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**NANOSTRUCTURED METAL-ORGANIC-FRAMEWORK-
DERIVED MATERIALS FOR ELECTROCHEMICAL
ENERGY STORAGE AND CONVERSION**

ZHANG SONGLIN

**SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
2021**

NANOSTRUCTURED METAL-ORGANIC-FRAMEWORK- DERIVED MATERIALS FOR ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION

ZHANG SONGLIN

School of Chemical and Biomedical Engineering

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

2021

Statement of Originality

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

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Zhang Songlin

Supervisor Declaration Statement

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

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Prof. Xiong Wen (David) Lou

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as the first author.

Chapter 4 is published as S. L. Zhang, B. Y. Guan, X. W. Lou, Co-Fe alloy/N-doped carbon hollow spheres derived from dual metal-organic frameworks for enhanced electrocatalytic oxygen reduction, *Small* 15, 1805324 (2019). DOI: 10.1002/sml.201805324.

The contributions of the co-authors are as follows:

- Prof Lou provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Guan.
- I co-designed the study with Prof Lou and performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Guan assisted in the synthesis of the materials.

Chapter 5 is published as S. L. Zhang, B. Y. Guan, X. F. Lu, S. B. Xi, Y. H. Du, X. W. Lou, Metal atom-doped Co₃O₄ hierarchical nanoplates for electrocatalytic oxygen evolution. *Advanced Materials* 32, 2002235 (2020). DOI: 10.1002/adma.202002235.

The contributions of the co-authors are as follows:

- Prof Lou suggested the initial project direction and edited the manuscript drafts.

- I wrote the drafts of the manuscript. The manuscript was revised by Dr Lu.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Xi and Dr Du conducted the X-ray absorption spectroscopy test and assisted in related data interpretation. Dr Lu assisted in the DFT calculation.

Chapter 6 is published as S. L. Zhang, X. F. Lu, Z. P. Wu, D. Y. Luan, X. W. Lou, Engineering Pt-Co nano-alloys in porous nitrogen-doped carbon nanotubes for highly efficient electrocatalytic hydrogen evolution, *Angewandte Chemie International Edition*, DOI: 10.1002/anie.202106547 (2021).

The contributions of the co-authors are as follows:

- Prof Lou provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Lu and Dr Wu.
- I co-designed the study with Prof Lou and performed all the laboratory work at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Wu assisted in the DFT calculation and the related data interpretation.

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Abstract

Transition metal-based materials are promising not only in energy storage devices such as batteries, supercapacitors, fuel cells, but also in the field of catalysis. Increasing attention is paid to push the limits of energy storage and conversion by the delicate design of nanomaterials. To this end, metal-organic-frameworks (MOFs) based materials are emerging as outstanding templates and precursors to create nanostructures with various promising functionalities, such as excellent chemical and mechanical stabilities, large specific surface areas, and adjustable pore structures, which are promising for the applications towards energy-related applications. The research work presented in this project focuses on the rational design and synthesis of MOF-derived materials with the desired structure and composition as well as their electrochemical applications. The main results and findings are summarized as follows.

1. Co-Fe alloy@N-doped carbon hollow spheres are designed and synthesized through a dual-MOF-assisted pyrolysis approach for electrocatalytic oxygen reduction reaction (ORR). In this case, dual MOFs shell and polystyrene core are coupled together by one-step encapsulation procedure, enabling the further alloying of metal centers during the pyrolysis stage. After the thermal treatment in N₂, the Co-Fe alloy particles originated from the conjunct ZIF-67, and MIL-101 are homogeneously distributed and serve as active sites in porous N-doped carbon nanoshells with nanometer precision. Benefiting from the rich active sites and porous conductive matrix, the catalyst exhibited an enhanced ORR performance with a half-wave potential ($E_{1/2}$) at 0.854 V.

2. A series of hollow hierarchical nanoplates (NPs) assembled by Co₃O₄ nanosheets doped with 13 metal atoms are developed through a cooperative etching-

coordination-reorganization method for electrocatalytic oxygen evolution reaction (OER). Novel two-dimensional ZIF-67 NPs are synthesized as templates to receive a Lewis acid etching and metal species coordination to form unique cross channels, and thus further converted to hollow Co_3O_4 hierarchical NPs constructed from ultrathin nanosheet subunits through a controllable solvothermal reaction, during which the metal species are doped into Co_3O_4 crystal lattice. Benefiting from the structural and compositional advantages, the as-derived Fe-doped Co_3O_4 hierarchical NPs manifest superior electrocatalytic activity towards OER with an overpotential of 262 mV at 10 mA cm^{-2} , a Tafel slope of 43 mV dec^{-1} , and excellent stability over 50 h at 100 mA cm^{-2} .

3. Ultrafine Pt-Co alloy nanoparticles (sub-10 nm) attached on the inner and outer shells of porous nitrogen-doped carbon nanotubes (NCNT) are synthesized through a MOF-assisted pyrolysis-replacement-reorganization method. During the thermal reorganization, the migration of Pt-Co nano-alloys to both surfaces ensures the maximized exposure of active sites while maintaining the robust attachment to the porous carbon matrix. Density functional theory calculations suggest a nearly thermodynamically-neutral free energy of adsorption of hydrogen intermediates and diversified active sites induced by alloying, thus resulting in a great promotion in intrinsic activity towards the hydrogen evolution reaction (HER). Benefiting from the delicate structural design and compositional modulation, the optimized $\text{Pt}_3\text{Co}@NCNT$ electrocatalyst manifests outstanding HER activity and superior stability in both acidic and alkaline media.

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List of abbreviations

LIBs: lithium-ion batteries

ORR: oxygen reduction reaction

OER: oxygen evolution reaction

HER: hydrogen evolution reaction

HOR: hydrogen oxidation reaction

Pt: platinum

Ru: ruthenium

Co: cobalt

Fe: iron

N: nitrogen

Ni: nickel

Mo: molybdenum

Cu: copper

Mn: manganese

Zn: zinc

Li: lithium

MoS₂: molybdenum disulfide

RuO₂: ruthenium oxide

IrO₂: iridium oxide

H₂SO₄: sulfuric acid

KOH: potassium hydroxide

HCl: hydrochloric acid

MOF: metal-organic framework

ZIF-67: zeolitic imidazolate framework-67

ZIF-8: zeolitic imidazolate framework-8

MIL-101: Matériaux Institut Lavoisier-101

PS: polystyrene

TMO: transition metal oxide

Co₃O₄: cobalt(II,III) oxide

FeCl₂·4H₂O: iron(II) chloride tetrahydrate

FeCl₃·6H₂O: Iron(III) chloride hexahydrate

Co(NO₃)₂·6H₂O: cobalt(II) nitrate hexahydrate

2-MIM: 2-methylimidazole

M_w: molecular weight

sc-Pt: single-crystalline platinum

LDH: layered double hydroxides

NC: nitrogen-doped carbon

NT: nanotube

ALD: atomic layer deposition

Ar: argon

N₂: nitrogen gas

H₂: hydrogen gas

DMF: dimethylformamide

EtOH: ethanol

DI: deionized

PVP: polyvinylpyrrolidone

CTAB: cetyltrimethylammonium bromide

1D: one-dimensional

2D: two-dimensional

3D: three-dimensional

XRD: X-ray diffraction

JCPDS: joint committee on powder diffraction standards

ICDD: international centre for diffraction data

FESEM: field-emission scanning electron microscopy

EDX: energy-dispersive X-ray spectroscopy

TEM: transmission electron microscopy

SAED: selected-area electron diffraction

HRTEM: high-resolution transmission electron microscopy

STEM: scanning transmission electron microscopy

ADF: annular dark-field

HAADF: high-angle annular dark-field

TGA: thermogravimetric analysis

ICP-AES: inductively coupled plasma atomic emission spectroscopy

BET: Brunauer-Emmett-Teller

DFT: density functional theory

DOS: density of states

XPS: X-ray photoelectron spectroscopy

Sat.: satellites

XAS: X-ray absorption spectroscopy

XAFS: X-ray absorption fine structure

XANES: X-ray absorption near edge structure

EXAFS: extended X-ray absorption fine structure

$E_{1/2}$: half-wave potential

j : current density

η : overpotential

RDE: rotating disk electrode

RHE: reversible hydrogen electrode

CFP: carbon fiber paper

Ag/AgCl electrode: silver chloride electrode

Hg/HgO: mercury/mercury oxide

SCE: saturated calomel electrode ($\text{Hg}_2\text{Cl}_2/\text{Hg}, \text{Cl}^-$)

SCE: saturated calomel electrode

LSV: Linear sweep voltammetry

CV: cyclic voltammetry

CP: chronopotentiometry

K-L plot: Koutecky-Levich plot

EIS: electrochemical impedance spectroscopy

ECSA: electrochemical surface area

TOF: turnover frequency

fcc: face-centered cubic

hcp: hexagonal close-packed

ΔG_{H^*} : Gibbs free energy of adsorption for the H^* intermediate

ΔG : Gibbs free energy difference

FT: Fourier transform

IFFT: inverse fast Fourier transform

SAA: single-atom alloy

PDA: polydopamine

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Chapter 1. Introduction

1.1. Background

To alleviate the reliance on non-renewable fossil fuels and ease the impact on climate change, the research tasks are imperatively assigned to renewable and clean energy innovation that includes discovering novel energy sources, upgrading economic and safe electrical storage systems, and promoting energy conversion efficiency. As a main secondary energy source, electricity bridges most natural energy (e.g., solar, wind, and tidal) to other forms of power for storage and resupply. In this regard, the storage and conversion efficiency of intermediate devices is inevitably tied up with the overall energy generation. For different applications, the requirements for energy storage systems are widely varying, including high capacity and energy density, long cycle life, rapid discharge/charge rates, stable performance, cost-effectiveness, and easy scale-up. One of the most notable achievements in energy storage is the commercialization of lithium-ion batteries (LIBs). LIBs are commonly engaged in portable electronic devices with high maturity. However, their charging speed, energy density, and power grid compatibility are still insufficient to address the varying needs fully. To address the impending needs and diverse types of applications, a suitable combination of energy storage systems may moderate the drawbacks of each electrochemical technique and satisfy the specific requirement of applications (**Figure 1.1**). One significant progress has been made by fuel cells, a representative for generating electricity through the reaction of hydrogen and oxygen, coupled with the water-splitting technology driven by electric energy. Fuel cells have been long anticipated to replace conventional heat engines due to their high performance and

infinite renewable characteristics, but commercially hindered by the significant driving force required by the overpotential due to the kinetic sluggish, aside from the material limits of costly platinum-based catalysts. Hydrogen serves as the primary energy carrier to produce electricity in fuel cells, which can be generated with high purity by water electrolysis.^[1] The essential part of these energy-related techniques are composed of various electrocatalytic reactions, involving oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) in fuel cells and oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in water electrolysis.

Figure 1.1. Characteristics of rechargeable batteries and hydrogen fuel cells. Reproduced with permission.^[2] Copyright 2018, Springer Nature.

Hence, investigating applicable methods to promote these reactions with low energy consumption has been regarded as the most urgent demand. To date, noble metals (Pt, Ru) and noble metal oxides ($\text{RuO}_2/\text{IrO}_2$) are widely regarded as the most efficient catalysts to achieve favorable reaction kinetics towards electrocatalytic HER, ORR, and OER. Nevertheless, the paucity and high cost of the noble metals (oxides)

restrains their mass manufacture in relevant energy devices. In recent years, with the remarkable advances in nanotechnology and (in)organic synthesis, current attempts turn to open up new opportunities to more efficient electrocatalytic materials with low or no utilization of noble metal constituents for practical applications.

Assuming the responsibility for promoting the reaction as well as sustained chemical and structural stability, active electrocatalyst/electrode materials are supposed to be nanostructured with complex organizations to acquire multiple enhancements. Significant research effort confirms that the structure-performance dependence gives direct access to realize the design of high-performance catalysts/electrodes. Specifically, nanoparticles characterized with large surface area endow sufficient active sites for surface-dependent pathways, such as adsorption/desorption, insertion/desorption, and surface oxidation/reduction reactions. Porous and hollow structures shorten the mass diffusion distance, which is highly promising as hosts for accommodating guest species. Moreover, nanosized precision grants enhanced activity to nanomaterials through unique morphological, electronic properties, and binding strength to reaction intermediates compared with bulk materials, further enabling regulations of activity and selectivity for a particular reaction. Hence, to integrate these characteristics, delicate compositional and structural designs are indispensably demanded.

1.2. Motivation

Recently, the emerging of nanostructured electrocatalysts opens up a new route to settle the aforementioned problems and enhance the overall properties of electrochemical devices. MOF has emerged as a family of periodic structures organized by coordination bonds between metal ion centers and organic linkers.

Benefiting from their structural advantages, typically ultrahigh porosity and internal surface area, MOF materials show strong promise on homogeneous and heterogeneous catalysis. Significantly, the extraordinary degree of variability for both metal nodes and linkers allows the compositional diversity, make MOF materials good candidates to meet broadened needs related to energy. MOFs materials can be possibly converted to various nanostructured materials to serve different duties in view of moderate chemical and physical instability. As thermal methods via solvothermal or pyrolysis and chemical reactions with desirable reagents are applied to MOFs precursors, numerous carbons, metal-based compounds are converted with inherent structural advantages of MOFs. Rational increment of the complexity favors the multifunctional properties, which could be realized via integrating MOFs and other functional materials with active sites in the early stage. Thus, the complex MOF-derived materials with diverse characteristics are regarded as possible solutions to solve the energy-related storage and conversion tasks.

1.3. Overall objective

This research project has been concentrated on rationally designing MOF-derived materials with well-defined nanostructures and tunable compositions to correlate the electrocatalytic performance with delicate material design. In order to improve the ORR kinetics, nanosized alloys are distributed on nitrogen-doped framework to promote the conductivity and maximize the exposed active sites. Further, hierarchical structures are designed to increase the surface area to lower the OER overpotential, while surface modulation is employed to improve the intrinsic catalytic properties of transition metal oxides (TMOs). Moreover, ultrafine Pt-alloy nanoparticles with strong metal-support interaction are delicately designed to enhance the HER performance in

acidic and alkaline media. To this regard, the overall objective could be generally categorized into the following aspects.

1.3.1. Synthesis of Co-Fe nanoalloy confined in nitrogen-doped carbon hollow spheres for enhanced electrocatalytic oxygen reduction

The employment of MOF composites as precursors is a potential direction to derive metal/carbon-based materials with high electrocatalytic activities. Mostly, the synthetic methods start from mono-MOF precursors to generate sole metal species and solid structures after the calcination. Hence, the rational design of multi-MOF composite as precursor could open new avenues to functional materials with high performance. To achieve this target, a dual-MOF-assisted synthesis method is developed for the synthesis of Co-Fe alloy confined in nitrogen-doped hollow spheres with tunable compositions. The specific effect observed in this project that ORR performance varies with catalysts prepared at different pyrolysis temperatures is also well-investigated and ascribed to the synergistic effect of Fe-Co alloy as well as the nitrogen content variations. The targeted structure provides rich active sites and porous conductive matrix and thus endow the material with enhanced activity and stability towards ORR.

1.3.2. Synthesis of metal-doped Co_3O_4 hierarchical nanoplates for electrocatalytic oxygen evolution

Another critical half-reaction, OER, always occurs on the anode of an electrolytic cell upon water splitting. However, the fact is that most metal compounds would always inevitably transform to hydroxides at high anodic potential, therefore jeopardizing the cyclability. Generally, Co_3O_4 is quite chemically stable but with a

high overpotential to induce OER in alkaline media. Incorporating secondary metal atoms is expected to enhance the intrinsic activity of Co_3O_4 towards OER efficiently. Meanwhile, to maximize the electrochemically active sites (ECSA), the hierarchical nanostructure is also necessary for advanced electrocatalysts. To this end, a cooperative etching-coordination-reorganization method is developed to construct metal-doped Co_3O_4 hierarchical nanoplates (NPs), started from Co-based MOF NPs. This method allows 13 metal species dope into Co_3O_4 lattice. Among them, Fe-doped Co_3O_4 hierarchical nanoplate exhibits the best OER activity with an overpotential of 262 mV@10 mA cm^{-2} and remarkable durability over 50 h@100 mA cm^{-2} .

1.3.3. Synthesis of Pt-Co nanoalloys in porous nitrogen-doped carbon nanotubes for electrocatalytic hydrogen evolution

Hydrogen is regarded as an efficient energy carrier and plays an important role in sustainable energy conversion. However, the essential method for hydrogen production-water electrolysis, is hindered by the high overpotential, which requires the efficient electrocatalysts to promote the processes. In this regard, a metal-organic framework-assisted pyrolysis-replacement-reorganization method is developed to obtain ultrafine Pt-Co alloy nanoparticles (sub-10 nm) attached on the inner and outer shells of porous nitrogen-doped carbon nanotubes (NCNT) with closed ends. During the thermal reorganization, the migration of Pt-Co nano-alloys to both surfaces ensures the maximized exposure of active sites while maintaining the robust attachment to the porous carbon matrix. The reaction performance is further verified by theoretical calculations, which imply that the Pt_3Co alloy provides a nearly thermodynamically-neutral free energy of adsorption of hydrogen intermediates with diversified active sites induced, thus giving access to boosted intrinsic activity towards HER. Thanks to the delicate material design, the $\text{Pt}_3\text{Co}@ \text{NCNT}$ electrocatalyst with optimized

structure and composition presents outstanding catalytic activity and superior stability towards HER in both acidic and alkaline media.

1.4. Organization

The overall layout of the thesis is listed below:

Chapter 1 briefly synthesizes the background, motivation, and overall objective of this research project. In Chapter 2, introductions about the electrochemical energy conversion process are provided, followed by the classification of electrocatalysts for ORR, OER, and HER. The synthesis methodology, characterization, and electrochemical test engaged in this research are displayed in Chapter 3. For electrocatalysis, the designed catalysts should be able to facilitate the electrochemical reactions and guarantee stability over tests, which therefore emphasize the importance of MOF-derived materials. In this regard, in Chapter 4, we demonstrate a dual-MOF-assisted pyrolysis strategy to explore the MOF-based derivations to transition metal/N-doped carbon composite. Further, precise structural and compositional control is applied to further enhance the exposure of active sites and boost the intrinsic activity of the electrocatalysts. In Chapter 5, a cooperative etching–coordination–reorganization method is developed to design secondary metal-doped ultrathin transition metal oxide nanosheet assembly with highly exposed surface area and modulated electronic structure. In Chapter 6, we further enhance the metal-support interaction of Pt-based alloy with porous nitrogen-doped carbon matrix through MOF-assisted pyrolysis-replacement-reorganization method to achieve high stability and catalytic activity in acidic and alkaline media. These materials demonstrate strong relationship between structure and electrochemical performance, which is also proved by the advances in electrochemical performance. The catalytic

performance of the three systems is carefully investigated. Lastly, Chapter 7 summarizes the overall results regarding the above systems, accompanied by outlooks for future works in material design and catalytic field.

Chapter 2. Literature Review

2.1. Overview of electrocatalysis

Sustainable energy conversion techniques, representative fuel cells, metal-air batteries, and water electrolysis are highly promising to ease the reliance on traditional fossil fuels. The relationship between chemistry and electricity enables the storage of excess energy into chemical bonds of molecules, such as H_2 , NH_3 , and methanol, which can also be released and utilized as fuels in ambient conditions (**Figure 2.1**). These highly reversible processes create close cycles for clean energy conversions. Among them, the water cycle based on elementary H_2 and O_2 reactions is the most promising one as H_2 possesses the highest energy density, and the reaction process is clean and sustainable. The water cycle is composed and operated by four electrochemical processes, which HER and OER are accompanied with the operation of water splitting, and HOR and ORR occur at electrodes of hydrogen fuel cells (**Figure 2.2**).

