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**Advanced Non-Noble Catalysts for Electrocatalytic Energy
Conversion Processes**

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Abstract

The key renewable-energy technologies, such as fuel cells, metal-air batteries, and water electrolyzers, provide sustainable solution to the aggravating energy and environment issues. They can convert chemical energy to electricity or fuel directly with high efficiency and low even zero greenhouse gas emission. However, the commercial success of these techniques has been greatly hampered by the prohibitive cost, low abundance, and limited stability of the state-of-the-art noble-metal electrocatalysts (Pt, IrO₂ or RuO₂) at the anodes and/or cathodes. Therefore, the development of cost-effective, highly active, and durable electrocatalysts is highly desirable for these techniques. This thesis aims to design and fabricate a series of advanced electrocatalysts for oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) which are the cathodic or anodic reactions of fuel cells, metal-air batteries and water electrolyzers.

The first part of the thesis focuses on ORR to fabricate a number of low cost transition metal oxides and carbon materials as the alternative to commercial Pt/C. Non-precious metal oxides such as Mn₃O₄ have been studied as Pt substitute due to their earth abundance and environmental compatibility. In addition, heteroatom-doped graphene which combines excellent electrical conductivity, high surface area, and rich active sites, displays good electrocatalytic performance. As a consequence, a hybrid material composed of Mn₃O₄ nanoparticles on nitrogen-doped graphene was firstly synthesized for ORR catalysis. Further, the shape effect of metal oxide nanoparticles (Mn₃O₄) on ORR activity has been examined, based on the fact that the heterogeneous ORR process involving the adsorption of reactants and desorption of products on the exposed facets of nanocrystals.

The second part of thesis is to study HER which is the primary step of sustainable H₂ production from electrochemical water splitting. Other than tuning the chemical composition and nanostructure of electrocatalysts, the HER performance can also be optimized through the manipulation of the electrode architectures. Heteroatom-doped graphene has been investigated as the HER catalyst, but its performance is limited due to the small amount of accessible active sites. In response, we hybridizes heteroatom-doped graphene with a highly active HER catalyst (porous C₃N₄ and 1T-WS₂) into three dimensional flexible hybrid film, which can be directly utilized as HER catalyst electrodes without substrates or binders. This new category of electrocatalysts can combine the facile HER kinetics and high HER activity. This work offers the possibility to tackle the bottleneck of HER electrocatalyst by tailoring the electrocatalytic performance at atomic scale.

The third part of thesis aims to design a bifunctional electrocatalyst for both HER and OER. The cobalt oxides are known as an efficient OER electrocatalyst, while cobalt phosphides are active HER electrocatalysts. Through adjusting the anion percentage of P and O elements in cobalt phosphoric oxides, we can obtain the optimized bifunctional catalyst for both HER and OER for overall water electrolysis. Moreover, the cation in cobalt phosphoric oxide is modulated by doping different amount of Fe, which can improve its water splitting ability further. As expected, the obtained catalyst electrode has displayed a superior water electrolysis performance, exhibiting the low driving potential and facile reaction kinetics, which might be associated with the three-dimensional conductive network beneficial for the electron and charge transportation, high accessibility of active sites, and the optimum cation and anion percentages.

Thesis Declaration Statement by Author

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no materials previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree.

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Chapter 1: Introduction

1.1 Significance of the project

Many advanced technologies for clean and sustainable energy conversion, for example fuel cells, metal-air batteries and water electrolyzers, are the subjects of extensive studies because they can convert chemical energy to electricity or fuel directly with high efficiency and low even zero pollution.¹⁻⁴ However, their sluggish electrode reactions such as oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) currently require large overpotential and great amount of precious electrocatalysts.⁵⁻⁷ The state-of-the-art electrocatalysts for these electrocatalytic processes are usually precious metals (Pt for ORR and HER, IrO₂ or RuO₂ for OER), which are with high cost (for example, ~\$40/g for Pt), low abundance (<10⁻⁶ % for Pt, Ir and Ru in earth crust) and environmental vulnerability and thus greatly limit the commercial success of the clean technologies.⁸⁻¹⁰ For these reasons, it is momentous but challenging to develop cost-effective, highly active, durable and environmental friendly electrocatalysts as noble metal alternatives to promote the sustainable energy technologies.

1.2 Research objectives

The major goals of this thesis are to gain insights to the reaction mechanisms of the key electrocatalytic processes (ORR, HER and OER) in the renewable fuel cells, metal-air batteries and water electrolyzers, and thus fabricate low-cost, active and durable electrocatalysts to substitute precious metal materials through facile synthesis. Specifically, the objectives of this thesis are:

- **Investigating** the heteroatom-doping effect of graphene on ORR performance and developing facile doping method to synthesize heteroatom-doped graphene with high doping amount;
- **Understanding** the reaction mechanisms of ORR promoted by hybrids of transition metal oxides (Mn₃O₄) on a conductive supporter like heteroatom-doped graphene;
- **Revealing** the shape dependence of ORR activity on transition metal oxides, and thus providing a new pathway to improve the ORR performance;
- **Understanding** the reaction mechanisms of HER in water electrolysis and optimizing the HER performance not only by tuning the chemical composition and nanostructure of catalysts but also by designing the electrode architecture.
- **Tuning** the catalyst's chemical composition by integrating active C₃N₄ nanolayers into N-doped graphene films, and modifying its nanostructure by introducing macropores (120 nm)

onto the two-dimensional C_3N_4 nanolayers, to design a three-dimensional film electrode ($C_3N_4@N$ -graphene film) which are highly facile for the HER kinetics.

- **Combining** high HER activity and facile HER kinetics to develop advanced HER catalyst electrodes by inducing highly active 1T- WS_2 nanolayers into P-doped graphene films.
- **Modulating** the anion and cation in metal oxides to fabricate a bifunctional catalyst electrode for HER and OER, to promote the overall water splitting. The optimum water splitting activity can be obtained by adjusting the percentages of P anion doping and Fe cation doping in cobalt oxide, displaying very low overpotential and facile reaction kinetics.

1.3 Thesis outline

This thesis is the outcomes of my PhD research presented in the form of journal publications. The chapters in this thesis are presented in the following sequence:

- **Chapter 1** introduces the significance of the thesis and outlines the objectives and key contributions to the field of research.
- **Chapter 2** reviews the literatures covering the recent advance of electrocatalysts synthesis, characterization, and their applications to key energy conversion reactions-ORR, HER and OER.
- **Chapter 3** presents a mesoporous hybrid material composed of Mn_3O_4 nanoparticles on nitrogen-doped graphene for highly efficient ORR.
- **Chapter 4** investigates shape control of Mn_3O_4 nanoparticles on nitrogen-doped graphene for enhanced oxygen reduction activity.
- **Chapter 5** designs and fabricates porous C_3N_4 nanolayers@N-graphene films as catalyst electrodes for highly efficient hydrogen evolution.
- **Chapter 6** develops 3D WS_2 nanolayers@heteroatom-doped graphene films as hydrogen evolution electrodes.
- **Chapter 7** devotes to atomic modulation in metal phosphoric oxides for a bifunctional overall water splitting electrocatalyst.
- **Chapter 8** presents conclusions and perspectives for future work on non-precious electrocatalysts synthesis, applications and mechanisms of the electrocatalytic reactions.

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Chapter 2: Literature Review

2.1 Introduction

This chapter gives a concise appraisal on the latest development of electrocatalysts for electrocatalytic ORR, HER and OER, including the facile experimental strategies, electrochemical reaction mechanisms and performance. Especially, the conductive heteroatom-doped graphene have been reviewed in detail, both as an electrocatalyst and the support to electrocatalysts.

2.2 Heteroatom-Doped Graphene-Based Materials for Energy-Relevant Electrocatalytic Processes

This section is included as it appears as a journal paper published by **Jingjing Duan**, Sheng Chen, Mietek Jaroniec, and Shi Zhang Qiao, Heteroatom-Doped Graphene-Based Materials for Energy-Relevant Electrocatalytic Processes, *ACS Catalysis*, 2015, 9, 5207-5234. It provides an overview of recent advances in non-precious electrocatalysts as precious metal alternatives for key electrocatalytic processes. The reaction mechanisms have been investigated, which provides guidance for the design and fabrication of advanced electrocatalysts.

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Chapter 3: Mesoporous Hybrid Material Composed of Mn₃O₄ Nanoparticles on Nitrogen-Doped Graphene for Highly Efficient Oxygen Reduction Reaction

3.1 Introduction and Significance

The commercial development of fuel cells and lithium-air batteries has been constrained by the scarcity and high cost of Pt/C used as the cathodic ORR catalysts. Therefore, new ORR catalysts with competitive ORR activity, durability and low cost are highly demanded to replace Pt/C. In this chapter, we prepared a new type of mesoporous hybrid material, composed of Mn₃O₄ nanoparticles and nitrogen-doped graphene, and investigated its ORR performance. It was found that this new type non-precious metal catalyst had high catalytic activity, excellent durability and completely tolerance to methanol. The highlights in this work include:

1. We have firstly synthesized a new type hybrid material of Mn₃O₄ nanoparticles on N-doped graphene using a solvothermal process. The liquid phase method to dope nitrogen onto graphene is more facile, less energy-cost and non-hazardous as compared with the widely used vapour-assisted approach.
2. We have for the first time investigated this hybrid material as non-precious ORR catalysts, which exhibited high ORR activity, excellent durability and completely tolerance to methanol. The mesoporous architecture resulted from nanoparticle assembly in the hybrid could boost the oxygen absorption and molecular transport during the catalytic process.
3. We have demonstrated an obvious synergetic effect between Mn₃O₄ nanoparticles and N-doped graphene, through an enhanced ORR activity of this hybrid compared to that of their physical mixture. The synergetic effect could be attributed to the covalently bonding between metal and graphene. Specifically, the newly formed metal-N-C and metal-O-C bonds could provide strong coupling between metal and graphene, which would introduce efficient charge transfer between them and improve the electroconductivity.

