Transitional metal based nanomaterials as catalysts for water electrolysis

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**NANYANG
TECHNOLOGICAL
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SINGAPORE

TRANSITIONAL METAL BASED
NANOMATERIALS AS CATALYSTS FOR WATER
ELECTROLYSIS

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Abstract

Growing concerns about fossil-fuel crisis and global warming make it urgent to explore renewable energy sources as alternatives to fossil fuels. Finding a green and efficient way to harvest, store and use renewable energy is highly necessary. As an energy carrier, hydrogen, has attracted massive attention due to its highest gravimetric energy density and free of CO₂ emissions. In addition, electrochemical water splitting provides a feasible and environmental method to produce hydrogen. However, the sluggish kinetics in both side electrodes makes it not economic. To decrease the energy consumption and speed up the reaction rate, efficient and earth abundant catalysts are urgently needed. In this thesis, we focus on the rational design and facile preparation of transition metal based nanomaterials, which are one group of promising catalysts.

Radio frequency (RF) plasma is emerging as a very efficient and environmentally friendly technology for surface modification and conversion reaction of solid electrode materials. In this thesis, we first applied the RF N₂ plasma to fabricate metal nitrides via the conversion reaction and studied their superior electrochemical performances as catalysts for water splitting. Transition metal nitrides possess high chemical stability and functional physical properties, such as superior corrosion resistance, high conductivity and high melting points. In addition, the introduced N atoms strongly affect the electronic structure of the metal by concomitant structural modification and/or charge transfer processes. They show excellent catalytic activities

in various areas due to their distinct electronic structure. However, in most previous reports, metal nitrides are prepared via annealing precursors under caustic and hazardous ammonia (NH_3) flow. Even worse, it requires long processing duration and high reaction temperature. In this method, earth abundant and nontoxic N_2 is used as nitrogen source and the processing duration is only a few minutes. We successfully converted dense NiMo alloy and Ni metal films into 3D porous nickel molybdenum nitride (NiMoN) and nickel nitride (Ni_3N), respectively. Attributed to the synergistic effect of Ni, Mo and N, high roughness factor and electron transport, the obtained NiMoN catalyst exhibits outstanding hydrogen evolution reaction (HER) performance, reaching the current density of 10 mA cm^{-2} at a small overpotential ($\sim 109 \text{ mV}$) with a long-term stability under different current densities.

In addition to dense metal precursors, nanostructured metal (hydr)oxides could also be converted into corresponding metal nitrides. For example, Co_3O_4 nanowire arrays were converted into CoN with the nanowire nanostructure preserved at room temperature in one minutes under N_2 plasma. We studied in detail their superior electrochemical performances for OER and compared to four control samples with different plasma treatment durations. The 1-min sample show best performance – small overpotential (290 mV) at 10 mA cm^{-2} and small tafel slope (70 mV Dec^{-1}) due to the complete conversion and well-preserved morphology. This method is new and should be applicable to a wide range of metal nitrides that can be useful in supercapacitors, Na-ion batteries, OER/HER, etc.

Transitional metal oxides, as a large and important class of chemical compounds, are easily available materials with various nanostructures, which endows them large specific surface areas. We found that there is a slow self-activation of metal oxides during the constant hydrogen evolution process due to the reduction of intermediate hydrogen. But the self-activation effect is only temporary and not stable. Hence pre-reducing of metal oxides should be a feasible method to improve their catalytic activity. Metal oxides (NiMoO_4 , Co_3O_4 and NiO) were pre-reduced by H_2 and C-plasma, respectively. Compared with traditional H_2 annealing reduction method, the carbon plasma treatment has a “One stone, two birds” effect - it not only creates lower-valence active sites on the surface, but also deposits a thin graphitic carbon shell simultaneously. This carbon shell protects the surface from re-oxidation and can maintain the catalytic activity for long time. Our C-plasma method opens a new door to make cheap metal oxides more catalytic efficient and stable for HER in harsh conditions.

In chapter 5, benefiting from the uniform dip coating and in-situ reduction of precursor, a series of ultrafine transition metal-based nanoparticles (Ni-Fe, Ni-Mo) embedded in N-doped carbon have been successfully fabricated as replacements for noble metal-based catalysts in electrolytic water splitting. The diameter of metal-based nanoparticles is around 2 nm, which increases the availability of active sites for electrocatalysis. The as-prepared catalysts demonstrate outstanding catalytic activities rendered by the synergistic effect of bimetal elements and N-dopants, the improved electrical conductivity and hydrophilism. Ni/Mo₂C@N-doped porous carbon

(NiMo-PVP) and NiFe@N-doped carbon (NiFe-PVP) produce low overpotential of 130 and 297 mV at a current density of 10 mA cm^{-2} as catalysts for HER and OER, respectively. In addition, the binder-free electrodes make them show long-term stability. The overall water splitting is also demonstrated based on the couple of NiMo-PVP || NiFe-PVP.

Finally, the achievements in each chapter are summarized in chapter 6. In addition, the plans for further research are also proposed.

Table of Contents

Acknowledgement	I
Abstract	III
Publications.....	IX
Chapter 1 Introduction	1
1.1 Background	1
1.2 Hydrogen evolution reaction.....	4
1.2.1 Mechanism	4
1.2.2 Current state of catalysts development for HER	7
1.3 Oxygen evolution reaction	12
1.3.1 Mechanism	12
1.3.2 Current state of catalysts development for OER	14
1.4 Important measurements and parameters for the study of electrocatalysts	18
1.5 Motivation, Objectives and Scope of thesis	22
Chapter 2 Fabrication and Characterization	25
2.1 Radio frequency plasma.....	25
2.1.1 Fabrication of 3D porous NiMoN and CoN nanowire arrays via N ₂ plasma .	27
2.1.2 Prereduction of metal oxides via carbon plasma	29
2.2 Dip-coating method.....	30
2.2.1 Preparation of hybrid of Ni/Mo ₂ C@N-doped porous carbon (NiMo-PVP)...	31
2.2.2 Preparation of hybrid NiFe nanoparticle@N-porous carbon (NiFe-PVP)	32
2.3 Sample characterization	32
2.4 Electrochemical characterization	32
Chapter 3 Nanostructured Metal Nitrides via N₂ RF Plasma for Electrolysis of Water Splitting	35
3.1 Introduction	36
3.2 Results and Discussion.....	37
3.2.1 Synthesis of 3D Porous NiMoN and Its HER Performance	37
3.2.2 Synthesis of CoN Nanowire Arrays and Its OER Performance	49
3.2.3 Overall water splitting of the NiMoN CoN electrolyzer	61

3.3 Conclusion	62
Chapter 4 Pre-reduction of Metal Oxides via Carbon Plasma as Catalysts for Hydrogen Evolution Reaction	64
4.1 Introduction	65
4.2 Results and Discussion.....	67
4.2.1 Pre-reduction of NiMoO ₄ nanowire arrays and their HER performance.....	67
4.2.2 Pre-reduction of Co ₃ O ₄ nanowire arrays and their HER performance	77
4.3 Conclusion	78
Chapter 5 Ultrafine metal nanoparticles/N-doped porous carbon hybrids coated on carbon fibers as flexible and binder-free water splitting catalysts	80
5.1 Introduction	81
5.2 Results and Discussion.....	83
5.2.1 Characterization of NiMo-PVP and its HER performance.....	84
5.2.2 Characterization of NiFe-PVP and its OER performance	94
5.3.3 Overall water splitting of NiMo-PVP NiFe-PVP	99
5.3 Conclusion	101
Chapter 6 Summary and Future Work.....	103
6.1 Conclusions	103
6.2 Comments and future work	105
References	107