Figure 2.1. Schematic overview of sustainable energy storage and conversion. From *Science* **2017**, 355, eaad4998. Reprinted with permission from AAAS.^[3]

Figure 2.2. (a) Schematic of the operation of electrolytic cell and fuel cell. (b) Linear sweep voltammetry (LSV) curves for the hydrogen-related and oxygen-related reactions. Reproduced with permission.^[4] Copyright 2018, American Chemical Society.

However, these conversions suffer from slow kinetics and thus present relatively low efficiency. For example, although H_2 can be produced from water electrochemically, the mass production and commercialization are still unrealistic due to the high cost of electricity comparing with the steam reforming method.^[5] In the view of half-cell electron transfer processes, the HER and HOR follow the two-electron transfer; meanwhile, ORR and OER go through the multistep electron transfer and thus presenting sluggish kinetics. To reduce the consumption of electricity, electrocatalysts are inevitably demanded to reduce the overpotential of the reactions. Two general strategies have emerged for the electrocatalytic activity improvement: (1) exposing more accessible active sites per gram/unit area or (2) boosting the intrinsic activity of each catalytic site.^[6] The strategies emphasize both the structural and compositional design of the catalysts to achieve the highest conversion efficiency. On the other hand, the practical efficiency of catalyst can hardly reach the theoretical expectations due to physical limits, e.g., the loading amount of catalyst can affect mass/charge transport in the electrode process.^[6]

In recent studies, nanostructured materials show superior activity over bulk materials owing to advances in surface-to-volume ratio, shape effect, and electronic properties. The enhanced surface area of catalysts can offer sufficient accessible active sites and shortened the diffusion path of ions. The shape design can expose certain facets of the nanostructure to facilitate a particular reaction. Furthermore, the geometric or strain effect can alter the electronic structure and result in the modified binding energy of intermediates. Hence, the employment of complex nanostructure can combine the essential properties and offers numerous possibilities for efficient electrocatalysis.

2.2. Oxygen Reduction Reaction (ORR)

Electrocatalytic ORR follows multistep electron transfer pathways, which engages four-electron ($4e^-$) and two-electron ($2e^-$) transfer pathways. The two different pathways target different practical usages; as for fuel cells and metal-air batteries, direct $4e^-$ transfer is favored with low energy consumption, while $2e^-$ transfer is mainly for the industrial preparation of H_2O_2 products.^[7] The reaction routes are subjected to the selection of electrode materials.

Overall reaction (Acidic media)

Reaction pathway

Overall reaction (Alkaline media)

Reaction pathway

Detailed ORR mechanism has been studied through both experimental and computational methods on different substrates, suggesting that the binding energy of intermediates with specific substrates controls the overall selectivity and activity towards ORR. Isotope measurements also indicate that the 4e^- process requires the cleavage of O-O bond, while the 2e^- process maintains the original O-O bond. Generally, Au, Hg, graphite, and metal oxides are potential substrates to catalyze O_2 to H_2O_2 electrochemically through 2e^- process, whereas the 4e^- process is typically carried out predominantly on Pt-based catalysts to generate H_2O as a product. Generally, the modification of ORR activity and selectivity fundamentally relies on exploiting electronic effects and support-induced surface-lattice strain by shifting the electronic structure of the catalyst, thus bringing alternations to the adsorption energy of reaction intermediates.

2.2.1. Pt and Pt alloys

Pt has been intensively studied and regarded as the most state-of-art ORR electrode since the 1960s. Commercially used Pt metals are usually attached to carbon black due to the concern of conductivity. The study of the ORR mechanism on single-crystalline Pt (sc-Pt) catalysts is quite mature as the geometric effect of planes and adsorption of electrolyte species are both demonstrated to change the ORR activity significantly (**Figure 2.3a**).^[8-9] As Pt elements are expensive and of low abundance on earth, to achieve large-scale commercialization, alloying Pt with non-noble metals is considered as a potential method to downsize the usage of Pt.^[10] Besides, based on intensive mechanism study on sc-Pt, the harsh operating conditions in fuel cell limits the practical usage of pure Pt NPs by deactivating Pt facets and resulting in degradation of ORR activities (Figure 2.3b).^[11] Notably, this drawback can be solved by structural and compositional reorganization and their interactions during the alloying process. Besides, the active facets and sites should be exposed as much as possible to maximize the electrocatalytic efficiency. In this regard, two approaches named “core-shell” and “skin-skeleton” are developed to construct the alloy nanostructure for different purposes (Figure 2.3c,d).^[12] Core-shell structured materials functioned with a Pt-rich surface and non-noble metal/alloy internal possess unique electronic properties and structure-induced strain effect, delivering enhanced catalytic performance to the ORR process.^[13-16] For skin-skeleton structures, Pt skin can be possibly generated through phase segregation of Pt layer from alloys through thermal treatment or acid leaching.^[17-18]

Figure 2.3. Structural and compositional evolution of sc-Pt and Pt alloy catalysts. Reproduced with permission.^[19] Copyright 2020, American Chemical Society.

2.2.2. Transition Metal Compounds and Alloys

Apart from the Pt-based materials and alloys, non-precious metal compounds also present comparable activity and stability towards ORR in alkaline solution, thus being considered potential alternatives to Pt catalysts.^[20] Several branches of transition metal compounds have recently been investigated for electrocatalytic applications, such as transition metal-nitrogen-carbon (M-N-C) materials, transition metal compounds and alloys.

Transition M-N-C complexes characterized with low cost, high activity, and strong tolerance to methanol cross-over effect are regarded as the most promising candidates among non-precious ORR catalysts. Starting from the investigation of electrocatalytic ORR performance using cobalt phthalocyanine by Jasinski *et al.* in 1964's,^[21] M-N-C materials are drawn intensive research interests, and numerous M-N-C formed

catalysts synthesized through different metal sources have emerged. Formerly, nitrogen ingredients in M-N-C materials are commonly originated from inorganic sources, e.g., ammonia, sodium azide;^[22-23] organic molecules, e.g., pyrrole, 1-methylimidazole, acetonitrile;^[24-26] nitrogen-containing polymers, e.g., polyaniline, polydopamine, and pyrolyzed macrocycles.^[27-31] Besides, as a branch of MOF materials, zeolitic imidazolate frameworks (ZIFs) containing both metal and N centers exhibit highly ordered structure than other precursors, thus could template the formation of M-N-C derivatives with better organization.^[32-33] Li's group has studied the synthesis of Fe-N-C^[34] and Co-N-C^[32] materials with high loading mass from ZIF-8/67 precursor and demonstrated the promising ORR performance (**Figure 2.4**). Though precursors and synthetic procedures are precisely optimized for the overall M-N-C catalysts, the activity and durability could hardly be paralleling with the state-of-art Pt. Breakthroughs on further enhancement might be achieved through advances on the following two governing parameters: (I) Elemental compositions as well as their interactions are determinations of active sites. Though controversies still focus on the exact catalytic sites and mechanisms of M-N-C catalyst, metal and nitrogen sources together with the carbon supports are believed to contribute to the overall performance. (II) Surface and porous structures affect the exposure of the active sites and mass/charge diffusion path. Typically, well-defined porous structures are required by precursors to go through thermal treatments to be partially inherited in the products.

Figure 2.4. (a) Synthetic procedure of Fe-N-C catalyst from ZIF-8. (b) TEM, (c-e) HAADF-STEM image and corresponding EDX mapping of Fe-N-C catalyst. Reproduced with permission.^[34] Copyright 2017, John Wiley and Sons.

Lately, binary transition metal compounds are widely investigated to attain enhanced catalytic performance compared with single metal compounds due to the common belief that the synergistic effect generated from mixing multiple transition metals could possibly enhance ORR activity. Inherently, the introduction of secondary cations (or anions) is expected to modulate the local electronic structures and geometric configurations of metal centers in host compounds to modify a series of relevant properties. Representatively, ternary NiMoN_x compound present much superior activity over binary NiMo/C and MoN/C (**Figure 2.5**).

Figure 2.5. LSV curves of NiMoN_x/C, Co_{0.6}Mo_{1.4}N₂, MoN/C and NiMo/C for ORR activity. Reproduced with permission.^[35] Copyright 2014, Royal Society of Chemistry.

2.2.3. Metal-Free Catalysts

Carbon-based nanomaterials are ideal support or individuals for the practical use due to their resistance to fuel crossover, environmental acceptability, broad availability and stability over the Pt-based or transition metal-based materials. The ongoing research brings in carbon nanomaterials with flexible structures to the catalytic field as a replacement of long used activated carbon and glassy carbon catalysts for specific processes, varying from graphite, graphene, and carbon nanofiber mesoporous carbon. For enhancement of the electrocatalytic performance, a series of heteroatoms, typically N, B, S, and Se, are introduced to tuning the surface electron structure. In this case, considerable efforts are also dedicated to probing the actual catalytic sites and mechanism of the doped carbon materials for specific catalytic processes. Dai *et al.* suggest that the advances in ORR performance granted by N sites are intrinsically ascribed to the positive charge density on the neighboring C atoms induced by the high electronegativity of N, thus favoring the O₂ absorption.^[36] Meanwhile, other dopants in carbon materials are served with various functions for certain pathways, which remain unrevealed and require further investigations.^[37] Among the various elements,

nitrogen is the most promising dopant in carbon nanomaterials. Generally, four kinds of nitrogen sites commonly exist in N-doped carbon materials, for the pyrrolic N atoms emerge as edge or defect, graphitic N atoms replaced the original carbon atom and confined in the graphitic structure, and pyridinic N atoms normally act as defect or as oxidized N in the carbon matrix.^[38] Although the dominant active site for ORR is still under debate, the degree of graphitization and overall N content are commonly believed to influence the ORR efficiency. Generally, although most ORR studies involving non-metallic nitrogen-doped carbon are namely “metal-free”, insufficient evidence is presented to rule out the effect of traced metals. As some of the “metal-free” materials are prepared through processes that involve metal sources, the contribution of traced metals to ORR performance should not be ignored. Notably, it is proved that the addition of trace amount (0.05%) of Fe source to nitrogen-doped carbon material would strongly affect the activity and selectivity of catalyst towards ORR.

2.3. Oxygen Evolution Reaction (OER)

The OER process is reversible to the ORR process; specifically, in ORR procedure, H₂O is oxidized to O₂. Similar to ORR, the OER processes are sensitive to the surface of the catalytic substrates, e.g., different facets may induce different reaction mechanisms. According to different pH values, the electrocatalytic OER goes through different pathways but shares the same thermodynamic potential as 1.23 V at 25 °C versus reversible hydrogen electrode (*vs.* RHE). Ordinarily, the realistic potential required to accelerate the OER progress has to be higher than the thermodynamic potential value. The extra potential, namely overpotential, is the combined result of

resistance in the catalytic system and activation barriers of reactions, thus being regarded as a crucial parameter to evaluate the OER progress.

Overall reaction (Acidic media)

Reaction pathway

Overall reaction (Alkaline media)

Reaction pathway

2.3.1. *RuO₂ and IrO₂*

Traditionally, rutile-type RuO₂ and IrO₂ are commonly regarded as benchmarked catalysts towards electrocatalytic OER with the highest activity in acidic and alkaline media.^[39] In view of the OER mechanism is thoroughly analysed by computation methods, the OER activity is revealed strong dependence on the intrinsic activities of the electrocatalyst such as local electronic structure, porosity and crystallinity, that leads to the higher demand of the sample structure and preparation steps. When promoting OER processes under high anodic potential (generally, RuO₂ > 1.4 V, and IrO₂ > 2 V), both RuO₂ and IrO₂ are unstable and oxidized to high oxidation state RuO₄/IrO₃ then dissolved in the solution (**Figure 2.6**).^[40-42] Their high catalytic

surfaces are irreversibly damaged after dissolution and no further to hold high activity. Ideas of alloying Ru with Ir and forming their bimetallic oxides are proposed, as their product turned out to be very effective and thermodynamically stable. Due to the interaction between metal sites and surface charge transfer, the existence of Ir in the bimetallic system can effectively suppress the deterioration without much performance loss. In this regard, doped bimetallic oxide system $\text{Ru}_x\text{Ir}_{1-x}\text{O}_2$ and core-shell structured $\text{IrO}_2@\text{RuO}_2$ in OER tests are designed, exhibiting significantly long-term stabilities and outstanding activities.

Figure 2.6. Electrocatalytic performance of state-of-art electrocatalysts in acidic and alkaline media. Reproduced with permission.^[39] Copyright 2014, John Wiley and Sons.

2.3.2. Transition metal (hydro-)oxides

Typically, the non-precious metal-based oxides and hydroxides can be divided into three classes for alkaline electrolytes, perovskite family (ABO_3), spinel family ($\text{A}^+\text{B}'_2\text{O}_4$), and layer structure type family. Besides, these (hydro-)oxides could be possibly considered as supports to accept single-atom doping to further improve the intrinsic activity of electrocatalytic OER.

Perovskite family (ABO_3). Perovskites can be denoted as ABO_3 formula, in which A represents the alkaline or rare-earth metal and B represents the transition metal. Both A and B occupy the octahedral voids regularly in space, for B can be considered

as taking the center place while B takes the corners of each unit cell (**Figure 2.7**). When concerning the $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ material designed by Matsumoto *et al.*, the electrocatalytic OER performance is found to increase with the amount of higher oxidation stated Co ions, implying that the OER performance is closely associated with the d-band electrons of perovskite.^[43] Bockris and Otagawa reported a tendency of OER activity as $\text{Ni} > \text{Co} > \text{Fe} > \text{Mn} > \text{Cr}$ in perovskite systems by doping different metal centers.^[44] Based on Tafel slopes and the fact that the activation energy of elemental steps changed with practical potentials, great influence has been found on their OER activity, showing a decrement from Ni to Fe samples due to the weakened B-OH bond strength.^[45] In recent years, revealed by the DFT calculations, moderate adsorption energy is suggested for the best catalytic activities towards OER that further highlight the Co- and Ni-based oxides.^[46]

Figure 2.7. (a) Structural illustration of ABO₃ type perovskite. (b,c) Theoretical correlations of perovskite compound and performance. Reprinted with permission.^[47] Copyright 2017, Royal Society of Chemistry.

Spinel family ($A'B'_2O_4$). Oxides in the spinel family follow the formula of $A'B'_2O_4$, in which A' and B' atoms represent alkaline earth metal, boron group, and 3d transition metal elements. To date, more than one hundred compounds are discovered in the spinel family. According to crystal field theory, the octahedral (O_h) and tetrahedral (T_d) sites of $A'B'_2O_4$ generate d-band splitting (O_h : $t_{2g}e_g$; T_d : $e_g t_{2g}$) of metal centers (**Figure 2.8**). As a result, spinels possess good electron conductivity and

stability in alkaline solutions under working conditions. Iron- and cobalt-based spinels are most seen in the spinel family, and secondary metal ions such as Ni, Mn, Cu, and Zn, act as dopants in the crystals. It is reported that the OER performance follows the trend of $\text{CoFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{MnFe}_2\text{O}_4$ when the second metals are incorporated in the ferrite system. However, the case for the cobalt-based system is slightly different from Ni, Cu, Li atoms doped into the $\text{M}_x\text{Co}_{3-x}\text{O}_4$ system is favorable for the OER activity, while the incorporation of Mn atoms would be harmful to the OER activity. Generally, bimetallic spinel systems present superior overall OER activity than the monometallic spinel oxides, which might be ascribed to the synergistic effect and modulated electronic structure of secondary metal centers. The coupling interaction between the electrocatalysts and substrates is also worth consideration, as the electroactive surface areas, electro-transfer, and the attachment of electrocatalysts to substrates could dominate the efficiency and durability of the catalytic materials. The spinel composition is to an extent able to avoid the deterioration under very high anodic potential by the phase transformation to metal oxyhydroxide phase with even higher OER performance, which also inspired researchers to probe the properties of layer structure-type systems.

Figure 2.8. (a) Structural illustration of $\text{A}(\text{Td})\text{B}(\text{Oh})_2\text{O}_4$ type spinel. (b) Cyclic voltammetry (CV) curves and (c) corresponding Tafel plots of samples. Reprinted with permission.^[47] Copyright 2017, Royal Society of Chemistry.

Layer structure type family. Layer structure type family contains transition metal hydroxides, denoted as $M(OH)_2$, and metal oxyhydroxides, denoted as $MOOH$, both of which are promising for delivering electrocatalytic OER with low overpotential. As the typical crystal structure for layer structured oxides is the layer-stacking configuration with proton interposing between layers to construct 2D layers, the layer structured oxides are also catalogued as layer double hydroxides (LDHs). As the research studies are gradually intensified in water splitting, the LDHs have been widely investigated as a platform to design advanced electrocatalysts with outstanding OER performance. As mentioned by Subbaraman *et al.*, the OER activity displays similar tendency as in the perovskite system as $Ni > Co > Fe > Mn$, which might be ascribed to the bond strength between Ni and OH is the most moderate.^[48] Besides, bringing in trace Fe impurity could also significantly upgrading the OER performance of $NiOOH$.^[49] With a gradual increment of Fe content to 25%, the overpotential of $Ni_{1-x}Fe_xOOH$ drops to 200 mV, suggesting that the OER performance of $NiOOH$ is tunable by introducing Fe atoms. DFT calculations propose that the Fe ions serve as active sites in $Ni_{1-x}Fe_xOOH$, responsible for the depression of overpotential.^[50-51] The enhancement of catalytic activity in Ni- and Co-based LDH is not exclusive for Fe element; introducing foreign Mn, Cr, W elements is demonstrated to have similar effects.^[52-53]

2.3.3. Non-metallic materials

Comparing to the intensive research of non-metallic materials in ORR, the studies for metal-free catalysts are just begun. Currently, these materials are mostly limited to heteroatom doped carbon, e.g., graphene and CNT, and carbon hybrids, e.g., C_3N_4 -CNT and graphene-CNT. These materials are commonly structured with high

electrochemically surface area to reach higher current density for the OER process. Nevertheless, the best of these materials, such as 3D structured non-metal electrocatalysts, and film-like electrodes, are still incomparable with the traditional metal OER catalysts.

2.4. Hydrogen Evolution Reaction (HER)

HER is a standard $2e^-$ transfer procedure which commonly follows Volmer-Heyrovsky or Volmer-Tafel pathways in mechanism. HER reaction rate presents high dependence on the binding strength of hydrogen to the surface of substrates, which can be evaluated by hydrogen absorption free energy (ΔG_{H^*}). Specifically, when the binding strength is too weak, the adsorption (Volmer) step will dominate and limit the overall reaction rate. On the other hand, when the binding strength is too strong, the desorption (Heyrovsky/Tafel) step will restrict the overall reaction speed. Hence, the ideal electrocatalyst for HER is supposed to reach a thermal-neutral stage for ΔG_{H^*} parameter to minimize the required overpotential, which is the so-called Sabatier principle. Rational regulation of binding energy of intermediates to the catalytic surface is highly demanded to design electrocatalyst with enhanced activity.^[54]

Overall reaction

(Acidic media)

(Alkaline media)

Reaction pathway

Figure 2.9. Volcano plot illustration of the experimental exchange current density vs. theoretical ΔG_{H^*} of various state-of-art electrocatalysts. Reprinted with permission.^[55] Copyright 2007, AAAS.

The volcano plot shown in **Figure 2.9** illustrates the relationship of exchange current density and computed ΔG_{H^*} parameter by DFT to theoretically predict the potential electrocatalytic performance of various materials. After experimental verification by researchers, MoS₂ presents lower exchange current density in experiments than in computational results because the ΔG_{H^*} -based model is insufficient to predict the deviations in the kinetic barrier among different types of materials. Notably, although MoS₂ thermally presents a near-neutral value in ΔG_{H^*} , it still exhibits lower exchange current density than noble metals. Thus, additional factors are believed necessary to provide corrections to the practical reaction rate. The kinetic barrier shows a strong dependence on pH value at certain potential vs. RHE and thus enables the relationship between current density and pH value. (**Figure 2.10**)^[56]

Figure 2.10. (a) Experimental and (b) computational pH-dependent current-voltage behavior for the HER/HOR on Pt-based electrode. Reproduced with permission.^[56] Copyright 2013, Springer Nature.