3.2 Mesoporous Hybrid Material Composed of Mn₃O₄ Nanoparticles on Nitrogen-Doped Graphene for Highly Efficient Oxygen Reduction Reaction

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Chapter 4: Shape Control of Mn₃O₄ Nanoparticles on Nitrogen-Doped Graphene for Enhanced Oxygen Reduction Activity

4.1 Introduction and Significance

Hybrid materials of non-precious transition metal oxide and nitrogen-doped graphene have displayed good ORR performance, making them potential substitutes of expensive Pt/C electrocatalyst which is widely used in fuel cells and metal-air batteries. Heterogeneous catalytic reactions such as ORR usually involve the adsorption of reactants and desorption of products on the surface of solid catalysts. The catalytic activity can be optimized by selectively exposing active crystal surface through anisotropic shape control of catalysts, which can be termed as shape-dependent catalysis. In this chapter, we have synthesized Mn₃O₄ nanocrystals with three different shapes (spheres, cubes and ellipsoids) on nitrogen-doped graphene and investigated their ORR performance. This new kind of non-noble electrocatalysts exhibits excellent ORR performance, and the hybrid with ellipsoidal Mn₃O₄ has shown the highest ORR activity among the three samples. The highlights in this work include:

1. We have for the first time prepared sphere, cube and ellipsoid-like Mn₃O₄ nanocrystals on nitrogen-doped graphene by simply adjusting the reaction conditions (temperature, duration and solvent). The liquid process to dope nitrogen onto graphene sheets is much more facile, lower energy-cost and less-hazardous than the vapour-assisted approach which is currently used for nitrogen doping.
2. These hybrid materials display excellent ORR performance. The electron transfer numbers are above 3.6, which can be assigned to the four-electron pathway. The durability is very good and about 80% of initial current can be retained even after 100 hour running. Significantly, the mesoporous architecture induced by freeze-drying can boost the oxygen absorption and molecular transport during ORR process. The effective nitrogen doping results in strong coupling between doped graphene and metal species, facilitating the electron transfer which favours the ORR process.
3. We have for the first time built the correlation between the shapes of transition metal oxide on nitrogen-doped graphene and their ORR performance. The hybrid with ellipsoidal Mn₃O₄ exhibits the highest ORR activity among three different shaped samples, with a high kinetic limiting current density of 11.69 mA cm⁻² at -0.60 V and an electron transfer number of 3.81. Based on the results, we have proposed that the different ORR activity is relevant to the different exposed facets of sphere, cube and ellipsoid-like Mn₃O₄ nanocrystals. The Mn₂O₄ terminated (001) facet of Mn₃O₄ is the most stable facet due to its lowest surface energy among all facets,

and may provide more ORR active sites because of its facile O₂ adsorption capacity and the high oxidation valence of Mn⁴⁺.

4.2 Shape Control of Mn₃O₄ Nanoparticles on Nitrogen-Doped Graphene for Enhanced Oxygen Reduction Activity

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Chapter 5: Porous C₃N₄ Nanolayers@N-graphene Films as Catalyst Electrodes for Highly Efficient Hydrogen Evolution

5.1 Introduction and Significance

Pt electrocatalyst for HER is very expensive, which has been the main obstacle in the commercial success of hydrogen economy. In this chapter, we develop a flexible film by integrating macroporous C₃N₄ (PCN) nanolayers with N-doped graphene sheets, which has displayed an unbeatable HER activity and an excellent durability. Furthermore, this self-supported three-dimensional film can be directly used as catalyst electrodes without substrates or binders, which may shed light on many other electrocatalytic processes such as ORR, OER and carbon dioxide reduction. This catalyst electrode is cheap, highly efficient and durable, providing new possibilities to promote the hydrogen economy. The highlights in this work include:

1. New material. The heterostructured film derived from PCN and N-graphene sheets has been obtained for the first time, which combines rich active sites and high electron conductivity. Also this is the first time to introduce pores into two-dimensional C₃N₄ nanolayers, which could greatly enlarge the surface area and maximize the active sites thus optimizing the catalytic activity.
2. Unbeatable HER performance. The flexible three-dimensional film has displayed extraordinary HER activity, facile kinetics and great durability. Especially, the exchange current density has been one of the highest values in the reported literatures.
3. Fascinating structure. The hierarchical porous structure in the film provides a high-accessible surface area and multidimensional mass-transport pathways; the strong coupling facilitates the electron transfer between graphene sheets and PCN nanolayers. Importantly, the self-supported film can be directly utilized as a HER catalyst electrode without supports, which could greatly improve catalyst/electrolyte contact area, avoid powder-catalyst agglomeration and peeling off from substrates during H₂-venting, guaranteeing a superior activity and an outstanding durability.
4. Interesting catalytic mechanism. There is a change of rate-determination-step during the HER process (Volmer to Heyrovsky step) because of the improved contact and electron transfer at the catalyst/electrolyte interface after some cyclic voltammetry cycles.

5.2 Porous C₃N₄ Nanolayers@N-graphene Films as Catalyst Electrodes for Highly Efficient Hydrogen Evolution

This chapter is included as it appears as a journal paper published by **Jingjing Duan**, Sheng Chen, Mietek Jaroniec, and Shi Zhang Qiao, Porous C₃N₄ Nanolayers@N-graphene Films as Catalyst Electrodes for Highly Efficient Hydrogen Evolution, *ACS Nano*, 2015, 9, 931-940.

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Author Contributions

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Chapter 6: 3D WS₂ Nanolayers@Heteroatom-Doped Graphene Films as Hydrogen Evolution Catalyst Electrodes

6.1 Introduction and Significance

The state-of-the-art Pt catalyst for electrocatalytic hydrogen evolution reaction (HER) is with high-cost and limited durability, which has greatly hampered the hydrogen economy development. Herein, we fabricate a three-dimensional (3D) self-supported HER catalyst electrode, by assembling two-dimensional (2D) WS₂ nanolayers and P, N, O-doped graphene sheets layer-by-layer into a hybridized film. This novel structure can be considered as the 3D van der Waals (vdW) heterostructure, which is a newly emerged paradigm in material science. The 3D vdW heterostructure as catalyst electrodes has exhibited superior HER performance, which may shed light on many other electrocatalytic processes such as oxygen reduction/evolution reaction and carbon dioxide reduction. The highlights in this work include:

1. A new HER catalyst electrode. The 3D vdW heterostructure derived from WS₂ nanolayers and P, N, O-doped graphene has been utilized as HER catalyst electrodes for the first time. Significantly, the self-supported heterostructured film can be directly utilized as HER catalyst electrodes without any binders, which could greatly improve catalyst/electrolyte contact area, and avoid active specie peeling off from substrates, guaranteeing a superior activity and durability.
2. Advantageous structure. The hierarchical pores in the film provide a high surface area and multi-dimensional mass-transport pathways, thus a minimal diffusion resistance. The 2D nanolayers of WS₂ after exfoliation have almost 100% exposure of surface atoms, increased surface area and utmost exposure active sites; the coupling between the two kinds of 2D materials facilitates the electron transfer during HER.
3. Extraordinary HER performance. The catalyst has displayed extraordinary HER activity (low overpotential of 125 mV *vs* RHE, to achieve a current density of 10 mA cm⁻²), facile kinetics (Tafel slope of 52.7 mV dec⁻¹), a high catalytic efficiency (a high exchange current density of 0.131 mA cm⁻²) and robust durability (less than 20% current degradation after operation for 20 hours).
4. Dual-active-site catalytic mechanism. The first kind of active sites originates from heteroatom doping. On the one hand, heteroatom doping improves the electroconductivity and thus HER kinetics; on the other hand, adjacent C atoms can be co-activated by heteroatoms as HER active sites through redistributing their charge and spin density, where the Gibbs free energy of proton absorption-desorption is lowered and gives rise to a synergistically enhanced HER activity. The second kind of active sites are from the 1T-WS₂ nanolayers due to the high concentration of the

strained metallic edges, which are also the main active sites.

6.2 3D WS₂ Nanolayers@Heteroatom-Doped Graphene Films as Hydrogen Evolution Catalyst Electrodes

This chapter is included in this thesis as it appears as a research paper published by **Jingjing Duan**, Sheng Chen, Benjamin A. Chambers, Gunther G. Andersson, and Shi Zhang Qiao, 3D WS₂ Nanolayers@Heteroatom-doped Graphene Films as Hydrogen Evolution Catalyst Electrodes, *Advanced Materials*, 2015, 27, 4234-4241.

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Contribution to the Paper	Discussion of research plan and material analysis.
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Contribution to the Paper	Research plan, material synthesis, characterization and analysis, HER performance evaluation and manuscript drafting.		
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Chapter 7: Atomic Modulation in Metal Phosphoric Oxides for a Bifunctional Overall Water Splitting Electrocatalyst

7.1 Introduction and Significance

To substitute the precious Pt/C at the cathode and IrO₂ at the anode in water electrolytic cells, bifunctional electrocatalysts are highly pursued for cathodic HER and anodic OER. Herein, we designed and fabricated a bifunctional catalyst electrode by cation Fe and anion P-doping into metal oxides (CoO) on nickel foam substrate. The obtained material can be directly utilized as catalyst electrodes without the electrode membrane assembling process and in the absence of any binders. The electrode has exhibited superior HER and OER performances with high activity, favourable kinetics, and outstanding overall water splitting activity, making itself a strong candidate to substitute precious metals. Mechanism study reveals that the atomic modulation of cation and anion play important roles to tune the electrocatalytic activity of as-prepared materials, and the optimum P and Fe-doping was obtained by simply adjusting the P and Fe sources. This work will increase the possibilities for the electrocatalyst design and synthesis to tackle bottleneck in electrocatalysis. The highlights in this work include:

1. The HER activity can be tuned by changing the P and Fe-doping percentages, displaying an optimum overpotential as low as 87.5 mV to obtain a current density of 10 mA cm⁻² and a small Tafel slope of 38.1 mV dec⁻¹ in alkaline, both of them are very close to commercial Pt/C (56.5 mV and 30.5 mV dec⁻¹).
2. The OER activity in basic electrolyte can also be optimized by adjusting the P and Fe-doping level. The obtained optimum OER activity shows overpotential of 274.5 mV to achieve a current density of 10 mA cm⁻² and a small Tafel slope of 57.1 mV dec⁻¹, which outperforms the benchmark IrO₂ catalyst (351.5 mV and 81.8 mV dec⁻¹).
3. The P-doping can be achieved by simply annealing treatment with P source (triphenylphosphine) in N₂ at elevated temperature (600 °C); while the Fe-doping can be obtained by adding Fe salts (Fe(NO₃)₃) in the first chemical bath deposition process.
4. The overall water splitting of P and Fe-doped material is also extraordinary, requiring overpotential of 333.5 mV to gain a 10 mA cm⁻² current density. The excellent electrocatalytic performance including high activity and durable stability can be assigned to the combination of abundant active species originated from the cation and anion doping, high accessibility of active sites and favorable electron and charge transportation resulted from the three-dimensional conductive porous network provided by nickel foam substrate.

7.2 Atomic Modulation in Metal Phosphoric Oxides for a Bifunctional Overall Water Splitting Electrocatalyst

This chapter is included in this thesis as it appears as a research paper submitted by **Jingjing Duan**, Sheng Chen, Sheng Dai, and Shi Zhang Qiao, Atomic Modulation in Metal Phosphoric Oxides for a Bifunctional Overall Water Splitting Electrocatalyst, to *Journal of American Chemistry Society*.