Publications

1. **Yongqi Zhang**, Bo Ouyang, Kun Xu, Xinhui Xia, Zheng Zhang, Rajdeep Singh Rawat and Hong Jin Fan, Prereduction of Metal Oxides via Carbon Plasma Treatment for Efficient and Stable Electrocatalytic Hydrogen Evolution, *Small*, 2018, 14, 1800340
2. **Yongqi Zhang**, Rajdeep Singh Rawat and Hong Jin Fan, Plasma for Rapid Conversion Reactions and Surface Modification of Electrode Materials, *Small methods* 2017, 1, 1700164
3. **Yongqi Zhang**, Xinhui Xia, Xun Cao, Bowei Zhang, Nguyen Huy Tiep, Haiyong He, Shi Chen, Yizhong Huang, Hong Jin Fan*, Ultrafine Metal Nanoparticles/N-Doped Porous Carbon Hybrids Coated on Carbon Fibers as Flexible and Binder-Free Water Splitting Catalysts, *Adv. Energy Mater.* 2017, 7, 1700220.
4. **Yongqi Zhang**, Guichong Jia, Huanwen Wang, Bo Ouyang, Rajdeep Singh Rawat and Hong Jin Fan*, Ultrathin CNTs@FeOOH nanoflake core/shell networks as efficient electrocatalysts for the oxygen evolution reaction, *Mater. Chem. Front.*, 2017, 1, 709
5. **Yongqi Zhang**, Bo Ouyang, Jing Xu, Guichong Jia, Shi Chen, Rajdeep Singh Rawat and Hong Jin Fan*, Rapid Synthesis of Cobalt Nitride Nanowires: Highly Efficient and Low-Cost Catalysts for Oxygen Evolution, *Angew. Chem. Int. Ed. Engl.* 2016, 55 (30), 8670
6. **Yongqi Zhang**, Bo Ouyang, Jing Xu, Shi Chen, Rajdeep Singh Rawat and Hong Jin Fan*, 3D Porous Hierarchical Nickel-Molybdenum Nitrides Synthesized by RF Plasma as Highly Active and Stable Hydrogen-Evolution-Reaction Electrocatalysts, *Adv. Energy Mater.*, 2016, 6 (11) 1600221
7. Bo Ouyang, **Yongqi Zhang** (equal contribution), Zheng Zhang, Hong Jin Fan, Rajdeep Singh Rawat, Nitrogen-Plasma-Activated Hierarchical Nickel Nitride Nanocorals for Energy Applications, *Small* 2017, 13, 1604265.
8. Bo Ouyang, **Yongqi Zhang** (equal contribution), Ying Wang, Zheng Zhang, Hong Jin Fan, Rajdeep Singh Rawat, Plasma surface functionalization induces nanostructuring and nitrogen-doping in carbon cloth with enhanced energy storage performance, *J. Mater. Chem. A*, 2016, 4 (45), 17801
9. Xinhui Xia, **Yongqi Zhang** (equal contribution), Zhanxi Fan, Dongliang Chao, Qinqin Xiong, Jiangping Tu, Hua Zhang, Hong Jin Fan, Novel Metal@Carbon Spheres Core-Shell Arrays by

-
- Controlled Self-Assembly of Carbon Nanospheres: A Stable and Flexible Supercapacitor Electrode, *Adv. Energy Mater.*, 2015, 5 (6), 1401709
10. Xinhui. Xia, **Yongqi Zhang** (equal contribution), Dongliang Chao, Qinqin Xiong, Zhanxi Fan, Xili Tong, Jiangping Tu, Hua Zhang, Hong Jin Fan, Tubular TiC fibre nanostructures as supercapacitor electrode materials with stable cycling life and wide-temperature performance, *Energy & Environ. Sci.*, 2015, 8 (5), 1559
11. Guichong. Jia, Huanwen Wang, Dongliang Chao, Haiyong He, Nguyen Huy Tiep, **Yongqi Zhang**, Zheng Zhang, Hong Jin Fan, Ultrathin MoSe₂@ N-doped carbon composite nanospheres for stable Na-ion storage, *Nanotechnology* 2017, 28, 42LT01
12. Huanwen Wang, Guichong Jia, Yuanyuan Guo, **Yongqi Zhang**, Hongbo Geng, Jing Xu, Wenjie Mai, Qingyu Yan, Hong Jin Fan, Atomic Layer Deposition of Amorphous TiO₂ on Carbon Nanotube Networks and Their Superior Li and Na Ion Storage Properties, *Adv. Mater. Interfaces* 2016, 3, 1600375.
13. Xinhui Xia, Dongliang Chao, **Yongqi Zhang**, Jiye Zhan, Yu Zhong, Xiuli Wang, Yadong Wang, Ze Xiang Shen, Jiangping Tu, Hong Jin Fan, Generic Synthesis of Carbon Nanotube Branches on Metal Oxide Arrays Exhibiting Stable High-Rate and Long-Cycle Sodium-Ion Storage, *Small* 2016, 12, 3048.
14. Huanwen Wang, Yu Zhang, Huixiang Ang, **Yongqi Zhang**, Huiteng Tan, Yufei Zhang, Yuanyuan Guo, Joseph. B. Franklin, Xing Long Wu, Madhavi Srinivasan, Hong Jin Fan, Qingyu Yan, A High-Energy Lithium-Ion Capacitor by Integration of a 3D Interconnected Titanium Carbide Nanoparticle Chain Anode with a Pyridine-Derived Porous Nitrogen-Doped Carbon Cathode, *Adv. Funct. Mater.* 2016, 26, 3082.
15. Xinhui Xia, Yadong Wang, Donghuang Wang, **Yongqi Zhang**, Zhanxi Fan, Jiangping Tu, Hua Zhang, Hong Jin Fan, Atomic-layer-deposited iron oxide on arrays of metal/carbon spheres and their application for electrocatalysis, *Nano Energy* 2016, 20, 244.
16. Xinhui Xia, Zhiliang Ku, Ding Zhou, Yu Zhong, **Yongqi Zhang**, Yadong Wang, Min Joon Huang, Jiangping Tu, Hong Jin Fan, Perovskite solar cell powered electrochromic batteries for smart windows *Mater. Horiz.* 2016, 3, 588.

Chapter 1 Introduction

1.1 Background

Energy is the driving force for development of human society. The rapid development of industrialization gives great convenience to our spirit and life, at the same time it also promotes the tremendous demands for energy.^[1] Generally, based on the intrinsic nature of energy sources, there are mainly two categories: non-renewable and renewable sources. Currently, nonrenewable fossil fuels (coal, oil and natural gas) occupy the main position in energy supplement. The mass extraction and consumption of them leads to serious environmental problems. And they could not be re-generated within a short span of time. As projected by the U.S. Energy Information Administration, the consumption of energy will be doubled between 2010 and 2040, from 524 quadrillion British thermal units (Btu) in 2010 to 820 quadrillion Btu.^[2] The serious energy crisis and environment issues caused by the exploitation of fossil fuels have affected the sustainable development of society.^[3] Renewable energies, such as solar, wind, tide, geothermal, are inexhaustible and the exploitation of them has very little influence in environment. Hence, exploiting and utilizing clean and renewable energy are vital for the sustainable development of society.^[4] However, these renewable energy sources are intermittent and inhomogeneous distributed, which results in great challenge for energy storage and transmission. To fully exploit them, efficient and affordable energy conversion and storage technologies are needed to convert them from current forms to others for storage and resupply.^[5, 6]

Hydrogen (H₂) has the highest specific energy density (142.35 kJ/kg) among any known fuels without CO₂ emissions and is considered as the future clean fuel.^[7] Converting these renewable energies into hydrogen via the electrolysis of water splitting and then supplying energy by fuel cells is considered as one of the most promising candidates.^[1, 8] More importantly, H₂O is not only the raw material for hydrogen production but also the only product after providing energy. In addition, compared to the current large-scale H₂ production method—steam reforming of hydrocarbons, water splitting does not need any high temperature and pressure reaction vessels and the produced H₂ is more pure.^[9, 10]