2.4.1. Pt and Pt/C

As aforementioned in Figure 2.10, Pt-based materials sit near the apex of the volcano plot towards HER, presenting both low ΔG_{H^*} value and high exchange current density. Similar to the ORR performance, sc-Pt also demonstrates its structural dependence in HER performance with a tendency of (110) > (100) > (111), which is in line with the trend of activation energy by Arrhenius plots.^[57] Recently, Gu et al. report the theoretical simulation and experimental verification of the superior electrochemical performance of jagged Pt nanowire towards alkaline HER.^[58] The complex surface morphology provides diverse active sites to serve different functions, such as absorption of reaction intermediates and reaction activation, giving rise to a four times increment in activity. According to their end-to-end computational results, the ΔG_{H^*} ranging from -0.2 to 0.0 eV shows more optimal for alkaline HER over the conventional thermal-neutral 0 eV. The ultrahigh activity was also unveiled by the low coordination of surface Pt with a coordination number less than 7. In addition, particle size is another critical factor for HER behavior. Sun *et al.* report the synthesis of Pt electrocatalysts ranging from NPs, clusters, and single atoms and compare their HER performance with commercial Pt/C catalysts.^[59] By precise controlling of the size and

density of Pt on substrates through the atomic layer deposition (ALD) method, the Pt single-atom catalyst presents near 37 times in terms of activity than commercial Pt/C catalysts with ultralong duration time (**Figure 2.11**). By gradually downsizing the Pt catalyst, the atomic utilization efficiency is significantly improved, and the active sites are mostly exposed to reaction agents. However, the reduction in size leads to the unsaturated coordination of the surface atoms, which requires exquisite control of the electronic structure to provide extra stabilization.

Figure 2.11. (a) LSV curve and (b) mass activities of ALD-Pt with different sizes loaded on NGN support and Pt/C catalysts. (c) Stability test of ALD50Pt/NGNs. (d) STEM image of ALD50Pt/NGNs after ALD. Scale bar, 20 nm. Reproduced with permission.^[59] Copyright 2016 Springer Nature.

Conventionally, the Pt/C degradation in alkaline media is a severe issue, which mechanism has been discussed in some recent works. Zadick and co-authors have investigated the structural evolution of Pt attached to carbon support in both acidic and alkaline media through electrochemical tests and transmission electron microscopy (TEM) observations.^[60] The TEM images display a severe degradation in 0.1 M NaOH

- 60% loss in electrochemical surface area (ECSA) after 150 cycles, which is three times worse than in acidic media. The dissolution/redeposition behavior is observed in acidic media, while near 63% Pt nanoparticles are detached from carbon support after 150 cycles in alkaline media. As the possible carbon corrosion has been excluded by the experimental results, the changes of interfaces between Pt nanoparticles and the carbon support are strongly responsible for the degradation in HER performance. The significant loss of Pt catalysts is further ascribed to modifying particle anchoring sites on the substrates. Another mechanism raised by Alinejad and co-workers attributes the severe degradation of Pt/C electrocatalysts to electrochemical Ostwald ripening, which is induced by the strong coalescence between the neighboring nanoparticles.^[61]

2.4.2. Pt-based alloys

To date, Pt-based materials still exhibit unparalleled electrocatalytic activity towards HER. To address the cost and stability issues, researchers have been focusing on alloying Pt with other metals, which can possibly improve the Pt atomic utilization efficiency and structural robustness. For example, a series of Pt-rare earth metal alloys (Ce, Sm, Ho) are developed to enhance the stability;^[62] meanwhile, PtRu alloy clusters with Pt-enriched surface presents superior durability over 50 h.^[63] The alloying effect with transition metal can not only provide structural stability but also modulate the electronic structure of Pt to achieve the high intrinsic activity. PtRu nanoclusters attached to black phosphorus nanosheets have been synthesized through the chemical reduction method by Li et al., combining the superior HER activity with outstanding stability by strong electronic interactions between PtRu and BP.^[64] Xie's group reports the design of nanostructured Pt-Ni alloy multipods in hexagonal close-packed (hcp) phase, which presents strongly enhanced intrinsic activity over commercial Pt/C and

face-centered cubic (fcc) Pt-Ni alloy.^[65] Ternary alloy is further tailored to enhance the Pt usage efficiency towards HER. Pt-Ni-Co alloy with hexapod structure is developed through chemical reduction coupled with selective etching of Ni, Co components. The usage of Co salt helps the formation of Pt-Ni-Co ternary phase by slowing down the growth of Pt nanoparticles.^[66] The PtNiCo hexapods show ten times higher performance than Pt/C in terms of specific activity, outperforming bimetallic PtNi alloys towards alkaline HER.

2.4.3. Transition metal-based materials

Recently, the transition metal-based materials show great potential in alkaline media to replace the benchmarked Pt/C catalyst with high cost-effectiveness. Moreover, the alkaline environment enables the application of various unstable materials in acidic media, involving transition metals,^[67] oxides,^[68-69] and sulfides^[70-71] based catalysts.

Transition metals and alloys. Ni-based and Co-based alloys have been broadly considered as potential replacement for Pt-based electrocatalysts towards HER owing to their outstanding performance and abundancy. The catalytic efficiency of these alloys is highly dependent on both composition and structure. For example, the Ni-based binary alloys are observed to possess the following order regarding the catalytic activity: Mo-Ni > Zn-Ni > Co-Ni > W-Ni > Fe-Ni > Cr-Ni.^[72] Meanwhile, various morphologies of binary alloys have been studied to relate the structure and activity, containing Ni-Mo powder,^[73] Ni-Cu nanocone,^[74] Ni-Cu foam,^[75] Ni-Mo film.^[76] The synthesis of MoNi₄ electrocatalysts supported by MoO₂ on Ni foam is reported by Zhang et al. through an annealing method (**Figure 2.12**).^[77] The designed 3D

structured electrode presents unparalleled HER activity with an ultralow overpotential of 15 mV at 10 mA cm^{-2} , outperforming commercial Pt/C catalysts in alkaline media.

Figure 2.12. (a) Illustration of synthetic procedure and (b,c) SEM images of MoNi₄ alloy supported by MoO₂ on Ni foam. (d) LSV curves and (e) Tafel plots of the MoNi₄/MoO₂/Ni foam electrocatalyst. Reprinted with permission^[78]. Copyright 2020, American Chemical Society.

As the nanoalloys are easily corroded, resulting in activity degradation, protective supports are of great necessity to be used together. Heteroatom-doped graphitic carbons are widely used to protect the metallic component to avoid corrosion by reducing the adsorption energy of metal.^[79-80] Du et al. demonstrate the design of binary NiFe alloy confined in N-doped graphitized carbon shell through pyrolysis of the MOF structure.^[81] The properties of the carbon shell can be modulated by the chemical state of Fe precursor. The electron transfer between NiFe alloy and carbon shell is responsible for the enhancement in durability.

Figure 2.13. Schematic illustration of the synthesis of CuCo@NC electrocatalysts. Reprinted with permission.^[82] Copyright 2017, John Wiley and Sons.

Similarly, CuCo alloys encapsulated in N-doped mesoporous carbon (CuCo@NC) are designed by Kuang et al. through thermal transformation of ZIF-67 precursor (**Figure 2.13**).^[82] The existence of Cu can elevate the N content by forming Cu-N bonds in the mesoporous carbon matrix. The CuCo@NC presents an ultrahigh surface area of $700 \text{ m}^2 \text{ g}^{-1}$ and leads to a low overpotential and outstanding stability for HER.

Transition metal compounds. Among the plethora of research regarding the transition metal compounds, Mo and W-based materials are regarded as the main branch of non-noble metal electrocatalysts and substrates for loading noble metals. The enhancement in their HER performance has been achieved by various designs, such as structural design, control of the synthetic method, modulation of electronic structure, and catalyst-support interaction. Zhang et al. report the growth of a few layers of MnO_2 nanosheets with plentiful O vacancies and secondary Mn^{3+} active sites on Ni foam, providing a favorable d-band center for hydrogen adsorption and rapid charge transfer to facilitate the HER process.^[83]

Figure 2.14. (a) Scheme of synthetic process of octahedron-structured MoN-NC. (b) TEM and (c) HRTEM of MoN-NC. (d) LSV curve and (e) Tafel plots of MoN-NC and control samples in 0.5 M H₂SO₄. Reprinted with permission.^[84] Copyright 2017, American Chemical Society.

Carbon protection is an applicable method to alleviate aggregation and tune the electronic structure of electrocatalysts. Zhu et al. report the design of MoN nanoparticles confined in N-doped carbon octahedron composite (MoN-NC) through a MOF-assisted control pyrolysis method (**Figure 2.14**).^[84] The designed MoN-NC demonstrates an outstanding HER performance in acidic media with an overpotential of 62 mV@10 mA cm⁻², surpassing bulk MoN counterpart and commercial Pt/C catalysts. Exfoliation is another common method to improve the catalytic activity of layered materials. In particular, 1T WS₂ nanosheets present enhanced exchange current density after exfoliation from 2H WS₂.^[85-86] Besides, doping secondary metal atoms into WS₂ can further modulate the electronic properties of the material. Co-doped WS₂/W₁₈O₄₉ with core-shell structure has been reported by Shi et al.^[87] and

Pt/WS₂ nanosheets have been reported by Tang et al.^[88], both of which present outstanding electrocatalytic activity compared to their WS₂ counterparts.

Chapter 3. Experimental Section

3.1. Synthesis Methodology

3.1.1. Hydrothermal/solvothermal treatment

Hydrothermal synthesis works on applying wet-chemical techniques for crystallizing substances in a sealed and heated solution with high reaction temperature and high vapor pressure. To ensure the high pressure, the hydrothermal synthesis is often performed in a steel pressure vessel named “autoclave”, where selected precursors are dispersed together with the solvent as illustrated in **Figure 3.1**.^[89] By precisely manipulating conditions of the reaction, such as solvent type, temperature and duration, the morphology and shape of the product are adjustable.

Figure 3.1. A schematic of a Teflon lined stainless steel autoclave typically used for hydrothermal synthesis. Reproduced with permission.^[89] Copyright 2014, Royal Society of Chemistry.

3.1.2. Galvanic replacement method

Galvanic replacement can be regarded as a spontaneous reduction/oxidation process, where one metal is oxidized by other metal center with higher reduction potentials, shown by the general formula: $M_{\text{noble}}^{n+} + n/m M \rightarrow M_{\text{noble}} + n/m Mm^{+}$.^[90]

The mechanism of the galvanic replacement is quite straightforward. The electrochemical reaction is carried out by the difference in reduction potential – higher reduction potential for the metal ion (M_{noble}^{n+}) and lower reduction for the secondary metal (M), contacted by the electrolyte. During the introducing of noble metal salt with higher reduction potential to a secondary metal, the selective corrosion occurs on the interface of the deposit layer and inner metal. The reaction is thermodynamically favoured owing to the difference in standard electrochemical potentials of metal species.^[91] By controlling the reaction condition, bimetallic materials with different structures and compositions can be fabricated.^[92-93]

3.2. Materials Characterization

Field-emission scanning electron microscopy (FESEM; JEOL-6700) is applied to depict the morphology, size and distribution of the designed materials. TEM imaging is performed on JEOL JEM2100F operating at 200 kV. The high acceleration voltage in TEM enables the electrons transmit through the specimen and provide a perspective view of the sample with high resolution. TEM instruments also offer different operation modes such as scanning transmission electron microscopy (STEM), and diffraction modes to provide additional structural information. Atomic-resolution high-angle annular dark-field (HAADF)-STEM imaging is performed on an aberration-corrected JEOL ARM200F, equipped with a cold field-emission gun and an ASCOR corrector operating at 200 kV. The Z-contrast in STEM arises from the differences in atomic number. The brightness of atomic column increases with higher atomic number of elements. The STEM-based energy-dispersive X-ray (EDX) spectroscopy is collected and processed in an Oxford Aztec EDX system. EDX spectroscopy can detect the characteristic X-rays of material impacted by high energy electron beam and

provide compositional information with elements from boron and up in the periodic table can be detected and identified. The compositions of the samples are analyzed by FESEM-based EDX spectroscopy. Elemental mapping images are recorded using TEM-based EDX spectroscopy (JEOL, JEM-2100F). EDX elemental mapping images, combined with the STEM images, offers further high-resolution elemental distribution of a specific area of sample. The structural information of materials is analyzed by X-ray diffraction (XRD; Bruker D2 Phaser X-ray Diffractometer) with Ni filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a current of 10 mA and a voltage of 30 kV.

X-ray absorption fine structure (XAFS) measurement are tested under a fluorescence mode at XAFCA facility of ICES which is built in Singapore synchrotron light source (SSLS). By conducting the XAFS measurements, information regarding the local structure and unoccupied local electronic states can be harvested and analyzed. The X-rays from the 2.5 GeV electron storage ring are monochromatized through the Si (III) double crystal. Typically, the samples are prepared as a compressed pellet and loaded into a cell. The energy is calibrated using metal foils. ATHENA program is applied for processing XAFS raw data with standard procedures, involving background-subtraction, normalization, and Fourier transformation to R-space.^[94-95]

3.3. Electrochemical Measurements

3.3.1. Electrochemical ORR measurements

The electrochemical test towards ORR are performed on glassy carbon disk with 5 mm in diameter that is polished with 0.05 μm alumina paste and then sonicated in distilled water and ethanol. Catalyst inks are prepared by dispersing 10 mg of catalyst materials in the mixture of ethanol (1.9 mL) and Nafion (5 wt%, 100 μL). The ink

solution is then sonicated for 30 min to get a uniform suspension. Then, 10 μL of the catalyst ink is deposited on the glassy carbon substrate to obtain a loading of 0.25 mg cm^{-2} . Platinum plate (1 cm^2) and SCE are selected as the counter electrode and reference electrode, respectively. All potentials in this study are measured against the SCE reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale by $E_{(\text{RHE})} = E_{(\text{SCE})} + 0.059 \text{ pH} + 0.242$. The electrochemical measurements are carried out at room temperature in a conventional three-electrode cell with 0.1 M KOH solution using an RDE setup from Pine Instrument Company connected to an Autolab potentiostat/galvanostat (Model PGSTAT-72637) workstation. The working electrode is scanned in 0.1 M KOH solution by CV and LSV at 10 mV s^{-1} . Before CV and RDE tests, the 0.1 M KOH solution is bubbled with oxygen for 30 min. The current densities in RDE data are normalized to the geometric area (0.196 cm^2) of the glassy carbon disk.

3.3.2. Electrochemical OER measurements

The electrochemical measurements towards OER are carried out on glassy carbon disk with 5 mm in diameter that is polished with 0.05-micron alumina paste and then sonicated in distilled water and ethanol. Catalyst inks are prepared by dispersing 1 mg of catalyst materials in the mixture of isopropanol (0.2 mL) and Nafion (5 wt%, 10 μL). The ink solution is then sonicated for 30 min to get a uniform suspension. Then, 10 μL of the catalyst ink is deposited on the glassy carbon substrate to obtain a loading of 0.25 mg cm^{-2} . Platinum plate (1 cm^2) and Ag/AgCl (KCl saturated) electrode are selected as the counter electrode and reference electrode, respectively. All potentials are measured against the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale by $E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + 0.059\text{pH} + 0.197$.

The electrochemical measurements are carried out at room temperature in a conventional three-electrode cell with 1.0 M KOH solution using a rotating disk electrode (RDE) setup from Pine Instrument Company connected to an Autolab potentiostat/galvanostat (Model PGSTAT-72637) workstation. Linear sweep voltammetry (LSV) is recorded with a scan rate of 5 mV s⁻¹ at the rotating speed of 1600 rpm to obtain the polarization curves. All the data presented are corrected for iR losses. The current densities in LSV are normalized to the geometric area (0.196 cm²) of the glassy carbon disk. Chronoamperometric measurements are performed on carbon fiber paper (CFP) substrates to activate the sample and evaluate the long-term stability.

3.3.3. Electrochemical HER measurements

Electrochemical measurements for HER were conducted on a CHI 760E electrochemical workstation with a conventional three-electrode cell at room temperature (~ 25 °C). The working electrode was prepared as follows: 3.0 mg of catalyst was dispersed in the mixture of ethanol (0.6 mL) and Nafion (5 wt%, 30 µL) under ultrasonication for 30 min. A homogeneous catalyst ink was obtained by sonicating the mixed solution for 5 min. Then, the above suspension (20 µL) was dropped on a piece of clean carbon fiber paper (0.5 cm × 0.5 cm) and dried at room temperature. The mass loading of catalysts was 0.4 mg cm⁻². For HER in 0.5 M H₂SO₄ (pH = 0), carbon rod and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. For HER in 1.0 M KOH (pH = 14), carbon rod and mercury oxide (Hg/HgO) electrodes were used as the counter electrode and reference electrode, respectively. The LSV curves were collected with a scan rate of 5 mV s⁻¹. The potentials were calibrated to reversible hydrogen electrode (RHE)

according to the Nernst equation: $E \text{ (V vs. RHE)} = E \text{ (V vs. Hg}_2\text{Cl}_2/\text{Hg,Cl}^-) + 0.241 + 0.0592 \times \text{pH}$ for pH = 0 test, and $E \text{ (V vs. RHE)} = E \text{ (V vs. Hg/HgO)} + 0.098 + 0.0592 \times \text{pH}$ for pH = 14 test. The ohmic drop correction was performed by the method of positive feedback, and the compensation level is 95%. All LSV curves were corrected with iR-compensation.

Chapter 4. Co–Fe alloy/N-doped carbon hollow spheres derived from dual metal–organic frameworks for enhanced electrocatalytic oxygen reduction[†]

4.1. Introduction

Oxygen reduction reaction (ORR) is an important electrocatalytic reaction for metal-air batteries and fuel cells.^[20, 96-100] Nevertheless, the efficiency of these electrochemical devices has been constrained by the sluggish kinetics of the ORR. So far, platinum (Pt)-based materials have been considered as the most active catalysts for ORR.^[14, 101-102] However, the scalable application of the catalysts for ORR cannot be realized if expensive Pt-based catalysts are not replaced by other low-cost and high-performance electrode materials. Transition metal/N-doped carbon composite materials consisting of metal-nitrogen coordinated sites as catalytically active centers in carbon matrix have recently been considered as potential alternative electrocatalysts for ORR.^[36, 103-105] In particular, the electrocatalysts with multi-metal-nitrogen coordinated sites have been demonstrated to further promote their catalytic activity and selectivity.^[106-108] In addition to the compositional control of the electrocatalysts, the enhancement of electrochemical performance can also be achieved by optimization of their nanostructures. Porous hollow particles with separated nanosized active sites and porous nanoshells have been widely used as nanoreactors in electrocatalysis. Apart from the shortened diffusion pathway for electrons/reactants, the discrete active sites in porous shells can also effectively prevent site overlap and thus increase the

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electrocatalytic activity and stability.^[109-111] However, controllable synthesis of hollow structured multi-metallic alloy/N-doped carbon catalysts with separated nanosized active sites and porous carbon matrix towards high electrocatalytic performance still remains a great challenge, because of the difficulty in achieving relatively even distribution of multiple metal species in composite precursors and inhibiting the aggregation of the *in situ* formed alloy nanoparticles at high temperature.