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Name of Principal Author (Candidate)	Jingjing Duan		
Contribution to the Paper	Research plan, materials synthesis, characterization and analysis, HER, OER and overall water splitting testing, and manuscript drafting.		
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Name of Co-Author	Sheng Chen		
Contribution to the Paper	Discussion of the research plan and material analysis.		
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Contribution to the Paper	Manuscript editing.		
Signature	<table border="1"> <tr> <td>Date</td> <td>29/10/2014</td> </tr> </table>	Date	29/10/2014
Date	29/10/2014		

Name of Co-Author	Prof. Shizhang Qiao		
Contribution to the Paper	Supervised development of work, helped in data interpretation and manuscript evaluation.		
Signature	<table border="1"> <tr> <td>Date</td> <td>30/10/2014</td> </tr> </table>	Date	30/10/2014
Date	30/10/2014		

Atomic Modulation in Metal Phosphoric Oxides for a Bifunctional Overall Water Splitting Electrocatalyst

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KEYWORDS: Overall water splitting, metal phosphoric oxide, atomic modulation, hydrogen evolution reaction, oxygen evolution reaction

ABSTRACT: To substitute the precious Pt/C at the cathode and IrO₂ at the anode in water electrolytic cells, this work reports a bifunctional electrocatalyst for HER and OER by doping Fe and P into metal oxide (CoO) on nickel foam substrate. This CoFePO material can be directly utilized as catalyst electrodes without the electrode membrane assembling process and in the absence of any binders. The electrode has exhibited superior HER and OER performances with high activity, favorable kinetics, and outstanding overall water splitting activity with an overpotential of 333.5 mV to gain a 10 mA cm⁻² current density. Mechanism study reveals that the atomic modulation of cation and anion play important roles to tune the electrocatalytic activity of as-prepared materials, and the optimum P and Fe-doping was obtained by simply adjusting the P and Fe sources. Furthermore, the extraordinary water electrolysis performance can be assigned to the strong and liable contact between active catalysts (CoFePO) and conductive nickel foam support which facilitates the electron and charge transfer during electrocatalytic processes, as well as the efficient cation and anion atomic modulation that greatly enlarge the active sites in the electrocatalyst.

1. INTRODUCTION

Water electrolysis ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) has been considered as the secure and sustainable technology to resolve the aggravating energy and environment crisis, because it can generate the clean H₂ energy with zero environmental emission and the only byproduct is O₂.^{1,2} However, the commercial Pt/C for the cathodic hydrogen evolution reaction (HER, $\text{H}_2\text{O} \rightarrow \text{H}_2$) and benchmark IrO₂ for the anodic oxygen evolution reaction (OER, $\text{H}_2\text{O} \rightarrow \text{O}_2$) are high-cost and low abundant, which greatly hampered the development of water electrolysis technology thus the commercial success of the promising H₂ economy.^{3,4} Currently, only ~4% of H₂ is generated by water electrolysis, thus there still is a huge space to promote the H₂ economy.¹ No doubt, the electrocatalysts for cathodic HER or anodic OER have been actively pursued recently to substitute the precious Pt/C or IrO₂, such as metal sulfides⁵⁻⁶ and phosphides⁷⁻⁸ for HER, metal oxides⁹ and hydroxides¹⁰ for OER.

Among the reported electrocatalysts, metal oxides especially cobalt oxides represent a class of conventional catalysts for OER in alkaline which feature low cost, nature abundance, diversity and critically, the inherent activity.¹¹ But the intrinsically inferior electrical conductivity of metal oxides largely hampers the electron transfer in

catalysts, which has been the major limitation for the advancement of OER performance. In response, nickel foam (NF) has been applied as the substrate for metal oxides because it can facilitate the electron and charge transportation during OER, and their 3D porous structure affords high accessibility to water molecules, lower bubble overpotential and mechanical robustness.¹²⁻¹³ Further, catalysts can directly grow on NF to avoid the utilization of insulating binders like nafion, which is considered to decrease the contact area between electrolyte and active species and deteriorate the conductivity of electrode, compromising part of the electrocatalytic activity.

Very recently, mixed metal oxides (Fe, Co, Ni) have outperformed the single metal oxides counterparts for OER catalysis, possibly correlating to the surface metal cation orbital occupation, electron transfer between different metals and their oxophilicity (like M-OH bond strength) which is believed to facilitate the initialization OER.^{9,14} As a result, cation doping at the lattice level is effective to modulate the electrocatalytic activity atomically.

On the other hand, most of the HER catalyst are investigated in acidic electrolyte, while in industry the water electrolysis is usually conducted in alkaline. So it is pressing to develop HER catalysts that are highly active and

stable in alkaline electrolyte. Recently, metal phosphides have shown potential HER performance in alkaline, which is related to their metallic conductivity, the “ensemble effect” that negatively charged P acts as the proton-acceptor and weakens the metal (positively charged, the hybrid acceptor) bond strength to promote the hydrogen adsorption, unlike the pure metals that adsorb hydrogen too strong making desorption of H₂ kinetically sluggish.¹⁵⁻¹⁶ Further, the mixed metal phosphides are reported to increase the HER activity of single metal phosphides following the HER volcano relationship.¹⁷ However, the surface instability resulted from the under-coordinated HER active P sites remains a challenge. In response, Jaramillo’s group has introduced S into MoP to suppress the surface oxidation, which was thought to degrade the HER performance by blocking protons reaching active sites and lowering the conductivity.¹⁸

Toward a bifunctional electrocatalyst for overall water splitting, the material requires not only rich active species for cathodic HER but also active species for anodic OER, making the surface oxidation of metal phosphides no longer a problem because it benefits the OER process. Herein, we developed a cobalt iron phosphoric oxide (CoFePO) by doping Fe and P into the metal oxide (CoO) lattice. The key of this study is to use metal hydroxide (CoFeOH) as the precursor, Fe salt (Fe(NO₃)₂) as the Fe source and triphenylphosphine (TPP) as the P source. The cation and anion doping percentages were tuned by simply adjusting the amount of Fe and P sources to optimize the HER and OER activity. Consequently, the obtained CoFePO has displayed outstanding water electrolysis performance, only requiring a low overpotential of 87.5 mV to achieve 10 mA cm⁻² current density for HER, 274.5 mV overpotential for OER, and 333.5 mV for the two-electrode overall water splitting. To our best knowledge, this is the first systematic work to investigate the P anion doping in metal oxides, which will provide a new direction to material design for exploring potential candidates as precious metal substitutes.

2. RESULTS AND DISCUSSION

2.1 RESULTS

2.1.1 Catalyst preparation, morphology and composition characterizations

As shown in Figure 1a, CoFePO was grown on NF (denoted CoFePO) by a two-step method using CoFe OH@NF as a precursor (obtained by a chemical bath deposition-CBD¹⁹ process), followed by an annealing treatment in N₂ with TPP as the P source. The CoFeOH nanowire clusters arranged vertically as an array on NF with Co, Fe and O distributed homogeneously (scanning electron microscopy-SEM, X-ray diffraction-XRD, energy dispersive X-ray spectroscopy-EDS and transmission electron microscopy-TEM in Figure 1b-c, S1-2). Then CoFePO was obtained by the topotactic transformation at an elevated temperature (600 °C) from CoFeOH, which retained the nanowire morphology of CoFeOH (Figure 1d-f, S3). Comparison of the TEM images of CoFeOH and CoFePO shows that the CoFePO nanowire was broken into ultra-small nanoparticles (several nanometers) under slight sonication, which

is different from CoFeOH retaining the intact nanowire shape. This phenomenon means CoFePO nanowires are actually composed by small nanoparticles arranged in the form of nanowires. According to the SEM EDS spectra and element mapping images, it is confirmed that a P element was successfully doped into the metal oxide (CoO) by the annealing treatment, which can be considered as an anion modulation method.

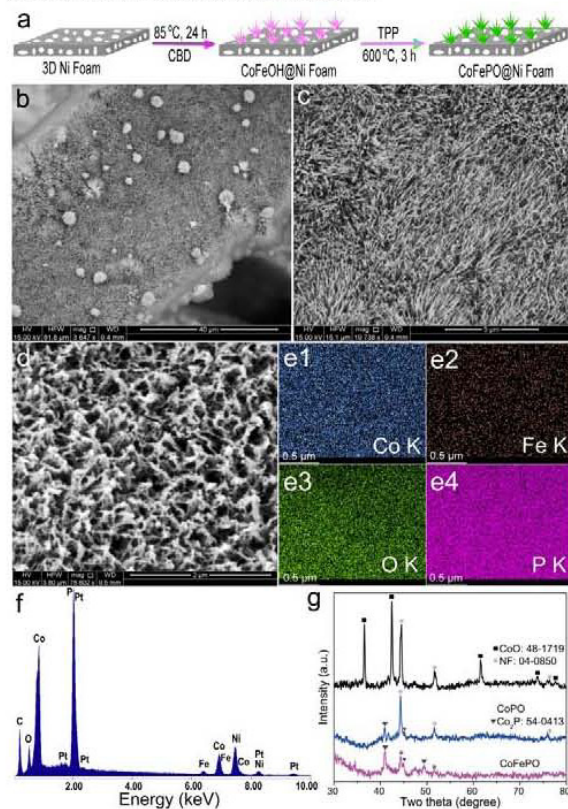


Figure 1. (a) Scheme of the preparation process of CoFePO. (b-c) FESEM images of CoFeOH. (d) FESEM image, (e1-4) SEM EDS element mapping images of Co K, Fe K, O K and P K, and (f) SEM EDS spectrum of CoFePO. (g) XRD patterns of as-prepared materials.

This hypothesis can also be confirmed by the transformation from cobalt hydroxide (CoOH) to cobalt oxide (CoO) and cobalt phosphoric oxide (CoPO). As displayed in Figure S4, the CoO was prepared by directly annealing CoOH in N₂, which also have the nanowire cluster-shape composed by nanoparticles (tens of nanometers), and only Co and O were detected (Ni from the NF substrate). The CoPO synthesized with the presence of P source can also keep the nanoparticle-arranged nanowire cluster shape, with Co, P, O and Ni distributed throughout the sample (Figure S5). Further, the above conclusions can be verified by the XRD patterns of as-prepared materials. In Figure 1g, except peaks from NF substrate, all the peaks of CoO sample can be assigned to CoO phase (JPCDS: 48-1719), CoPO and CoFePO samples attributed to Co₂P (JPCDS: 54-0413). Therefore, the cation and anion modu-

lation can be achieved by adjusting metal salt precursors and annealing treatment using P sources.

