2 h, 3 h, 5 h, 8 h, 10 h, 15 h. All the inset images are FEEM images focusing on one MOF microstructure at the corresponding reaction time.

MOF products at different reaction times were observed by FESEM to study the growing process. As summarized in Figure 6.4, the initial nanoplates (ca. 600 nm) were formed at 2 h. At $t = 3$ h, the small plate structures grew along one direction and transformed into oval and layered structure, with length being ca. 3 μm . From 3 – 5 h, the layered structure grew layer by layer based on the preformed one dimensional layered structure. From 8 – 15 h, no obvious variation was observed for the MOF, indicating the formation of fully mature hybrid MOF microstructure. This layer-by-layer configuration is beneficial for electrochemical process, such as mass and charge transfer, gas release, thereafter promoting electrocatalytic activity and stability,^[36] as evidenced by linear sweeping voltammogram (LSV), Tafel plot and i - t curves in Figure 6.9.

Figure 6.5 HRTEM of CoO_x-MoC/NC-2 displaying the lattice fringe of MoC and Co₃O₄.

Figure 6.6 FESEM images of the hybrid MOF produced without PVP (a) and with PVP (b).

6.2.2 Physical Characterization

Figure 6.7 (a) XRD patterns of CoOx-MoC/NC-1, CoOx-MoC/NC-2, CoOx-MoC/NC-3 derived from the hybrid MOF, (b) Raman spectra recorded at 532 nm laser excitation, (c) XPS data showing Co 2p spectrum of CoOx-MoC/NC-2, (d) XPS data showing Mo 3d spectrum of CoOx-MoC/NC-2.

XRD was used to study the crystal composition of CoOx-MoC/NC. Figure 6.7a shows diffraction peak at 25°, which was graphitic carbon's crystal plane of (002). Whereas the characteristic diffraction peaks at 32°, 36.5°, 48.2°, 64.9°, and 67° can be indexed to MoC, respectively.^[37] Three strong peaks of cobalt oxides and two metallic cobalt can also be observed.^[38] Furthermore, CoOx-MoC/NC-2 has a higher crystalline phase, which may endow it with better electrical conductivity. Raman spectroscopy was conducted to study the products of CoOx-MoC/NC.^[39] Figure 6.7b shows the typical Raman spectra of CoOx-MoC/NC 1-3, notably, the two typical D band (1334 cm⁻¹) and G band (1597 cm⁻¹) of carbon are seen. Here IG/ID of CoOx-MoC/NC-2 is calculated to be 1.31 with apparent D

peak and G peak, proving the formation of graphitized carbon. On contrary, the CoOx-MoC/NC 1 and CoOx-MoC/NC-3 have the IG/ID of 1.21, 1.25, respectively. As the comparisons, Ding et al produced carbon materials by hydrothermal impregnation with a IG/ID ratio of 1.14;^[40] while Presser et al reported onion-like carbon (OLC) calcined at 1300 °C and 1750 °C, the OLC calcined at 1300 °C had a IG/ID ratio of 0.4, the OLC calcined at 1750 °C had a IG/ID ratio of 0.625.^[41] Therefore, this work achieved high graphitic degree with lower calcination temperature (600 °C). Previous work reported that the graphitic carbon could improve the electronic conductivity of the products.^[42] Therefore, the high graphitic degree of CoOx-MoC/NC-2 would play a beneficial role in boosting the electrochemical oxygen evolution performance, by acting as efficient electron highway and mass reservoir for the electrochemical process (Figure 6.1).

Figure 6.8 XPS data of O 1s.

X-ray photoelectron spectroscopic (XPS) is a technique for investigation of surface composition, this work used it to characterize CoOx-MoC/NC. In the spectra of Co 2p spectra (Figure 6.7c), cobalt oxide and metallic cobalt were detected.^[43] As demonstrated in Figure 6.7c, the peak of Co 2p_{3/2} and Co 2p_{1/2} are located at 780 and 805 eV, respectively. The deconvoluted peaks of 780 and 786.7 eV are corresponding to Co₃O₄, the peaks of 778.5 and 805 eV are corresponding to metallic cobalt, and metallic cobalt occupies 67.2%. For Mo 3d spectrum, the fitting of the Mo 3d peak shows that there are four valence states for Mo (Mo⁰, Mo³⁺, Mo⁴⁺, Mo⁶⁺) on the surface of MoC nanoparticles.^[44] Mo⁰ and Mo³⁺ are corresponding to Mo-Mo and Mo-C bonds in MoC,

respectively (Figure 6.7d). For O 1s spectra of CoO_x-MoC/NC (Figure 6.8), it displays two peaks, they are designated as O1 and O2, respectively.^[45] The metal-oxygen bond is corresponding to the peak O1(532.0 eV), and the defects because of low oxygen is corresponding to the peak O2(538.1 eV). The apparent peak of O2 indicates plenty of defects induced by oxygen vacancies, such defects are beneficial for the conductivity enhancement and increase of the kinetics of surface redox reactions, thereafter enhancing the overall electrocatalytic performance.

6.2.3 Electrochemical Performance

Figure 6.9 (a) LSV of different electrocatalysts with rotation disk electrode at 1600 rpm, (b) Tafel plot of different electrocatalysts, (c) Plot of current density (at 1.14 V vs RHE) vs scan rate, (d) Chronoamperometric responses of CoO_x-MoC/NC-2 (at 1.56 V vs RHE) and IrO₂ (at 1.63 V vs RHE) in 1 M KOH at rotating disk electrodes (1600 rpm) for 36 000 s.

Linear sweeping voltammetry (LSV) was conducted to measure the electrocatalytic activities of the as-synthesized catalysts toward OER in a three-electrode configuration.^[46] To investigate the importance of the ratio of Co/Mo, CoOx-MoC/NC was prepared by using various precursor atomic ratios (35.8:1, 21:1, 10.3:1), namely, CoOx-MoC/NC-1, CoOx-MoC/NC-2, and CoOx-MoC/NC-3, respectively. The electrocatalytic performance of commercial IrO₂/C was tested for comparative study. All the catalysts' performances were depicted in Figure 6.9a, CoOx-MoC/NC-2 shows the lowest overpotential of 330 mV at 10 mA cm⁻², which is the working current of solar fuel synthesis for practical applications,^[47] and it is smaller than those of CoOx-MoC/NC-1 (370 mV), CoOx-MoC/NC-3 (390 mV) and IrO₂/C (400 mV). More importantly, CoOx-MoC/NC-2 showed an onset potential of 1.52 V (vs RHE), which was the smallest one among the four samples. Moreover, the overpotential at 10 mA cm⁻² of CoOx-MoC/NC-2 is the smallest among the reported cobalt based oxygen evolution electrocatalysts, such as Co₃O₄/NiCo₂O₄ (340 mV),^[48] Ni-Co-oxide nanocages (380 mV).^[49] More importantly, Tafel plots (Figure 6.9b) were drawn to investigate the reaction kinetics for oxygen evolution reaction. The Tafel slope of CoOx-MoC/NC-2 is 89 mV dec⁻¹, it demonstrates that CoOx-MoC/NC has the smallest Tafel slope among the four catalysts, suggesting the fast catalytic reaction kinetics of CoOx-MoC/NC-2.

Figure 6.10 CVs of (a) CoOx-MoC/NC-1, (b) CoOx-MoC/NC-2, (c) CoOx-MoC-3 and IrO₂/C in the range of 1.095~1.155 V vs. RHE, measured in 1.0 M KOH solution, respectively.

Co atoms on the surface are first oxidized into CoOOH to form a CoOOH/Co complex as the actual active sites, evidenced by the oxidation peak of Co²⁺ to Co³⁺ near 1.08 V (Figure 6.9a, inset), which are beneficial to the oxidation of OH⁻ into oxygen.^[50] Interestingly, the oxidation peak of Co²⁺ to Co³⁺ for CoOx-MoC/NC-2 shifts to a more negative value and became more intense compared with that for CoOx-MoC/NC-1 (1.18 V) and CoOx-MoC/NC-3 (1.12 V), while IrO₂/C showed no oxidation peak around this potential region, demonstrating that the synergistic effect between MoC and Co generated in the hybrid structures contributes to the formation of CoOOH species and more active sites are exposed on the composites, which subsequently promote the OER performance. This trend is also consistent with the composition ratio of Co/Mo as evidenced by EDX. It is speculated a high ratio of Co/Mo does not contribute to conductivity enhancement; whereas a low ratio

of Co/Mo may not be able to provide sufficient catalytic site, which is unfavorable for the OER. These results show that an appropriate ratio of Co/Mo should be optimized in order to obtain excellent OER catalyst.

Table 6.1 Summary of Electrochemical Performances of CoOx-MoC/NC and IrO₂/C.