In recent years, MOFs have been regarded as promising precursors to derive metal/carbon-based functional materials for various energy-related applications.^[112-114] Nevertheless, most MOFs-derived synthetic methods are based on simple MOF precursors.^[115] As such, their derived metal/carbon-based composite materials often possess sole metal species and solid structures after thermal treatment under inert atmosphere.^[116-117] Therefore, rational design and preparation of relatively complex MOF composite precursors via the introduction of other MOFs or functional materials as co-precursors might be a suitable way for synthesis of hollow structured multi-metal/carbon-based electrocatalysts.^[106, 118]

In this chapter, we report a dual-MOF-assisted synthesis of Co-Fe alloy@N-doped carbon hollow spheres as an efficient electrocatalyst for ORR. Distinct from previous studies, the present synthetic approach relies on confined nanospace thermal transformation reaction of Fe-based MIL-101 nanoparticles in Co-based ZIF-67 nanoshell (**Figure 4.1**). The introduction of the second MOF nanoparticles into a MOF shell as co-precursor ensures evenly confined pyrolysis of MIL-101 nanocrystallites inside ZIF-67 nanoshell and easy production of small bimetallic Co-Fe alloy nanoparticles in N-doped carbon framework, which cannot be fabricated by direct pyrolysis of sole MIL-101 or ZIF-67. Benefiting from the rich catalytically active sites and porous conductive matrix, the as-prepared Co-Fe alloy@N-doped carbon hollow

spheres manifest excellent electrocatalytic performance with enhanced activity and stability.

Figure 4.1. Schematic illustration of the formation process of Co-Fe alloy/N-doped carbon hollow spheres. PS@MIL-101/ZIF-67 core-shell composites are synthesized from coprecipitation of PS spheres, MIL-101 nanocrystallites and Co^{2+} ions in the presence of organic ligand 2-MIM. The PS@MIL-101/ZIF-67 core-shell composites are further converted to Co-Fe alloy/N-doped carbon hollow spheres via the annealing treatment under N_2 atmosphere.

4.2. Experimental Measurements

4.2.1. Materials synthesis

Synthesis of ZIF-67 particles. To synthesize ZIF-67 particles, 3 mL of 20 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ methanol solution and 5 mL of 160 mM 2-MIM methanol solution are mixed and then allowed to react at room temperature for 2 h without stirring. The product is then collected by centrifugation and washed with ethanol several times.

Synthesis of the MIL-101 nanocrystallites. Briefly, 0.29 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is dissolved in 40 mL of dimethylformamide (DMF, solution A), refluxing at 160 °C for 15 min. The 0.2 of 2-aminoterephthalic acid powder is dissolved in 10 mL of DMF (solution B). Then the solution B is added into the solution A dropwise. The reaction

mixture is stirred for another 10 min, before lifted up from oil bath. After cooling to room temperature, the dark brown product is recovered and washed with ethanol several times. Then the as-prepared MIL-101 nanocrystallites are dispersed in 10 mL of methanol solution of PVP (0.5 g, $M_w = 55000$), and the mixture is further stirred at room temperature for 12 h. The PVP-functionalized MIL-101 nanocrystallites are collected by centrifugation, washed by methanol several times, and dispersed in 5 mL of methanol for further use.

Synthesis of PS spheres. The PS spheres are synthesized according to a previously reported method. In a typical synthesis, 0.11 g of sodium lauryl sulfate and 0.1 g of potassium persulfate are dissolved in 70 mL of aqueous alcohol (50 mL of ethanol and 20 mL of deionized water) in a 250 mL two-neck flask. Prior to use, the styrene is treated with 10 % sodium hydroxide solution in a separatory funnel three times in order to remove the anti-polymerizer. Then 4.5 mL of styrene is added into the flask under nitrogen atmosphere and rapid stirring, and the emulsion solution is heated to 70 °C to polymerize for 8 h. After the polymerization reaction has come to completion, keeping the reaction condition, another 4.5 mL of styrene diluted with four times volume absolute alcohol was added to react for another 8 h. Then the obtained PS spheres with the particle size of about 1.3 μm are collected by centrifugation and dispersed in 10 mL of ethanol solution of PVP (0.5 g, $M_w = 55000$), and the mixture is further stirred at room temperature for 12 h. The PVP-functionalized PS spheres are collected by centrifugation, washed by ethanol several times, and dispersed in 30 mL of methanol for further use.

Synthesis of the PS@MIL-101/ZIF-67 core-shell particles. To synthesize PS@MIL-101/ZIF-67 core-shell particles, 1 mL of MIL-101 nanocrystallites suspension, 0.05 mL of PS spheres suspension, 3 mL of 20 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

solution, and 5 mL of 160 mM 2-MIM solution are mixed and then allowed to react at room temperature for 2 h without stirring. The product is then collected by centrifugation, washed with methanol several times, and vacuum dried overnight.

Synthesis of the Co-Fe alloy/NC hollow spheres. The obtained PS@MIL-101/ZIF-67 core-shell particles are placed in a ceramic boat, heated to 200 °C at a ramp rate of 5 °C min⁻¹ and maintained for 2 h in a tube furnace under nitrogen atmosphere. The temperature in the furnace is further raised to 700 °C at a ramp rate of 5 °C min⁻¹ and kept at that temperature for 2 h. After that, the furnace is cooled down to room temperature naturally.

4.3. Results and Discussion

4.3.1. Formation and characterization of Co-Fe alloy/NC hollow sphere structure

Monodisperse polystyrene (PS) spheres are synthesized through an emulsion polymerizing method (**Figure 4.2a-c**),^[119] while another co-precursor MIL-101 nanocrystallites are prepared via a hydrothermal method (Figure 4.2d-f).^[120] The surfaces of both PS spheres and MIL-101 nanoparticles are further functionalized with polyvinylpyrrolidone (PVP). The growth of MIL-101/ZIF-67 composite nanoshells on PS templates is conducted by adding MIL-101 nanoparticles, Co(NO₃)₂, and 2-methylimidazole (2-MIM) into the suspension of PS spheres. Due to the nucleophile functional groups on the surface of PS spheres and MIL-101 nanocrystallites, the Co²⁺ ion and 2-MIM tend to form ZIF-67 shells on the PS surface and MIL-101 surface. With the thickness of ZIF-67 shell gradually increasing, the ZIF-67 shells are combined together and fix MIL-101 nanocrystallites on the surface of PS spheres. The amount of captured MIL-101 nanocrystallites is highly depended on the concentration of the MIL-101 in the solution, which will result in different molar Fe to Co ratio in

final alloy product. The dark purple PS@MIL-101/ZIF-67 product is produced after 2 hours at room temperature (**Figure 4.3**). FESEM image reveals the morphology of the resultant PS@MIL-101/ZIF-67 spheres (Figure 4.2g). Uniform PS@MIL-101/ZIF-67 composite spheres are fully covered with MIL-101 nanocrystallites. TEM images show that PS@MIL-101/ZIF-67 core-shell spheres consist of many MIL-101 nanoparticles evenly distributed in the dual-MOF composite nanoshells (Figure 4.2h,i).

Figure 4.2. (a,d,g) FESEM and (b,c,e,f,h,i) TEM images of (a-c) PS spheres, (d-f) MIL-101 nanocrystallites, and (g-i) PS@MIL-101/ZIF-67 core-shell composites.

Figure 4.3. Photographs of the mixed solution for the preparation of the PS@MIL-101/ZIF-67 core-shell composites.

As shown in the powder X-ray diffraction (XRD) patterns, the PS@MIL-101/ZIF-67 composite spheres exhibit a similar diffraction pattern as ZIF-67 (**Figure 4.4**). Compared with the diffraction peaks of ZIF-67, the unique peaks associated with MIL-101 at around 10° are very weak, probably due to its low-degree crystallinity. Additionally, the existence of MIL-101 in the PS@MIL-101/ZIF-67 product is further demonstrated by energy-dispersive X-ray spectroscopy (EDX) measurement (**Figure 4.5**).

Figure 4.4. XRD patterns of PS@MIL-101/ZIF-67 core-shell composites, MIL-101 nanocrystallites and ZIF-67 polyhedra.

Figure 4.5. EDX analysis of (a) PS@MIL-101/ZIF-67 core-shell composites, (b) MIL-101 nanocrystallites, (c) PS spheres.

Besides, the density of MIL-101 nanocrystallites encapsulated in composite nanoshells and shell architecture can be finely tuned by adjusting the amount of MIL-101 nanocrystallites and concentration of Co^{2+} ions and 2-MIM added in the reaction system (**Figure 4.6-4.8**). During this process, the optimal amount of MIL-101 suspension is found to be 1.0 mL to form Co-Fe alloy with molar Co to Fe ratio of around 7:3 in the upcoming thermal treatment.

Figure 4.6. (a-e) FESEM and (f-o) TEM images of PS@MIL-101/ZIF-67 core-shell composites prepared with different amount of MIL-101 suspension: (a,f,k) 0.125 mL, (b,g,l) 0.25 mL, (c,h,m) 0.5 mL, (d,i,n) 1.5 mL and (e,j,o) 3 mL.

Figure 4.7. (a-d) FESEM and (e-l) TEM images of PS@MIL-101/ZIF-67 core-shell composites prepared with different concentration of $\text{Co}(\text{NO}_3)_2$ solution: (a,e,i) 5 mM, (b,f,j) 10 mM, (c,g,k) 40 mM and (d,h,l) 80 mM.

Figure 4.8. (a-c) FESEM and (d-i) TEM images of PS@MIL-101/ZIF-67 core-shell composites prepared with different concentration of 2-MIM solution: (a,d,g) 40 mM, (b,e,h) 80 mM and (c,f,i) 320 mM.

The Co-Fe alloy/N-doped carbon hollow spheres are fabricated via annealing treatment of the PS@MIL-101/ZIF-67 precursors at 700 °C under N₂ atmosphere. The pyrolysis product is denoted as Co-Fe/NC-700, where the number in the sample abbreviation represents pyrolysis temperature. The role of the pyrolysis is to conduct thermal reduction for Fe³⁺ and Co²⁺ ions by carbon, while controlling the degree of alloying and the size of nanoparticles by heating temperature. The FESEM images of the Co-Fe/NC-700 spheres reveal that the sample maintains its original morphology after the annealing process (**Figure 4.9a-c**). The structure of the Co-Fe/NC-700 spheres is further elucidated by TEM image (Figure 4.9d). The hollow nanostructures are produced as the result of the decomposition of PS cores after the thermal treatment. Meanwhile, the Fe³⁺ and Co²⁺ ions in the dual-MOF shells are transformed to Co-Fe alloy nanoparticles, and the organic ligands in each MOF serve as nitrogen and carbon sources for the formation of N-doped carbon frameworks. The organic ligands are gradually carbonized during the elevation of temperature to form N-doped carbon. The Fe³⁺ and Co²⁺ ions are then reduced by new generated carbon under the N₂ protection to form small alloy nanoparticles on the interface of ZIF-67 and MIL-101. Closer examination on a Co-Fe/NC-700 hollow sphere shows the porous texture of the obtained nanoshell, which consists of many small Co-Fe alloy nanoparticles (Figure 4.9e,f). High-resolution TEM (HRTEM) image shows the lattice fringes of the alloy nanoparticles, which can be correlated to the (110) planes of Co_{0.7}Fe_{0.3} alloy phase (Figure 4.9g). The selected area electron diffraction (SAED) pattern also verifies the alloy phase of the sample (Figure 4.9h).

Figure 4.9. (a-c) FESEM images, (d-f) TEM images, (g) HRTEM image, (h) SAED pattern, and (i) HAADF-STEM and elemental mapping images of Co-Fe/NC-700 hollow spheres.

Distinct from these Co-Fe alloy/N-doped carbon hollow spheres with well-defined structure, a mixture of aggregated Fe-Fe₃C large particles and carbon nanocages (Fe-Fe₃C/NC-700) as well as Co/N-doped carbon solid particles (Co/NC-700) are produced by direct pyrolysis of MIL-101 nanocrystallites and ZIF-67 polyhedra at 700 °C (**Figure 4.10, 4.11**), respectively. Therefore, the encapsulation of MIL-101 nanocrystallites in the ZIF-67 nanoshell is not only essential to successfully produce bimetallic Co-Fe alloy through high-temperature transformation reaction, but also to realize the confined nanospace pyrolysis to form small alloy nanoparticles in carbon matrix. The crystalline structure of the Co-Fe alloy is further determined by powder XRD analysis (**Figure 4.12a**). The diffraction pattern of the Co-Fe/NC-700

product is indexed to $\text{Co}_{0.7}\text{Fe}_{0.3}$ and $\text{Co}_{0.72}\text{Fe}_{0.28}$ alloy phases (JCPDS card No. 50-795 and 51-740). The EDX analysis reveals the existence of Fe, Co, C, and N elements in the pyrolysis product (Figure 4.12b). These elements are homogeneously distributed in the shells of Co-Fe/NC-700 hollow spheres (Figure 4.9i).

Figure 4.10. TEM images of (a,b) Fe- Fe_3C /NC-700 and (c,d) Co/NC-700 particles.

Figure 4.11. XRD pattern of (a) Fe- Fe_3C /NC-700 particles, (b) Co/NC-700 particles.

Figure 4.12. (a) XRD pattern (b) EDX spectrum of Co-Fe/NC-700 hollow spheres.

For comparison, Co-Fe/N-doped carbon samples with different crystalline phases are prepared by tuning the pyrolysis temperature from 600 °C to 900 °C. FESEM and TEM characterizations confirm that the Co-Fe/NC-600, Co-Fe/NC-800 and Co-Fe/NC-900 samples show similar features in morphology and structure as Co-Fe/NC-700 hollow spheres (**Figure 4.13-4.15**).

Figure 4.13. (a,b) FESEM and (c,d) TEM images of Co-Fe/NC-600 hollow spheres.

Figure 4.14. (a,b) FESEM and (c,d) TEM images of Co-Fe/NC-800 hollow spheres.

Figure 4.15. (a,b) FESEM and (c,d) TEM images of Co-Fe/NC-900 hollow spheres.

The crystalline structure and composition for each composite material are further determined by XRD and X-ray photoelectron spectroscopy (XPS) analysis (**Figure 4.16, 4.17**). When the pyrolysis temperature is increased from 600 °C, to 800 °C, then to 900 °C, the crystalline phase of the resultant products is varied from low-crystallinity Co/Fe species, to mixture of Co-Fe alloy, metallic Fe and Co, then to mixture of metallic Fe and Co (Figure 4.16a). XPS measurements further reveal the valence state and content of different elements in Co-Fe/NC products. Most Fe and Co elements in the Co-Fe/NC-600 sample exhibit high oxidation valence (Figure 4.16b,c), possibly due to incomplete reduction of metal species under low pyrolysis temperature

of 600 °C. When the temperature is further increased to 700 °C, the amount of Fe and Co elements with high oxidation valence quickly decreases. Metallic Fe⁰ and Co⁰ become dominant, revealing the formation of Co-Fe alloy. By further increasing the temperature from 800 °C to 900 °C, the metallic Fe⁰ and Co⁰ gradually decreases, possibly because of the inferior stability of the *in situ* formed metallic Fe and Co compared with alloy.^[121] As the metal-nitrogen coordinated sites in the carbon matrix are the catalytically active centers of the electrocatalysts, the number of active centers strongly relies on N content for each sample.^[122-125] The high-resolution N 1s spectra (Figure 4.16d) reveal the existence of four types of nitrogen species, pyridinic-N at ~398.7 eV, pyrrolic-N at ~400.1 eV, graphitic-N at ~401.1 eV and oxidic-N at ~403.2 eV. Among these Co-Fe/N-doped carbon composites, the Co-Fe/NC-700 sample exhibits higher N content than other three control samples.

Figure 4.16. (a) XRD patterns and (b-d) XPS spectra of Co-Fe/NC composites prepared at different annealing temperatures of 600 °C, 700 °C, 800 °C and 900 °C. High-resolution spectra of (b) Fe 2p, (c) Co 2p and (d) N 1s.

Figure 4.17. XPS spectra of Co-Fe/NC composites prepared at different annealing temperatures of 600 °C, 700 °C, 800 °C and 900 °C. (a) Survey spectra and high-resolution spectra of (b) C 1s and (c) O 1s.

4.3.2. Electrochemical measurements

The electrocatalytic activity of the Co-Fe/NC, Co/NC and Fe-Fe₃C/NC samples are investigated by RDE measurements in O₂-saturated KOH solution (**Figure 4.18a**). Both Co-Fe/NC-700 and Co-Fe/NC-800 samples consisting of Co-Fe alloy nanoparticles show superior ORR activity over the commercial Pt/C catalyst (20 wt.%; Johnson Matthey) in terms of half-wave potential (0.854 V and 0.842 V vs. 0.835 V). Compared with these catalysts with bimetallic alloy nanoparticles, Co-Fe/NC-900, Co-Fe/NC-600, Co/NC-700 and Fe-Fe₃C/NC-700 consisting of separated Co and/or Fe-based active sites manifest inferior half-wave potentials of 0.820 V, 0.787V, 0.808 V and 0.766 V (**Figure 4.18a**; **Figure 4.19**), respectively. The improved electrocatalytic activity of bimetallic alloy catalysts might be attributed to the optimization of binding energy of O species via alloying Fe and Co in N-doped carbon matrix.^[107] Of note, Co-Fe/NC-700 hollow spheres show similar Tafel slope as Pt/C catalyst, further confirming the remarkable electrocatalytic activity for the Co-Fe/NC-700 sample.

RDE measurements at different rotating speeds from 100 to 2500 rpm are further used to study the electrocatalytic kinetics of the Co-Fe/NC-700 sample (**Figure 4.20a**). The electron number (n) per O_2 involved in the ORR for the Co-Fe/NC-700 sample is calculated via the corresponding Koutecky-Levich (K-L) plots (**Figure 4.20b**, Supporting Information). The n value is determined to be about 3.81, suggesting that the oxygen reduction is dominated by the four-electron process. As the most active catalyst, the stability test of the Co-Fe/NC-700 sample is further examined via chronoamperometric response (**Figure 4.18c**). 97.7% of the original current density is maintained for the Co-Fe/NC-700 electrode after 8 h, whereas the commercial Pt/C catalyst exhibits much higher current loss of 12.8%. The Co-Fe/NC-700 retains its structure and composition after stability test (**Figure 4.21**).

Figure 4.18. Electrocatalytic performance evaluation of Co-Fe/NC composites prepared at different annealing temperatures of 600 °C, 700 °C, 800 °C and 900 °C. (a) LSV curves in O_2 -saturated 0.1 M KOH solution with a sweep rate of 10 mV s $^{-1}$ at the rotating speed of 1600 rpm. (b) Tafel slopes curves. (c) Chronoamperometric response at 0.5 V for 8 h. (d) Chronoamperometric response at 0.5 V after the introduction of 30 mL of methanol into 150 mL of 0.1 M KOH solution.

Figure 4.19. LSV curves of Co-Fe/NC-700, Fe-Fe₃C/NC-700, Co/NC-700 and a commercial Pt/C catalyst in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ at the rotating speed of 1600 rpm.

Figure 4.20. (a) LSV curves of Co-Fe/NC-700 in O₂-saturated 0.1 M KOH solution with a sweep rate of 10 mV s⁻¹ at different rotating speeds ranging from 100 to 2500 rpm. (b) Corresponding Koutecky-Levich plots (j^{-1} vs. $\omega^{-1/2}$) at different potentials from 0.3 to 0.7 V from the LSV curves.

The Co-Fe/NC-700 sample and the commercial Pt/C catalyst are further compared by investigating the methanol crossover through chronoamperometric response. A significant reduction in the current density can be detected by the addition of methanol for the Pt/C catalyst, whereas the current density is not sensitive to the addition of methanol in the case of the Co-Fe/NC-700 catalyst (Figure 4.18d). The overall electrocatalytic performance of Co-Fe/NC-700 material is comparable to many metal/carbon-based electrocatalysts.^[126-128]

Figure 4.21. (a) FESEM image and (b) XRD pattern of Co-Fe/NC-700 hollow spheres after electrochemical stability test for 8 h.