2.1.2 Electrochemical measurements

2.1.2.1 Three-electrode testing

To examine the water-splitting performance of as-obtained materials, both the cathodic HER and anodic OER processes were evaluated at first (without iR-correction for all the curves in this paper). In Figure 2a, the CoFePO displays remarkable HER activity with a low overpotential of 87.5 mV to achieve 10 mA cm⁻² current density ($\eta_{10\text{-HER}}$), which is very close to 56.5 mV of commercial Pt/C, and much smaller than 165.5 mV of CoPO without Fe, 191.5 mV of CoO without Fe and P, and 358.5 mV of NF substrate. Moreover the HER kinetics were demonstrated using the Tafel plots (Figure 2b), where CoFePO has favorable HER kinetics with a small Tafel slope (38.1 mV dec⁻¹), which is also close to Pt/C (30.5 mV dec⁻¹), and smaller than CoPO (63.4 mV dec⁻¹) and CoO (88.4 mV dec⁻¹) and NF (128.1 mV dec⁻¹). Generally, a Volmer-Heyrovsky mechanism is determined on CoFePO, with Heyrovsky step (electrochemical desorption step) as the rate-determination-step (RDS).²⁰ Therefore, with the highest HER activity and most facile kinetics, the as-synthesized CoFePO with both Fe and P doping has the best HER performance among all studied samples, which is one of the best among reported materials in basic electrolyte.^{16, 21-22}

The electrochemical impedance spectra (EIS) testing was conducted to evaluate the electron and charge transfer ability during the electrochemical process.⁶ Surprisingly, the system resistance (R_s , tested at 1.023 mV vs. RHE where no faradic reaction happens) of CoFePO (1.42 Ω cm²) is higher than that of CoPO (0.82 Ω cm²), meaning a lower conductivity of CoFePO than CoPO (Figure S6a); the charge transfer resistance (R_{ct} , measured at -0.227 V vs. RHE where HER process happens) of CoFePO (0.81 Ω cm²) is also larger than CoPO (0.57 Ω cm²), suggesting the CoFePO has a lower charge transfer ability than CoPO (Figure S6b). Therefore, it leaves a puzzle why CoFePO with a lower electron and charge transfer ability than CoPO shows a higher HER property?

We sought to the electrochemical active surface area (ECSA), which represents the amount of active sites in electrocatalysts, to solve this mystery (Figure S7 and inset 1-2 in 2f).¹⁷ The cyclic voltammetry (CV) curves were tested between 0.823 and 1.023 V vs. RHE in which range no faradic processes happened. Divided by the average specific capacitance (40 $\mu\text{F cm}^{-2}$) of reported materials, the calculated ECSAs are 1145.1, 860.6, 457.6 and 72.6 for CoFePO, CoPO, CoO and NF, respectively. The ECSA was improved 0.88 times after P doping comparing CoO with CoPO, possibly because the annealing process introduces P into the crystal lattice of CoO thus generating nanoporous and macropores in and between the nanowires, respectively (see Figure S4b-c and Figure S5b-c, the roughness was enhanced obviously and the nanowires become incomplete). While after Fe-doping, the ECSA was improved 1.5 times from CoPO to CoFePO, possibly resulting from more generated pores and much smaller nano-

particles (from tens of nanometers to several nanometers). As a result, the HER turn over frequency (TOF) at overpotential of 300 mV calculated from the above ECSA was compared in the inset of Figure 2b and Table S1, that TOF of CoFePO (16.87 s⁻¹) was greatly improved after Fe doping (2.62 s⁻¹) and P doping (CoO: 0.82 s⁻¹).²³

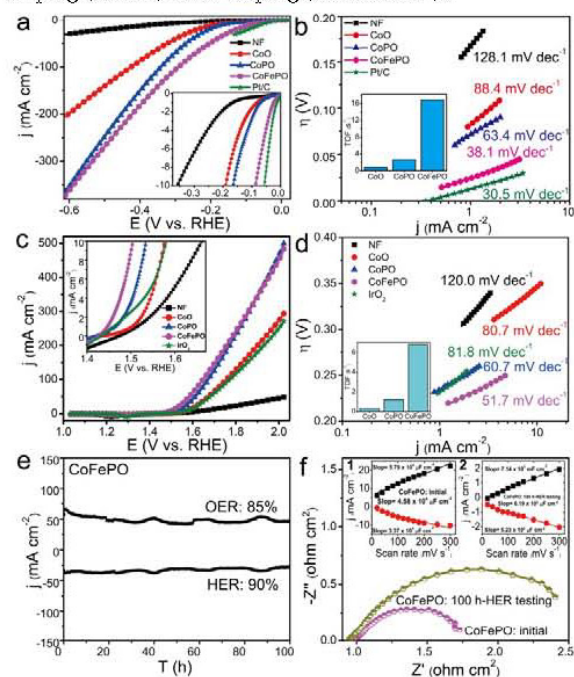


Figure 2. (a) Polarization curves obtained during HER, inset is the polarization curves under 10 mA cm⁻², and (b) Tafel plots of CoFePO, CoPO, CoO, NF and Pt/C, inset is the TOF values. (c) Polarization curves obtained during OER, inset is the polarization curves under 10 mA cm⁻², and (d) Tafel plots of CoFePO, CoPO, CoO, NF and IrO₂, inset is the TOF values. (e) Chronoamperometric response of CoFePO tested in HER and OER processes for 100 h, respectively, and (f) Nyquist plots of CoFePO before and after 100 h HER testing, insets are the ECSA change. All the testing is conducted in 1M KOH.

On the other hand, the anodic OER property of as-obtained materials was also tested (Figure 2c-d). Unexpectedly, CoFePO also displays the highest OER activity requiring the overpotential of 274.5 mV to achieve 10 mA cm⁻² current density ($\eta_{10\text{-OER}}$, obtained by subtracting 1.5045 V vs. RHE from 1.23 V), which is smaller than that of the benchmark IrO₂ (351.5 mV), CoPO (304.5 mV), CoO (346.5 mV) and NF (431.5 mV). The CoFePO OER kinetics is interpreted by the smallest Tafel slope (51.7 mV dec⁻¹), which is also the most favorable one as compared to that of IrO₂ (81.8 mV dec⁻¹), CoPO (60.7 mV dec⁻¹), CoO (80.7 mV dec⁻¹) and NF (120.0 mV dec⁻¹). The low $\eta_{10\text{-OER}}$ and Tafel slope of CoFePO material are smaller than many reported materials, indicating its extraordinary OER property.^{14, 24} Similarly with HER, the R_{ct} of CoFePO is higher than that of CoPO, indicating the charge transfer ability of CoFePO is worse than CoPO during OER process (Figure S8a). But with a much higher ECSA, CoFePO still dis-

plays a larger TOF (6.8 s^{-1} , inset in Figure 2d) for OER tested at 400 mV, than CoPO (1.2 s^{-1}) and CoO (0.3 s^{-1}).²³ Therefore, the CoFePO after cation and anion doping in atomic level not only have the best HER property, but also has the outstanding OER property, both of which are ace-high among reported materials.^{14, 16, 21-22, 24}

A promising electrocatalyst also require the durable stability during practical operation. We estimated the stability of CoFePO for HER and OER, respectively (Figure 2e-f). As a result, over 90% of the initial current density can be retained after 100 hour (h) HER process, while 85% of the initial current density remained after 100 h OER process. Therefore, CoFePO is a robust electrode both for HER and OER.^{10, 16} In addition, the charge transfer ability decreases slightly after 100 h HER and OER processes (Figure 2f and S8b). The ECSA also decreases a little bit after 100 h reaction, probably because of the collapse of the pores and damage of nanowires. All the above obtained electrochemical parameters are summarized in Table S1 for HER and Table S2 for OER.

2.1.2.2 Two-electrode testing

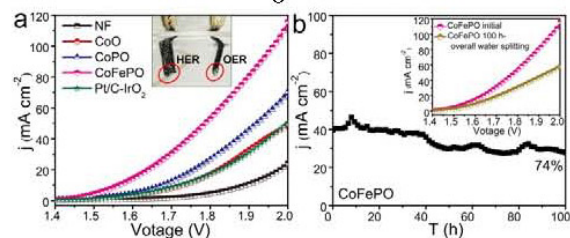


Figure 3. (a) Polarization curves tested in a home-made two-electrode system using NF-NF, CoO-CoO, CoPO-CoPO, CoFePO-CoFePO and Pt/C-IrO₂ as both the cathodes and anodes, (b) Chronoamperometric response in the two-electrode system using CoFePO, inset is the polarization curves before and after the 100 h-stability testing. The testing was conducted in 1M KOH.

The above results indicate CoFePO is a good candidate to catalyze the overall water splitting process. Figure 3a shows the polarization curves in a home-made two-electrode system using as-prepared materials both as cathodes and anodes. The overpotential to obtain a current density of 10 mA cm^{-2} (η_{10}) for CoFePO is as low as 333.5 mV, which outperforms the state-of-the-art Pt/C-IrO₂ counterparts (491.5 mV), CoPO-CoPO (445.5 mV), CoO-CoO (500.5 mV) and NF-NF (659.5 mV). Under electrolysis process, obvious bubbles can be observed on the surface of the electrodes (see inset in Figure 3a and supporting video). The electrode can retain 74% of the initial current density after 100 h operation. Additionally, the electron and charge transfer resistance increased obviously owing to the decreased electron and charge transfer ability of CoFePO after the long-term water-splitting process (Figure S9).

2.2 DISCUSSION

2.2.1 Catalyst

To gain insight into the extraordinary water-splitting performance, X-ray photoelectron spectroscopy (XPS) was tested to investigate the composition, element valence

status and their change before and after cation and anion doping (Figure 4). The deconvolution of Co $2p_{3/2}$ spectrum in CoO sample (Figure 4a) shows three peaks at 779.9 eV, 781.9 eV and 786.2 eV that are consistent with the reported CoO.²⁵ With P-doping into CoO, the main peak of Co $2p_{3/2}$ (780 eV) down-shifts to 778.8 eV in CoPO, which indicates the newly formed Co-P bonding substitutes a part of Co-O bonding.^{17, 26} Meanwhile, the B.E. of O 1s (Figure 4b) up-shifts from 529.7 eV in CoO to 532.1 eV in CoPO, possibly indicating that parts of O-Co bonding are replaced by O-P bonding. By comparing the survey scans of CoO and CoPO (Figure S10), new peaks emerged which can be assigned to P 2s and P 2p. The deconvolution of high resolution P 2p XPS spectrum of CoPO (Figure 4c) displays three peaks at 129.6 eV ($2p_{3/2}$), 130.6 ($2p_{1/2}$) and 133.3 eV (PO_4^{3-}). The lower B.E. of $2p_{3/2}$ in CoPO than that of P $2p_{3/2}$ (130.2 eV of P⁰) suggests strong bondings between metal and P (Co-P).^{17, 26-27} Based on above results, P was successfully doped into the lattice of CoO to form CoPO.