Catalyst	Onset potential (V vs RHE)	Overpotential@10mA/cm ² (mV vs RHE)	Co oxidation potential (V vs RHE)	Tafel slope (mV/dec)
CoOx-MoC/NC-1	1.55	370	1.18	126.3
CoOx-MoC/NC-2	1.52	330	1.08	89.8
CoOx-MoC/NC-3	1.57	390	1.12	131.5
IrO ₂ /C	1.57	400	N.A.	126.2

The high electrocatalytic activity of CoOx-MoC/NC may be explained by their large electrochemical active surface areas (EASAs).^[51] Typically ECSAs were represented by double-layer capacitance, thus the EASAs of CoOx-MoC/NC and IrO₂/C were obtained by measuring their double-layer capacitances (C_{dl}) (Figure 6.10). As displayed in Figure 6.9c, the C_{dl} of CoOx-MoC/NC-2 (257.00 mF cm⁻²) is larger than those of IrO₂/C powders (3.04 mF cm⁻²) and CoOx-MoC/NC-1, 3 (38.00, 100.50 mF cm⁻²), indicating CoOx-MoC/NC-2 owns a much higher ECSA than CoOx-MoC/NC-1 and CoOx-MoC/NC-3.

Figure 6.11 (a) nitrogen adsorption–desorption isotherm, and (b) pore size distribution.

To study the stability of CoOx-MoC/NC under an alkaline solution, a continuous oxygen evolution reaction was conducted at a constant overpotential using IrO₂/C and CoOx-MoC/NC. As shown in Figure 6.9d, For CoOx-MoC/NC, the current density tended to increase at the preceding 5,000 s, and then kept a stable current density until 36,000 s, its final current density is 112% of its initial value; As a comparison, i-t plot of IrO₂/C shows a severely serrated curve, which is mainly because the forming gas (O₂) cannot be released easily. On the contrary, the well stability of CoOx-MoC/NC is ascribed to the superior and well-constructed 3D hierarchical structure, which is assembled by nanowire and comprise plethora of cavity and channel space, these interconnected pores facilitate gas diffusion and release easily.^[52, 53] Nitrogen adsorption-desorption isotherm was conducted to study the surface area and pore size of the products of CoOx-MoC/NC-2, the result showed a surface area of 69.36 m²/g and that the dominant pore size range was 1-20 nm (Figure 6.11), which facilitated the gas diffusion. Moreover, the high electrochemical active surface area (250 mF/cm²) can also aid to verify that large surface area endows the catalyst with outstanding electrochemical performance. Besides, the increase of activity should come from the activation effect of the layered carbon structure. In particular, the forming oxygen inside the stacked layered carbon structure may continuously open and expose more catalytic sites for oxygen evolution. Therefore, the current density increased in the i-t curve during the preceding 5,000 s.

The aforementioned superior electrochemical behaviors of the microstructure may be ascribed to three reasons. First, Co/Mo compositional tuning, MoC has been found to promote the water splitting electrochemical reaction, whereas a low ratio of Co/Mo may not be able to provide sufficient catalytic sites, which is unfavorable for OER. Thus, the finely tuned Co/Mo composition exhibited enhanced oxygen evolution catalytic performance. Second, N-dopant from PVP with graphitic carbon contributes to highly conductive properties,^[54,55] which serves as the charge reservoir for the electrochemical reaction. Third, hierarchically 3D structure assembled from nanowires not only produces the well-arrayed electroactive catalytic site, but also lead to facile charge transfer and gas diffusion, which collaborates to endow the microstructure with outstanding electrochemical reaction kinetics, active surface area, activity and long term stability.^[56-58]

6.3 Conclusion

To conclude, a novel route was designed and carried out to construct hierarchical microstructure CoOx-MoC/NC by introduction of Mo atoms into Cobalt based MOF and the assistance of PVP as structure directing agent. A facile water-based method was adopted to tune the composition of the template cobalt based MOF, and use PVP (usually for metal nanoparticles surfactant) to optimize the MOF structure. Moreover, these hierarchically structured CoOx-MoC/NCs derived from hybrid MOFs displayed superior electrochemical oxygen evolution performances. Their excellent performances arise from the well arrayed electroactive nanoparticles and 3D interconnected configuration. For the first time, this work reports the parallel realization of MOF-templated bimetallic electrocatalyst synthesis and construction of efficient structure. Moreover, this study demonstrates a good example of fundamentally improving electrochemical behaviors tailored for electrochemical applications, by tuning composition and optimization of micro-architecture, with the assistance of template and polymers.

References

- [1] X. J. Shi, K. Zhang, K. Shin, M. Ma, J. Kwon, I. T. Choi, J. K. Kim, H. K. Kim, D. H. Wang and J. H. Park, *Nano Energy*, **2015**, 13, 182-191.
- [2] D. W. Hwang, J. Kim, T. J. Park and J. S. Lee, *Catal Lett*, 2002, 80, 53-57.
- [3] A. Kudo and Y. Miseki, *Chem Soc Rev*, **2009**, 38, 253-278.
- [4] A. T. Swesi, J. Masud and M. Nath, *Energ Environ Sci*, **2016**, 9, 1771-1782.
- [5] X. Y. Yu, Y. Feng, B. Y. Guan, X. W. Lou and U. Paik, *Energ Environ Sci*, **2016**, 9, 1246-1250.
- [6] T. Kwon, H. Hwang, Y. J. Sa, J. Park, H. Baik, S. H. Joo and K. Lee, *Advanced Functional Materials*, **2017**, 27.
- [7] I. Kwak, I. S. Kwon, J. Kim, K. Park, J. P. Ahn, S. J. Yoo, J. G. Kim and J. Park, *J Phys Chem C*, **2017**, 121, 14899-14906.
- [8] Y. H. Fang and Z. P. Liu, *Journal of the American Chemical Society*, **2010**, 132,

- 18214-18222.
- [9] Y. Lee, J. Suntivich, K. J. May, E. E. Perry and Y. Shao-Horn, *J Phys Chem Lett*, **2012**, 3, 399-404.
- [10] J. Rosen, G. S. Hutchings and F. Jiao, *Journal of the American Chemical Society*, **2013**, 135, 4516-4521.
- [11] B. S. Yeo and A. T. Bell, *Journal of the American Chemical Society*, **2011**, 133, 5587-5593.
- [12] Y. F. Sun, S. Gao, F. C. Lei, J. W. Liu, L. Liang and Y. Xie, *Chem Sci*, **2014**, 5, 3976-3982.
- [13] S. Mao, Z. H. Wen, T. Z. Huang, Y. Hou and J. H. Chen, *Energ Environ Sci*, **2014**, 7, 609-616.
- [14] X. Y. Lu and C. Zhao, *Journal of Materials Chemistry A*, **2013**, 1, 12053-12059.
- [15] Y. Z. Chen, C. M. Wang, Z. Y. Wu, Y. J. Xiong, Q. Xu, S. H. Yu and H. L. Jiang, *Advanced Materials*, **2015**, 27, 5010-5016.
- [16] B. Nohra, H. El Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo and A. Dolbecq, *Journal of the American Chemical Society*, **2011**, 133, 13363-13374.
- [17] B. Y. Xia, Y. Yan, N. Li, H. B. Wu, X. W. Lou and X. Wang, *Nature Energy*, **2016**, 1.
- [18] J. Tang and Y. Yamauchi, *Nature chemistry*, **2016**, 8, 638-639.
- [19] L. He, Y. Liu, J. Liu, Y. Xiong, J. Zheng, Y. Liu and Z. Tang, *Angewandte Chemie International Edition*, **2013**, 52, 3741-3745.
- [20] M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao and Z. Tang, *Nature*, **2016**, 539, 76-80.
- [21] M. Jahan, Z. Liu and K. P. Loh, *Advanced Functional Materials*, **2013**, 23, 5363-5372.
- [22] S. L. Zhao, H. J. Yin, L. Du, L. C. He, K. Zhao, L. Chang, G. P. Yin, H. J. Zhao, S. Q. Liu and Z. Y. Tang, *Acs Nano*, **2014**, 8, 12660-12668.
- [23] R. R. Salunkhe, Y. V. Kaneti and Y. Yamauchi, *ACS nano*, **2017**.
- [24] M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa and Y. Yamauchi, *Journal of the American Chemical Society*, **2012**, 134,

2864-2867.

- [25] J. Tang, R. R. Salunkhe, J. Liu, N. L. Torad, M. Imura, S. Furukawa and Y. Yamauchi, *Journal of the American Chemical Society*, **2015**, 137, 1572-1580.
- [26] Z. X. Yan, G. Q. He, P. K. Shen, Z. B. Luo, J. M. Xie and M. Chen, *Journal of Materials Chemistry A*, **2014**, 2, 4014-4022.
- [27] D. V. Esposito, S. T. Hunt, Y. C. Kimmel and J. G. G. Chen, *Journal of the American Chemical Society*, **2012**, 134, 3025-3033.
- [28] T. G. Kelly, K. X. Lee and J. G. G. Chen, *J Power Sources*, **2014**, 271, 76-81.
- [29] T. Huang, Y. Chen and J. M. Lee, *Acs Sustain Chem Eng*, **2017**, 5, 5646-5650.
- [30] K. M. Koczkur, S. Mourdikoudis, L. Polavarapu and S. E. Skrabalak, *Dalton T*, **2015**, 44, 17883-17905.
- [31] X. F. Lu, L. F. Gu, J. W. Wang, J. X. Wu, P. Q. Liao and G. R. Li, *Advanced Materials*, **2017**, 29.
- [32] S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, **2001**, 412, 169-172.
- [33] J. S. Yu, S. Kang, S. B. Yoon and G. Chai, *Journal of the American Chemical Society*, **2002**, 124, 9382-9383.
- [34] X. P. Zhang, L. Huang, Y. J. Han, M. Xu and S. J. Dong, *Nanoscale*, **2017**, 9, 5583-5588.
- [35] X. W. Lou, D. Deng, J. Y. Lee, J. Feng and L. A. Archer, *Advanced Materials*, **2008**, 20, 258-262.
- [36] S. Biswas and L. T. Drzal, *Chemistry of Materials*, **2010**, 22, 5667-5671.
- [37] H. L. Lin, Z. P. Shi, S. N. He, X. Yu, S. N. Wang, Q. S. Gao and Y. Tang, *Chem Sci*, **2016**, 7, 3399-3405.
- [38] G. X. Wang, Y. Chen, K. Konstantinov, M. Lindsay, H. K. Liu and S. X. Dou, *J Power Sources*, **2002**, 109, 142-147.
- [39] D. W. Kim, H. S. Kil, J. Kim, I. Mochida, K. Nakabayashi, C. K. Rhee, J. Miyawaki and S. H. Yoon, *Carbon*, **2017**, 121, 301-308.
- [40] M. Xie, J. Yang, J. Liang, X. Guo and W. Ding, *Carbon*, **2014**, 77, 215-225.
- [41] D. Weingarth, M. Zeiger, N. Jäckel, M. Aslan, G. Feng and V. Presser, *Advanced Energy Materials*, **2014**, 4.