Compared with other MOF-derived synthetic methods reported previously, this strategy employs dual-MOF precursors consisting of discrete Fe-based MIL-101 nanoparticles evenly encapsulated in Co-based ZIF-67 shells. Additionally, the nanospace-confined thermal transformation process guarantees even pyrolysis and conversion of Fe^{3+} and Co^{2+} ions in dual-MOF nanoshells to Co-Fe alloy, and prohibits excessive growth of active alloy nanoparticles in porous carbon matrix. The enhanced ORR performance of the Co-Fe alloy/N-doped carbon sample might be attributed to the following aspects. First, the bimetal-nitrogen coordinated active sites might grant high catalytic activity by optimizing the binding energy of O species through alloying Fe and Co.^[107] Second, the sufficiently separated small Co-Fe alloy nanoparticles and N-doped carbon matrix render large active surface. Also, the porous structure and graphitic carbon effectively facilitate the mass/charge transport throughout these hollow particles, thus promoting the oxygen reduction process.

4.4. Summary

In this chapter, a dual-MOF-assisted pyrolysis approach is developed to synthesize Co-Fe alloy/N-doped carbon hollow spheres. The feature of this new approach is that

each Co-base ZIF-67 nanoshell can effectively encapsulate many Fe-based MIL-101 nanocrystallites. These PS@dual-MOF composite nanostructures can be converted into a hollow structured electrocatalyst consisting of separated Co-Fe alloy nanoparticles in the porous N-doped carbon framework. The as-prepared Co-Fe alloy/N-doped carbon hollow spheres show enhanced electrocatalytic activity for oxygen reduction reaction compared with the catalysts consisting of separated Fe or/and Co species. This multi-MOF composite precursor approach can be applied for the design and construction of many other functional materials for different energy-related applications.

Chapter 5. Metal Atom-Doped Co₃O₄ Hierarchical Nanoplates for Electrocatalytic Oxygen Evolution[†]

5.1. Introduction

The oxygen evolution reaction (OER) is of critical importance as the key electrocatalytic reaction in water splitting devices and rechargeable metal-air batteries.^[3, 129-134] Nevertheless, the multi-step proton-coupled electron transfer processes involved in OER lead to the sluggish kinetics, which severely constrains the energy conversion efficiency.^[135] To date, noble metal oxides, in particular RuO₂ and IrO₂, are demonstrated to be the most effective electrocatalysts for OER.^[136] However, due to the scarcity and preciousness of the noble metal constituents, mass production of OER catalysts cannot be fulfilled unless replaced by other earth-abundant materials with comparable OER activity.^[11, 47, 137] Transition metal oxides (TMOs), in particular Co₃O₄ which contains highly oxidized redox couples, have recently been considered as promising alternatives to noble metal oxides for efficient OER in alkaline media.^[138-140] However, the activity of reported Co₃O₄-based catalysts can rarely be comparable to the high activity of noble metal oxides. Surface modulation is an efficient way to enhance the intrinsic activity by lowering the high driving force required by overpotential through tuning their surface structure and electronic properties.^[141-143] Among various surface modulation strategies, the incorporation of a secondary metal atom into the lattice of TMOs has been demonstrated to remarkably improve their

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catalytic performance.^[70, 144-145] Therefore, rational introduction of isolated metal atoms into the crystal lattice of Co₃O₄ host is expected to promote its electrocatalytic OER activity.

In addition, design and construction of peculiar nanoarchitectures for electrocatalysts has been regarded as another efficient strategy for the enhancement of electrocatalytic performance by exposing more electrochemically active sites.^[146] Particularly, hierarchical nanostructures can offer great benefits for the construction of advanced electrocatalysts because they combine the advantages of both low dimensional building blocks and hierarchically porous structures.^[147] Low-dimensional nanosized building blocks, especially ultrathin nanosheets or nanoneedles, can not only expose abundant catalytically active sites, but also shorten the charge transport distance.^[148] Moreover, hierarchically macro-/mesoporous structures are particularly beneficial for increasing the efficiency of mass transport, and thus promoting the formation and release of gas-phase catalytic products.^[149-150] Based on these design rationales mentioned above, hollow nanostructures assembled by heteroatom-doped Co₃O₄ ultrathin nanosheets could serve as excellent catalysts for OER.

Metal-organic frameworks (MOFs) have become a rapidly expanding research area in the past two decades.^[151-154] The most distinctive advantage of MOFs is their designable frameworks formed via modular self-assembly reactions of metal ions/clusters and organic ligands.^[155-157] Although their chemical instability often prevents them from being used directly as electrocatalysts for OER, it offers us many possibilities to chemically convert to various nanostructures, in which some advantages of MOFs can be well inherited.^[158-159] Here, we report a cooperative etching-coordination-reorganization strategy for the introduction and stabilization of

isolated metal atoms in hierarchical Co_3O_4 hollow nanoplates (NPs) with cross channels (**Figure 5.1**). Novel NPs of Co-based zeolitic imidazolate framework-67 (ZIF-67) are employed as the precursors for the synthesis of metal atom-doped Co_3O_4 electrocatalysts. By introducing the guest metal salt as a Lewis acid into the reaction system, the acid etching reaction induces the transformation of ZIF-67 from solid NPs to hollow NPs with unique cross channels. Meanwhile, the guest metal species is adsorbed on the inner and outer surfaces of the hollow ZIF-67 NPs. After a solvothermal reaction, these hollow ZIF-67 NPs are transformed into hierarchical Co_3O_4 NPs assembled by ultrathin nanosheets. Moreover, the adsorbed metal atoms are successfully incorporated into the octahedral sites of Co_3O_4 . Owing to the structural and compositional merits, the Fe-doped Co_3O_4 hierarchically hollow NPs (designated as Fe- Co_3O_4 HHNPs) exhibit superior OER performance with a small overpotential of 262 mV to reach the current density of 10 mA cm^{-2} , enhanced kinetics with a Tafel slope of 43 mV dec^{-1} , and excellent stability at ultrahigh current densities, which are much better than that of Co_3O_4 HHNPs and even commercial RuO_2 catalysts in alkaline solution.

Figure 5.1. The schematic synthesis process of cross-channeled Fe- Co_3O_4 HHNPs.

5.2. Experimental Measurements

5.2.1. Materials synthesis

Synthesis of ZIF-67 nanoplates. To synthesize ZIF-67 nanoplates, 0.124 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 21 mL of deionized water containing 0.0288 g of cetyltrimethylammonium bromide (CTAB, solution A). The solution B (5 mL of aqueous solution containing 1.2 g of 2-methylimidazole) is rapidly injected into solution A and stirred rapidly at room temperature for 1 h. Then the mixed solution is transferred into a Teflon-lined stainless-steel autoclave and kept at 120 °C for 10 h. After cooling to room temperature, the ZIF-67 nanoplates are collected by centrifugation, washed with ethanol once, and dispersed in 10 mL of ethanol for further usage.

Synthesis of Fe-doped ZIF-67 nanoplates with cross channels. A Lewis acid etching method is used to synthesize Fe-doped ZIF-67 nanoplates with cross channels. 1 mL of ZIF-67 nanoplates solution is rapidly injected into 10 mL of 0.8 mg mL⁻¹ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ethanol solution. After aging for 10 min, the solution turns green. The product is collected by centrifugation, washed with ethanol several times, and dispersed in 5 mL of ethanol for further usage.

Synthesis of Fe-doped Co_3O_4 hierarchically hollow nanoplates (Fe- Co_3O_4 HHNPs). To prepare hierarchical cross-channeled Fe- Co_3O_4 hollow nanoplates, the 5 mL of Fe-doped ZIF-67 nanoplates are first diluted to 20 mL by ethanol, after addition of 5 mL of H_2O , transferred to a 50 mL round-bottomed flask, heated by oil bath, underwent a solvothermal treatment to 90 °C with magnetic stirring of 600 rpm and kept for 15 min till the color fully turns black. After that, the product is collected by centrifugation, washed with ethanol several times, and vacuum dried overnight.

Synthesis of ZIF-67 nanoplates with cross channels. Brønsted acid etching is used to synthesize ZIF-67 nanoplates with cross channels. 1 mL of ZIF-67 nanoplates suspension prepared above is rapidly injected into 10 mL of 1.16×10^{-3} M and 2.32×10^{-3} M HCl ethanol solution. After aging for 10 min, the solution turns blue. The product is collected by centrifugation, washed with ethanol several times, and dispersed in 5 mL of ethanol for further usage.

Synthesis of Co_3O_4 hierarchically hollow nanoplates. To prepare hierarchical Co_3O_4 hollow nanoplates, the 5 mL of ZIF-67 nanoplates (after acid etching) is first diluted to 20 mL by ethanol, after addition of 5 mL of H_2O , transferred to a 50 mL round-bottomed flask, heated by oil bath, underwent a solvothermal treatment to 90°C with magnetic stirring of 600 rpm and kept for 30 min till the color fully turns black. After that, the product is collected by centrifugation, washed with ethanol several times, and vacuum dried overnight.

Synthesis of M-doped ZIF-67 plates with cross channels. Certain amount of metal salts is dissolved in 10 mL of ethanol or methanol solution without further pH control, noted as solution A (2 mg mL^{-1} for $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ ethanol solution, 1 mg mL^{-1} for ZrCl_4 ethanol solution, 1 mg mL^{-1} for NbCl_5 ethanol solution, 1 mg mL^{-1} for WCl_6 ethanol solution, 4 mg mL^{-1} for $\text{Mn}(\text{Ac})_2$ methanol solution, 4 mg mL^{-1} for $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ methanol solution, 4 mg mL^{-1} for $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ methanol solution, 4 mg mL^{-1} for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ethanol solution, 4 mg mL^{-1} for ZnCl_2 ethanol solution, 4 mg mL^{-1} for $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ethanol solution, 4 mg mL^{-1} for SnCl_2 ethanol solution, 4 mg mL^{-1} for BiCl_3 ethanol solution). The prepared 2 mL of ZIF-67 plates is rapidly injected into solution A and aged for several minutes. The M-ZIF-67 product is further collected by centrifugation, washed with ethanol several times, and dispersed in 5 mL of ethanol for further usage.

Synthesis of different isolated metals doped Co_3O_4 (M- Co_3O_4 HHNPs). The synthetic methods for M- Co_3O_4 are similar to that of the Fe- Co_3O_4 sample. To prepare the M-doped Co_3O_4 nanosheet-constructed hollow plates, the 5 mL of M-doped ZIF-67 plates is first diluted to 20 mL by ethanol, after addition of 5 mL of H_2O , transferred to a 50 mL round-bottomed flask, heated by oil bath, underwent a solvothermal treatment to 90 °C with magnetic stirring of 600 rpm and kept for 15 min till the color fully turns black. After that, the product is collected by centrifugation, washed with ethanol several times, and vacuum dried overnight.

5.2.2. Computational methodology

Spin-polarized density functional theory (DFT) calculations were performed in the plane wave and ultrasoft pseudopotential as implemented in Quantum ESPRESSO.^[160] The adsorption energies were calculated with Perdew–Burke–Ernzerhof (PBE) exchange functional correction.^[161] The effective U-J terms, from linear response theory,^[162] were 3.0 and 3.5 for Fe and Co, respectively. The kinetic energy cutoffs of 35 Ry and 350 Ry were chosen for the wave functions and augmented charge densities. All the atomic structures for the models were fully relaxed with self-consistency criteria of 10^{-6} Ry and all atomic coordinates were converged to within 10^{-3} Ry/bohr for maximal components of forces. The occupancy of the one-electron states was calculated using an electronic temperature of $k_{\text{B}}T=0.01$ Ry for surfaces. All energies were extrapolated to $T = 0$ K. Vacuum slab of 12 Å was used for surface isolation to prevent interaction between two surfaces. All the atoms were relaxed to simulate bulk structure and relax top layer in slab system. Reciprocal space was sampled by the Γ -centered Monkhorst-Pack scheme with $5*3*1$ for slab, $5*5*1$ for DOS calculation.

The correction calculated using the harmonic approximation for every adsorbate and surface, with typical values of +0.35 eV, +0.05 eV and +0.40 eV for HO*, O* and HOO* respectively.

Final ΔG_{i^*} formula can be summarized by:

$$\Delta G_1 = \Delta E_{OH^*} + 0.35 \text{ eV} - eU$$

$$\Delta G_2 = \Delta E_{O^*} - \Delta E_{OH^*} - 0.30 \text{ eV} - eU$$

$$\Delta G_3 = \Delta E_{OOH^*} - \Delta E_{O^*} + 0.35 \text{ eV} - eU$$

$$\Delta G_4 = \Delta E_{OO^*} - \Delta E_{OOH^*} - eU$$

It is worth mentioning that some structures cannot be normally optimized under different adsorption conditions. Therefore, the linear relationship between the adsorbed species is predicted by using the previous reports of Nørskov and coworkers.^[163]

5.3. Results and Discussion

5.3.1. Formation processes

Figure 5.2. Schematic illustration and structural characterizations of ZIF-67 NPs, cross-channelled Fe-ZIF-67 NPs and Fe-Co₃O₄ HHNPs. (a) The schematic synthesis process of cross-channelled Fe-Co₃O₄ HHNPs. (b-j) FESEM (b,e,h) and TEM (c,d,f,g,i,j,k) images of ZIF-67 NPs (b-d), cross-channelled Fe-ZIF-67 NPs (e-g) and Fe-Co₃O₄ HHNPs (h-k). (l) HRTEM images of Fe-Co₃O₄ HHNPs, and (m) HAADF-STEM image and elemental mapping images of one Fe-Co₃O₄ HHNP.

ZIF-67 NPs are first prepared through a surfactant-assisted hydrothermal reaction. FESEM and TEM images reveal that these ZIF-67 NPs are uniform with an average side length of about 900 nm and thickness of about 160 nm (**Figure 5.2b-d**). After a Lewis acid etching treatment in 0.8 mg mL⁻¹ FeCl₂ ethanol solution for 10 min at room

temperature, orthogonal channels are formed in ZIF-67 NPs. Figure 5.2e shows a typical FESEM image of the as-formed NPs with internal cross channels. The average particle size does not change significantly during the etching process. TEM images confirm the existence of orthogonal channels in each nanoplate (Figure 5.2f,g). Energy-dispersive X-ray (EDX) spectroscopy reveals that a small amount of Fe species is incorporated into the as-formed cross-channeled ZIF-67 NPs (thereafter denoted as Fe-ZIF-67), where the molar ratio of Fe to Co is about 1:22.9 (**Figure 5.3**).

Figure 5.3. EDX analysis of cross-channeled Fe-ZIF-67 NPs, showing the molar ratio of Fe to Co is about 1:22.9.

Next, the as-prepared Fe-ZIF-67 NPs are refluxed in a mixed solvent of ethanol and water to gradually form Fe-Co₃O₄ nanosheets. Finally, Fe-ZIF-67 NPs are completely transformed into Fe-Co₃O₄ HHNPs with cross channels. EDX analysis of the product shows the existence of Fe, Co and O elements in the sample (**Figure 5.4**). The disappearance of the N element verifies that the Fe-ZIF-67 sample is completely converted to Fe-Co₃O₄ HHNPs after the solvothermal treatment. The low Fe/Co molar ratio of 1:30.6 suggests that the Fe atoms might be doped into the lattice of Co₃O₄ in the form of isolated atoms. The content of Fe and Co is also revealed to be 3.1 and

70.2 wt% with an atomic ratio of 0.05 by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement.

Figure 5.4. EDX analysis of cross-channeled Fe-Co₃O₄ HHNPs, showing the molar ratio of Fe to Co is 1:30.6.

Figure 5.2h shows an FESEM image of the as-derived Fe-Co₃O₄ HHNPs at a low magnification. The sample retains its nanoplate morphology, but the surface becomes very rough after the solvothermal treatment. The structure of the Fe-Co₃O₄ HHNPs is further elucidated by TEM, showing the hierarchically porous structure with orthogonal channels and nanosheet subunits (Figure 5.2i,j). A closer examination of the nanosheet subunits reveals that the thickness of the nanosheets is only about 2 nm (Figure 5.2k).

Figure 5.5. N₂ sorption isotherms of Fe-Co₃O₄ HHNPs.

N₂ sorption measurements reveal that the Fe-Co₃O₄ HHNPs possess a porous structure with a relatively high specific surface area of about 60 m² g⁻¹ (**Figure 5.5**). High-resolution TEM (HRTEM) image (Figure 5.2l) shows the lattice fringes of the ultrathin nanosheets, which can be ascribed to the (311) planes of cubic spinel Co₃O₄ (JCPDS card No. 42-1467). As revealed by HAADF-STEM and elemental mapping results, Fe, Co and O elements are evenly distributed throughout the Fe-Co₃O₄ HHNP (Figure 5.2m).

5.3.2. Materials characterization

To further investigate the impact of the etching-coordination process on ZIF-67 NPs, X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) spectroscopies are conducted to characterize the crystalline phase and coordination configurations of Co and Fe in Fe-ZIF-67 NPs. As shown in **Figure 5.6a**, XRD pattern of the Fe-ZIF-67 NPs is the same as that of ZIF-67 NPs, suggesting that the Fe species is doped into the ZIF-67 NPs. The existing forms of the metal elements are first revealed by extended X-ray absorption fine structure (EXAFS) analysis. In Figure 5.6b, the Fourier transform (FT) of Fe K-edge EXAFS of Fe-ZIF-67 shows a dominating peak of Fe-N at 1.53 Å, which overlays with the Co-N peak at 1.56 Å for the CoN₄ moiety, suggesting the incorporated Fe centers partially substitute for the Co sites in the CoN₄ imidazole tetrahedra.^[164] The similar pattern in EXAFS further confirms that Fe atoms have taken the Co positions (**Figure 5.7a**). The FT of EXAFS profile of Fe-ZIF-67 also exhibits minor signals located at 2.60 Å and 3.04 Å, which respectively arise from Fe-C and Fe-Fe from the second neighbor correlation.^[148] The FT of Co K-edge EXAFS (Figure 5.6b) and the normalized X-ray absorption near-edge structure (XANES) spectra (Figure 5.6c) of Fe-ZIF-67 are observed in excellent accordance

with unetched ZIF-67, confirming the good reservation of the original coordination structure of ZIF-67 after the etching-coordination treatments.

Figure 5.6. Phase and structural characterizations of Fe-ZIF-67 NPs and Fe-Co₃O₄ HHNPs. (a) XRD patterns of ZIF-67 NPs and Fe-ZIF-67 NPs. (b) Fourier transform (FT) of EXAFS $k^3\chi(k)$ spectra of Fe-ZIF-67 with Fe foil and ZIF-67 as the references. (c) Normalized Fe K-edge (up), Co K-edge (bottom) XANES spectra of Fe-ZIF-67 with Fe foil, Co foil, ZIF-67 as references. (d) XRD patterns of Co₃O₄ HHNPs and Fe-Co₃O₄ HHNPs together with the standard pattern of Co₃O₄. (e) FT of EXAFS $k^3\chi(k)$ spectra of Fe-Co₃O₄ with Fe foil and Co₃O₄ as references. (f) Normalized Fe K-edge (up), Co K-edge (bottom) XANES spectra of Fe-Co₃O₄ with Fe foil, Co foil and Co₃O₄ as the references.

Figure 5.7. EXAFS spectra of the (a) Fe-ZIF-67 NPs, (b) Fe-Co₃O₄ HHNPs.