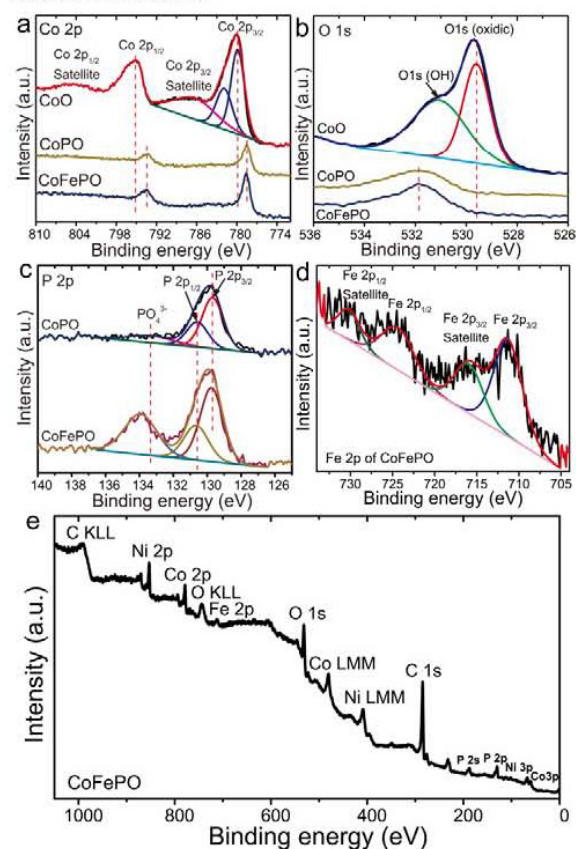


Figure 4. XPS spectra of (a) Co 2p, (b) O 1s, (c) P 2p, (d) Fe 2p and (e) survey scan of as-prepared CoFePO, CoPO and CoO materials.

The B.E. of Co 2p and O 1s in CoFePO are located at 779.0 eV and 532.3 eV, respectively, which are close to those of CoPO, suggesting the presence of P in CoFePO in the form of P-Co and P-O bonding. However, the Co 2p B.E. in CoFePO still increases a little bit in comparison to

CoPO (778.8 eV), probably because of the Fe-doping into CoPO. The O 1s B.E. displays the same trend by increasing from 532.1 eV to 532.3 eV which further confirms the Fe-doping into CoO. The deconvolution of P 2p in CoFePO shows peak at 129.8 eV ($2p_{3/2}$), 130.7 eV ($2p_{1/2}$) and 133.9 eV (PO_4^{3-}), which are also marginally higher than those in CoPO. Similarly, a new Fe 2p peak is observed by comparing the survey scans of CoFePO and CoPO (Figure 4e and S10b). The deconvolution of high resolution Fe 2p spectrum can be assigned to Fe $2p_{3/2}$ (711.3), Fe $2p_{3/2}$ satellite (715.9 eV), Fe $2p_{1/2}$ (724.4) and Fe $2p_{1/2}$ satellite (730.2 eV).⁷ Based on the B.E. shifts of Co2p, O1s, P2p and newly appeared Fe 2p peak, it can be proposed that Fe was also successfully doped into CoFePO similar to the case of P.

By comparing the HER, OER and overall water splitting activities of as-prepared CoO, CoPO and CoFePO materials, it is seen that P-doping into metal oxide can improve both the HER and OER activity, which has been scarcely reported in the literature. The Fe doping into metal phosphoric oxide (CoPO) can also greatly enhance the electroactivity of electrocatalyst. Therefore, both the cation and anion modulation can facilitate the electrocatalytic water splitting, displaying high activity and facile kinetics.

2.2.2 Anion modulation of P/O in metal phosphoric oxide

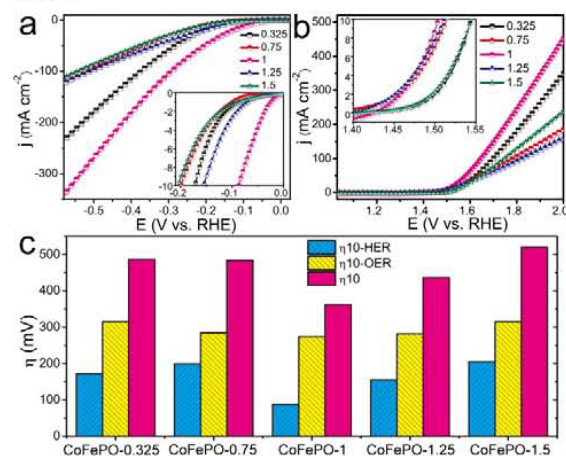


Figure 5. (a) HER and (b) OER polarization curves of CoFePO materials with different amount P source (0.325, 0.75, 1, 1.25 and 1.5). (c) Overpotentials to achieve a current density of 10 mA cm^{-2} .

Next, we investigated how the doping percentage affects the catalytic activity by adjusting the amount of P source. For reliable comparison, we set the amount of P source (TPP) used in the best catalyst-CoFePO as CoFePO-1, and prepared CoFePO-0.325, CoFePO-0.75, CoFePO-1, CoFePO-1.25 and CoFePO-1.5 via a similar procedure (Figure 5). The η_{10} -HER, η_{10} -OER and η_{10} (calculated by adding η_{10} -HER and η_{10} -OER) are summarized in Figure 5c to compare their water splitting performances. The η_{10} for overall water splitting promoted by CoFePO-0.325 is 487 mV, which increases to 484 mV of CoFePO-0.75 and then decreases greatly to 362 mV for CoFePO-1. Further elevating P content, the η_{10} increases to 437 mV for CoFePO-1.25, and then 520 mV for CoFePO-1.5. Therefore, the optimum p-doping percentage

was in CoFePO-1. These controlled experiments also indicate the anion modulation played an important role for the optimization of water-splitting performance.

2.2.3 Cation modulation of Co/Fe

Besides anion doping, the cation doping like Fe-doping into CoPO can also facilitate the kinetics of water electrolysis. Therefore, we conducted a detailed investigation on the effect of the amount of Fe-doping on the water splitting activity. Firstly, set the amount of Fe source used to prepare CoFePO as 1, then we doubled the amount of Fe to prepare CoFePO-Fe-2, and the CoPO without Fe can be considered as CoFePO-Fe-0. As displayed in Figure S11, the η_{10} is 470 mV without Fe-doping, and decreased to 362 mV in CoFePO-Fe-1, but further increased to 598 mV by using more Fe precursor. Therefore, there is an optimum Fe-doping amount in the cation modulation to tune the electrocatalytic activity, which is in CoFePO-Fe-1.

3. CONCLUSIONS

In summary, we have fabricated a bifunctional electrocatalyst for HER and OER by the cation and anion atomic modulation of metal oxides. The as-prepared CoFePO nanowire clusters grew on NF have displayed outstanding HER and OER performance with low overpotentials and durable stability. The overall water splitting activity is superior with a η_{10} as low as 335.5 mV, making CoFePO a promising candidate to substitute the expensive Pt/C and IrO₂ electrocatalysts. Further analyses have been conducted to modulate the P anion and Fe cation in metal oxide (CoO), thus providing a new pathway for the material design and synthesis in the field of electrocatalysis. It is believed that this work will boarden the horizon of water electrolysis and materials chemistry.

ASSOCIATED CONTENT

Supporting Information. The supporting information file includes the characterization of morphology, composition and electrocatalytic measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no completing financial interest.

ACKNOWLEDGMENT

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Atomic Modulation in Metal Phosphoric Oxides for a Bifunctional Overall Water Splitting Electrocatalyst

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KEYWORDS: Overall water splitting, metal phosphoric oxide, atomic modulation, hydrogen evolution reaction, oxygen evolution reaction

This supporting information includes the experimental section and supported figures.

Experimental Section

Materials preparation:

Ni foam (NF) was cleaned by sonicating in acetone, ethanol and Milli-Q water for 30 mins successively before used as substrates. Metal hydroxide (CoFeOH) was grown on NF by a chemical bath deposition (CBD) method.¹ In a typical procedure, 291 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 40.4 mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 4 mL Milli-Q water. In the meantime, 792 mg urea was dissolved in 1.2 mL water. After mixing the above two solutions in a glass vessel, the cleaned NF (1 cm x 3 cm) was immersed and the reaction system was kept at 85 °C for 24 hours (h). Then the as-obtained CoFeOH@NF was washed with water for three times and dried at 60 °C.

The dried CoFeOH@NF was mixed with with 2.103 g Triphenylphosphine (TPP) and heated at 600 °C for 3 h in N₂ atmosphere with a heating rate of 2 °C min⁻¹. The obtained material was denoted as CoFePO.

To prepare the sample without Fe (CoPO), only 291 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 4 mL H₂O, and the solution was mixed with 1.2 mL H₂O with 720 mg urea. The followed procedure is similar to that of CoFePO.

Characterization:

The morphologies of samples were characterized using transmission electron microscopy (TEM, Tecnai G2 Spirit) and scanning electron microscopy (SEM, QUANTA 450). Energy dispersive X-ray spectroscopy (EDS) was measured on QUANTA 450 SEM. The high resolution TEM analysis was conducted on FEI Titan Themis TEM machine. X-ray diffraction (XRD) patterns were recorded on a Philips 1130 X-ray diffractometer (40 kV, 25 mA, Cu K α radiation, $\lambda=1.5418$ Å). X-ray photoelectron spectroscopy (XPS) was performed in an ultra-high vacuum apparatus built by SPECS (Berlin, Germany) at 200 W using a non-monochromatic X-ray source for Mg. The valence band XPS was performed using an Al anode. The XPS spectra were referenced to the carbon 1s peak (285 eV).

Electrochemical measurements:

HER and OER analyses were performed in a three-electrode glass cell on a CHI 650 workstation (Pine Research Instruments, US) using Ag/AgCl/KCl (4 M) as a reference electrode, graphite rod as a counter electrode and the prepared materials as working electrodes. The two-electrode overall water splitting testing was conducted in a home-made glass cell with the obtained material both as the cathode and anode. The loading mass of metals for CoFePO sample was 2.187 mg cm^{-2} , therefore, the same amount of Pt and IrO₂ was coated on NF for comparison. Specifically, 10.935 mg of Pt/C or 2.55 mg IrO₂ was dissolved in 1 mL of ethanol, and the obtained suspension was coated on NF (1 x 1cm) and dried under ambient conditions. Then 50 μL of 1% nafion was drop on the dried NF. In addition, 20 μL Pt/C powder suspensions (2 mg mL^{-1}) was casted on rotating disk electrode (0.196 cm^2) to compare with the sample on NF.

The polarization curves were collected at a scan rate of 1 mV S^{-1} . Electrochemical impedance spectra (EIS) were recorded under AC voltage amplitude of 5 mV with frequencies from 1 Hz to 1×10^5 Hz. The series resistance (R_s) data was obtained in the high frequency zone. All measurements were carried out in N₂-saturated 1M KOH to eliminate dissolved O₂. All potentials were calibrated to RHE by adding a value of $(0.197 + 0.059 \times \text{pH}) \text{ V}$.

Turn over frequency (TOF):

The values of TOF were calculated by assuming that every metal atom was involved in the catalysis (lower limits)²:

$$\text{TOF} = j/4 \times F \times n$$

where j is the current density (A cm^{-2}), F is Faraday's constant ($96485.3 \text{ C mol}^{-1}$) and n is moles of electrocatalysts (mol cm^{-2}).