- [42] J. Zhang, C. P. Yang, Y. X. Yin, L. J. Wan and Y. G. Guo, *Advanced Materials*, **2016**, 28, 9539-9544.
- [43] J. S. Mondschein, J. F. Callejas, C. G. Read, J. Y. C. Chen, C. F. Holder, C. K. Badding and R. E. Schaak, *Chemistry of Materials*, **2017**, 29, 950-957.
- [44] H. Huang, C. C. Du, S. Y. Wu and W. B. Song, *J Phys Chem C*, **2016**, 120, 15707-15713.
- [45] C. R. Parkinson, M. Walker and C. F. McConville, *Surf Sci*, **2003**, 545, 19-33.
- [46] Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi and K. Hashimoto, *Nat Commun*, **2013**, 4.
- [47] C. C. L. McCrory, S. H. Jung, J. C. Peters and T. F. Jaramillo, *Journal of the American Chemical Society*, **2013**, 135, 16977-16987.
- [48] L. Han, X. Y. Yu and X. W. D. Lou, *Advanced Materials*, **2016**, 28, 4601-4605.
- [49] H. Hu, B. Y. Guan, B. Y. Xia and X. W. Lou, *Journal of the American Chemical Society*, **2015**, 137, 5590-5595.
- [50] K. Juodkazis, J. Juodkazyte, R. Vilkauskaitė and V. Jasulaitienė, *J Solid State Electr*, **2008**, 12, 1469-1479.
- [51] L. A. Stern, L. G. Feng, F. Song and X. L. Hu, *Energ Environ Sci*, **2015**, 8, 2347-2351.
- [52] J. Xie, X. Zhang, H. Zhang, J. Zhang, S. Li, R. Wang, B. Pan and Y. Xie, *Advanced materials*, **2017**, 29.
- [53] D. T. Dam and J. M. Lee, *Acs Appl Mater Inter*, **2014**, 6, 20729-20737.
- [54] Z. R. Ismagilov, A. E. Shalagina, O. Y. Podyacheva, A. V. Ischenko, L. S. Kibis, A. I. Boronin, Y. A. Chesalov, D. I. Kochubey, A. I. Romanenko and O. B. Anikeeva, *Carbon*, **2009**, 47, 1922-1929.
- [55] H. Yin, H. Tang, D. Wang, Y. Gao and Z. Tang, *Acs Nano*, **2012**, 6, 8288-8297.
- [56] S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao and L. Zhang, *Nature Energy*, **2016**, 1, 16184.
- [57] H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat Commun*, **2015**, 6, 6430.
- [58] S. Zhao, H. Yin, L. Du, G. Yin, Z. Tang and S. Liu, *Journal of Materials Chemistry A*, **2014**, 2, 3719-3724.

Chapter 7

Hybrid of layered double hydroxide and carbon with iridium doping for oxygen evolution

Layered double hydroxides have been intensively studied in various areas such as electrocatalytic applications. However, it remains a vacancy to employ these materials as seeds to design and fabricate heterostructures with desired crystal architectures as well as tailorable compositions for catalysis. Herein, for the first time this work reports a strategy for the synthesis of binary hybrid hydroxide microstructures which were wrapped by few-layer carbon with iridium doping. The preformed nickel hydroxides enable the epitaxial overgrowth of cobalt hydroxide due to their similar crystal lattice, resulting in the formation of hybrid NiCo layered double hydroxides heterostructures. Moreover, the NiCo layered double hydroxides were coated by few-layer carbon, which was eventually doped by iridium. The results show that NiCo-Ir hybrid microarchitecture with tunable compositions display excellent electrocatalytic behaviors towards the oxygen evolution in alkaline medium, due to their microstructural advantages with few-layer carbon and electronic interaction of iridium/hydroxides. This work develops a general paradigm of seed based growth of hierarchical layered double hydroxide heterostructure with much improved surface area and distinct porous nature. These results validate the potential applications of these materials in electrocatalysis after few-layer carbon coating and iridium doping via aqueous modification.

7.1 Introduction

Layered double hydroxide (LDH) is composed of metal cations, intercalated anions and hydroxyl groups structured in repetitive layers. In general, ease of replacement of the anions which are located in the interlayer enables the incorporation of a wide variety of anions, including simple inorganic/organic anions as well as biomolecules such as DNA.^[1,2] This has led to an intense interest in the use of LDH intercalates for advance applications. For example, drug molecules such as ibuprofen, have been incorporated in LDH, where the as-obtained composites are feasible to be utilized in the controlled release system by designing a multiscale structure that reduces the overdosage of medication.^[3] Recently, LDH has been extensively investigated in electrochemical applications, for example, supercapacitors, oxygen evolution, electrochemical sugar and hydrogen peroxide detection.^[4-7] In terms of electrochemical application, previous studies typically used hard templates such as nickel foam and titanium mesh to produce a macroscale structures.^[8,9] These methods require sophisticated pretreatment of the hard templates, while the surfactant molecules which assemble the hydroxides on the templates tends to block available active sites, thus limiting the practical application of layered double hydroxides. Considering the strong dependence of electrochemical behaviors on the layered double hydroxides' microstructural characteristics, the design of well-controlled microscale architecture is urgently desirable so as to produce an efficient and tailorable materials for proper use of LDH.^[10]

Controlled synthesis of heterostructures is extensively studied because of their novel electronic and catalytic properties arising from the synergism of their individual components.^[11] For example, studies of heterostructures had been focused on noble metals,^[12] MOFs,^[13] semiconductors,^[14] and even the hybrid of MOF@COF.^[15] Aqueous epitaxial synthesis has been known as a feasible and low-cost method towards the construction of heterostructures with desired chemical composition and microarchitecture,^[16] which can be tailored for various applications. Intensive works have been investigated on the fabrication of heterostructures in view of their porous nature and derived hierarchical structure which is beneficial for electrochemical reaction, especially for gas-evolving reaction. For example, sponge-like Au/Pt core/shell have been

synthesized with substantial enhancement in the electrocatalytic behavior deriving from improved surface area.^[17] Nonetheless, the synthesis of LDH heterostructural crystals with well-controlled microarchitectures was not well documented. Therefore, this work aimed at fabrication of the heterostructure of LDH, which were subsequently used as a platform for electrocatalyst development. Besides, LDH showing poor conductivity has been demonstrated in several studies. For instance, Kim et al used graphene-encapsulated NiAl layered double hydroxides to fabricate high-performance electrochemical capacitors;^[18] whereas, hydroxides that are present in LDH are generally not active enough to reduce the overpotential that is required for oxygen evolution as depicted from Ye et al.^[19] It is noteworthy that in this study, improvement of oxygen evolution can be observed in Au/LDH, however such analysis requires the installation of laser (532 nm) irradiation which limits the scalability. Driven by these concerns, metallic iridium and carbon layer was supported on the LDH nanosheets for an efficient oxygen evolution catalyst. Ir can improve electronic structure as reported by Teng et al,^[20] whereas the charge transfer can be facilitated with the installation of carbon layer. Therefore, by integrating the structural benefits (porous, high surface area and 2D assembly) of heterostructured hydroxides and compositional advantages (electronic modification, improved conductivity) of iridium doping and carbon coating, a well-designed microarchitecture of NiCo-LDH/Carbon/Ir should be a promising next-generation electrocatalyst.

For this purpose, an epitaxial seeded growth of hybrid LDH via all solution process was performed. First, nickel hydroxides were fabricated in ethanol solution at room temperature. Using nickel hydroxides as the seeds, cobalt hydroxides layers were grown in ethanol solution at room temperature. In the next step the NiCo LDH were coated by a few-layer carbon, which was eventually doped by iridium. Such all-solution process demonstrates this method is a facile and energy saving route, contributing a cheap and scalable method to the industry. Notably, after doping, the compositional advantages from the iridium doping and carbon coating were well developed without affecting the overall morphology. The NiCo-Ir LDH displays plethora of macro/mesopores, high BET surface area, electrochemical active surface area (EASA), superior catalytic activity and long term stability. Thus, this work adds a new member to the family of epitaxially grown structure.