We next investigate the local structure of Fe and Co centers in Fe-Co₃O₄. Both XRD patterns of the obtained Co₃O₄ and Fe-Co₃O₄ products can be well indexed to the cubic spinel Co₃O₄ phase (JCPDS card No. 42-1467; Figure 5.6d). X-ray photoelectron spectroscopy (XPS) analysis is further carried out to study the surface chemical states of Fe-Co₃O₄ HHNPs. The survey spectrum (**Figure 5.8a**) shows the presence of C, O, Co, and Fe, which is consistent with the EDX result. The peak-fitting analysis of Co 2p spectrum (Figure 5.8b) suggests that there are two chemical states, corresponding to Co²⁺ at 781.6 eV and 797.3 eV and Co³⁺ at 780.4 eV and 796.0 eV.^[139] The high-resolution O 1s spectrum (Figure 5.8c) can be deconvoluted into two peaks, namely the Co-O peak at 530.4 eV and Co-O-H peak at 531.7 eV.^[164] The Fe 2p spectrum (Figure 5.8d) shows a pair of relatively weak peaks for Fe³⁺ at 711.7 eV and 724.9 eV, which also confirms the successful incorporation of Fe atoms.

Figure 5.8. XPS spectra of Fe-Co₃O₄ HHNPs: (a) survey spectrum and (b-d) high-resolution spectra of Co 2p (b), O 1s 2p (c), Fe 2p (d).

The FT of Fe K-edge EXAFS spectrum of Fe-Co₃O₄ illustrates a dominating peak centered at 1.50 Å, which is assigned to the Fe-O bonding at the first shell (Figure 5.6e). In contrast to Fe foil, the Fe-Fe coordination peaks at 2.20 Å and 3.47 Å are

absent in Fe-Co₃O₄, ruling out the existence of aggregated Fe clusters or particles. From EXAFS spectra (Figure 5.7b) of Fe-Co₃O₄, the Fe K-edge exhibits similar oscillation shape to Co K-edge ranging from 3 to 10 Å⁻¹ by wavenumber (*k*), which suggests that Fe atoms have been successfully doped into the Co₃O₄ lattice. The disordered structure of Fe centers is verified by the lower magnitude of Fe K-edge than the Co K-edge. The main peak of the Fe K-edge has shifted to lower *k* compared with the Co K-edge in EXAFS spectra of Fe-Co₃O₄, implying that the Fe dopants mainly occupy the octahedral sites of high oxidation state Co(III), which has been demonstrated by the similar magnitude of Co EXAFS spectra of Fe-Co₃O₄ and Co₃O₄.^[165] The Co K-edge XANES profiles of Fe-Co₃O₄, Co₃O₄ and Co foil are also evaluated to study the local structure regarding Fe coordination in Co₃O₄. As shown in Figure 5.6f, the Co XANES spectrum of Fe-Co₃O₄ resembles that of Co₃O₄, indicating the similar valence of Co species in both samples.

Figure 5.9. Synthetic etching-coordination and hydrolysis processes. (a-e) TEM images of single ZIF-67 NP (a) and (b-e) the corresponding products obtained by etching in 10 mL of FeCl₂·4H₂O ethanol solution with different concentrations for 10 min: (b) 0.4 mg mL⁻¹, (c) 0.8 mg mL⁻¹, (d) 1.2 mg mL⁻¹, and (e) 1.6 mg mL⁻¹. (f-j) TEM images of the products obtained by hydrolysis of cross-channelled Fe-ZIF-67 NPs etched in 0.8 mg mL⁻¹ for different durations: (f) 0 min, (g) 3 min, (h) 6 min, (i) 9 min, and (j) 15 min.

To investigate the structural evolution process and conversion mechanism, the etching reaction is carried out in FeCl₂ ethanol solutions with different ion

concentrations. When $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is added into ethanol, it will hydrolyze to generate the acidic environment for the etching process. When the ZIF-67 NPs (**Figure 5.9a**) are dispersed in 0.4 mg mL^{-1} FeCl_2 ethanol solution for 10 min, the etching process begins selectively at the center of four side surfaces forming a thin cross in each nanoplate (**Figure 5.9b**). When the concentration is increased to 0.8 mg mL^{-1} , the orthogonal channels are enlarged (**Figure 5.9c**). By increasing the FeCl_2 concentration to 1.2 then to 1.6 mg mL^{-1} , the orthogonal channels are further expanded (**Figure 5.9d**) until the nanostructure breaks down into four separate parts (**Figure 5.9e**). In addition, we have also investigated the transformation process from Fe-ZIF-67 NPs to Fe- Co_3O_4 HHNPs under the solvothermal treatment. As elucidated by the TEM images of the samples collected at different reaction stages, the hydrolysis process starts at the outer surface and channel walls of the Fe-ZIF-67 precursor simultaneously, and the Fe-ZIF-67 residue is gradually consumed and converted into hierarchical hollow nanoplates constructed from ultrathin Fe- Co_3O_4 nanosheets (**Figure 5.9f-j**).

Figure 5.10. TEM images of (a) ZIF-67 NP and (b,c) products obtained by acid etching in 10 mL of (b) $1.16 \times 10^{-3} \text{ M}$ and (c) $2.32 \times 10^{-3} \text{ M}$ HCl ethanol solution for 10 min.

It is found that the etching process is largely ascribed to the Lewis acidity of FeCl_2 salt. Control experiments are conducted by replacing the FeCl_2 ethanol solution with a low concentration HCl solution. As expected, the exactly same etching processes can be observed, resulting in cross-channeled ZIF-67 NPs (**Figure 5.10**). With this understanding, the present method can easily be extended for incorporation

of many other metals into ZIF-67 NPs, ranging from III B to V A group in the periodic table, to generate metal-doped ZIF-67 (M-ZIF-67) NPs with cross channels. During this process, the ZIF-67 NPs are steadily etched by protons released from the hydrolysis of metal cations, generating a cross-channeled structure for M-ZIF-67 NPs. Remarkably, similar nanostructures can be formed with the addition of 13 metal salts in total, which can be transformed to corresponding M-Co₃O₄ HHNPs after the solvothermal treatment. **Figure 5.11a** presents the overview of M-ZIF-67 NPs and corresponding M-Co₃O₄ HHNPs (M = Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, W, In, Sn, Bi, and La). TEM images of M-ZIF-67 NPs and M-Co₃O₄ HHNPs are displayed in Figure 5.11b.

Figure 5.11. Universality of the cooperative etching-coordination-reorganization approach for different M-Co₃O₄ HHNPs. (a) The 13 metal elements in the periodic table for M-Co₃O₄ HHNPs. (b) TEM images of M-ZIF-67 NPs (left) and M-Co₃O₄ HHNPs (right) of 12 metal elements.

5.3.3. Electrochemical measurements

For the Co₃O₄ HHNPs decorated with 6 first row transition elements (M=Mn, Fe, Co, Ni, Cu, and Zn), electrocatalytic OER tests are carried out (**Figure 5.12**). From the criteria of overpotential and Tafel slope, the Fe-Co₃O₄ electrocatalyst exhibits the best performance and thus is selected as the main sample for further detailed investigation of the effects of atomic doping and nanostructure engineering on the OER performance.

Figure 5.12. (a) LSV curves and (b) Tafel plots of cross-channelled M-Co₃O₄ HHNPs.

The electrocatalytic activity of Fe-Co₃O₄, Co₃O₄ and commercial RuO₂ catalysts toward OER is investigated in alkaline solution (1.0 M KOH). **Figure 5.13a** shows the *iR*-compensated LSV curves. The Fe-Co₃O₄ catalyst requires an overpotential of 262 mV to reach the current density of 10 mA cm⁻², which is 52 and 126 mV lower than that required for the Co₃O₄ and commercial RuO₂ catalysts respectively to achieve the same current density. Moreover, the current density of the Fe-Co₃O₄ catalyst can reach 100 mA cm⁻² at the overpotential of 303 mV, which is 120 mV lower than that of Co₃O₄ sample. In sharp contrast, the commercial RuO₂ catalyst is not able to deliver a current density of 100 mA cm⁻² in the applied potential range. The lowest overpotential and fastest current density rise of Fe-Co₃O₄ demonstrate the importance of heteroatom doping and nanostructure engineering for enhancing the electrocatalytic activity. The Tafel plots of these catalysts are investigated to get some insight into their OER kinetics. As can be seen in Figure 5.13b, the Fe-Co₃O₄ catalyst exhibits enhanced reaction kinetics with the lowest Tafel slope of 43 mV dec⁻¹ compared with 72 mV dec⁻¹ (for Co₃O₄) and 83 mV dec⁻¹ (for RuO₂), which is consistent with the fastest current density rise of Fe-Co₃O₄ in Figure 5.13a.

Figure 5.13. Electrocatalytic OER performance. (a) LSV curves, (b) Tafel plots, and (c) $(j_a - j_c)/2$ as a function of scan rate of Fe-Co₃O₄ HHNPs, Co₃O₄ HHNPs, and commercial RuO₂ catalysts. (d) ECSA-normalized LSV curves (Inset: a bar chart of the ECSA), (e) potential-dependent TOF curves, (f) the corresponding bar graph of the ECSA-normalized current density (red) and TOF values (blue) at the overpotentials of 300 mV, and (g) EIS Nyquist plots for different electrocatalysts. (h,i) Chronopotentiometry curves of (h) Fe-Co₃O₄ HHNPs and commercial RuO₂ at the current density of 10 mA cm⁻², and (i) Fe-Co₃O₄ HHNPs at the current densities of 10, 50, 100 mA cm⁻² for 50 h.

Electrochemically active surface area (ECSA) of the catalysts is calculated based on the double-layer capacitance (C_{dl}).^[166] The cyclic voltammograms (CVs) are obtained in the voltage range of 1.18 - 1.28 V in which there are no redox processes. From the CVs, the C_{dl} is extracted by plotting $(j_a - j_c)/2$ versus scan rate, where j_a and j_c are the anode and cathode current densities at 1.23 V respectively (**Figure 5.14**).

Figure 5.14. Cyclic voltammogram (CV) curves at different scan rates for (a) Fe-Co₃O₄ HHNPs, (b) Co₃O₄ HHNPs, and (c) commercial RuO₂ nanoparticles.

The Fe-Co₃O₄ catalyst exhibits the highest C_{dl} of 20.2 mF cm⁻², which is much higher than that of Co₃O₄ (7.0 mF cm⁻²) and commercial RuO₂ (1.7 mF cm⁻²) catalysts (Figure 5c). As expected, the Fe-Co₃O₄ catalyst possesses the largest ECSA of 504 cm² (normalized per cm² of electrode area), which is much higher than that of Co₃O₄ (175 cm²) and commercial RuO₂ (42 cm²) (Figure 5.13d). Importantly, from the ECSA-normalized LSV curves (Figure 5.13d), the Fe-Co₃O₄ catalyst still exhibits the highest activity. To further elucidate the intrinsic mechanism for the enhancement of OER activity, per-site turnover frequency (TOF) is employed to compare the practical performance of catalysts. The TOF value is calculated based on the assumption that all metal atoms are active sites, and the number of metal atoms is obtained from ICP-AES results.^[167] The corresponding potential-dependent TOF curves show the enhanced intrinsic activity per site in Fe-Co₃O₄ compared to Co₃O₄ and RuO₂ (Figure 5.13e). We have also provided a bar graph of ECSA-normalized current densities and TOF values at an overpotential of 300 mV (Figure 5.13f). As can be seen, the Fe-Co₃O₄ catalyst has shown much higher current density and TOF value (0.033 mA cm⁻²; 0.0169 s⁻¹) than Co₃O₄ (0.006 mA cm⁻²; 0.0016 s⁻¹) and RuO₂ (0.003 mA cm⁻²; 0.0003 s⁻¹), suggesting that the Fe dopants significantly influence the coordination environment and symmetry of Co sites, thus greatly improve the intrinsic activity of active Co sites. Greatly increased TOF values by this heteroatom doping strategy are

commonly observed in previous studies.^[148, 168] Clearly the enhanced electrocatalytic activity of Fe-Co₃O₄ can be mainly attributed to the Fe doping. This is also verified by electrochemical impedance spectroscopy (EIS) that the Fe-Co₃O₄ catalyst exhibits nearly identical charge transfer resistance as Co₃O₄ (Figure 5.13g).^[169]

The long-time operational stability is a major challenge for the practical application of electrocatalysts, which is more severe under a large catalytic current density. As shown in the chronopotentiometry tests (Figure 5.13h), the potential of commercial RuO₂ increases rapidly within 0.6 h even at a small current density of 10 mA cm⁻², which could be attributed to the formation of soluble high oxidation state Ru species under highly anodic potential.^[170] In contrast, benefiting from the high stability and reversibility of the spinel structure, the Fe-Co₃O₄ catalyst shows a negligible change of OER potential under the same constant current density after continuous operation for 50 h (Figure 5.13i), suggesting the superior structural and phase stability of the Fe-Co₃O₄ catalyst. We have also carried out water oxidation at higher current densities of 50 mA cm⁻² and 100 mA cm⁻², where only insignificant potential rise is observed after 50 h (Figure 5.13i). The structural and compositional evolutions during the electrochemical tests are also investigated for further understanding of the high stability. The Fe-Co₃O₄ catalyst is harvested from the electrode after the stability test for 50 h at 10 mA cm⁻². It is observed from FESEM and TEM images that the structure of HHNPs is well preserved (**Figure 5.15**).

Figure 5.15. (a) FESEM and (b) TEM images of Fe-Co₃O₄ HHNPs after the stability test for 50 h.

Moreover, post-mortem XRD characterization shows that no additional crystalline phase is observed and the overall crystal structure remains as Co_3O_4 after the long-term OER test (**Figure 5.16**).

Figure 5.16. XRD patterns of Fe- Co_3O_4 HHNPs before and after the stability test for 50 h.

XPS Co 2p spectra show that the $2p_{1/2}$ and $2p_{3/2}$ peaks of Fe- Co_3O_4 after the stability test are shifted toward lower binding energy, suggesting partial surface oxidation of Co^{2+} to Co^{3+} (**Figure 5.17**).

Figure 5.17. Co 2p spectra of Fe- Co_3O_4 HHNPs before and after the stability test for 50 h.

HRTEM images of Fe- Co_3O_4 before and after the stability test show that some crystalline Co_3O_4 on surface is oxidized to form a layer of amorphous high-valent oxyhydroxide (**Figure 5.18**), which is consistent with results reported in literature.^[171]

Figure 5.18. HRTEM images of Fe-Co₃O₄ HHNPs (a) before and (b) after the stability test for 50 h.

The electrocatalytic performance of these Fe-Co₃O₄ HHNPs in alkaline electrolyte is among the best when compared with numerous Co-based electrocatalysts (Table 5.1).

Table 5.1. Comparisons of the OER activity of Fe-Co₃O₄ with other recently reported Co-based catalysts.

Catalyst	Electrolyte	Overpotential / mV @10 mA cm ⁻²	Reference
Fe-Co ₃ O ₄	1 M KOH	262	This work.
Co ₃ O ₄ /N-rmGO	1 M KOH	310	Nat. Mater. 2011 , 10, 780.
CoO _x -ZIF/C	1 M KOH	318	Adv. Funct. Mater. 2017 , 27, 1702546.
Plasma engraved Co ₃ O ₄	0.1 M KOH	300	Angew. Chem. Int. Ed. 2016 , 55, 5277.
CoO _x @CN supported on Ni foam	1 M KOH	260	J. Am. Chem. Soc. 2015 , 137, 2688.
NiCo-UMOFNs	1 M KOH	250	Nat. Energy 2016 , 1, 16184.
A-CoS _{4.6} O _{0.6} PNCs	1 M KOH	290	Angew. Chem. Int. Ed. 2017 , 56, 4858.
Gelled FeCo oxyhydroxides	1 M KOH	277	Science 2016 , 352, 333.
SC CoO NRs	1 M KOH	330	Nat. Commun. 2016 , 7, 12876.
Fe ₃ O ₄ @Co ₉ S ₈	1 M KOH	320	Adv. Funct. Mater. 2016 , 26,

/rGO-2			4712.
Co@Co ₃ O ₄ /N C-2	0.1 M KOH	390	Angew. Chem. Int. Ed. 2016 , 55, 4087.
Co ₃ O ₄ /porous carbon	0.1 M KOH	360	Adv. Funct. Mater. 2014 , 24, 7655.
Au@Co ₃ O ₄ core-shell nanocrystals	1 M KOH	350	Adv. Mater. 2014 , 26, 3950.
FeCoO _x	0.1 M KOH	400	J. Am. Chem. Soc. 2014 , 136, 17530.
Co-UNMs	1 M KOH	307	ACS Catal. 2018 , 8, 1913.
CoO/Co ₃ O ₄	1 M KOH	260	Angew. Chem. Int. Ed. 2020 , 59, 6929.
Co ₂ Mo ₃ O ₈ @N C-800	1 M KOH	331	Angew. Chem. Int. Ed. 2020 , 10.1002/anie.202004533.
Co ₃ O ₄ /CeO ₂ NHs	1 M KOH	270	Adv. Mater. 2019 , 31, 1900062.
Co ₃ O ₄ /Co-Fe oxide DSNBs	1 M KOH	297	Adv. Mater. 2018 , 30, 1801211.
F-CoOOH/NF	1 M KOH	270	Angew. Chem. Int. Ed. 2018 , 57, 15471.

The enhanced OER performance is mainly attributed to the Fe doping of Co₃O₄ ultrathin nanosheets, as well as the hierarchical structure. Some preliminary density functional theory (DFT) calculations are performed to understand the effect of Fe doping on the enhanced electrocatalytic activity. For Co₃O₄ catalysts, the adsorption energy difference from the O* to OH* intermediates at the reactive sites are suggested to have dominant effect on the overall OER activity.^[172-173] After incorporating isolated Fe atoms into the lattice of Co₃O₄, the DFT result shows that the adsorption energy difference from OH* to O* is significantly reduced from 1.90 eV to 1.54 eV (Figure 5.19, 5.20), suggesting the rate-determining step (RDS) is OH⁻ + HO* = O* + H₂O(l) + e⁻.

Figure 5.19. (a) The optimized Fe-Co₃O₄ model for calculation. (b) Crystal model of Co₃O₄.

Figure 5.20. Free energy diagram for the OER process over Co sites.

In view of the ultrathin (~ 2 nm) nature of these Fe-Co₃O₄ nanosheets, all doped Fe atoms should exist near the surface.^[174-175] It is thus easy to understand that the doping of even small amount of Fe atoms will have profound enhancement in electrocatalytic activity as suggested by the DFT results.

5.4. Summary

In this chapter, hierarchical cross-channeled hollow nanoplates constructed with ultrathin Co₃O₄ nanosheets have been prepared by a facile etching-coordination-reorganization method. Importantly this method allows simultaneous incorporation of a secondary metal species. In total, 13 metal elements have been successfully doped

into the ultrathin Co_3O_4 nanosheets in the form of isolated metal sites. As an example, the doping of Fe atoms in the octahedral sites of Co_3O_4 has greatly enhanced the intrinsic electroactivity of the obtained Fe- Co_3O_4 catalyst for the oxygen evolution reaction (OER). The ultrathin nanosheet subunits and highly porous structure with cross-channels expose abundant active sites and facilitate the charge and mass transport. Significantly, the as-prepared Fe- Co_3O_4 electrocatalyst exhibits remarkable catalytic activity toward OER with an overpotential of 262 mV to reach the current density of 10 mA cm^{-2} , and show excellent stability even at a high current density of 100 mA cm^{-2} for 50 h.