Electrochemical active surface area (ECSA):

Electrochemical capacitance measurements were used to determine the active surface area of each catalyst. To measure the electrochemical capacitance, the potential was swept between 0.823 to 0.923 V vs. RHE at different scan rates (20, 40, 60, 80, 100, 120, 140, 160, 200, 250 and 300 mV s^{-1}). We measured the capacitive currents in a potential range where no faradic processes are observed, i.e. at 0.923 V vs. RHE. The measured capacitive currents were plotted as a function of scan rate and a linear fit determined the specific capacitance. The specific capacitance can be converted into an ECSA using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. The specific capacitance for a flat surface is generally found to be in the range of 20-60 $\mu\text{F cm}^{-2}$, therefore, an average value $40 \mu\text{F cm}^{-2}$ was used in the calculation.

Mass activity:

The values of mass activity (A g^{-1}) were calculated using the following equation²:

$$\text{Mass activity (A g}^{-1}\text{)} = j/M$$

where M is the electrocatalyst loading amount (mg cm^{-2}) and j is the measured current density (mA cm^{-2}).

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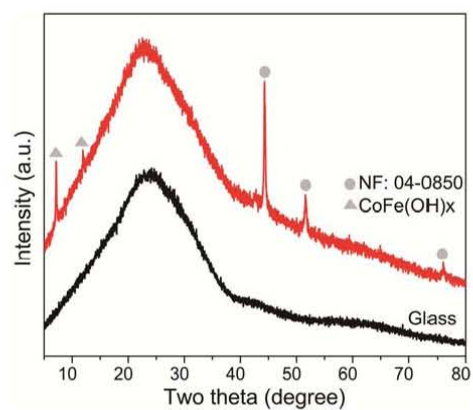


Figure S1. XRD patterns of as-prepared CoFeOH and glass substrate. The CoFeOH@NF was bath-sonicated for half an hour to peel off CoFeOH from the NF substrate, and the dispersion was dropped on glass substrate for XRD measurements.

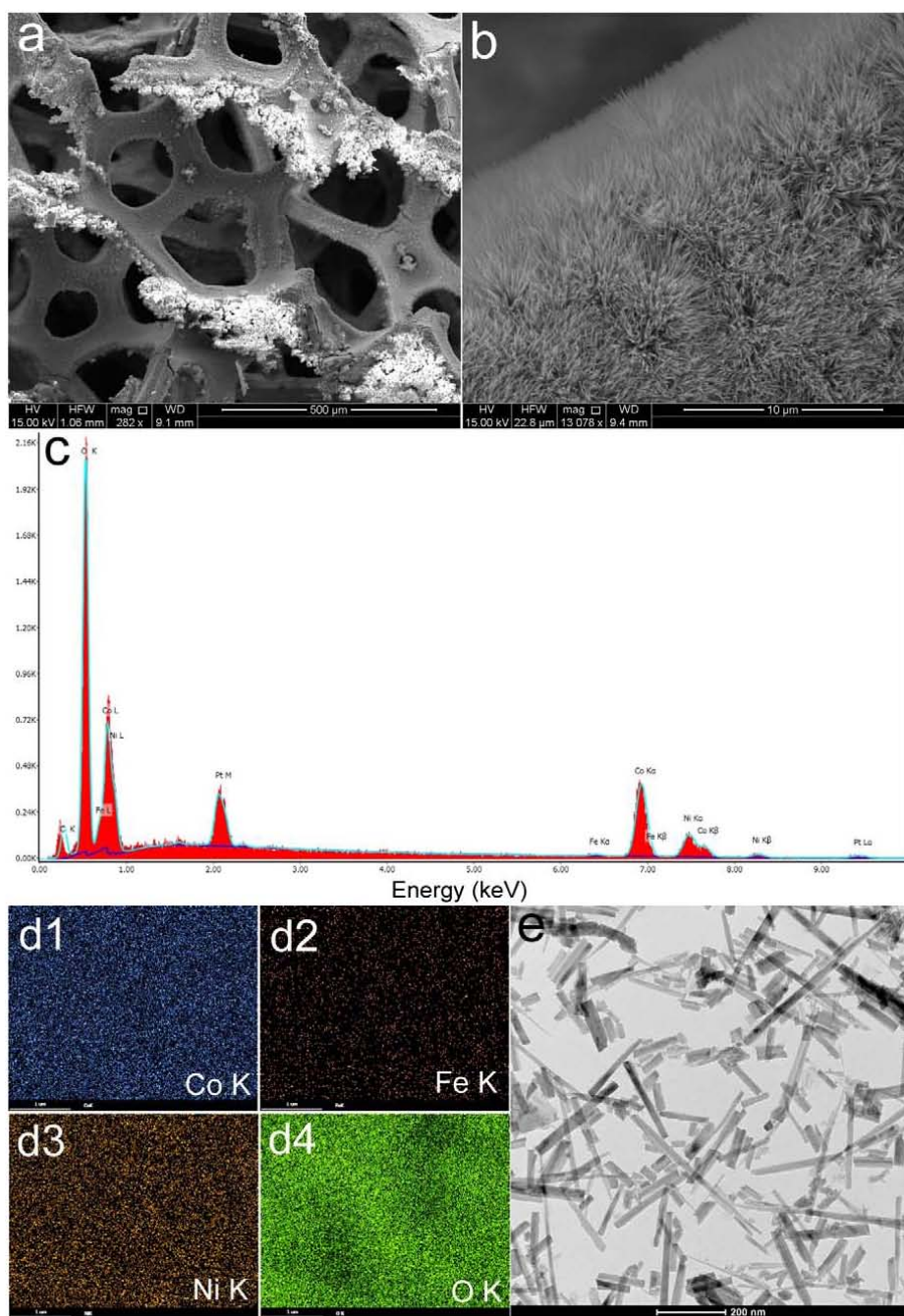


Figure S2. (a-b) FESEM images, (c) SEM EDS spectrum, (d1-4) SEM EDS element mapping of Co K, Fe K, Ni K and O K, and (e) TEM image of CoFeOH.

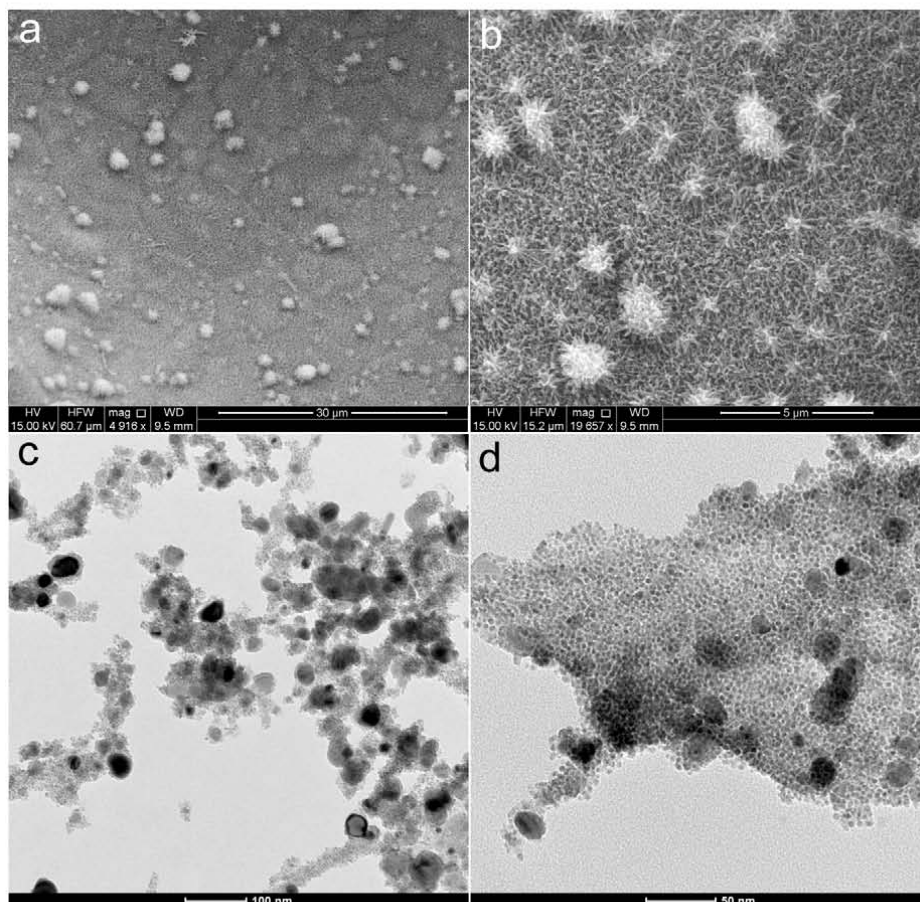


Figure S3. (a-b) FESEM images and (c-d) TEM images of CoFePO

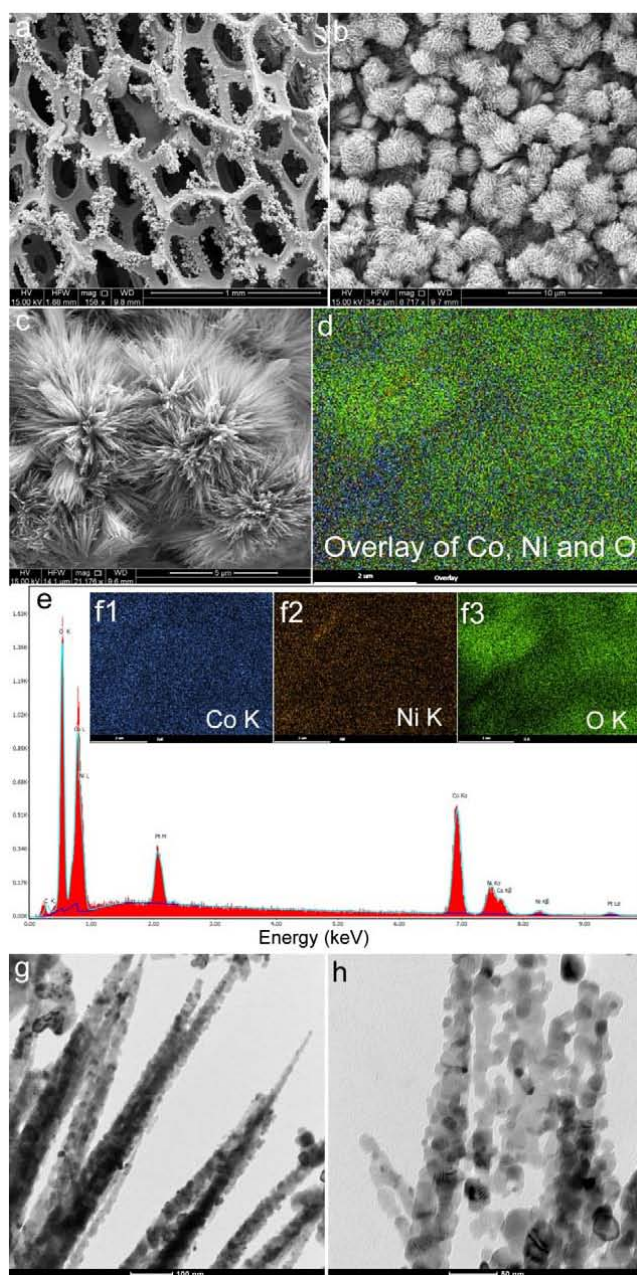


Figure S4. (a-c) FESEM images, (d) Overlay of SEM EDS mapping of Co K, Ni K and O K, (e) EDS spectrum and (f1-3) SEM EDS element mapping images of Co K, P K, Ni K and O K obtained on Figure S4c of CoO sample.