Moreover, this work provides a general epitaxial seeded growth of hybrid and hierarchical layered double hydroxides with a demonstration of its potential in electrocatalysis. Considering the vast compatibility of layered double hydroxides and porous nature of this well designed heterostructure, the synthetic route developed by this work possess great potential not only in catalysis, but also in other energy conversion and storage applications.

Figure 7.1 Design and synthesis of NiCo-Ir microarchitecture for efficient oxygen evolution.

7.2 Principle Outcomes

7.2.1 Structure characterization

Figure 7.1 shows the synthesis procedure is an all-solution formation of all products. In the first step, nickel hydroxides were synthesized at room temperature, in which 2-methylimidazole acts as the alkaline ions provider. Their FESEM images were shown in Figure 7.2a,b. For the first time, the nickel hydroxide single particles were formed at room temperature without using the surfactant. Next, cobalt hydroxides were growing epitaxially, using nickel hydroxides as seeds by using cobalt nitrate as precursor. FESEM images of NiCo LDH depict a well-defined microarchitecture of the hybrid LDH, comprising

nanosheet subunits (Figure 7.2c,d). The nanosheets were the subunit, with the overall thickness of 19 nm. Similarly, NiCu LDH can be fabricated in the same way. The hybrid NiCo LDHs were used as scaffolds in aqueous reaction system so as to fabricate carbon wrapped and iridium doped NiCo LDH hybrid microarchitectures. The FESEM images depicts that the subunit grew thicker after this step, with thickness being around 25 nm, indicating that the growing of few-layer carbon and Ir nanoparticles on the preformed NiCo LDH. The final step, which is the development of few-layer carbon coating and iridium doping on the preformed NiCo hydroxides in water solution was performed via a one-pot hydrothermal reaction by using glucose, 2-methylimidazole and iridium chloride as precursors.

Figure 7.2 (a,b) FESEM images of Ni hydroxides; (c,d) FESEM images of NiCo hydroxides; (e,f) FESEM images of NiCo-Ir hydroxides.

Figure 7.3 (a,b) TEM images of NiCo hydroxides; (c) TEM images of NiCo-Ir; (d) HRTEM images of NiCo-Ir showing the few-layer carbon and iridium doping.

The nickel hydroxides produced from the ethanol solution were washed by ethanol via centrifugation to remove any residual precursor molecules, which the light green powder collected were dried at 60 °C overnight. Observation on the field emission scanning electron microscope (FESEM) reveals that the surface of the nickel hydroxides is rough and wrinkled (Figure 7.2a, b). The edges of the wrinkled surface of nickel hydroxides can be served as the initial growing site for the overgrown layers of cobalt hydroxides. While NiCo LDH (Figure 7.2c,d) show that the nanosheet subunits are well segregated, NiCo

LDH inherited the ordered structure of nickel hydroxides after the overgrowth of cobalt hydroxides. The hybrid of NiCo LDH are still isolated with no packing. However, the nanosheets were evenly grown on the surface of NiCo LDH in a well-ordered way, with van der Waals force and hydrogen bonding of hydroxides as demonstrated by FT-IR being the possible assembling force (Figure 7.6b). The ultrathin nanosheets (Figure 7.2c, d) interlaced with each other, while the outer surface was well separated from neighboring interlaced nanosheets. This creates cavity space and pores where the electrolytes can access and travel around the inner NiCo LDH microstructure, augmenting the number of electroactive sites with facilitated evolving and releasing of gas (Figure 7.2e,f). Additionally, the integration of nanosheet subunits at the surface of core nickel hydroxides should protect the inner core as scaffolds, which would well maintain the overall structure during the electrochemical gas-evolving process. The NiCo LDH is further studied by TEM, which shows identical structural traits as shown in the FESEM images, the NiCo hydroxides possess nanosheet subunits, with a clear seed inside. The TEM elemental mapping (Figure 7.5) shows the existence of cobalt, demonstrating the growth of cobalt hydroxide nanosheet on the surface. For the NiCo-Ir with carbon layer microstructure, iridium is doped onto NiCo LDH by a one-pot hydrothermal reaction. As shown in Figure 7.2 e, f, the morphology of their precursors, NiCo LDH was well retained. FESEM images displays abundant macropores with supported iridium clusters on the nanosheet. Further studies of The NiCo-Ir via TEM also shows the identical structural traits as shown by FESEM images. More importantly, the iridium clusters (2-3 nm) are firmly and densely deposited into the carbon layer by keeping contact with the hydroxide nanosheets (Figure 7.1), which lays the structural basis and compositional benefits for their well displayed electroactive sites and efficient intrinsic properties for electrocatalysis (Figure 7.10).

Figure 7.4 HRTEM of NiCo-Ir showing the crystal plane of (003).

Figure 7.5 Elemental mapping of NiCo hydroxide after calcination in argon atmosphere.

7.2.2 Physical characterization

UV-Vis was used to study the interaction of the precursors including IrCl_3 , glucose, 2-methylimidazole before the step of simultaneous few-layer carbon coating and iridium doping. Figure 7.6a presents the UV-vis spectra of IrCl_3 , glucose, 2-methylimidazole, IrCl_3 /glucose, IrCl_3 /2-methylimidazole, IrCl_3 /glucose/2-methylimidazole dissolved in

water. For the UV-vis spectrum of glucose and 2-methylimidazole, characteristic peak in the specified range was not detected. On the other hand, the UV-Vis spectrum of IrCl_3 demonstrated four characteristic peaks. Notably, as compared to the adsorption band of IrCl_3 , the absorption bands in Ir^{3+} solution disappear after mixing with 2-methylimidazole; while the absorption bands in Ir^{3+} /glucose solution remain after the addition of glucose. These results confirm the complexation of Ir^{3+} /2-methylimidazole, while there is no complexation of Ir^{3+} /glucose. Besides, the spectrum of Ir^{3+} /glucose/2-methylimidazole shows the similar peak due to the complexation of Ir^{3+} /2-methylimidazole. N groups in 2-methylimidazole can interact with transitional metal ions, which has been reported by previous work.^[21] The complexation of Ir^{3+} /2-methylimidazole verified that the precursors are homogeneously mixed at molecular level without precipitation, before the hydrothermal step for simultaneous carbon coating and iridium doping was carried out. Moreover, glucose provides additional carbon source for the formation of carbon layers on the preformed NiCo hydroxides to enhance the overall electrocatalytic performances (Figure 7.11). The transformation of such homogeneously mixed precursor under hydrothermal condition leads to few-layer carbon doped with iridium clusters on the preformed NiCo hydroxides (Figure 7.3 e,f).

Figure 7.6 (a) UV-Vis spectra of some precursors; (b) FT-IR spectra of Ni, NiCo, NiCo-Ir; (c) XRD patterns of Ni, NiCo, NiCo-Ir; (d) Nitrogen adsorption-desorption isotherm and pore size distribution of Ni, NiCo, NiCo-Ir; inset is the pore size distribution.

Fourier-Transform Infrared (FT-IR) was conducted to study the chemical compositions and functional groups of the products. Figure 7.6b shows the FT-IR spectra of nickel hydroxide, NiCo hydroxide and NiCo-Ir. A sharp peak around 2369 cm^{-1} that corresponds to hydrogen bonding in the interlayer was detected due to the appearance of interlayer water molecules in the layered double hydroxide. The broad peak at 1670 cm^{-1} arises from the bending mode of water molecules. The peaks (1380 cm^{-1} and 980 cm^{-1}) are designated to the nitrate ions from the precursors such as nickel nitrate and cobalt nitrate. However, weaker intensity of nitrate peak was detected for the spectrum of NiCo-Ir due to the coverage of surface carbon. While the peak at 470 cm^{-1} is from the Ni-O vibrational modes, and for the

spectrum of NiCo hydroxides, the Ni-O peak is weaker, which possibly due to the formation of hydroxides heterostructure.^[22]

Figure 7.7 High-resolution XPS spectra of (a) Ni 2p, (b) Co 2p (c) Ir 4f and (d) C 1s core levels in NiCo-Ir-5 products.

The crystallographic structure of the nickel hydroxide, NiCo hydroxide and NiCo-Ir products were studied using X-ray diffraction, as shown in Figure 7.6c. The nickel hydroxides show the typical peaks which are indexed as (003), (006), (101) and (110) diffraction planes of $\text{Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$ (JCPDS:38-0715). Similarly, NiCo hydroxides share those similar peaks, with some peaks being not apparent. This may be due the overgrowth of cobalt hydroxides on the nickel hydroxide seeds. In view of their similar crystal planes with close diffraction angles, it is not easy to differentiate intensity peaks at the same diffraction angle for the two hydroxides.^[23] Notably, a large interlayer space (003) ($d_{003} = 0.672 \text{ nm}$) is formed due to the intercalation of counter anion (NO_3^-) into the layered double hydroxide interlayers as observed by HRTEM (Figure 7.4). This enlarged interlayer

space is favorable for the transport of charges within the heterostructure, leading to the fast kinetics,^[24] as evidenced by the tafel plot in Figure 7.10. For NiCo-Ir, its spectrum inherits most of the major peaks from the hybrid layered double hydroxides. More importantly, the XRD pattern of NiCo-Ir products show one broad peak around 72° , which locates between the (220) plane (69°) of face-centered cubic (fcc) Ir (JCPDS No. 06-0598) and (220) plane (76°) of fcc Co (JCPDS No. 15-0806), which proves the alloyage of iridium and cobalt. This alloyage effect would directly lead to the electronic improvement endowed by iridium tuning.