Chapter 6. Engineering Pt-Co Nano-alloys in Porous Nitrogen-Doped Carbon Nanotubes for Highly Efficient Electrocatalytic Hydrogen Evolution[†]

6.1. Introduction

Hydrogen is an ideal zero-carbon energy carrier and has a strategic position in the development of the sustainable future society.^[2, 176] As an essential hydrogen production technology, renewable energy-driven electrolysis of water for hydrogen production urgently needs highly efficient electrocatalysts to reduce overpotential and improve energy conversion efficiency.^[177-178] Electrocatalysts usually show faster kinetics towards the hydrogen evolution reaction (HER) under acidic and alkaline environments over neutral media because of the relatively high ionic concentration of H^+ and OH^- respectively, thus representing practicable conditions for industrial water electrolysis.^[179-180] So far, carbon-supported platinum (Pt), “the Holy Grail” of HER electrocatalyst, presents the most optimal adsorption and recombination of hydrogen intermediates (e.g., H^*) among other carbon-supported metals, ensuring the low overpotential and fast kinetics towards HER in acidic media.^[181] However, nanoparticle (NP) agglomeration and metal dissolution during the long-term operation will result in the loss of active sites, which is mainly responsible for the rapid degradation of catalytic activity and stability in acidic electrolyte.^[121, 182] In contrast, hydrogen production by water-alkali electrolysis is favored by the industry due to its unlimited reactant availability, good manufacturing safety, stable output, and high

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product purity.^[183-185] However, limited by the low abundance of H^+ ions in alkaline media, the initiation of HER requires massive dissociation of water molecules, leading to a two to three orders of magnitude decrease in reaction rate than that in acidic media.^[186-189] Therefore, it still remains challenging in developing Pt-based electrocatalysts with outstanding activity, fast kinetics, long-term stability, and high tolerance in both strongly acidic and alkaline environments.

To overcome the challenges associated with Pt-based catalysts, delicate design of the carbon support and alloy composition is advantageous for enhancing the stability in acidic media and boosting activity in alkaline media. For example, enhancing the metal-support interaction can considerably alleviate the aggregation of NPs and induce the synergistic effect to promote the activity.^[190-191] Among various supports, nitrogen-doped porous carbon materials are primarily developed in view of their strong anchoring effect, conductive network, and high surface area.^[147, 192-194] On the other hand, nano-alloying can effectively promote the water dissociation for alkaline HER with lower Pt usage to boost HER properties.^[65] Alloying Pt with 3d-transition metal can effectively reduce the precious metals usage at the expense of non-noble metals, adjust the electronic structure of Pt for enhanced hydrolysis, introduce diversified active sites, and thus boost the intrinsic activity for HER.^[195] Besides, due to the large lattice mismatch between Pt and 3d-transition metals, the alloying process is expected to induce lattice strain and altered surface properties, which often lead to enhancement in catalytic efficiency.^[196-197] In conventional designs, noble metal particles are usually attached on the surface of porous carbon support or embedded inside, it will be difficult to achieve high utilization efficiency and catalytic stability simultaneously.^[63, 158] To this end, it is desirable to control the spatial distribution of alloy NPs on the carbon support with maximized exposure of active sites.

Metal-organic frameworks (MOFs), assembled by metal ions/clusters and organic ligands with distinct crystalline structures, are highly designable precursors/templates for engineering the nanoarchitecture of derived materials through many controlled thermal annealing and wet chemical reactions.^[198-200] Among them, zeolitic imidazolate frameworks (ZIFs) possessing high structural stability can be thermally converted to porous nanostructures without significant morphological changes.^[201-203]

6.2. Experimental Measurements

6.2.1. Materials synthesis

Preparation of ZIF-67 nanorods (ZIF-67 NRs). 3.6 g of 2-methylimidazole is dissolved in 30 mL of deionized water containing 0.126 g of cetyltrimethylammonium bromide (CTAB, solution A). Solution B (3 mL of aqueous solution containing 0.372 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) is rapidly injected into solution A and stirred rapidly at room temperature for 5 min. Then the mixed solution is transferred into a Teflon-lined stainless-steel autoclave and kept at 120°C for 10 h. After cooling to room temperature, the ZIF-67 NRs are collected by centrifugation, washed with ethanol several times, and dispersed in 30 mL of ethanol for further usage.

Preparation of ZIF-67@PDA NRs. 5 mL of the ZIF-67 NR ethanol solution and 10 mg of dopamine hydrochloride are dispersed into a Tris ethanol solution (10 mM, 20 mL) with magnetic stirring for 30 min. The resultant ZIF-67@PDA NRs products are collected by centrifugation, washed three times with ethanol, and dispersed in 5 mL of ethanol for further usage.

Synthesis of Co@N-doped carbon nanotubes (Co@NCNT). The obtained ZIF-67@PDA NRs are placed in a ceramic boat, heated to 300°C at a ramp rate of 1 °C

min⁻¹, and maintained for 2 h in a tube furnace under nitrogen atmosphere. The temperature in the furnace is further raised to 500°C at a ramp rate of 1 °C min⁻¹ and kept at that temperature for 1 h. After that, the furnace is cooled down to room temperature naturally.

Preparation of Pt₃Co@NCNT. 10 mg of as-prepared Co@NCNT and 2 mL of 10 mg mL⁻¹ K₂PtCl₄ water solution were added to 8 mL of deionized water under magnetic stirring. The resulting solution was stirred at 80°C for 24 h. After the reaction, the precursor (denoted as pre-Pt₃Co@NCNT) was collected by centrifugation, washed once with ethanol, and dried at 70°C overnight. The obtained precursors were then placed in a ceramic boat, heated to 300°C at a ramp rate of 2 °C min⁻¹ and maintained for 1 h then heated to 500°C at a ramp rate of 2 °C min⁻¹ and maintained for 8 h in a tube furnace under nitrogen atmosphere. After that, the furnace was cooled down to room temperature naturally.

Preparation of PtCo@NCNT. 10 mg of as-prepared Co@NCNT and 1.25 mL of 10 mg mL⁻¹ K₂PtCl₄ water solution were added to 8.75 mL of deionized water under magnetic stirring. The resulting solution was stirred at 50°C for 18 h. After the reaction, the precursor (denoted as pre-PtCo@NCNT) was collected by centrifugation, washed once with ethanol, and dried at 70°C overnight. The obtained precursors were then placed in a ceramic boat, heated to 300°C at a ramp rate of 2 °C min⁻¹ and maintained for 1 h then heated to 500°C at a ramp rate of 2 °C min⁻¹ and maintained for 8 h in a tube furnace under nitrogen atmosphere. After that, the furnace was cooled down to room temperature naturally.

6.2.2. Computational details

Theoretical calculations were performed in the Materials Studio program equipped with the DMol³ package. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correction potential was used. A double-numerical basis set with polarization functions was applied. To calculate the hydrogen atom adsorption free energy, three-layer slab (111) surface models with the bottom two layers fixed were used. Pure Pt, Pt₃Co, and PtCo alloy models were calculated. A 15 Å vacuum space was applied along the z-direction in a 2×4 unit cell. A 9 × 5 × 1 Monkhorst-Pack k-point mesh was used. On each surface model, different adsorption sites were tested for seeking the most stable configuration. The free energy difference (ΔG) of the hydrogen atom was calculated by $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE , ΔZPE , T , and ΔS denote the total energy difference, zero-point energy change, temperature, and entropy difference, respectively. In this work, the total energy difference of $\Delta ZPE - T\Delta S$ was calculated to be 0.25 eV.

6.3. Results and Discussion

6.3.1. Formation processes

Herein, we first synthesize novel Co-based ZIF-67 nanorods (NRs) as the starting material. We then report a pyrolysis-replacement-reorganization strategy to obtain ultrafine Pt-Co alloy NPs (sub-10 nm) supported on the inner and outer shells of porous nitrogen-doped carbon nanotubes (designated as Pt-Co@NCNT) with closed ends. The detailed synthesis process is shown in **Figure 6.1**. In the first step, ZIF-67 NRs coated with polydopamine (PDA) are thermally transformed to Co NPs confined in porous N-doped carbon nanotubes (designated as Co@NCNT). By a simple galvanic replacement reaction with a K₂PtCl₄ solution, the Co NPs are converted to Pt-

Co NPs confined in the nanotubes (denoted as pre-Pt-Co@NCNT). Thermal annealing is further used to improve the Pt-Co alloy crystallinity, which at the same time induces the migration of alloy NPs to the inner and outer shells of the nanotubes. Owing to the optimized electronic structure brought by alloying and strong metal-support interactions, the obtained Pt₃Co@NCNT electrocatalyst exhibits high activity and ultralong stability towards HER in both acidic and alkaline media.

Figure 6.1. Schematic illustration for the synthesis of Pt-Co@NCNT.

6.3.2. Materials characterizations

ZIF-67 NRs with a square cross section are first synthesized through a surfactant-assisted solvothermal method. The FESEM, TEM, and HAADF-STEM images display the uniform NR structure with an average length of about 1 μm and width of about 100 nm (**Figure 6.2**).

Figure 6.2. (a) FESEM, (b,c) TEM, and (d) HAADF-STEM images of ZIF-67 NRs.

A thin layer of PDA is then coated on ZIF-67 NRs to form ZIF-67@PDA NRs (**Figure 6.3**). The X-ray diffraction (XRD) pattern confirms that ZIF-67@PDA NRs retain the crystalline phase of ZIF-67 (**Figure 6.4**).

Figure 6.3. (a) FESEM, (b,c) TEM, and (d) HAADF-STEM images of ZIF-67@PDA NRs.

Figure 6.4. XRD patterns of ZIF-67 NRs and ZIF-67@PDA NRs.

Next, ZIF-67@PDA NRs are annealed at 500 °C under N₂ atmosphere for the conversion of ZIF-67 to sub-20 nm of Co NPs confined in N-doped carbon matrix, while forming a porous nanotube structure in Co@NCNT (**Figure 6.5a**). The hollow interior structure is revealed by TEM and HAADF-STEM images (Figure 6.5b,c) together with many enclosed metallic Co NPs (**Figure 6.6**). After the galvanic replacement reaction with K₂PtCl₄, the Co NPs are converted to pre-Pt₃Co NPs thus forming the pre-Pt₃Co@NCNT structure (Figure 6.5d,e).

Figure 6.5. Morphology characterization and formation progress of pre-Pt₃Co@NCNT. (a) FESEM, (b) TEM, and (c) HAADF-STEM images of Co@NCNT. (d) TEM and (e) HAADF-STEM images of a pre-Pt₃Co@NCNT. (f, g) TEM and (h, i) atomic-scale HAADF-STEM images of a corner of the pre-Pt₃Co@NCNT.

Figure 6.6. XRD pattern of Co@NCNT.

A closer examination around one end of the resultant pre-Pt₃Co@NCNT shows the dense distribution of pre-Pt₃Co NPs in the nanotube (Figure 6.5f,h, **Figure 6.7**). High-resolution TEM (HRTEM) and HAADF-STEM images (Figure 6.5g,i) show obvious lattice fringes with an interplanar spacing of 0.226 nm, which can be well indexed to the (100) planes of cubic Pt (ICDD card No. 00-004-0802).

Figure 6.7. (a-e) EDX elemental mapping images and (f) corresponding HAADF-STEM image of a corner of pre-Pt₃Co@NCNT.

This observation shows that crystalline Pt₃Co alloy NPs are not formed after the galvanic replacement reaction, and the pre-Pt₃Co@NCNT product shows relatively poor crystallinity as shown by the XRD pattern (**Figure 6.8**).

Figure 6.8. XRD patterns of pre-Pt₃Co@NCNT and pre-PtCo@NCNT.

The pre-Pt₃Co@NCNT sample is then subjected to thermal reorganization under N₂ atmosphere to generate crystalline Pt₃Co@NCNT (**Figure 6.9**).

Figure 6.9. FESEM images of Pt₃Co@NCNT. The Pt₃Co@NCNT can perfectly preserve the uniform NR morphology after the annealing process.

Unexpectedly, the thermal reorganization process leads to the migration of Pt₃Co alloys to both inner and outer surfaces of the porous carbon shell, which is highly advantageous for exposing active sites and shortening the charge/mass transfer distance (**Figure 6.10a,b**). The corresponding energy-dispersive X-ray (EDX) line scanning and elemental mapping images (**Figure 6.10b-d**) clearly demonstrate that Pt₃Co NPs are uniformly distributed on the nanotube.

Figure 6.10. Structural characterizations of $\text{Pt}_3\text{Co@NCNT}$ and PtCo@NCNT . (a) TEM image, (b) HAADF-STEM image with EDX line scanning, and corresponding (c, d) EDX elemental mapping images of a $\text{Pt}_3\text{Co@NCNT}$. (e) SAED pattern, (f) HRTEM image of $\text{Pt}_3\text{Co@NCNT}$. (g) the corresponding IFFT image of area g in (f), and (h) atomic-scale HAADF-STEM image of a Pt_3Co NP. (i) TEM image, (j) HAADF-STEM image with EDX line scanning, and corresponding (k, l) EDX elemental mapping images of a PtCo@NCNT . (m) SAED pattern and (n) HRTEM image of PtCo@NCNT . (o, p) the corresponding IFFT images of area o and p in (n), and (q) atomic-scale HAADF-STEM image of a PtCo NP.

XRD results (**Figure 6.11**) confirm the face-centered cubic (fcc) structure of Pt_3Co NPs (ICDD card No. 00-029-0499). Furthermore, the (111), (200), and (220) planes of Pt_3Co NPs are confirmed by selected area electron diffraction (SAED, Figure 6.10e). A HRTEM image shows the presence of ultrafine nanoalloys with an average size of around 5 nm (Figure 6.10f), which is in line with the broad peaks shown in the XRD pattern. The corresponding inverse fast Fourier transformation (IFFT) image shows the interplanar distance of 0.222 nm, which belongs to the (111) planes of

Pt₃Co (Figure 6.10g). HAADF-STEM is applied to probe the atomic structure of a single Pt₃Co NP.

Figure 6.11. XRD patterns of as-synthesized Pt₃Co@NCNT and PtCo@NCNT. Compared with the standard Pt pattern and the pre-Pt₃Co@NCNT sample, the peak positions of Pt₃Co@NCNT are shifted to higher angles, suggesting Co atoms/clusters are fused into Pt lattice with a lattice contraction.

As shown in Figure 6.10h, a 2-nm Pt₃Co NP is observed along the [001] zone axis,^[204] verified by a diffractogram of the same area (**Figure 6.12**).

Figure 6.12. Diffractogram of the center particle in Figure 6.10h.

As Co and Pt possess different Z-contrast in HAADF-STEM, the Co columns can be differed from Pt columns due to the low intensity. Most Co columns are surrounded by Pt columns at both edges and corners in each unit cell, confirming the partially ordered structure of Pt₃Co NPs (Figure 6.10h). The chemical composition around one

corner of Pt₃Co@NCNT is examined by EDX results (**Figure 6.13**). The projected distributions of Pt and Co elements are overlaid perfectly with a molar ratio of about 2.9, which is in line with the inductively coupled plasma atomic emission spectroscopy (ICP-AES) result.

Figure 6.13. (a-e) Elemental mapping and (f) HAADF-STEM images of a corner of Pt₃Co@NCNT. (g) EDX analysis of a corner of Pt₃Co@NCNT. (h) EDX line scanning results for Co, Pt, C, N along the pathway marked in Figure f.

Through the same preparation method, ultrafine Pt-Co alloy NPs with an atomic Pt/Co ratio of about 1:1 can also be obtained forming the sample designated as PtCo@NCNT (Figure 6.10i, **Figure 6.14**).

Figure 6.14. FESEM images of PtCo@NCNT.

HAADF-STEM, corresponding EDX elemental mapping, and line scanning images confirm that the uniform distribution of Pt and Co with a molar ratio close to 1 (Figure 6.10j-l). The ICP-AES results also confirmed the content of Pt (25.2 wt%) and Co (7.8 wt%). The molar Pt to Co ratio is 0.98:1, in accordance with the composition of PtCo alloy with molar ratio of 1:1. XRD patterns (Figure 6.11) indicate that the PtCo NPs can be indexed to the hexagonal closed-packed (hcp) crystal structure. The SAED pattern (Figure 6.10m) shows the (101), (110), and (112) planes of PtCo NPs, in agreement with the standard XRD pattern (ICDD card No. 01-071-7408). The HRTEM and corresponding IFFT images show the highly crystalline structure of PtCo alloy with highly exposed (110) and (101) planes (Figure 6.10n-p). The atomic-resolution HAADF-STEM image in Figure 6.10q displays the layered distribution of Pt and Co at the atomic level. Nitrogen sorption measurements show that both Pt₃Co@NCNT and PtCo@NCNT possess a highly porous nanostructure with a large specific surface area of 115.2 and 124.2 m² g⁻¹, respectively (**Figure 6.15**).

Figure 6.15. Nitrogen sorption isotherms of (a) Pt₃Co@NCNT and (b) PtCo@NCNT.

6.3.3. Electrochemical measurements

The electrocatalytic HER performance of Pt₃Co@NCNT and PtCo@NCNT catalysts is first investigated in acidic media (0.5 M H₂SO₄) by a standard three-electrode system. For comparison, the HER performance of a commercial Pt/C catalyst (the average size of Pt particles is 2 ~ 3 nm, **Figure 6.16**) is also measured under the same test conditions.

Figure 6.16. Atomic-scale HAADF-STEM images of a commercial Pt/C catalyst.

Figure 6.17. Electrocatalytic HER performance of Pt₃Co@NCNT and PtCo@NCNT in (a-d) 0.5 M H₂SO₄, (e-h) 1.0 M KOH. (a) LSV curves, (b) a bar graph of comparative TOF values at two different overpotentials, (c) Tafel plots and (d) chronopotentiometric curves recorded at 10 mA cm⁻² of Pt₃Co@NCNT, PtCo@NCNT, and Pt/C in 0.5 M H₂SO₄ solution. (e) LSV curves, (f) a bar graph of comparative TOF

values at two different overpotentials, (g) Tafel plots, and (h) chronopotentiometric curves recorded at 10 mA cm⁻² of Pt₃Co@NCNT, PtCo@NCNT, and Pt/C in 1.0 M KOH solution.

Figure 6.17a shows the iR-compensated LSV curves of the samples at a scan rate of 5 mV s⁻¹. The Pt₃Co@NCNT catalyst shows the best activity with only a small overpotential of 42 mV required to reach 10 mA cm⁻², while the required overpotentials of PtCo@NCNT and Pt/C are 64 and 47 mV respectively to reach the same current density. At the overpotential of 70 mV, the Pt₃Co@NCNT can reach a high current density of 100 mA cm⁻², which is much larger than that of PtCo@NCNT (13.3 mA cm⁻²) and benchmark Pt/C (34.6 mA cm⁻²). To further interpret the enhancement of HER activity, turnover frequency (TOF) is calculated to compare the intrinsic activity of catalysts (**Figure 6.17b**, **Figure 6.18a**).

Figure 6.18. TOF of Pt₃Co@NCNT, PtCo@NCNT, and commercial Pt/C in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.

Specifically, the Pt₃Co@NCNT catalyst presents an outstanding TOF value of 1.95 s⁻¹ at an overpotential of 100 mV, which is 6.5 times and 2.3 times that of PtCo@NCNT and Pt/C respectively at the same condition. As shown in **Figure 6.17c**, the Pt₃Co@NCNT catalyst shows enhanced kinetics with a lower Tafel slope (27.2 mV dec⁻¹) compared with PtCo@NCNT (48.5 mV dec⁻¹) and Pt/C (31.4 mV dec⁻¹).

The HER performance of Pt₃Co@NCNT in 0.5 M H₂SO₄ is also comparable to that of some recently reported Pt-based catalysts (**Table 6.1**).

Table 6.1. The comparison of the electrocatalytic activities of Pt₃Co@NCNT, PtCo@NCNT, and Pt/C with some representative Pt-based HER electrocatalysts recently reported in 0.5 M H₂SO₄ solution.

Catalysts	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Reference
Pt₃Co@NCNT	42	27.2	This work.
PtCo@NCNT	64	48.5	
Pt/C(20%)	47	31.4	
Pt/C-20%	~50	~30	[205]
Pt/C-40%	45	30	[206]
Pt@PCM	105	63.7	[207]
Pt₃Ni₄ NWs/C	40	N.A.	[189]
PtTe₂ NSs	~40	N.A.	[208]
Pt/np-Co_{0.85}Se	58	26	[174]
Pt-MoS₂	53	40	[209]
PtRu/RFCs	46.6	46.7	[63]
Pt@CIAC-121	48	58	[210]
Pt ML/Ag NF/Ni foam	70	53	[211]
er-WS₂-Pt	~45	27	[88]

η_{10} : Overpotential (mV) at a current density of 10 mA cm⁻².