Electrolysis water splitting is the process that decomposing of water into hydrogen gas and oxygen gas during an electric current being passed through the water and converting electric energy into chemical energy. Anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER) are the two half-cell reactions during the electrolysis of water splitting.^[11] As shown in **Figure 1.1**, hydrogen evolution via electrolysis of water splitting proceeds in electrolytic cell, which is mainly composed of anode, cathode and electrolyte. The overall reaction function is as the following.^[12]

Figure 1.1 Schematic of the water electrolysis

As it is well-known, the hydrogen production via electrolysis of water is not favorable in thermodynamic and kinetic terms. External electric energy is required to promote the reaction. The minimum necessary voltage to start the water splitting reaction, i.e. theoretical decomposition voltage (E^0), could be calculated under standard conditions (1 atm and 298.15 K) by:

$$\Delta G = nFE^0 \quad (1.2)$$

where ΔG , the change of the Gibbs free energy, is 237.1 kJ/mol; n , the number of electrons transferred, is 2; and F , the Faraday constant, is 96485 C/mol. So E^0 is 1.23 V. However, as shown in **Figure 1.2**, a larger applied potential than the E^0 is always required due to complex electron and ion transfer processes. Specifically, $\sum \eta$ is the summary of the overpotentials (activation energy at both electrodes, and the mass transport of gaseous products away from the electrode surfaces). R is the total ohmic series resistance including external circuit resistance, electrolyte and electrodes. In practical, the voltage to drive the reaction of water splitting at i could be expressed as:

$$E_{\text{electrode}} = E_0 + iR + \sum \eta \quad (1.3)$$

Hence, researchers could improve the energy conversion efficiency in the following

two aspects: i) the development of highly activity catalysts with smaller overpotential, and ii) the reduction of overall systematic resistance. The state-of-art catalysts are all noble metal-based materials (Pt, Ir, Ru).^[13] However, the scarcity on earth and high cost of these noble metals make it unpractical to large scale application. Hence, it is highly desirable to look for low cost electrocatalysts with superior electrochemical performance.

Figure 1.2 Schematic of the potentials involved in water splitting under standard conditions.

1.2 Hydrogen evolution reaction

1.2.1 Mechanism

HER, a reduction reaction takes place at the cathode with hydrogen cations accepting electrons from electrode to form hydrogen gas. The mechanism of HER is strongly influenced by the pH value of electrolytes.^[14]

In acidic solution, the HER process proceeds as the following steps:^[15]

i) The discharge of proton (H^+) on the catalyst surface with the formation of an absorbed hydrogen atom ($^*\text{H}_{\text{ads}}$):

ii) The $^*\text{H}_{\text{ads}}$ further discharges with a proton to produce a hydrogen molecule: during this process, there are generally two steps:

Or

iii) Coupling of two $^*\text{H}_{\text{ads}}$ to produce a hydrogen molecule:

In neutral and alkaline solutions, H_2O molecular takes part in the HER reaction instead of H^+ due to the high pH value. The symbol of “*” represents the hydrogen absorption site.

Ideally, Tafel plot derived from the polarization curve could provide helpful information to study the HER mechanism. In acid solution, if the rate limiting step is the equation (1.6), (1.7), or (1.8), Tafel slope should be around 120, 40, and 30 mV Dec^{-1} , respectively. If the Tafel value located in the range of between 30~40 or 40~120 mV Dec^{-1} , the limiting steps will be Heyrovsky-Tafel or Volmer-Heyrovsky.^[16] In alkaline conditions, the mechanism is still unclear. For the HER catalyst of Pt/C, it is controlled by the Volmer step with a Tafel slope of ~30 mV dec^{-1} . However, it should be noted that there are many other factors to disturb the

Tafel slope, such as applied potential, mass transport in porous structure and the presence of adsorbents.

Figure 1.3. Exchange currents vs. metal-hydrogen bond strength.^[17]

In molecular scale, the M-H bond strength plays a vital role in determining the rate and type of mechanism for the electrochemical evolution of hydrogen. As previous discussed, in the Volmer step, the strong M-H bond strength facilitates the catalyst attract the H^+ or H_2O to form $H_{(a)}$. While in the Heyrovsky and Tafel steps, the desorption of $H_{(a)}$ is needed to form H_2 molecules. During this process, weaker M-H bond promotes the reaction to carry on. So a proper M-H bond strength is required to get the optimal catalyst. Volcano plot (the relationship of M-H and exchange current density) is a facile tool to direct the design of ideal catalysts. As shown in **Figure 1.3**, the value of exchange current density reaches a maximum value at Pt. This is in consistent with experiment result that Pt is the most active HER catalyst. The M-H

bond strengths of these left metals are weaker or stronger. Hence, alloying them is a choice to get optimal M-H bond strength for HER. In addition, according to the hypo-hyper theory, heteroatoms (metal or nonmetal atom) are able to influence the Fermi-level of present metal. So metal alloys, metal oxides, sulfides, nitrides, carbides, phosphides and so on are extensively studied as catalysts for HER.^[17]

1.2.2 Current state of catalysts development for HER

1.2.2.1 Noble metal (Pt) based materials

Until now, the most efficient catalysts for HER are still Pt-based materials. The scarcity on earth and high cost seriously hinder their large-scale application. Many strategies have been done to reduce the content of Pt in catalysts, such as covering a layer of Pt on porous substrate and alloying Pt with other non-noble metals. For example, Chen's group^[18] prepared monolayer Pt on WC substrates. When the monolayer Pt deposited on substrate with high specific surface area, its HER performance is comparable to that of 5-10 nm Pt nanoparticles. While a huge reduction in Pt loading, accompanying with the cost of whole electrode. PtNi₃ bimetallic concave octahedrons were reported by Yang's group.^[19] In these particles, large amount of Pt atoms are deposited on the frames, making them show comparable HER performance as Pt catalyst.

In recent years, single atom technique has been developed to make the maximum use of the catalytic materials.^[20] For example, Cheng et. al. downsized the Pt nanoparticles to single atoms via the atomic layer deposition method to utilize nearly

all platinum atoms. The obtained single atom material depicts an obviously enhanced catalytic activity and long-term stability in comparison with the state-of-the-art commercial 20% Pt/C.^[20] Although the Pt loading is reduced, the cost is still uneconomic for large-scale application and finding excellent non-noble metal catalysts is still urgent.

1.2.2.2 Non-noble metal catalysts

a) Metals and their alloys

The M-H bond is formed between the electron in H atom and the uncoupled d-space electron. According to the volcano curve, precious metal, Pt, has an optimal strength of M-H bond. It is clear that no pure metal could possess comparable high catalytic activity for HER to the noble metal of Pt.^[17] So in the past decades, alloying two or more metals from the two branches of “volcano” curve, respectively, has attracted tremendous researches as a straightforward approach to prepare catalysts with desirable HER performance.^[21, 22] The hypo-hyper theory also confirms that the combination of hypo-d orbit metals (such as Fe, Co, Ni) and hyper-d orbit metals (W, Mo, La) have a synergistic effect for HER.^[23] For example, Molybdenum atom owns unique outer shell electron structure. The non-filling d-space has a strong attract effect to the out most electrons of Nickel atom, which is favorable for HER. In all bi-metal alloys, Ni-Mo alloy is considered as one of promising HER catalyst. However, the poor electrochemical stability of transition metal catalysts makes them fade quickly under intermittent and harsh (alkaline and acid) HER conditions. Protecting these

metal nanoparticles via depositing a thin layer carbon as the protection shell is a feasible choice to improve their stability.^[22, 24] In chapter 4, we pre-reduced NiMoO₄ nanowire to form Ni₄Mo nanoparticles via C-plasma method with a thin layer of carbon deposited simultaneously. Introducing the third component (non-metal elements) to form stable compounds is another feasible method to improve their stability.

b) Transition metal chalcogenides, nitrides, phosphides and carbides

Transition metal compounds with nonmetal elements (C, N, O, S, Se P etc.) show some properties in common, such as high chemical and physical stability, superior corrosion resistance and high conductivity. In addition, these elements are abundant on earth. The introduction of those nonmetal atoms could strongly affect their electronic structure of the metal hosts by concomitant structural modification and/or charge transfer processes.^[25, 26] These characteristics make them attract tremendous research in the past few decades in various applications such as catalysts, catalyst supports and energy storage materials.