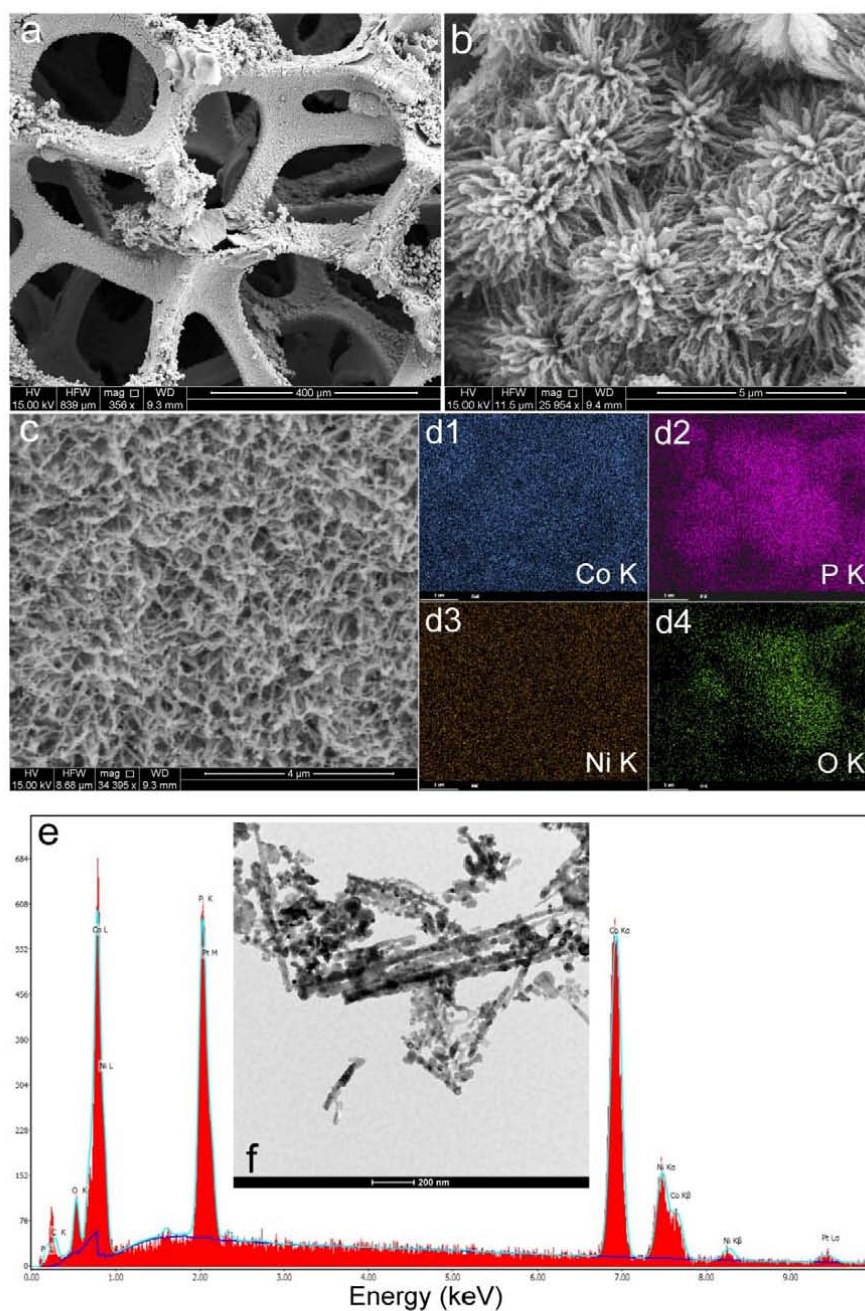


Figure S5. (a-c) FESEM images, (d1-4) SEM EDS element mapping images of Co K, P K, Ni K and O K, (e) SEM EDS spectrum obtained on Figure c, and (f) TEM image of CoPO sample.

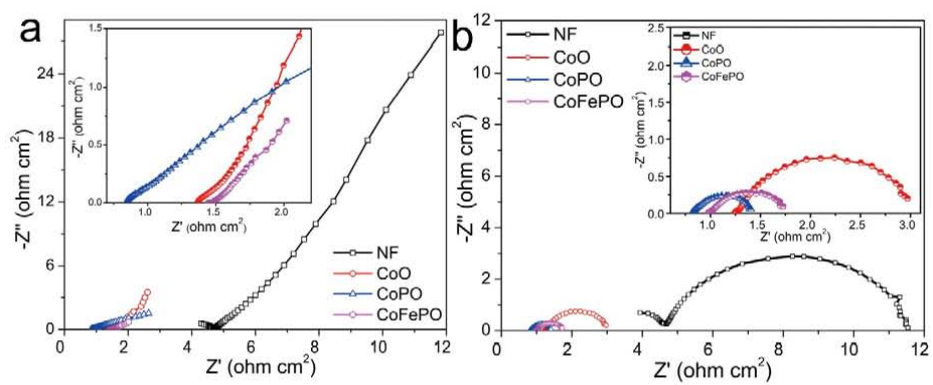


Figure S6. EIS spectra of as-prepared materials measured at (a) 1.023 V and (b) -0.227 V vs. RHE.

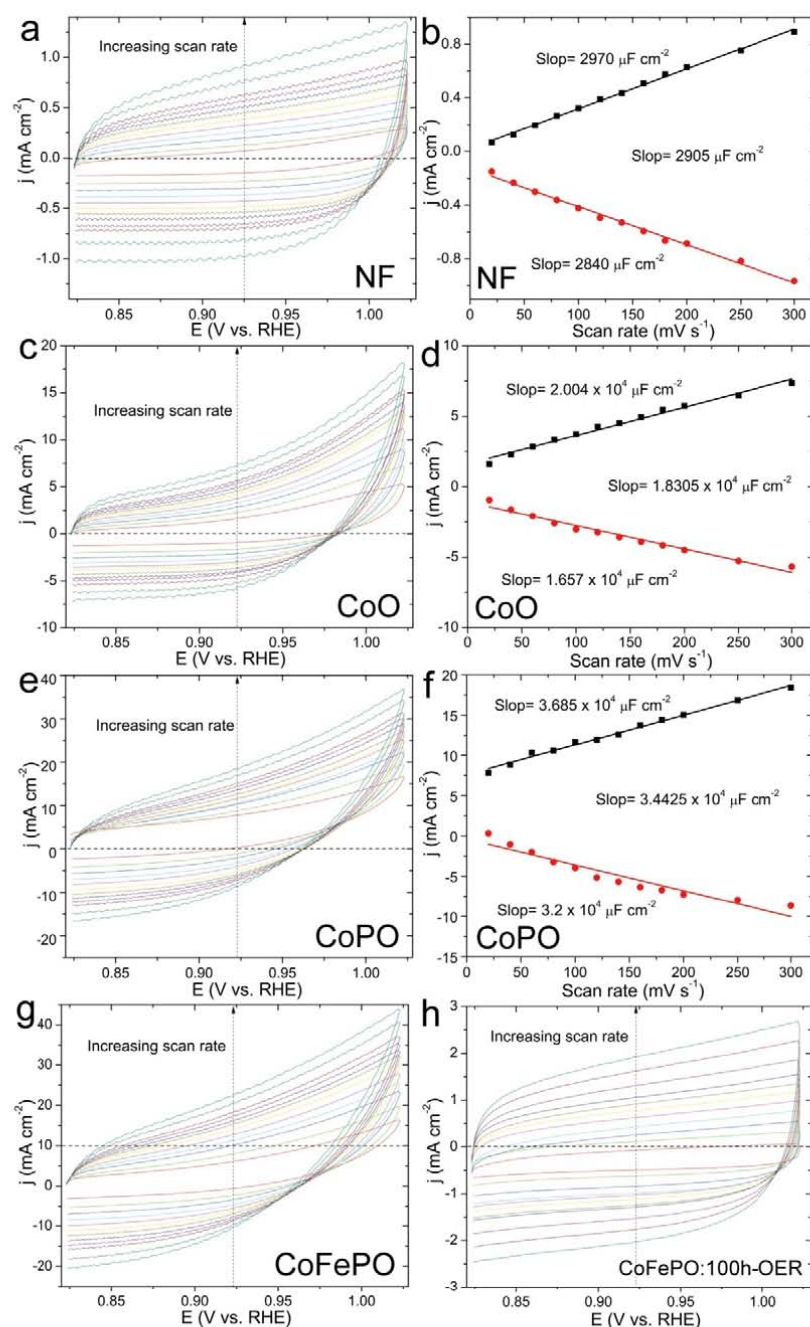


Figure S7. Electrochemical capacitance measurements to determine the surface area of as-prepared electrodes. (a, c, e, g, h) CVs of NF, CoO, CoPO and CoFePO measured at different scan rate and (b, d, f) The measured capacitive currents plotted as a function of scan rate.

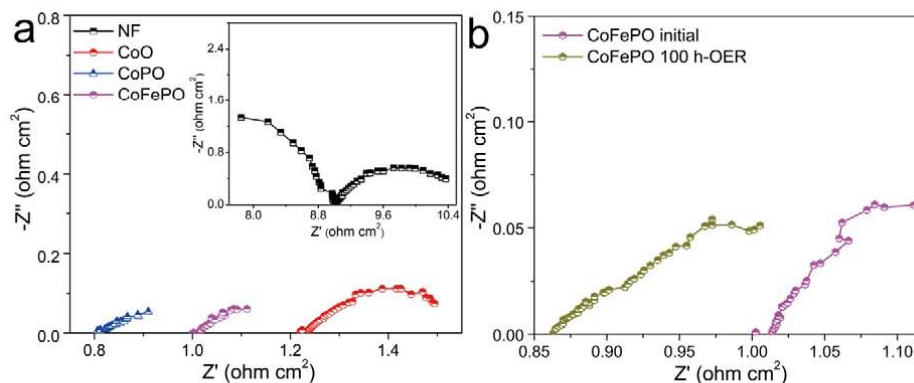


Figure S8. EIS spectra measured at 1.023 V vs. RHE on (a) as-prepared materials (b) CoFePO before and after 100 h-OER testing.