Figure 7.8 Pore size distribution of nickel hydroxides, nickel cobalt hydroxides and NiCo-Ir.

N₂ physisorption measurements (at 77 K) were also conducted to investigate the porous structure, surface area and pore size distribution of the as-prepared nickel hydroxides, NiCo hydroxides and NiCo-Ir, as shown in Figure 7.6d. Nickel hydroxides, NiCo hydroxides and NiCo-Ir possess BET surface areas of 95.9 m² g⁻¹, 124.9 m² g⁻¹ and 86.0 m² g⁻¹ respectively. NiCo hydroxides possess larger surface area than that of nickel hydroxides, which may be due to the overgrown cobalt hydroxide nanosheet network on nickel hydroxide seeds, which should also aid to confirm that the heterostructure was made. This shows that this seeded growth would produce highly porous materials. Moreover, these curves show H3 loops (based on the classification by the IUPAC technical report) with the possible formation of macropores by non-rigid aggregates composed by plate-like particles.^[25] Thus, these BET results are well-agreed with the FESEM observations. More importantly, from the plot of pore size distribution (Figure 7.6d inset), the nanosheet network displays

macropores and mesopores mostly in the range of 50 – 100 nm, which is consistent with the structural observation by FESEM as shown in Figure 7.2e,f. The dominating peak of the pore size distribution lies at 22 nm. These macro/mesopores formation is due to the interlaced nanosheet configuration. The coexistence of these macro/mesopores in the nanosheet network creates cavity space for electrolyte transport, gas evolving and release, and provides more electroactive surface area for electrochemical reaction, all of which contribute to its highly electrocatalytic active behaviors.^[26]

Figure 7.9 XPS of NiCo-Ir-5 survey scan showing the existence of Ni, Co, Ir, C, N and O.

Figure 7.10 XPS of NiCo-Ir-5 for (a) N 1s, (b) O 1s.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical composition and their valence state of NiCo-Ir (Figure 7.7). All the three products show existence of Ni, Co, Ir, C, N, O. For Ni 2p spectrum, it can be deconvoluted into two peaks: Ni 2p 3/2 is located at 856 eV, Ni 2p1/2 is located at 874 eV, both accompanied by their satellite peaks, which confirms the Ni²⁺ oxidation state. The C 1s spectrum contains mainly one peak at 284.5 eV which is attributed to graphitic C-C bond. For N 1s spectrum, the peak of Pyridinic-N, pyrrolic-N and quaternary-N are observed at 398 eV, 400 eV and 401.8 eV, respectively. While the pyrrolic-N is dominant, indicating the existence of nitrogen-doped carbon (Figure 7.9a). For Ir 4f spectrum of NiCo-Ir, it can be deconvoluted into four peaks, which are at located at 61 eV, 62.5 eV, 63.6 eV and 65.5 eV, respectively; the four peaks are corresponding to the binding energies of Ir⁰ 4f 7/2, Ir⁴⁺ 4f7/2, Ir⁰ 4f5/2 and Ir⁴⁺ 4f 5/2, respectively (Figure 7.7c), showing the coexistence of Ir⁰ and Ir⁴⁺ in NiCo-Ir. Ir⁰ can tune the overall electronic structure, while the high valence of Ir⁴⁺ can serve as a buffer for the electron transport during the oxygen oxidation process.^[27] For Co 2p spectrum of NiCo-Ir, it can be deconvoluted into two peaks, which are located at 781 eV and 797 eV with their accompanied satellite peaks; the two main peaks are corresponding to the peaks of Co 2p3/2 and Co 2p1/2 (Figure 7.7b), respectively. Moreover, for O 1s spectrum, it can be deconvoluted into two primary peaks: the peak of metal hydroxides is located at 531.5 eV, the peak of surface-adsorbed oxygen/hydroxyl groups is located at 532.4 eV (Figure 7.9b).^[28]

7.2.3 Electrochemical performances

Figure 7.11 (a) LSV of NiCo-Ir-3, NiCo-Ir-5, NiCo-Ir-7 and IrO₂/C with rotation disk electrode at 1600 rpm; (b) Tafel plot of NiCo-Ir-3, NiCo-Ir-5, NiCo-Ir-7 and IrO₂/C; (c) Plot of current density (at 1.14 V vs RHE) versus scan rate; (d) Current density - time curve of NiCo-Ir-5 (at 1.47 V vs RHE) and IrO₂/C (at 1.63 V vs RHE) in 1 M KOH, the duration is 36 000 s.

Linear sweeping voltammetry (LSV) was used to test the as-obtained composites' electrocatalytic behaviors towards oxygen evolution reaction.^[29] In order to study the influence of the usage of iridium, NiCo-Ir with various iridium atomic ratios (3.9 %, 5.3 %, 7.1 %) were produced, which were denoted by NiCo-Ir-3, NiCo-Ir-5, NiCo-Ir-7, respectively. Meanwhile, the commercial IrO₂/C towards OER was tested for comparative investigation. As shown in Figure 7.10a, NiCo-Ir-5 displays an overpotential of 240 mV at 10 mA cm⁻² (10 mA cm⁻² is used as as reference current density because of the practical operation current of solar fuel synthesis.^[30] Therefore, the overpotential at 10 mA cm⁻² of NiCo-Ir-5 is much smaller than those of NiCo-Ir-3 (272 mV), NiCo-Ir-7 (285 mV) and

IrO₂/C (400 mV). On the other hand, NiCo-Ir-5 displayed the smallest onset potential of 1.40 V versus RHE (the onset potential is calculated from tafel plot, i.e. the potential when the tafel curve starts to deviate from the linear region) (Figure 7.10b). The samples of NiCo hydroxides, NiCo-Ir (produced with 2-methylimidazole) and NiCo-Ir (produced with glucose) were also tested by linear sweeping voltammetry, with an overpotential (@10 mA cm⁻²) of 1.63 V, 1.57 V and 1.58 V (Figure 7.11), respectively. Combined with the results of UV-Vis, these results show that 2-methylimidazole mainly acted as coordinator with Ir³⁺, while glucose acted as the carbon source. These combinations allows the formation of a molecularly uniform carbon layer and well-distributed iridium clusters. Carbon coating played important role in improving the electrocatalytic performances. More importantly, the onset potential of NiCo-Ir-5 is lower than that of the typical benchmark for oxygen evolution, such as the conventional precious metal (IrO₂/C, 1.57 V) at the identical condition. Additionally, the overpotential@10 mA cm⁻² of NiCo-Ir-5 is the smallest, among the previously reported Ni and/or Co based oxygen evolution electrocatalysts, and also is smaller than that of iridium-containing electrocatalysts, such as NiCo@NiCoO₂/C (1.57 V),^[31] NiCo layered double hydroxides (1.59 V)^[32] and Cu-doped IrO₂ (1.64 V).^[33] Furthermore, the catalytic reaction kinetics were studied for electrochemical oxygen evolution by plotting their Tafel plots (Figure 7.10b). The Tafel slope of NiCo-Ir-5 is 76.7 mV dec⁻¹, while NiCo-Ir-3, NiCo-Ir-7 and IrO₂/C has Tafel slope of 88.9 mV dec⁻¹, 86.7 mV dec⁻¹, 139.6 mV dec⁻¹. Therefore, NiCo-Ir-5 shows the smallest Tafel slope among the four products, demonstrating the outstanding electrochemical reaction kinetics of the well-designed NiCo-Ir-5.

At the potential of c.a. 1.30 V (vs RHE), an oxidation peak was clearly observed, which corresponds to the typical conversion of Ni(II) to Ni(III). Nickel atoms on the surface are partially oxidized into NiOOH as the actual surface active site (Figure 7.10a), which subsequently catalyze the oxidation of OH⁻ into molecular oxygen.^[34] Notably, the oxidation peak of Ni(II) to Ni(III) for NiCo-Ir-5 (10.88 mA cm⁻²) became higher compared with that for NiCo-Ir-3 (5.82 mA cm⁻²) and NiCo-Ir-7 (1.98 mA cm⁻²), while IrO₂/C did not show any oxidation peak around this potential range. Iridium may tune the electronic structure of nickel hydroxides by charge redistribution of the hydroxides, contributing to a

decrease in the activation energy of the water molecules with improved oxygen evolution performance.^[9] This trend of the current density of oxidation peak is consistent with the compositional percentage of iridium. It is speculated that a low ratio of iridium does not contribute sufficiently to electronic improvement; while a high ratio of iridium may block the actual catalytic sites, which is detrimental to the oxygen evolution. These results demonstrate that a proper ratio of iridium metals should be adopted when designing and producing superior oxygen evolution electrocatalysts.

Figure 7.12 LSV of NiCo hydroxide, NiCo-Ir produced with glucose, NiCo-Ir produced with 2-methylimidazole, in 1.0 M KOH solution.