Transition metal chalcogenides: Metal oxides, as a large and important class of chemical compounds, are easily available materials with various nanostructures, which offer high specific surface area.^[27] However, most of them fail to play an important role in hydrogen evolution due to low electrical conductivity, sluggish catalytic kinetics and poor long-term stability. Recently, partially reduction of metal oxides have been an effective method to improve their HER activities.^[28] Many metal oxides, such as MnMoO₄,^[29] NiMoO₄,^[21] and WO₃,^[30] have been hydrogenated and shown obvious

enhanced HER activities.

Metal sulfides and selenides,^[31-33] such as MoS₂, WS₂, MoSe₂ and WSe₂ are a hexagonally packed layered structure. MoS₂ owns a variety of distinct surface sites and faster electron and hole mobility along basal planes than perpendicularly between sheets.^[34] Based on the density functional theory (DFT), the Mo($\bar{1}010$) edge of MoS₂ own the most optimal hydrogen binding energy (0.08 eV), which is very close to the optimum value of 0 eV.^[35] However, due to the lowest energy theory, the surface of bulk MoS₂ is composed of the thermodynamically favored basal plane sites, which are catalytically inert. So increasing the edges of MoS₂ or activating the basal plane is necessary to improve the catalytic activity of MoS₂ layers for HER. For example, Zheng et al.^[35] activated the basal plane of monolayer MoS₂ by introducing S-vacancies and strain. The S-vacancies work as new catalytic sites. Adjusting the S-vacancy and strain are able to yield the optimal hydrogen adsorption free energy (ΔG_H).

Transition metal nitrides (TMNs) and transition metal carbides (TMCs): TMCs and TMNs have been attracted intense attention as catalysts owing to their advantageous physical properties, such as high melting points, high electrical conductivity and excellent chemical stability.^[36] Group IVB-VIB metal-based nitrides and carbides are referred to as interstitial alloys. Relative to corresponding host metal, TMCs and TMNs have the similar behavior like noble metals for electrochemical reactions. For example, molybdenum carbides^[37] have been reported extensively as HER catalysts. More importantly, the introduction of another metal to form bimetal-based nitrides

and carbides could also improve their catalytic activity as previously mentioned bimetal alloys. For example, NiMoN nanoparticles and nanosheets were reported by Li's group^[38] and Sasaki's group^[39], respectively. And both exhibited excellent HER performance in alkaline and acidic electrolyte. 3D porous NiMoN with improved HER performance will be introduced in detail in Chapter 3.

Transition metal phosphides: Phosphorus can react with most elements to form a diverse class of compounds. Their bond ranges from ionic for the alkali and alkaline earth metals to covalent for the main group elements and metallic or covalent for the transition elements. Metal-rich transition metal based-phosphides, MP or M₂P, are considerably more stable than the phosphorus-rich compositions and show promising application as catalysts for water splitting. Basically, phosphides show the similar physical properties to corresponding compounds such as nitrides and carbides. They have high thermal and chemical stability and are good conductors of electricity and heat.^[40, 41] When applied as HER catalysts, they show high activity, stability in all pH value media from strong acidic solutions to strong alkaline solutions.^[42]

1.2.2.3 Metal-free catalysts

Metal-free materials are another important class of catalysts, which are mainly carbon materials and doped with cheap earth-abundant elements (N, S and P).^[43-45] Experimental results and theoretical calculation have demonstrated that chemical doping is an effective method to realize functions of carbon material as metal-free catalyst. Chen et al. synthesized nitrogen and sulfur co-doped nano-porous graphene

as HER catalyst.^[46] The experiment results show that the coupling of S and N dopants in graphene lattice are able to produce a synergistic effect on tuning the (ΔG_H) to acquire better HER performance. However, compared to their excellent ORR catalytic activity, their HER performance is rather poor. More work should be taken to improve their catalytic performance.

1.3 Oxygen evolution reaction

1.3.1 Mechanism

Compared with HER, OER is the more complex reaction as it involves in four protons coupled oxygen-oxygen bond formation.^[47] Hence, it requires higher overpotential. For OER, via giving electrons to the anode, oxygen gas is generated on anode.^[48]

This process is a four electron reaction processes:

$$\Delta G_1 = \Delta G_{\text{HO}^*} - \Delta G_{\text{H}_2\text{O}(\text{l})} - eU + k_b T \ln \alpha_{\text{H}^+}$$

$$\Delta G_2 = \Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*} - eU + k_b T \ln \alpha_{\text{H}^+}$$

$$\Delta G_3 = \Delta G_{\text{HOO}^*} - \Delta G_{\text{O}^*} - eU + k_b T \ln \alpha_{\text{H}^+}$$

$$\Delta G_4 = \Delta G_{O_2} - \Delta G_{HOO^*} - eU + k_b T \ln \alpha_{H^+}$$

The * indicates an oxygen vacancy site at the electrode surface. In these process, there are three intermediates HO*, O* and HOO*. All of them can be using as a descriptor to estimate the oxygen evolving activity and construct the free energy diagrams. Previous studies have shown that the activity can be plotted as a function of only one of them. The same as HER catalysts, a volcano-shaped relationship is formed between catalytic activity and descriptor. If the surface binds oxygen too strongly, the formation of HOO* is the limited step, whereas for surfaces that bind oxygen too weakly, the limited step is the oxidation of HO*.

The scale of the potential determining step can be derived from the free energy diagram. The last step to become downhill among ΔG_{1-4} with the potential increasing is the limiting reaction step in the four-step mechanism.

$$G^{OER} = \max[\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0] \quad (1.15)$$

For which ΔG_{1-4}^0 are ΔG_{1-4} at $U = 0$ (pH=0 and T=298 K). So the theoretical overpotential at standard conditions is given by equation (1.16):

$$\eta^{OER} = (G^{OER}/e) - 1.23 \text{ V} \quad (1.16)$$

Figure 1.4 shows the energy diagrams for the ideal catalyst, LaMnO₃ (strong binding), SrCoO₃ (intermediate binding) and LaCuO₃ (weak binding). For ideal catalyst, the reaction free energies of four charge transfer steps have the same magnitude at zero potential (1.23 eV). So at equilibrium potential, all the reaction free energies are zero. In practical, such ideal catalyst does not exist. As shown in Figure 1.4 b, c and d, all steps are uphill at U=0. At U=1.23 V, the standard equilibrium

potential for oxygen evolution, some of steps become downhill but some of other steps remain uphill. At the G^{OER} potential, the potential-determining step also becomes downhill.

Figure 1.4 Standard free energy diagram at zero potential ($U=0$ V), equilibrium potential ($U=1.23$ V), and at the potential for which all steps become downwards: a) the ideal catalyst, b) LaMnO_3 , c) SrCoO_3 , and d) LaCuO_3 . Standard free energies at $U=0$ for e) the ideal catalyst, f) LaMnO_3 , g) SrCoO_3 , and h) LaCuO_3 .^[48]

1.3.2 Current state of catalysts development for OER

1.3.2.1 Noble metal based materials

Noble metal-based materials, ruthenium oxide (RuO_2) and iridium oxide (IrO_2), are still the efficient OER catalysts.^[49] Many calculations as well as experiments demonstrated their efficient catalysis performance both in basic and acid electrolyte. However, the scarcity on earth and the high cost limit their scale-up industry application. The same as Pt for HER, loading these noble metal oxide on high conductivity and low cost materials is a feasible strategy to reduce the cost of the whole device.^[50] Due to the fascinating chemical and physical properties (excellent

chemical stability, high corrosion resistance and high conductivity), nanostructured transition metal carbides and nitrides have attracted tremendous research as the support material for catalyst.^[51] The ideal result is to deposit monolayer noble metal atoms on the surface of supporter to make full utilization of them.