Chronopotentiometry tests show that the Pt₃Co@NCNT catalyst is much more stable than PtCo@NCNT over the 35-h operation, while both of which show much enhanced stability than Pt/C (Figure 6.17d). This observation highlights the important

effects of the designed carbon support and catalyst composition on the electrocatalytic performance.^[191] After the stability test, there is no apparent change in morphology for both Pt₃Co@NCNT and PtCo@NCNT (**Figure 6.19**).

Figure 6.19. HAADF-STEM images, corresponding EDX line scan and elemental mapping images of (a-d) Pt₃Co@NCNT and (e-h) PtCo@NCNT after HER test in 0.5 M H₂SO₄ (a,b,e,f) and 1.0 M KOH (c,d,g,h) for 50 h.

Importantly, the Pt₃Co@NCNT catalyst also exhibits superior activity in alkaline media (1.0 M KOH). As displayed in Figure 6.17e, to reach the current density of 10 mA cm⁻², the Pt₃Co@NCNT catalyst requires an overpotential of only 36 mV, which is 17 mV and 30 mV lower than that required for PtCo@NCNT and Pt/C catalysts respectively. At the overpotential of 100 mV, the Pt₃Co@NCNT catalyst can deliver a current density of 100 mA cm⁻², which is 2.4 and 5 times that of PtCo@NCNT and Pt/C catalysts respectively. TOF is also calculated to further evaluate the enhancement in intrinsic activity (Figure 6.17f, 6.18b). Specifically, the Pt₃Co@NCNT catalyst shows a TOF value of 0.31 s⁻¹ at an overpotential of 60 mV, much higher than that of

PtCo@NCNT (0.13 s^{-1}) and Pt/C (0.11 s^{-1}). In addition, at a relatively large overpotential of 100 mV, the TOF of Pt₃Co@NCNT can reach 0.94 s^{-1} , which is about 2.2 and 3.8 times that of PtCo@NCNT (0.43 s^{-1}) and Pt/C (0.25 s^{-1}). The Pt₃Co@NCNT catalyst exhibits a Tafel slope of 34.8 mV dec^{-1} , which is much smaller than that of PtCo@NCNT (54.1 mV dec^{-1}) and Pt/C (65.9 mV dec^{-1}) (Figure 6.17g). With the outstanding HER activity in 1.0 M KOH, the Pt₃Co@NCNT catalyst outperforms most of the reported Pt-based high-performance electrocatalysts (Table 6.2).

Table 6.2. The comparison of the electrocatalytic activities of Pt₃Co@NCNT, PtCo@NCNT, and Pt/C with some representative Pt-based HER electrocatalysts recently reported in 1.0 M KOH solution.

Catalysts	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
Pt ₃ Co@NCNT	36	34.8	This work.
PtCo@NCNT	51	54.1	
Pt/C(20%)	66	65.9	
Pt ₅ /HMCS	46.2	48.1	[181]
Pt/C-20%	53.7	56.6	
PtNi/C	41.7	85.5	[212]
Pt/C-20%	108.9	134.4	
Pt ₃ Ni ₂ -NWs	60	N/A	[189]
Pt NWs/SL-Ni(OH) ₂	~70	N/A	[213]
Pt ₁ /N-C	46	36.8	[214]
Pt/C-20%	57	39.8	
Pt-Co(OH) ₂ /C	32	70	[215]
Pt/CC	75	93	

Pt/np-Co_{0.85}Se	58	39	[174]
er-WS₂-Pt	48	65	[88]
PtRu NCs/BP	64	43	[64]
hcp Pt-Ni alloy	65	78	[65]

η_{10} : Overpotential (mV) at a current density of 10 mA cm⁻².

Remarkably, the Pt₃Co@NCNT catalyst shows negligible decay in activity after continuous operation for 100 h at 10 mA cm⁻² (Figure 6.17h), which should benefit from the strong metal-support interaction as well as the nanoalloy composition.^[60, 216-217] On the other hand, the PtCo@NCNT catalyst shows more significant activity loss over the course of a 70-h chronopotentiometry test. As expected, the commercial Pt/C catalyst shows drastic activity loss during the initial 20 h. After the stability test, the catalysts are further characterized (Figure 6.19). It is important to find that the atomic Pt/Co ratio remains around 3:1 in the Pt₃Co@NCNT catalyst according to the line scanning results. This result confirms that Pt₃Co NPs are highly stable in alkaline media.^[218] On the contrary, the PtCo@NCNT catalyst shows a lower Co content than Pt, suggesting partial dissolution of Co in PtCo NPs.^[217]

6.3.4. Computational results

Some preliminary density functional theory (DFT) calculations are further performed to understand the enhancement of intrinsic activity brought by nanoalloying. The Gibbs free energy of adsorption for the H* intermediate (ΔG_{H^*}) is regarded as a crucial descriptor for evaluation of HER performance,^[219] requiring a “just right” ΔG_{H^*} value located at or very close to zero.^[220] Upon alloying Pt with the 3d-transition metal Co, the ΔG_{H^*} value has been greatly regulated towards a thermodynamically favorable position, which is approaching zero (**Figure 6.20**). Specifically, the ΔG_{H^*} value on the Pt (111) surface model is calculated to be -0.22 eV.

It shifts to -0.17 eV on the PtCo (111) surface and further increases to -0.07 eV on the Pt₃Co (111) surface, gradually approaching to a thermodynamically-neutral position. These calculation results agree well with our experimental observations, where the HER activity is in the order of Pt < PtCo < Pt₃Co in alkaline media in which the alloy surface structure is believed to be stable.^[221-222]

Figure 6.20. (a) DFT calculation models of Pt (111), Pt₃Co (111), and PtCo (111). Pt in blue, Co in orange. (b) Free energy diagrams for H* adsorption.

Besides the overall optimized HER energetics, the surface active sites on the Pt₃Co alloy have been diversified due to the formation of bimetallic alloys. A number of configurations reflecting different active sites have been examined for evaluating the HER activity. On the Pt (111) surface, the most stable configuration of H* adsorption is identified on the Pt top site, and there is a big gap of greater than 0.1 eV of the ΔG_{H^*} value on other sites, suggesting the unicity of the active site (**Figure 6.21**).

Figure 6.21. (a) Model and (b) free energy diagram of H^* on Pt (111) surface (t: Pt top site; b: PtPt bridge site; h: PtPtPt hcp site; f: PtPtPt fcc site).

In contrast, the Pt_3Co (111) alloy surface provides diversified active sites due to the alloy combination and the synergistic effect (**Figure 6.22**). The most stable adsorption configuration locates at the three-fold PtPtCo fcc hollow site with a ΔG_{H^*} value of -0.07 eV, while slightly weaker bindings are found on the Pt top site (-0.02 eV) and PtPtCo hcp site (0 eV). It is noted that the Co site in Pt_3Co alloy can never solely act as the HER active site due to its extremely unfavorable H^* binding. These results demonstrate that more types of active sites can actively catalyze the HER on the Pt_3Co (111) alloy surface model. In alkaline media, 3d-transition metals like Co can stably exist on the catalyst surface. However, in acidic electrolyte, the evidence showing the presence of Pt-Co alloy on the catalyst surface is insufficient and challenging. Recently, a PtPdCu ternary oxygen reduction reaction electrocatalyst has been proved to be active and stable in the acidic media due to realloying.^[223] This agrees well with our experimental observations showing limited amount of Co leaching after the durability test in acidic electrolyte and demonstrates great promise of nano-alloy electrocatalysts in acidic media.

Figure 6.22. (a) Model and (b) free energy diagram of H^* on Pt_3Co (111) surface (t_{Pt} : Pt top site; t_{Co} : Co top site; f_{Co} : PtPtCo fcc site; h : PtPtCo hcp site; f_{Pt} : PtPtPt fcc site).

6.4. Summary

In this chapter, ultrafine Pt-Co alloy nanoparticles confined on the inner and outer surfaces of porous nitrogen-doped carbon nanotubes with closed ends have been synthesized through a MOF-engaged pyrolysis-replacement-reorganization method. Benefiting from the synergistic effects of the bimetallic alloy components, the intrinsic activity of the obtained Pt₃Co@NCNT catalyst is remarkably enhanced, which is reflected by the high electrocatalytic activity towards HER in both acidic and alkaline media. Moreover, the exquisite porous carbon shell structure host prevents the ultrasmall Pt₃Co NPs from aggregation thus ensuring long-term durability. Theoretical calculations further reveal that the enhanced HER intrinsic activity originates from the optimized ΔG_{H^*} value and diversified active sites in the Pt₃Co alloy catalyst. The current strategy may provide a new thought for controlling the spatial distribution of alloy NPs in carbon support, thus improving their high utilization efficiency with superior stability in energy-related fields.

Chapter 7. Concluding Remarks and Outlook

7.1. Concluding Remarks

The research project focuses on developing MOF-derived nanostructured materials to enhance the elementary electrochemical processes, including ORR, OER, and HER. We have demonstrated that the rational regulation of the structure and composition is an effective way to modulate the reactivity and selectivity of the electrocatalysts with well-discussed mechanisms. In view of the nanostructure, the design of morphology, including particle shape and size, can help adjust active sites' exposure. The spatial distribution and interparticle distance will affect the diffusion and aggregation. The porous structure facilitates the mass/charge transfer and shortens the retention time of the reaction intermediates. Defects are usually introduced to the original nanoparticles by doping secondary metal atoms or alloying, tuning the electronic structure, and enhancing the reaction activity. This research introduces novel synthetic methods starting from MOF precursors to achieve delicate control of morphology, nanostructure, chemical composition, and defects to generate highly efficient electrocatalysts towards energy conversion.

Firstly, we develop a novel dual-MOF-assisted pyrolysis method for the synthesis of Co-Fe alloy embedded in N-doped carbon hollow spheres. ZIF-67 nanoshell encapsulates the MIL-101 nanocrystallites during their growth on PS spheres. The PS@dual-MOF with dual metal centers is further thermally transformed to a hollow sphere structured N-doped carbon matrix comprising of various separated Co-Fe alloys with strong metal-support interactions. With the delicate structural and compositional design, the Co-Fe/NC-700 catalyst presents outstanding ORR activity in terms of the half-wave potential of 0.854 V in 0.1 M KOH and ultralong stability of 8

h with 97.7 % retention of initial current density, outperforming the single-MOF derived counterparts and commercial Pt/C catalysts.

Moreover, MOF-assisted etching-coordination reorganization method has been developed to construct the ultrathin Co_3O_4 nanosheet assembly with hierarchical cross-channelled hollow nanoplate structure. Considering Co_3O_4 is chemically stable at high anodic potential but with low activity to induce OER in alkaline, secondary metal atom doping is employed to tune the electronic structure of Co_3O_4 for enhancing the intrinsic activity. Among the 13 metal atom-doped Co_3O_4 samples, Fe- Co_3O_4 HHNPs present the most promising electrocatalytic performance towards OER. The doped Fe atoms occupy the octahedral sites of Co_3O_4 , boosting the intrinsic activity significantly. Furthermore, the porous nanostructure and nanosheet subunit ensure the maximized exposure of active sites and shortened mass/charge transport. As a result, the designed Fe- Co_3O_4 shows remarkable electrocatalytic OER activity in terms of overpotential of 262 mV at 10 mA cm^{-2} and excellent stability for 50 h at 100 mA cm^{-2} .

In addition, MOF-engaged pyrolysis-replacement-reorganization synthesis is developed for engineering ultrafine Pt-Co alloy nanoparticles (sub-10 nm) attached on the inner and outer shells of porous nitrogen-doped carbon nanotubes (NCNT) with closed ends. The synergistic effect between Pt and Co component in the bimetallic Pt-Co alloy endows the obtained $\text{Pt}_3\text{Co@NCNT}$ catalyst with outstanding electrocatalytic HER activity in both acidic and alkaline media. The mechanism is revealed by DFT calculation that alloying Pt with Co provides more an optimized ΔG_{H^*} value and diversified active sites in Pt_3Co alloy towards HER. The synthetic strategy ensures the even spatial distribution of Pt_3Co nanoalloys in the delicate porous carbon matrix, thus improving the high utilization efficiency of Pt with outstanding durability in energy conversion fields.

In summary, this research project has systematically studied the design of nanostructured MOF-derived materials and their applications towards energy conversion reactions. The combination of compositional and structural advantages is crucial for enhancing the electrochemical performance of catalysts. Based on our design and synthetic strategy, our electrocatalysts present superior activity and outperform the state-of-art commercial catalysts (Pt/C and RuO₂). Firstly, the Co-Fe/NC-700 derived from dual-MOF structure manifests the strong metal-support interaction and synergistic effect by alloying. Meanwhile, the pyrolysis condition is precisely investigated to optimize the chemical composition and spatial distribution of the nanocrystallites. Secondly, the Fe-Co₃O₄ HHNPs derived from ZIF-67 nanoplate are assembled with ultrathin nanosheets, which offers the maximized exposure of the active sites and facilitates the mass/charge transfer. The introduction of secondary metal centers modulates the electronic structure of Co₃O₄ to enhance the intrinsic activity, which is demonstrated by the experiment and DFT calculation. Lastly, Pt₃Co@NCNT derived from ZIF-67 nanorod manifest unique structure with ultrafine Pt-Co alloy nanoparticles (sub-10 nm) attached on the inner and outer shells of porous nitrogen-doped carbon nanotubes with closed ends. The surface distribution of alloy gives access to maximized contact with the reactants while maintain the carbon support protection to avoid degradation during stability test. Highly crystallized Pt₃Co generated by thermal reorganization provides a nearly thermodynamically-neutral free energy of adsorption to hydrogen intermediates and diversified active sites, enhancing the electrocatalytic performance intrinsically. These findings and developments in this project will expand the horizon in the structural and compositional design of novel electrocatalysts and also offer new solutions to overcome the challenges for efficient energy conversion applications.

7.2. Outlook

Although various nanostructures with different compositions have been developed and demonstrated as efficient catalysts in the electrocatalytic field, the deployment of advanced nanostructured catalysts derived from MOF material is still at the early stage. Therefore, researchers still face challenges in improving the activity and selectivity of electrocatalysts for specific reactions. In this regard, several potential suggestions are listed below for future research perspectives.

- 1) Strain engineering has shown great promise in modulating the nanomaterial's electronic structure and chemical reactivity and thus gives access to further promotion in electrocatalytic performance.^[224-228] Recent research progress has demonstrated that the elastic strain in nanoparticles is highly affected by the synthetic method.^[224, 229] Traditional strategies to induce the elastic strain include the generation of the core-shell structure by surface coating and edge engineering of transition metal chalcogenides, which can be further applied to MOF-derived materials with smaller particle size and stronger metal-support interaction. Structural designs such as crystal shape, particles size, alloying/dealloying, atom doping, protective support can be further extended to control the strain engineering in MOF-derived materials, which could possibly generate efficient electrocatalysts with high stability.
- 2) To further enhance the utilization efficiency of noble metal component, single-atom alloy (SAA) material has received considerable research attention.^[230-231] The catalytic performance is strongly related to metal-metal interactions between the metal support and isolated single atoms by tuning the original electronic structures.^[232] MOF materials are high tailorable framework and ideal precursors for receiving secondary metal atom doping with controllable

doping amount, which has also been demonstrated by our previous MOF-assisted synthesis of Fe-Co₃O₄ catalyst in Chapter 5. Followed by different synthesis method, the atom-doped MOF precursor can be further transformed to single-atom alloy confined in N-doped carbon matrix with designed structure.

- 3) The structural and compositional evolution during the electrochemical tests remains controversial. Series of materials are regarded as pre-catalyst for receiving further transformations during the electrochemical processes, such as the transformation of RuIrZnO_x h-nanobox pre-catalyst to RuIrO_x catalyst,^[233] ZIF-67 to CoOOH,^[234] Fe-Co-P nanobox to Fe-Co-P-O catalyst,^[235] most of which transformation processes are characterized by indirect methods rather than in situ imaging. In situ TEM imaging can provide a platform to observe the dynamic changes of the electrocatalysts and offer in depth understanding of the reaction mechanism on electrocatalysis, such as evolution of metal-support interface, migration of the grain boundary, and dealloying and realloying dynamic, etc, which might also give access to the direct usage of MOF material in electrocatalysis.

Complete List of Publications

- [1] **S. L. Zhang**, X. F. Lu, Z. P. Wu, D. Y. Luan, X. W. Lou,* Engineering Pt-Co Nano-alloys in Porous Nitrogen-Doped Carbon Nanotubes for Highly Efficient Electrocatalytic Hydrogen Evolution, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.202106547 (2021).
- [2] **S. L. Zhang**, B. Y. Guan, X. F. Lu,* S. Xi, Y. Du, X. W. Lou,* Metal Atom-Doped Co₃O₄ Hierarchical Nanoplates for Electrocatalytic Oxygen Evolution, *Adv. Mater.*, 32, 2002235 (2020).
- [3] **S. L. Zhang**, B. Y. Guan,* X. W. Lou,* Co-Fe Alloy/N-Doped Carbon Hollow Spheres Derived from Dual Metal-Organic Frameworks for Enhanced Electrocatalytic Oxygen Reduction, *Small*, 15, 1805324 (2019).
- [4] **S. L. Zhang**, B. Y. Guan,* H. B. Wu, X. W. Lou,* Metal-Organic Framework-Assisted Synthesis of Compact Fe₂O₃ Nanotubes in Co₃O₄ Hosts with Enhanced Lithium Storage Properties, *Nano-Micro Lett*, 10, 44 (2018).
- [5] Y. Huang, **S. L. Zhang**, X. F. Lu,* Z. P. Wu, D. Y. Luan, X. W. Lou,* Trimetallic Spinel NiCo_{2-x}Fe_xO₄ Nanoboxes for Highly Efficient Electrocatalytic Oxygen Evolution, *Angew. Chem. Int. Ed.*, 60, 11841 (2021).
- [6] Y. J. Fang, **S. L. Zhang**, Z. P. Wu, D. Y. Luan, X. W. Lou,* A highly stable lithium metal anode enabled by Ag nanoparticles embedded nitrogen-doped carbon macroporous fibers, *Sci. Adv.*, 7, eabg3626 (2021).
- [7] X. F. Lu, **S. L. Zhang**, E. Shangguan, P. Zhang, S. Y. Gao,* X. W. Lou,* Nitrogen-Doped Cobalt Pyrite Yolk-Shell Hollow Spheres for Long-life Rechargeable Zn-Air Batteries, *Adv. Sci.*, 7, 2001178 (2020).

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- [9] Y. Wang, S. B. Wang, **S. L. Zhang**, X. W. Lou,* Formation of Hierarchical FeCoS₂-CoS₂ Double-Shelled Nanotubes with Enhanced Performance for Photocatalytic Reduction of CO₂, *Angew. Chem. Int. Ed.*, 59, 11918 (2020).
- [10] S. B. Wang, Y. Wang, **S. L. Zhang**, S. Q. Zang, X. W. Lou,* Supporting Ultrathin ZnIn₂S₄ Nanosheets on Co/N-Doped Graphitic Carbon Nanocages for Efficient Photocatalytic H₂ Generation, *Adv. Mater.*, 31, 1903404 (2019).
- [11] Z. P. Wu, H. B. Zhang, S. Zuo, Y. Wang, **S. L. Zhang**, J. Zhang, S. Q. Zang,* X. W. Lou,* Manipulating The Local Coordination And Electronic Structures For Efficient Electrocatalytic Oxygen Evolution, *Adv. Mater.* in press.

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