The electrocatalytic oxygen evolution behavior was studied by the measurement of the electrochemical active surface area (EASA) using CV with different scan rates, as shown in Figure 7.12.^[35] The EASAs of NiCo-Ir catalysts were measured using double-layer capacitance (C_{dl}), which is typically used to represent EASA (Table 7.1). For comparison, the C_{dl} of NiCo-Ir-5 (38.9 mF cm^{-2}) is much higher than those of IrO_2/C powders (5.4 mF cm^{-2}), NiCo-Ir-3 (13.9 mF cm^{-2}) and NiCo-Ir-7 ($13.8, 12 \text{ mF cm}^{-2}$), indicating the increase of double layer capacitance with NiCo-Ir-5 owns a much higher EASA than those of NiCo-Ir-3 and NiCo-Ir-7.

Figure 7.13 CVs of (a) NiCo-Ir-3, (b) NiCo-Ir-5, (c) NiCo-Ir-7 and (d) IrO₂/C in the range of 1.095 - 1.155 V vs. RHE, measured in 1.0 M KOH solution, respectively.

Table 7.1 Electrochemical oxygen evolution behaviors of NiCo-Ir and IrO₂/C

Catalyst	Onset potential (V vs RHE)	Overpotential@10mA/cm ² (mV vs RHE)	Ni oxidation peak (mA/cm ²)	Tafel slope (mV/dec)	EASA (mF/cm ²)
NiCo-Ir-3	1.46	272	5.82	88.9	13.9
NiCo-Ir-5	1.40	240	10.88	76.7	38.9
NiCo-Ir-7	1.43	285	1.98	86.7	13.8
IrO ₂ /C	1.57	400	N.A.	139.6	5.4

The long-term stability of the products were further conducted with a continuous electrocatalytic oxygen evolution at a constant potential using IrO₂/C and NiCo-Ir-5. As shown in Figure 7.10d, the current density of NiCo-Ir-5 tends to have a gradual increase at the beginning, with its final current density is reported to be c.a. 117% of its original value. As a comparison, i-t plot of IrO₂/C shows an apparent dropping curve, which may be

attributed to the difficulty of the evolving gas to be released. While the well stability of NiCo-Ir-5 is ascribed to its abundant macro/mesopores and the protection effect of carbon layers, which contributes abundant cavity space for mass transport. Moreover, these macro/mesopores facilitate gas evolving and releasing easily.^[36] As shown in the BET tests, the products of NiCo-Ir-5 showed a clear facilitation of gas diffusion in view of its accessible surface area of 86 m²/g with the macro/mesopore size range was 50 - 100 nm (Figure 7.6d). Therefore, the BET surface area and high electrochemical active surface area verified that large surface area endows the catalyst with outstanding electrochemical performances. Besides, the gradual increase of the current density of NiCo-Ir-5 may stem from the activation effect of the layered double hydroxides: the evolving gas within the interlaced layered hydroxide structure may effectively open and thus expose electrocatalytic sites for oxygen evolution, as such, the current density of NiCo-Ir-5 increased during the testing time.

Figure 7.14 Compositional advantages and structural benefits of NiCo-Ir microarchitecture as an oxygen evolving electrocatalyst.

Therefore, the greatly enhanced electrocatalytic oxygen evolution behaviors of NiCo-Ir-5 may be ascribed to the following reasons: (1) the NiCo LDH possess various macro/mesopores which are beneficial for gas evolving reaction; (2) the hydroxide nanosheet assembled in the form of flower-like structure was well presented in their catalytic sites; (3) the iridium doping may substantially tune the electronic structure of the catalytic site atoms by charge redistribution from iridium, therefore, the doping facilitates adsorption of hydroxyl groups and oxygen species;^[9] while the carbon coating endows the products with good conductivity as well ultralong stability due to the protection effect.^[37] As such, the hybrid NiCo hydroxides structure have the excellent properties for

electrocatalysis, such as porous nature and well-assembled microstructure, such potential has been demonstrated as a useful platform for catalytic applications in oxygen evolution.

7.3 Conclusion

In summary, an epitaxial seeded growth of hybrid layered double hydroxide heterostructure on nickel hydroxides was developed for the first time, via an all-solution-procedure at room temperature. The hybrid hydroxides were wrapped by a few-layer carbon doped with iridium, to endow them with high performances towards electrocatalytic oxygen evolution reaction. The hybrid materials inherit the structural benefits, at the same time gaining the compositional advantages from the iridium doping and carbon coating. The NiCo-Ir LDH displays plethora of macro/mesopores, high BET surface area, electrochemical active surface area (EASA), and displayed superior catalytic activity, long term stability as compared to IrO₂/C and most reported electrocatalysts. These findings demonstrate the potential of this well-controlled synthesis of hybrid hydroxides in the area of electrocatalysis. This work adds a new member to the epitaxial growth structure. Moreover, this work provides a general epitaxial seeded growth of hierarchical layered double hydroxides with a demonstration of its potential in electrocatalysis. It is believed that the synthetic procedure developed here may offer new opportunities for the preparation of intricate hybrid materials with desired microarchitectures and tailorable compositions catering to their catalytic properties and other applications.

References

- [1] L. Desigaux, M. Ben Belkacem, P. Richard, J. Cellier, P. Leone, L. Cario, F. Leroux, C. Taviot-Gueho and B. Pitard, *Nano Lett*, **2006**, 6, 199-204.
- [2] V. R. L. Constantino and T. J. Pinnavaia, *Inorg Chem*, **1995**, 34, 883-892.
- [3] R. Rojas, M. C. Palena, A. F. Jimenez-Kairuz, R. H. Manzo and C. E. Giacomelli, *Appl Clay Sci*, **2012**, 62-63, 15-20.
- [4] H. Sim, C. Jo, T. Yu, E. Lim, S. Yoon, J. H. Lee, J. Yoo, J. Lee and B. Lim, *Chem-Eur J*, **2014**, 20, 14880-14884.

- [5] F. Song and X. L. Hu, *Nat Commun*, **2014**, 5.
- [6] Z. J. Yin, J. J. Wu and Z. S. Yang, *Biosens Bioelectron*, **2011**, 26, 1970-1974.
- [7] H. R. Cho, J. H. Lee, S. H. Cho and H. G. Ji, *B Korean Chem Soc*, **2016**, 37, 401-403.
- [8] J. Jiang, A. L. Zhang, L. L. Li and L. H. Ai, *J Power Sources*, **2015**, 278, 445-451.
- [9] J. F. Zhang, J. Y. Liu, L. F. Xi, Y. F. Yu, N. Chen, S. H. Sun, W. C. Wang, K. M. Lange and B. Zhang, *J Am Chem Soc*, **2018**, 140, 3876-3879.
- [10] J. A. Syed, J. Ma, B. G. Zhu, S. C. Tang and X. K. Meng, *Adv Energy Mater*, **2018**, 8.
- [11] M. B. Cortie and A. M. McDonagh, *Chem Rev*, **2011**, 111, 3713-3735.
- [12] S. H. Choi, H. B. Na, Y. I. Park, K. An, S. G. Kwon, Y. Jang, M. Park, J. Moon, J. S. Son, I. C. Song, W. K. Moon and T. Hyeon, *J Am Chem Soc*, **2008**, 130, 15573-15580.
- [13] J. Tang, R. R. Salunkhe, J. Liu, N. L. Torad, M. Imura, S. Furukawa and Y. Yamauchi, *J Am Chem Soc*, **2015**, 137, 1572-1580.
- [14] J. Y. Park, S. W. Choi, J. W. Lee, C. Lee and S. S. Kim, *J Am Ceram Soc*, **2009**, 92, 2551-2554.
- [15] Y. W. Peng, M. T. Zhao, B. Chen, Z. C. Zhang, Y. Huang, F. N. Dai, Z. C. Lai, X. Y. Cui, C. L. Tan and H. Zhang, *Adv Mater*, **2018**, 30.
- [16] F. R. Fan, D. Y. Liu, Y. F. Wu, S. Duan, Z. X. Xie, Z. Y. Jiang and Z. Q. Tian, *J Am Chem Soc*, **2008**, 130, 6949.
- [17] S. J. Guo, Y. X. Fang, S. J. Dong and E. K. Wang, *J Phys Chem C*, **2007**, 111, 17104-17109.
- [18] S. X. Wu, K. S. Hui, K. N. Hui and K. H. Kim, *Acs Appl Mater Inter*, **2017**, 9, 1395-1406.
- [19] G. G. Liu, P. Li, G. X. Zhao, X. Wang, J. T. Kong, H. M. Liu, H. B. Zhang, K. Chang, X. G. Meng, T. Kako and J. H. Ye, *J Am Chem Soc*, **2016**, 138, 9128-9136.
- [20] W. X. Du, Q. Wang, D. Saxner, N. A. Deskins, D. Su, J. E. Krzanowski, A. I. Frenkel and X. W. Teng, *J Am Chem Soc*, **2011**, 133, 15172-15183.
- [21] D. H. Shin, Y. G. Ko, U. S. Choi and W. N. Kim, *Ind Eng Chem Res*, **2004**, 43, 2060-2066.