1.3.2.2 Non-noble metal based materials

Figure 1.5 The relation between the OER catalytic activity and the occupancy of the e_g -symmetry electron of the transition metal^[52]

a) *Perovskite*: ABO_3 is the basic structure of perovskite, A and B are both cations. A is larger than B. In general, A is a lanthanide or an alkaline earth element, and B is a transition metal surrounded by 6 oxygen atoms. The flexible composition characteristic of perovskites makes it easy to tune the electronic structure to get optimal catalytic activity. The chemical, physical and electronic properties can be tuned via doping or partial replacement at these sites. In most cases, the outer orbital electrons of A ions have no effect on the electronic properties. The energy of the

conduction band is effected by the electrostatic potential of the A ion and its size determines a possible deviation of the crystal structure from the ideal cubic form.^[47]

The d-band pervoskites were researched by Sato et al.^[53] They proposed that the oxide has a broad σ^* band and the oxidation state of transition metal cation (B site) in the oxide determine the OER performance. After several decades, Yang et al. have proposed a design principle for high activity perovskite catalysts based on orbital principle^[52] (**Figure 1.5**). They found that the e_g orbital of surface transition metal ions take part in σ -binding with surface adsorbed anions, which influence the binding of oxygen related intermediate species on B-sites and in turn the OER activity. The peak of OER activity was predicted to be at an e_g occupancy close to unity, with high covalence of transition metal-oxygen bonds. Predicted by the volcano plot, they found that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\sigma}$ is the most promising OER catalyst among those materials they studied.

b) Transition-metal chalcogenides, nitrides, phosphides and carbides

3d transition metal-based materials (Mn, Fe, Ni and Co) have attracted tremendous research and exhibited promising potential as OER catalysts. Markovic's group has systematically studied these metals and found that the binding strength of M-OH is in governing the activity. The activity trend is $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni}$. Recent studies have confirmed that the active material of transition metal chalcogenides, nitrides, phosphides and carbides are corresponding metal oxyhydroxides. As mention in 1.2.2, the introduced inter-lattice non-metal atoms can tune the electron structure of host metals and make it possible to get optimal activity catalysts.^[54]

Cobalt metal is abundant on earth and Co-based materials are widely studied as OER catalysts. The catalytic properties of Co_3O_4 on different substrates, with different nanostructure were systematically investigated. The catalytic activities on different crystal planes have also been studied through both theoretical calculations and experiments.^[55] Mechanism on the transformation of Co_3O_4 under reaction situation was studied. They found that the superoxides on the surface, oxo Co(IV), are active sites.

Researchers further improved the performance of Co_3O_4 by doping with a third element such as Li, Ni, Cu, Zn, Fe, etc.^[56, 57] For example, Chen et.al synthesized nanostructure NiCo_2O_4 on carbon cloth, which shows a superior performance than that of IrO_2 .^[58] Replacing or partially replacing the oxygen by other nonmetal atoms, such as N, C, S, B, P, etc.,^[54, 59-61] is another important and feasible method to improve the catalytic activity of Co-based catalyst. Detailed information of CoN as OER catalyst is introduced in Chapter 3.

1.3.2.3 Metal-free catalysts

Non-metal materials are another class of important catalyst, which are mainly carbon materials doped with N, O, H, S, P etc.^[62-64] Recently, N-doped carbon materials have emerged as efficient OER catalysts.^[65] And research results showed that the active sites are pyridinic-nitrogen atoms. A series of researches of carbon-based catalysts for OER have been researched by Qiao's lab.^[65, 66] They designed the N,O-dual doped graphene-CNTs hydrogel film which is easily fabricated

by filtration of graphene and CNT with layer-by-layer method. The synergistic effect of graphene and CNT brought about a current density of 5 mA cm⁻² at the overpotential of 368 mV in 0.1 M KOH.^[66] g-C₃N₄/CNT catalyst was also developed due to the high N concentration of C₃N₄, which plays a vital role in catalytic activity.^[67] Recently, carbon materials doped with one or two nonmetal materials attract more and more attention due to the synergistic effect.^[64, 66]

1.4 Important measurements and parameters for the study of electrocatalysts

To evaluate an electrocatalyst either for OER or HER, there are some basic parameters that include overpotential at a defined current density, Tafel slope, exchange current density, specific surface area, Faradaic efficiency and stability performance. In general, to facilitate the comparison, all potential values are calibrated with respect to reversible hydrogen electrode (RHE) via the following equation: $E(\text{RHE}) = E_{\text{test}} + 0.059 \times \text{pH} + E_0$. The specific parameters of common reference electrodes are showing in the following **Table 1.1**:

Table 1.1 Standard potentials of common reference electrodes

Electrode name	Electrode reaction	E_0 vs. RHE (1 atm, 298 K)	Abbreviation
Silver Chloride Electrode	Ag/AgCl, KCl (0.1 M)	0.2881	N.A.
	Ag/AgCl, KCl (3 M)	0.210	
	Ag/AgCl, KCl (sat'd)	0.197	
	Ag/AgCl, NaCl (3 M)	0.286	
	Ag/AgCl, NaCl (sat'd)	0.194	
Saturated Calomel	Hg/HaCl ₂ , KCl (sat'd)	0.241	SCE

Electrode			
Normal Calomel Electrode	Hg/HaCl ₂ , KCl (1 M)	0.280	NCE

1) Overpotential (η) at a defined current density is usually adapted as the primary evaluation measure of electrocatalytic activity. Due to the lots of thermodynamic and kinetic hindrances, the operating potential of certain reaction is generally over the reversible theoretical potential, which is 0 and 1.23 V vs. RHE for HER and OER, respectively. Onset potential: the lowest (for OER) or the highest (for HER) potential at which a reaction product is formed at a given electrode and at defined conditions. It is a very important parameter to evaluate the catalytic activity and make the comparison with other catalysts. The general method to determine onset potential is Tangent method as shown in **Figure 1.6**.

Figure 1.6 Tangent method to determine onset potential

However, this method is very arbitrary, so in most papers, the over-potential at 1

mA cm^{-2} (η_1) or 10 mA cm^{-2} (η_{10}) are chosen for comparison.

2) Tafel slope (b) and exchange current density(j_0):

Figure 1.7 Tafel plot for an anodic process

The Tafel slope is a parameter that evaluate the mechanism under electrocatalytic reaction, which is derived from an equation (1.17) describes the relation of current density and overpotential of an electrocatalyst. [68]

$$\eta = a + b \log(j) \quad (1.17)$$

Conventionally, these two important physical parameters are derived from this equation: the Tafel slope and the exchange current density. The relationship is shown in **Figure 1.7**.