Table S1. Parameters for HER

Materials	η_{10} (V)	Tafel slope (mV dec ⁻¹)	ECSA	Mass loading (mg cm ⁻²)	$j@\eta=0.3V$ (mA cm ⁻²)	TOF (s ⁻¹)	Mass activity@ $\eta=0.3$ V
NF	0.3585	128.1	72.625		6.372		
CoO	0.1915	88.4	457.625	6.89	40.334	0.818	5.854
CoPO	0.1655	63.4	860.625	6.98	69.469	2.616	9.953
CoFePO	0.0875	38.1	1145.125	2.187	105.521	16.873	48.25
Pt/C	0.0565	30.5					

Table S2. Parameters for OER

Materials	η_{10} (V)	Tafel slope (mV dec ⁻¹)	ECSA	Mass loading (mg cm ⁻²)	$j@\eta=0.4V$ (mA cm ⁻²)	TOF (s ⁻¹)	Mass activity@ $\eta=0.4$ V
NF	0.4315	120.0	72.625		7.414		
CoO	0.3465	80.6	457.625	6.89	29.04	0.295	4.215
CoPO	304.5	60.0	860.625	6.98	63.66	1.20	9.12
CoFePO	274.5	51.7	1145.125	2.187	85.16	6.809	38.94
IrO ₂	351.5	81.8		2.187	25.48		11.65

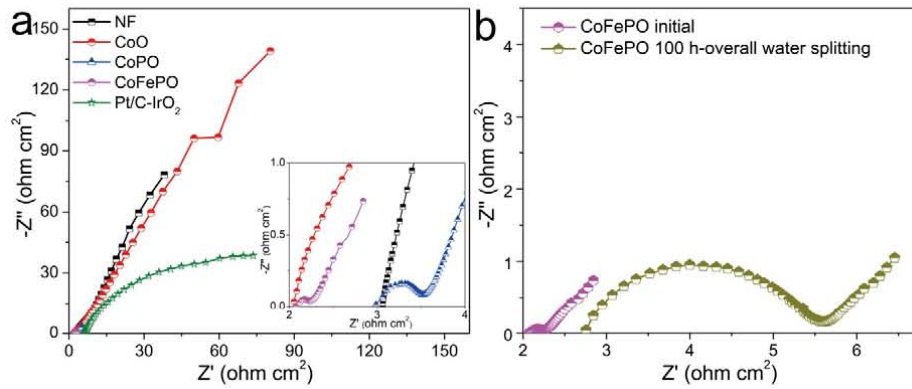


Figure S9. EIS spectra measured at voltage of 1 V on (a) as-prepared materials, (b) EIS spectra before and after 100 h-overall water splitting of CoFePO.

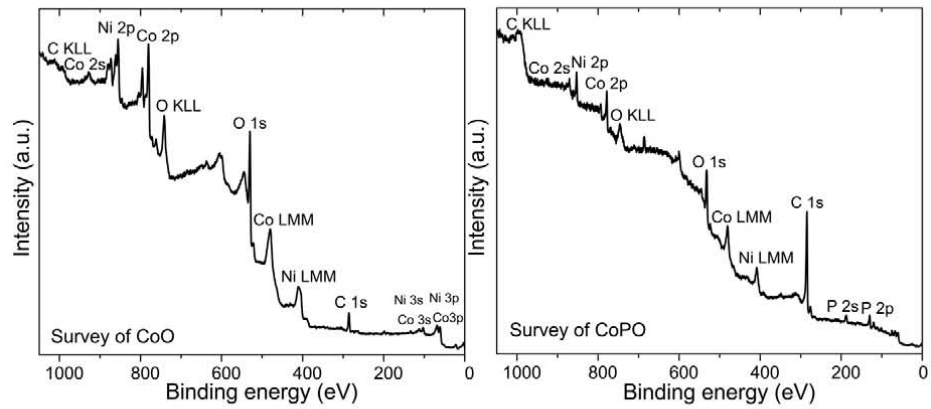


Figure S10. XPS survey scans of CoO and CoPO samples.

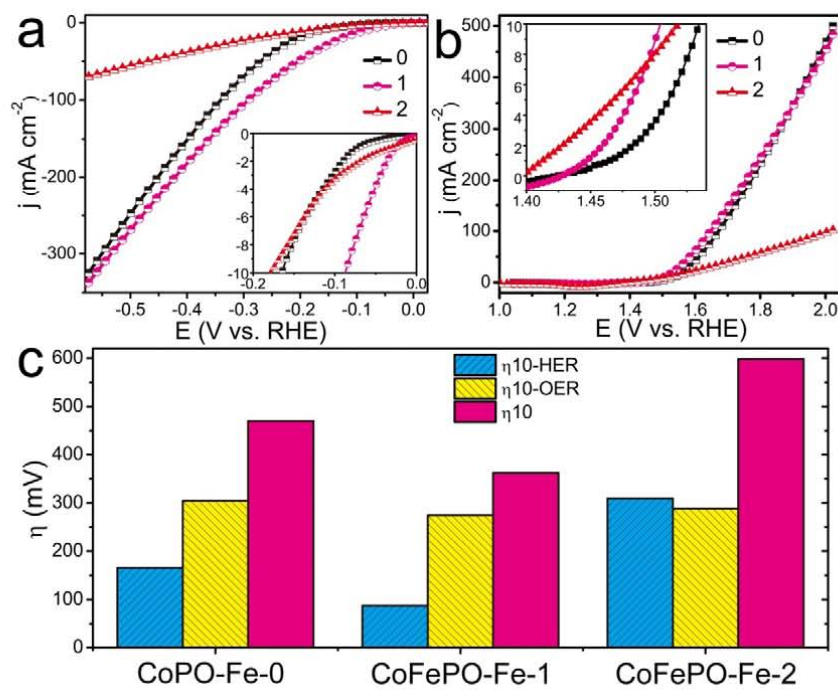


Figure S11. (a) HER and (b) OER polarization curves of CoFePO materials with different Fe contents (0, 1 and 2). (c) Overpotentials to achieve a current density of 10 mA cm⁻².

Chapter 8: Conclusions and Perspectives

8.1 Conclusions

This thesis is devoted to gain insights into the mechanisms and kinetics of some key electrocatalytic processes, such as ORR, HER and OER, and to develop the low cost, active and durable electrocatalysts as precious-metal alternatives. Based on the research in this thesis, the following conclusions can be drawn:

- (1) The electrocatalytic activity can be effectively improved by doping graphene with heteroatoms (N, B, S and/or P), because its adsorption and desorption capability of reactants, intermediates and products is modified by introduced charge and spin densities on C atoms nearby dopants. In the hybrids consisting of heteroatom-doped graphene and transition metal oxides, the doped graphene not only acts as the conductive support for anchoring nanoparticles, but also contributes to the catalytic activity by providing additional active sites. Therefore, the prepared Mn_3O_4 @N-doped graphene hybrid displays high ORR activity, excellent durability, and absolute tolerance to methanol. Significantly, the strong coupling effects are present in such hybrids, which not only improve the stability of electrocatalysts but also enhance their electrocatalytic activity by forming active metal-dopant sites to facilitate the electron transfer between metal and doped graphene.
- (2) As the heterogeneous ORR process involves the adsorption of reactants and desorption of products on the exposed facets of nanocrystals, the dependence of ORR activity on the shape of metal oxide nanoparticles has been further studied. Mn_3O_4 nanoparticles with three different shapes (spheres, cubes, and ellipsoids) on nitrogen-doped graphene sheets are prepared through a two-step liquid-phase procedure. Among them, the ellipsoidal sample exhibits the highest ORR activity with a positive onset-potential of $-0.13\text{ V vs Ag/AgCl}$ and a high kinetic limiting current density of 11.69 mA cm^{-2} at $-0.60\text{ V vs Ag/AgCl}$. The ORR activity is firstly correlated to the shape of Mn_3O_4 nanocrystals, and specifically to the exposed crystalline facets.
- (3) The mechanism study indicates the HER performance is not only related to the activity but also the kinetics regarding the mass transport during electrocatalytic processes. HER performance was optimized by tuning the chemical composition, catalyst nanostructure and importantly the electrode architecture, by adapting the three dimensional hybridized graphene films. Their remarkable structural properties, such as high specific surface areas, 3D conductive networks, and hierarchical porous structures, can facilitate the electron transport and ion diffusion during electrocatalytic processes, greatly facilitating the

reaction kinetics. Integrating highly active HER catalysts of porous C_3N_4 and 1T- WS_2 nanolayers into the 3D heteroatom-doped graphene film combines high activity and facile kinetics together which leads to unbeatable HER performance. Moreover, the 3D free-standing architectures can be used as working electrodes without membrane electrode assembly process, thus avoiding the catalyst agglomeration and peeling off from supports, and assuring good activity retention during catalytic processes.

- (4) The overall water splitting process has been studied, and a bifunctional electrocatalyst has been designed and fabricated by cation and anion doping of metal oxides. The P anion doping into metal oxide was achieved by annealing treatment with P source, and the doping content was adjusted by changing the amount of P source, which further can be used to optimize the HER and OER activity. The Fe cation doping can be tuned by the addition of Fe salts in the precursor preparation, which can improve the electrocatalytic activity further. Additionally, the three-dimensional conductive network provided by nickel foam substrate is highly facile for the electron and charge transportation, resulting favourable reaction kinetics. As a result, superior overall water splitting performance was obtained by combining the high activity (rich active species generated by cation and anion doping), facile kinetics and high accessibility of active sites (three-dimensional conductive porous structure).

8.2 Perspectives

Although significant progress for electrocatalytic ORR, HER and OER has been made in this thesis, there are still some challenges in the future research.

- (1) Most of the graphene-doping methods require high temperatures and harsh conditions, which impede the large-scale production and commercialization of heteroatom-doped graphene. It is highly desirable to develop facile and green synthesis of heteroatom-doped graphene based materials. In addition, there are always several doping structures coexisting in the doped graphene sheets. The controlled synthesis of doped graphene with single doping configuration is necessary to study the effect of one specific configuration on electroactivity, since the different doping configurations are known to play diverse roles in electrocatalysis.
- (2) Moreover, despite that the achieved catalytic activity is close to that of noble metals (Pt, IrO_2 and RuO_2), there is still a big challenge to make non-precious-metal materials commercially competitive to precious metals especially in terms of the large-scale production and operation under harsh electrochemical conditions. Therefore, some new metal compounds other than metal oxides may be tried as electrocatalysts, such as metal

phosphides, metal carbides, metal nitride and their hybrids, because of their good resistivity to acidic or basic conditions and also abundant resource.

- (3) Further, the reaction mechanisms are still inconclusive in many electrochemical systems because of the continuous development of new materials. As a result, more theoretical study combining experiments and calculations is needed to resolve this fundamental problem.

We believe that further explorations in this exciting electrocatalytic area will contribute to green energy systems with all the above problems solved.

Appendix: Publications during Ph.D

Papers in refereed journals:

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