- [22] H. Y. Gao, G. Wang, M. Yang, L. Tan and J. Yu, *Nanotechnology*, **2012**, 23.
- [23] L. Y. Jiang, Y. W. Sui, J. Q. Qi, Y. Chang, Y. Z. He, Q. K. Meng, F. X. Wei, Z. Sun and Y. X. Jin, *Appl Surf Sci*, **2017**, 426, 148-159.
- [24] C. Yu, Z. B. Liu, X. T. Han, H. W. Huang, C. T. Zhao, J. Yang and J. S. Qiu, *Carbon*, **2016**, 110, 1-7.
- [25] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K. S. W. Sing, *Pure Appl Chem*, **2015**, 87, 1051-1069.
- [26] D. T. Dam and J. M. Lee, *Electrochim Acta*, **2013**, 108, 617-623.
- [27] Y. K. Zhang, C. Q. Wu, H. L. Jiang, Y. X. Lin, H. J. Liu, Q. He, S. M. Chen, T. Duan and L. Song, *Adv Mater*, **2018**, 30.
- [28] H. Y. Jin, S. J. Mao, G. P. Zhan, F. Xu, X. B. Bao and Y. Wang, *J Mater Chem A*, **2017**, 5, 1078-1084.
- [29] H. S. Jeon, M. S. Jee, H. Kim, S. J. Ahn, Y. J. Hwang and B. K. Min, *Acs Appl Mater Inter*, **2015**, 7, 24550-24555.
- [30] C. C. L. McCrory, S. H. Jung, J. C. Peters and T. F. Jaramillo, *J Am Chem Soc*, **2013**, 135, 16977-16987.
- [31] H. Xu, Z. X. Shi, Y. X. Tong and G. R. Li, *Adv Mater*, **2018**, 30.
- [32] H. F. Liang, F. Meng, M. Caban-Acevedo, L. S. Li, A. Forticaux, L. C. Xiu, Z. C. Wang and S. Jin, *Nano Lett*, **2015**, 15, 1421-1427.
- [33] W. Sun, Y. Song, X. Q. Gong, L. M. Cao and J. Yang, *Chem Sci*, **2015**, 6, 4993-4999.
- [34] Y. H. Chung, I. Jang, J. H. Jang, H. S. Park, H. C. Ham, J. H. Jang, Y. K. Lee and S. J. Yoo, *Sci Rep-Uk*, **2017**, 7.
- [35] L. A. Stern, L. G. Feng, F. Song and X. L. Hu, *Energ Environ Sci*, **2015**, 8, 2347-2351.
- [36] T. Huang, Y. Chen and J. M. Lee, *Acs Sustain Chem Eng*, **2017**, 5, 5646-5650.
- [37] W. Ma, R. Z. Ma, C. X. Wang, J. B. Liang, X. H. Liu, K. C. Zhou and T. Sasaki, *Acs Nano*, **2015**, 9, 1977-1984.

Chapter 8

Implications/Impact/Outstanding Questions

In this thesis, the focus is on the synthesis and structural engineering of novel electrocatalysts, i.e., preparation of 3D palladium nanoassemblies, and metal organic frameworks derived hybrids and hybrid materials of CoOx-MoC. Moreover, investigation of their properties in electrocatalytic applications, such as electrooxidation of formic acid, hydrogen evolution and oxygen evolution are conducted. Next, conclusions drawn from the findings and the impacts of these findings for developing an efficient electrocatalyst are presented. Following on, the outcomes reflected on the hypotheses are discussed. In the reconnaissance work and future work section, future design and synthesis of electrocatalysts are addressed.

8.1 General Discussion

Currently, the world is facing energy depletion and environmental issues. Electrochemical energy conversion and storage has been identified as an ideal solution to tackle these serious problems. However, these energy storage devices (fuel cell and water splitting) have suffered from electrocatalysts' low performances which result in low energy efficiency. Therefore, this thesis has developed several synthetic methods and novel materials to improve the performances of electrocatalysts. The research outcomes can be summarized as following: (1) Palladium nanoassemblies were prepared by a polymer-assisted route, the growing process of the nanostructures was also observed chronologically, these results would be highly beneficial for electrocatalyst development (Chapter 4); (2) Layered two-dimensional MOFs were obtained via low-temperature hydrothermal method, after which the MOFs were calcined to produce the electrocatalyst, which inherited their precursor's porosity as well as two-dimensionality (Chapter 5); (3) A hierarchical cobalt MOF was synthesized from the two-dimensional MOF with PVP being structure-directing agents, at the same time, molybdate was loaded into the MOFs. As such, the Co-Mo-MOFs were calcined to prepared electrocatalysts for oxygen evolution (Chapter 6); (4) NiCo LDH was fabricated firstly, then it was coated by carbon with iridium doping for enhanced performances of electrochemical oxygen evolution.

The ultimate goal for this study is to improve the performance of the electrochemical reactions so as to achieve a high energy efficiency in high energy conversion storage devices. In Chapter 4, Pd precursor complexed with structure-directing agents, after the hydrothermal reaction, the three-dimensional Pd nanoassemblies were formed and fabricated for electrooxidation of formic acid. In Chapter 5, composites of cobalt/N-carbon for HER were produced as highly efficient catalysts. In Chapter 6, the hybrid of cobalt oxides and molybdenum carbides was derived MOFs for oxygen evolution. In Chapter 7, a heterostructure of layered double hydroxides was prepared for the application of electrochemical oxygen evolution reaction. The details of the outcome reflected on the hypothesis for individual chapter will be discussed in the following four sections (section 8.1.1, 8.1.2, 8.1.3 and 8.1.4). Therefore, such works will provide inspiration for production

of next-generation electrocatalysts, which contribute greatly to the clean energy community.

8.1.1 Outcome reflected on hypothesis #1

In Chapter 4, the hypothesis is to test hierarchical nanoassembly structure has abundant pores, which contribute to more surface area as compared to nonporous material. The results show that by rational design of 3D nanoarchitecture of palladium (porous nature) with the assistance of polymers, the nanoarchitecture has abundant pores and high surface area. In addition, the 3D Pd nanoassemblies were tested for formic acid electro-oxidation. Importantly, the Pd nanoassemblies displayed prominent electrocatalytic behaviors for formic acid electrooxidation. Based on the results, it seems like there is a relationship between the structure and properties (characterized using TEM). It is proposed that the high surface area can provide more active site and cavity space, which can facilitate gas involving reaction, respectively. Therefore, construction of efficient 3D structure of the electrocatalyst was suggested to be the key for improving the electrochemical performances in formic acid electrooxidation. By introducing cross-linking and structure-directing agents, the morphology of structure can be manipulated to produce open various pores. As such, Pd nanoassemblies displayed greater catalytic activity due to their advantageous features arising from the interconnected three-dimensional configuration.

The first hypothesis of producing the noble metal surface creates porous nature of anode materials is proven to be true, while the objective of designing palladium nanoassemblies that improve the electrocatalytic behaviors for formic acid electrooxidation has been met.

8.1.2 Outcome reflected on hypothesis #2

In Chapter 5, it is proposed that by chemically co-doping, such as nitrogen into the carbon hybrid structures, the doping of the nitrogen could improve electronic structure. This formation is very important for the physical and chemical process in hydrogen evolution processes. The results show that the N-doped CoOx electrode exhibits the lowest onset

overpotential as compared to Pt/C. In particular, by integration of the advantageous properties of cobalt and N-carbon, the hybrid materials of Co/N-Carbon showed enhanced electrocatalytic activity and long-term stability. More importantly, accelerating degradation test was conducted on the products by using thousands of cycles of CV, in which the Co/N-Carbon displayed negligible variation in terms of overpotential. Based on the hypothesis, the N heteroatom behaves as beneficial role in improving the electrochemical hydrogen evolution. It is speculated that doping reagent provide electron-rich N atoms, which might contribute to improving the electronic conductivity of the products.

The second hypothesis is that nitrogen-doping can improve electronic conductivity in HER with a lower overpotential, such hypothesis is confirmed. The aim of designing a 2D Co/N-carbon materials to facilitate fast ion transport that decreases overpotential is also achieved.

8.1.3 Outcome reflected on hypothesis #3

In Chapter 6, it is proposed that by chemical hybridization, such as Mo into the cobalt oxide structures, the electronic structure of the MoC could tune to facilitate active site (CoOOH) formation in OER. This formation is very important for the catalytic processes. According to experimental results (as described in Chapter 6), CoOOH is usually the active site for electrocatalytic oxygen evolution reaction. The results show that the sample of CoOx-MoC exhibits the low onset overpotential and overpotential at 10 mA cm^{-2} . Based on the hypothesis, the molybdenum carbides played important roles in improving the electrochemical oxygen evolution performances of cobalt oxides. Therefore, a proper usage amount of molybdenum should be adopted to obtain excellent oxygen evolution electrocatalysts. As excessive molybdenum usage may block the catalytic sites, insufficient molybdenum usage might not contribute to tuning effect.

The third hypothesis suggests that by hybridizing (for examples: Mo) cobalt oxides, it is possible to adjust the ratio of dopant and the cobalt oxides in order to improve oxygen evolution activity, this hypothesis is proven to be correct. More importantly, the goal of

fabricating a hybrid of cobalt oxide and molybdenum with suitable composition and optimized structure to improve the electrocatalytic performances of oxygen evolution is attained.