The catalyst with a lower Tafel slope has efficient charge transfer ability across its interface since Tafel slope and charge transfer coefficient are inversely related. In general, the steady state polarization curve of an electrocatalytic process can be achieved by converting the iR -compensated polarization curves, which is conducted

at very slow scan rates (e.g. 2 mV s^{-1}) The corresponding Tafel slope can also be obtained via the galvanostatic or potentiostatic measurements of steady state potential or current density with very small intervals within the potential window of electrocatalytic process.^[47]

3) Specific surface area and mass activity

The comparison of bulk materials with increased surface area and reduced mass would be not fair. To evaluate the activity of nanostructured catalysts, the current must be normalized. There are mainly two methods to normalize the current. Mass activity, the current density is divided by the catalyst loading, which is mainly used to evaluate the catalysts that differ in morphology and topography. Similarly, for these catalyst with the same mass but different surface area needs another parameter to compare their catalytic performance. In such cases, the current is generally normalized by the Brunauer-Emmett-Teller (BET) or surface area electrochemical surface area (ECSA) of the catalysts. To determine the ECSA, there are nearly nine methods are available. Among them, the double layer capacitance method is extensively used. The merits and demerits of current normalization methods has been summarized by Anantharaj et.al as shown in the following **Table 1.2**.^[26]

Table 1.2 Merits and demerits of various current normalization methods

Normalization method	Merits	Demerits
Geometrical surface area	<ul style="list-style-type: none"> ➤ Widely accepted and used method ➤ Fair comparison with existing literature ➤ Good for planar electrodes, such as foils and deposited thin film 	<ul style="list-style-type: none"> ➤ Does not reflect the intrinsic catalytic property of the catalyst ➤ May vary depending on catalyst loading and its optimization ➤ Geometrical area of the substrate electrode is not equal to the actual surface of the catalyst.
ECSA	<ul style="list-style-type: none"> ➤ Can reflect the intrinsic catalytic property of catalyst ➤ Loading sensitive 	<ul style="list-style-type: none"> ➤ Difficulties in determining ECSA ➤ Large experimental inaccuracies between one method to other
BET surface area	<ul style="list-style-type: none"> ➤ Ease of determination of BET surface area ➤ Would be most suitable for porous materials and catalysts 	<ul style="list-style-type: none"> ➤ Comparison with existing report would be tedious ➤ Does not reflect the intrinsic catalytic property ➤ All gas adsorption sites are not electrochemically active sites. Hence will lead to large errors.
Mass of loaded catalyst	<ul style="list-style-type: none"> ➤ Loading sensitive ➤ Regardless of type of catalyst, it directly cares about the loading ➤ Suitable when same material has been taken in different loading 	<ul style="list-style-type: none"> ➤ Not suitable for planar and thin film electrodes. ➤ Direct comparison with theory and experiment is not feasible ➤ Does not reflect the intrinsic catalytic property of the material. ➤ Comparison between catalysts of varying particle size, density, morphology and topography is not possible. ➤ Comparison with existing reports is also not possible

1.5 Motivation, Objectives and Scope of thesis

On considering the electrochemical performance of catalysts (onset potential, Tafel slope and stability) are largely depended on the intrinsic properties of electrode materials. Therefore, the proper design and fabrication of electrode materials are expected to significantly determine their catalytic performance. As previously discussed, the electrocatalytic processes for water splitting are generally occurred on the quasi-surface of electrode materials. So regardless of the intrinsic activity, reducing the dimension of bulk materials into nano-scale with specific nanostructure and high specific surface area is one of feasible methods to improve the utilization of

catalysts. The objective in this thesis is to achieve highly stable and active catalysts towards water splitting from the above two aspects.

TMNs have attracted enormous attention because of their high chemical stability and functional physical properties, such as superior corrosion resistance, high conductivity and high melting points. However, in most previous reports, metal nitrides are prepared via annealing precursors under caustic and hazardous ammonia (NH_3) flow. Even worse, it requires long processing duration and high reaction temperature, which may destroy their nanostructure. In chapter 3, we are focusing on the developing of a novel and green RF plasma assisted method for the synthesis of porous metal nitrides. The optimization of synthesis conditions and the evaluation of electrochemical performance in water splitting are introduced in detailed. The advantages of N_2 RF plasma method will also be discussed.

Except N_2 plasma, C-based plasma could also apply to the modification of electrode materials. For example, transitional metal oxides, as a large and important class of chemical compounds, are easily available materials with various nanostructures, which endows them large specific surface areas. We first found that there is a slow self-activation of metal oxides during the constant hydrogen evolution process due to the reduction of intermediate hydrogen. But the self-activation effect is temporary and not stable. Hence, pre-reducing of metal oxides should be a feasible method to improve their catalytic activity. Chapter 4 is focused on the pre-reducing of metal oxides (NiMoO_4 , Co_3O_4 and NiO) by H_2 annealing and C-plasma treatment and exploring their electrochemical performance as HER catalysts. Although the catalytic

activity is improved for samples pre-reduced via H₂ annealing, the improvement is ultra-unstable. So we applied C-plasma to the modification of metal oxides, which not only enhance the catalytic activity, but also improve their stable performance via the carbon shell deposited simultaneously during C-plasma.

Bimetal-based catalysts of two proper transition metals are generally more active than individual constituents for HER and/or OER. In Chapter 3 and 4, we also found that the NiMo based materials deliver high catalytic activity. In addition, N-doped carbon materials are not only an excellent catalyst supporter but also an effective catalyst for electrolysis. Until now, there are only few catalysts combining the bimetal material and N-doped carbon material together. The available few reports are in powder form and need polymer binders, which are not favorable for the electrochemical test. In chapter 5, a series of ultrafine transition metal-based nanoparticles (Ni-Fe, Ni-Mo) embedded in N-doped carbon have been successfully fabricated as replacements for noble metal-based catalysts in electrolytic water splitting via a dip-coating method with metal-assisted etching effect. Dip-coating, as a general coating technique in the industry, could fabricate electrode materials on a large-scale.

The summary and future work is presented in chapter 6.

Chapter 2 Fabrication and Characterization

2.1 Radio frequency plasma

Plasma, as the fourth fundamental state of matter first proposed by Irving Langmuir, consists of a set of charged and neutral particles, in which the positive and negative ions are completely free and showing a high chemical activity.^[69] Macroscopically, plasmas are electrically neutral, while on the molecular level they contain particles like electrons, positive and negative ions. Excited neutral species including radicals, atoms and molecules are also existent. In comparison with the ordinary gas, liquid and solid phases, most of these species in plasma deliver electronically excited states, exhibiting a highly reactive environment for chemical reactions. Therefore, it has received considerable interests in different areas, especially nano-material processing.

The plasmas used in plasma nanotechnology can be broadly classified into low temperature (cold) plasmas and high temperature (hot) plasmas.^[70] The low temperature plasmas are mainly produced by ac or dc electric gas discharge or by gas discharges initiated by RF or microwave electromagnetic fields. Normally, the cold plasmas are described by relation $T_e \gg T_i = T_g$, where T_e , T_i , and T_g are temperatures of electrons, ions, and background gas, respectively.^[69] Here, we mainly focus on the low pressure discharges initiated by RF, also called RF plasma. The electron temperature is ultrahigh (10^4 - 10^5 K) compared with the gas temperature (less than 5×10^2 K or near ambient). High energy plasma treatment is a very powerful and versatile method in enhancing the efficiency of material synthesis, lowering the reaction temperature and

shortening the reaction duration. Lots of reactions that are difficult to achieve at lower temperatures are becoming feasible under high-energy plasma ambient. In this thesis, a series of nanostructured metal nitrides, such as 3D porous nickel molybdenum nitride (NiMoN) and cobalt nitride nanoarrays, were fabricated and reported. In addition, the application of carbon plasma in prereduction of metal oxides to improve their HER performance was also studied. The setup of RF plasma and the photo of home-made RF plasma equipment are shown in **Figure 2.1**.

Figure 2.1 RF plasma setup

2.1.1 Fabrication of 3D porous NiMoN and CoN nanowire arrays via N₂ plasma

Preparation of NiMoN: The NiMoN was prepared by a combination of pulse electrodeposition (PED) and RF-plasma method. First, the precursor NiMo alloy was prepared via an optimal PED method in an electrolyte consisting of 0.2 M NiSO₄·6H₂O, 0.03 M (NH₄)₂MoO₄·2H₂O and 0.3 M Na₃C₆H₅O₇·2H₂O. The pH value was adjusted to 10 via ammonia (wt. 25%). The PED was performed in a conventional two-electrode glass cell with a cleaned carbon cloth used as substrate, and Pt plate as the counter electrode. The deposition was conducted at 25 °C at a cathodic current density of 30 mA cm⁻² and 2 Hz frequency for 7200 cycles. Then, the sample was taken out and washed repeatedly with distilled water and dried in oven at 90 °C. The average mass loading is about 2.5 mg cm⁻².

The NiMo alloy thin films deposited on carbon cloth was then subjected to the N₂ RF plasma treatment in order to convert them into NiMoN. In brief, after the precursor inserted into the reactor chamber of RF-PECVD system, the pressure of chamber was pumped down to 0.2 mbar under nitrogen flow (100 sccm). When the temperature of chamber increased to 450 °C, the RF-plasma discharge was conducted at 250 W and 13.56 MHz for 15 min. After the RF plasma, the average mass loading decreased to around 1.1 mg cm⁻². For the phases of NiMoN, the nitridation process is unlike a conventional diffusion-limited solid-state reaction. Instead, the energetic nitrogen radicals (N*, and N⁺, N₂⁺, etc.) in the plasma can cause sputtering of the NiMo. The ablated Ni and Mo atoms react with active nitrogen atoms to produce the NiMoN phase.

Preparation of porous Ni₃N on carbon cloth: The porous Ni₃N on carbon cloth was prepared by the combination of electrodeposition (ED) method and RF plasma method. In brief, the clean carbon cloth was used as the substrate for the growth of Ni film. The ED electrolyte consisted of 0.05 M NiSO₄ and 0.01 M NH₄Cl. The ED was performed in the conditions as the PED of NiMo alloy and conducted at a constant cathodic current density of 5 mA cm⁻² for 15 min. Then the sample was taken out and rinsed with distilled water. The average mass loading is about 1.5 mg cm⁻². The N₂ RF-plasma for Ni alloy was conducted at the same parameters as NiMo alloy except reducing the duration to 5 min to keep the loading mass around 1.1 mg cm⁻².

Preparation of N-doped MoO₂ (MoON) on carbon cloth: The MoO₂ was also synthesized by PED firstly. The electrolyte consisted of 0.05 M ammonium molybdate. The pH value was adjusted via ammonia to 9. The deposition was performed in the conditions as the PED of NiMo alloy and conducted at a cathodic current density of 5 mA cm⁻² and 2 Hz for 3600 cycles. The N₂ RF-plasma for MoO₂ was also conducted under the similar conditions of NiMo alloy. The average mass loading almost has no change and is around 1 mg cm⁻².

Preparation of cobalt nitride nanowire arrays: The CoN nanowire arrays grown on nickel foam were prepared by the following process. Firstly, as previously reported, the Co₂(OH)₂CO₃ nanowire arrays were prepared by a hydrothermal method.^[71] The hydrothermal solution contained 2 mmol Co(NO₃)₂, 4 mmol NH₄F, 10 mmol urea and 60 mL de-ionized (DI) water. Then the solution was transferred into Teflon-lined stainless-steel autoclave liners after continuously stirred for 5 min. A piece of pressed

nickel foam, which was cleaned by ethanol and DI water, was immersed into the reaction solution. Part of substrate was protected from solution contamination by uniformly coating with a polytetrafluoroethylene tape to use it as the current collector. The liner was sealed in a stainless-steel autoclave and maintained at 120 °C for 4 h. Samples were washed with DI water, dried in oven at 60 °C and then annealed in furnace at 300 °C under Ar atmosphere for 1.5 h leading to the formation of Co₃O₄. The average mass loading was about 1.5 mg cm⁻². Finally, the as-prepared Co₃O₄ arrays were directly subjected to the N₂ RF plasma treatment at room temperature to obtain CoN. The RF-plasma discharge was conducted at 300 W and 13.56 MHz for different treatment time (30 s, 1 min and 3 min). For the phase of CoN, the nitridation process is the same to that of NiMoN. N-based energetic ions and radicals react with Co₃O₄. Some of them bonded with oxygen atoms to form NO_x and were then removed. The rest penetrates in the nanowire to form CoN.

2.1.2 Prereduction of metal oxides via carbon plasma

Synthesis of carbon pre-reduced NiMoO₄ nanowire arrays: First, Nickel acetate (NiAc₂·4H₂O, 1.24g) and ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, 1g) were added to a mixed solution (30 mL deionized (DI) water and 30 mL ethylene glycol) under magnetic stirring to give a green solution and transferred into autoclave liner. Then, a piece of cleaned carbon cloth was immersed vertically into the reaction solution. The liner was sealed in a stainless-steel autoclave and maintained at 140 °C for 10 h. After cooling to room temperature, sample was washed with DI water, dried in oven at

60 °C and then annealed in furnace at 450 °C under Ar atmosphere for 30 min to remove moisture. The average mass was about 1.2 mg cm⁻². Finally, the NiMoO₄ were directly subjected to C-plasma to be modified. The plasma discharge was carried out under 450 °C and 0.2 mbar at 300 W and 13.56 MHz for different treatment time, i.e., 15, 30 and 60 s and the resulting products were denoted as C-15s, C-30s and C-60s, respectively. And ethanol as the reduction gas and carbon source.

For comparison, the obtained NiMoO₄ was partially reduced via heating under H₂/Ar (2:98) atmosphere at 450 °C for 1 h with 100 sccm.

Co₃O₄ nanowire arrays grown on Ni foam were fabricated as stated in chapter 2.1.1.^[72] And the plasma parameters are the same as these for NiMoO₄ and the treatment time was 30 s.

For the C-plasma, the reduction mechanism is attributed to the interaction between C radicals and target samples, which is similar to that of general CVD approach. In C-plasma, C radicals in plasma are generated due to the intense collision of molecules in radio frequency field, resulting in large amounts of C-radicals. In comparison, a limited number of reactive C-species can be achieved in general CVD method at high temperature. In terms of that, the superior properties of C-plasma in the reduction of metal oxides are the low reaction temperature and short reaction duration, which make it possible to preserve the nanostructure of metal oxides well.

2.2 Dip-coating method

Dip coating method is an industrial coating process, which is used to manufacture bulk products. There are mainly five steps during dip-coating process: immersion, start-up, deposition, drainage and evaporation. In the continuous process, steps are carried out directly after each other. There are many factors to determine the final state of dip coating thin films. The thickness can be fabricated by controlling many factors, such as functionality of the initial substrate surface, submersion time, withdraw speed, number of dipping coating cycles, solution composition, concentration and temperature. The dip coating method can give an uniform, high quality film every on bulky, complex shapes. In this thesis, we fabricated a series of metal nanoparticles on carbon cloth via dip coating method.

2.2.1 Preparation of hybrid of Ni/Mo₂C @ N-doped porous carbon (NiMo-PVP)

First, 0.4 g polyvinyl pyrrolidone (PVP), as Nitrogen source and thickening agent, was dissolved into 10 mL ethylene glycol (EG) under continuous stirring. And then 0.58 g Ni(NO₃)₂·6H₂O and 0.35 g (NH₄)₆Mo₇O₂₄·4H₂O were added separately to form the homogeneous solution as Ni source and Mo source, respectively. The cleaned carbon cloth was dipped into the solution for 10 min under ultrasonic condition to get uniform precursor film. Afterward, the dipped carbon cloth was dried in oven at 120 °C and then annealed in furnace at 1000 °C under Ar atmosphere for 2 h. The average mass loading was around 0.5 mg. For comparison, following solutions were prepared for dipping, solution with PVP replaced by 0.4 g polyethylene glycol (PEG) for hybrid of Ni/Mo₂C @ porous carbon (NiMo-PEG), solution without Mo source for Ni @

N-doped porous carbon (Ni-PVP) and solution without Ni source for Mo₂C @ N-doped porous carbon (Mo-PVP).