8.1.4 Outcome reflected on hypothesis #4

In Chapter 7, the hypothesis is that fabrication of heterostructure of layered double hydroxides may display novel and superior properties in electrocatalysis. The experimental results showed successful synthesis of binary hybrid hydroxide microstructures as a platform for electrocatalyst fabrication. Moreover, the nickel-cobalt layered double hydroxides were coated by a carbon layer, which was doped by iridium. The final products showed excellent electrochemical behaviors of oxygen evolution reaction. The excellent electrochemical oxygen production can be attributed to their compositional and structure advantages. Therefore, rational design of microarchitecture and selection of composition has been confirmed as a proper strategy to develop novel electrocatalysts.

The last hypothesis of producing the heterostructure of layered double hydroxides would induce porous nature is proven to be true, such porous nature combined with the theoretically high electroactive behaviors of layered double hydroxides would endow the final products with prominent performances in oxygen evolving reaction.

8.2 Reconnaissance and Outstanding questions

In viewing of recent advancements, plenty of research area is waiting for us to explore. Based on the current progress discussed in this thesis, some suggestions will be given on the potential works which can be conducted in the future.

8.2.1 Preparation of new metal nanostructures using the polymer-assisted method

Palladium metals nanostructures display various improved properties with the assistance of polymers. The mechanistic study in the part will induce other studies on polymer-

assisted synthesis of nanostructures. Metal nanostructure are a class of materials widely used in energy conversion and storage.^[1-3] The ability to design and produce desired metal nanostructure is quite fascinating to make good use of metals and to integrate various advantages of different metals, thus optimizing their performance for targeted applications.

Particularly, the 3D porous structures provide a smooth way to transport electrons through their porous space, which are attractive for energy storage and conversion applications.^[4, 5] For example, the work in chapter 4 of the thesis has demonstrated that the Pd nanoassembly hybrid material shows great promising potential in formic acid oxidation. Moreover, it is reported that the palladium nanostructures show excellent behaviors for electrocatalytic hydrogen evolution reaction (HER).^[6, 7] In addition to the palladium materials, synthesis of other noble metal materials is also fascinating. For example, it has been demonstrated that the nanostructure of platinum, one of the most attractive materials for electrocatalysis, can be designed by aqueous process.^[8, 9] The as-prepared metal materials have better electrocatalytic performances as compared with that of commercial Pt black, which is the benchmark for electrocatalysis. In this work, only Pd nanomaterials were presented (Chapter 4). Except that, other kinds of nanostructures, such as Rhodium, PdPt, PtAg materials, are expected to be prepared using the similar method, i.e., polymer-assisted formation by hydrothermal and/or solvothermal method. Moreover, it is expected that the hybridization process can induce some unique physical and electronic properties and the prepared hybrid materials show optimized or improved performance for electrochemical applications.^[10, 11]

8.2.2 Preparation of new hybrid materials based on metal organic frameworks for other applications

As introduced in the Literature Review in Chapter 5, it has been known that the 2D MOFs can be transformed to carbon, metal oxides, and metal embedded in nitrogen-doped carbon upon heat treatment, and the derivative hybrid materials have shown great potential in electrocatalysis and electrochemical lithium ion batteries.^[12, 13] Therefore, by utilization of

2D MOFs as precursors, after proper doping, such as sulfidation and phosphidation, it is valuable and promising to improve the performance of MOF-derived electrocatalysts.

However, it is rarely reported to co-dope MOFs with sulfur and phosphorus precursor simultaneously. In the thesis, the carbon matrix of the hybrid materials has been doped by nitrogen after heat treatment, and it is supposed nitrogen-doping can improve electronic conductivity in HER, which significantly increase the HER kinetics, leading to a lower HER overpotential. Therefore, it is possible to improve the electrochemical performances, by doping the MOFs with sulfur and phosphorus precursors, finely tuning the experimental conditions, such as reaction time and reaction temperature. In addition, the synergism of sulfur and phosphorus co-doping are potentially promising for improving the performance of electrocatalysts.^[14, 15]

8.2.3 Preparation of metal/MOF composites for electrochemical applications

Currently, the branch of layered MOFs is growing bigger. For example, MOF, hybrid of MOF and other 2D materials, have been reported for various applications.^[16, 17] The layered materials enable us to engineer their structures and functionalities for promising applications. However, most of the research works focus on the direct calcination of new 2D layered nanosheets, while hybrid of Pd, Pt loaded on MOFs, are rarely investigated. Therefore, synthesis of new hybrid layered materials, integrating the advantageous properties of 2D MOFs and noble metals should contribute to the scientific community with excellent electrocatalysts. The works presented chapter 6 can serve as valuable example for the study.

Moreover, with the advancement of synthetic methods and characterization protocols, the investigation on single atoms supported on MOFs has been realized. For example, Li Yadong et al and coworkers prepared high-quality single-atom nickel atoms supported on ZIF-67 in solution and studied their electrocatalytic performances.^[18] This study provides a good example for precisely testing the electrochemical property of a single atom catalysts. Therefore, continually fabrication of novel layered MOFs is valuable for exploration of the

structure-property relationship of new hybrid layered MOFs and promising for practical applications.

References

- [1] Y. H. Bing, H. S. Liu, L. Zhang, D. Ghosh and J. J. Zhang, *Chem Soc Rev*, **2010**, 39, 2184-2202.
- [2] J. W. Hong, S. W. Kang, B. S. Choi, D. Kim, S. B. Lee and S. W. Han, *Acs Nano*, **2012**, 6, 2410-2419.
- [3] C. Z. Zhu, H. Li, S. F. Fu, D. Du and Y. H. Lin, *Chem Soc Rev*, **2016**, 45, 517-531.
- [4] Z. Y. Shih, C. W. Wang, G. B. Xu and H. T. Chang, *J Mater Chem A*, **2013**, 1, 4773-4778.
- [5] S. Z. Wang, L. Kuai, Y. C. Huang, X. Yu, Y. D. Liu, W. Z. Li, L. Chen and B. Y. Geng, *Chem-Eur J*, **2013**, 19, 240-248.
- [6] S. Ghasemi, S. R. Hosseini, S. Nabipour and P. Asen, *Int J Hydrogen Energ*, **2015**, 40, 16184-16191.
- [7] A. Safavi, S. H. Kazemi and H. Kazemi, *Fuel*, **2014**, 118, 156-162.
- [8] M. M. Shahid, P. Rameshkumar, A. Pandikumar, H. N. Lim, Y. H. Ng and N. M. Huang, *J Mater Chem A*, **2015**, 3, 14458-14468.
- [9] N. Xu, H. W. Li and Y. Q. Wu, *Anal Chim Acta*, **2017**, 958, 51-58.
- [10] Q. A. Jiang, L. H. Jiang, H. Y. Hou, J. Qi, S. L. Wang and G. Q. Sun, *J Phys Chem C*, **2010**, 114, 19714-19722.
- [11] F. Maroun, F. Ozanam, O. M. Magnussen and R. J. Behm, *Science*, **2001**, 293, 1811-1814.
- [12] X. J. Wang, J. W. Zhou, H. Fu, W. Li, X. X. Fan, G. B. Xin, J. Zheng and X. G. Li, *J Mater Chem A*, **2014**, 2, 14064-14070.
- [13] F. Zou, X. L. Hu, Z. Li, L. Qie, C. C. Hu, R. Zeng, Y. Jiang and Y. H. Huang, *Adv Mater*, **2014**, 26, 6622-6628.
- [14] W. H. Li, S. H. Hu, X. Y. Luo, Z. L. Li, X. Z. Sun, M. S. Li, F. F. Liu and Y. Yu, *Adv Mater*, **2017**, 29.

- [15] S. A. Wohlgemuth, R. J. White, M. G. Willinger, M. M. Titirici and M. Antonietti, *Green Chem*, **2012**, 14, 1515-1523.
- [16] D. Kufer, I. Nikitskiy, T. Lasanta, G. Navickaite, F. H. L. Koppens and G. Konstantatos, *Adv Mater*, **2015**, 27, 176-180.
- [17] J. Yan, C. E. Ren, K. Maleski, C. B. Hatter, B. Anasori, P. Urbankowski, A. Sarycheva and Y. Gogotsi, *Adv Funct Mater*, **2017**, 27.
- [18] C. M. Zhao, X. Y. Dai, T. Yao, W. X. Chen, X. Q. Wang, J. Wang, J. Yang, S. Q. Wei, Y. E. Wu and Y. D. Li, *J Am Chem Soc*, **2017**, 139, 8078-8081.

List of Publications

Journal articles

- [1] D. T. Dam, T. Huang and J.-M. Lee, Sustainable Energy & Fuels, **2017**, 1, 324-335.
- [2] T. Huang, Y. Chen and J.-M. Lee, Acs Sustain Chem Eng, **2017**, 5, 5646-5650.
- [3] T. Huang, Y. Chen and J. M. Lee, Small, **2017**, 13, 1702753.
- [4] T. Huang, S. K. Moon and J.-M. Lee, Sustainable Energy & Fuels, **2017**, 1, 450-457.

Conference Presentation

- [1] Layered Hybrid Structure of Cobalt/N-Doped Carbon Derived from Metal-Organic Frameworks for Electrocatalytic Hydrogen Evolution. Tan Huang , Jong-Min Lee, American Chemical Engineer Annual Meeting, Minneapolis, United States of America, 2017.