2.2.2 Preparation of hybrid NiFe nanoparticle @ N-porous carbon (NiFe-PVP)

The process is similar as mentioned above. 0.4 g PVP, 0.58 g Ni(NO₃)₂·6H₂O and 0.8 g Fe(NO₃)₃·9H₂O were added into 10 mL EG in sequence under continues stirring as N, Ni and Fe sources respectively. Cleaned carbon cloth was dipped into the solution for 10 min under ultrasonic condition at 50 °C. Then carbon cloth was dried in oven at 120 °C and annealing in furnace at 1000 °C for 2 h under Ar atmosphere. Similarly, samples without Ni or Fe were also prepared for comparison.

2.3 Sample characterization

The microstructure and phase of samples were characterized by field-emission electron microscopy (FESEM, FEI SIRION), X-ray diffraction (XRD, RIGAKU/Max-2550 with Cu K α radiation), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F). The surface compositions were determined by X-ray photoelectron spectroscopy (XPS, PHI 5700). The C 1s spectrum for adventitious carbon (284.8 eV) was used for charge correction. The average mass loading is confirmed by the balance (B-220C) and Thermogravimetric Analysis (TA Instruments, New Castle, DE, USA)

2.4 Electrochemical characterization

Electrochemical performances of samples were tested in a three-electrode glass cell controlled by an electrochemical workstation (Zahner zennuim Germany). The samples

prepared were used as the working electrode. Pt plate and carbon rod (D=8 mm) were used as the counter electrode for OER and HER, respectively. And Ag/AgCl (3 M KCl) was used as the reference electrode, respectively. The electrolyte was 1 M KOH. Without specification, all potentials in this manuscript are referred to the reversible hydrogen electrode (RHE). The conversion of potential between E(RHE) and E(Ag/AgCl) obeys the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \times \text{pH} + 0.210 \text{ V}$. Current density was calculated based on the geometric area of electrode. All samples were firstly conducted the cyclic voltammetry (CV) test to get a stable curve at 50 mV s^{-1} . The linear sweep voltammetry (LSV) tests were conducted at a scan rate of 5 mV s^{-1} . The Tafel plots were derived from LSV curves, which were tested at the scan rate of 1 mV s^{-1} . The electrochemical impedance spectroscopies (EIS) were carried out at the current density of 10 mA cm^{-2} , in a frequency from 100 kHz to 50 mHz with an AC amplitude of 5 mV. The stability test was carried out at different fixed current densities (10, 30, and 50 mA cm^{-2}) for 20 h each. Overall water electrolysis was carried out in a two-electrode configuration for 60 h at 30 mA cm^{-2} .

The Faradaic efficiency was estimated using volumetric method. The evolved oxygen gas on CoN nanowire arrays electrode was collected in a 10 mL graduated tube, which was filled with electrolyte. Fixed current electrolysis was carried out at 10 mA for about 3.5 h under standard conditions (25 °C, 1 atm). The time points at each 1 mL of collected O₂ gas were recorded. The accumulated charge passing through the working electrode were calculated by the equation ($Q=It$).

Chapter 3 Nanostructured Metal Nitrides via N₂ RF Plasma for Electrolysis of Water Splitting

Transition metal nitrides have attracted enormous attention because of their high chemical stability and functional physical properties, such as superior corrosion resistance, high conductivity and high melting points. However, in most previous reports, metal nitrides are prepared via annealing precursors under caustic and hazardous ammonia (NH₃) flow. Even worse, it requires long processing duration (a few hours) and high reaction temperature (over 500 °C). Here, a facial, environmental-friendly and efficient RF N₂ plasma method has been developed for the synthesis of metal nitrides. N₂ gas is chose as nitrogen source and the processing duration is only a few minutes.

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3.1 Introduction

Transition metal nitrides, referred as interstitial alloys, have attracted much attention in electrocatalysis because of their superior corrosion stability, low electrical resistance, high stability.^[36, 74] Their density of states in *d*-band of the parent metals can be modified by introduction of nitrogen atoms. The resulted smaller deficiency in the *d*-band occupation of the metal makes the nitride surface exhibit an electron donating ability, which is similar to group VIII noble metals. Accordingly, metal nitrides are expected to exhibit a much higher catalytic activity than their corresponding parent metals.^[10] Moreover, both theoretical and experimental investigations indicate that bimetallic catalysts are more amendable to optimize the electrocatalytic performance than the corresponding individual compounds.^[23, 39, 75] Jaksic et al. have postulated the Brewer hypo-hyper-*d*-electronic theory to demonstrate that the interactive effect between Ni and Mo yields a synergism for the HER.^[76] In accordance with the “volcano plot”, the activity for the evolution of hydrogen is a function of the M-H (metal hydride) bond strength and exhibits a peak value for metal Pt, which has an optimal M-H bond strength.^[17] Therefore designing a material on the molecular scale which combines an M-H weakly metal (Ni) with an M-H strongly metal (Mo) is a feasible method to acquire ideal catalysts.

In first part of this work, we employed a novel method to synthesize 3D porous nickel molybdenum nitride on carbon cloth (NiMoN) by treating electrodeposited NiMo alloy films with N₂ plasma at a relatively low reaction temperature (450 °C) and shorter duration (15 min). The obtained bimetallic nitrides exhibit a 3D porous

hierarchical structure with outstanding catalytic performance for HER.

In addition to dense metal precursors, nanostructured metal (hydro)oxides as a large and important class of chemical compounds, are easily available materials with various nanostructures, which endows them large specific surface area, could also be converted into corresponding metal nitrides via N_2 plasma treatment. Here we take Co_3O_4 as an example to demonstrate the ultrafast and convenient conversion. Within just one minute at room temperature, the nitriding process is complete while the nanoarray structure is well reserved. The obtained CoN nanowires function as a highly active and stable non-noble OER electrocatalyst with a low overpotential of 290 mV to reach 10 mA cm^{-2} (η_{10}), a small Tafel slope of 70 mV dec^{-1} , and good stability over 30 h in 1 M KOH. Overall water splitting is also demonstrated by employing all-nitride nanostructure electrodes. This method is generic and can be applied for the synthesis of various metal nitrides with tailored nanostructure.

3.2 Results and Discussion

3.2.1 Synthesis of 3D Porous NiMoN and Its HER Performance

Figure 3.1 SEM images of PED NiMo alloy deposited for (a) 1800 cycles, (b) 3600 cycles and (c) 7200 cycles

The SEM images of NiMo alloy films at different cycles are shown in **Figure 3.1**. It is obvious that small particles start to grow on the surface of the carbon cloth at the early stage (deposited for 1800 pulse cycles) (Figure 3.1a) and grow bigger and denser after increasing the deposition pulse cycle to 3600 times (Figure 3.1b). As shown in Figure 3.1c, the surface of carbon cloth fibers is fully covered by a layer of dense NiMo alloy particles after being deposited for 7200 pulse cycles.

Figure 3.2 SEM images of NiMo alloy at different N_2 plasma activation duration (a) 5 min, (b) 10 min and (c) 15 min.

Subsequently, the as-prepared NiMo alloy films are directly treated by N_2 plasma. The N_2 plasma treatment time has an evident effect to the sample morphology (**Figure 3.2**). After exposing in N_2 plasma for 5 min, many dendrites form on the surface of film (Figure 3.2a). These dendrites grow longer (10 min) (Figure 3.2b) and finally interconnect to form a 3D porous hierarchical structure (15 min), as shown also in Figure 3.2c. The porous dendritic structure of nitrogen plasma treated sample points to strong sputtering of NiMo particles and thus helps us understand the NiMoN phase formation mechanism. The nitrogen plasma is mainly composed of excited states of N^* , and N^+ , N_2^+ . The energetic nitrogen ions cause the sputtering of NiMo particles

resulting in sputtered Ni and Mo atoms which react with excited nitrogen atoms and then recrystallize to produce the $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}$ phase.

Figure 3.3 EDX for (a) electrodeposited NiMo alloy deposited for 7200 cycles (b) NiMoN under 15min N_2 plasma treatment

The metal Mo cannot be electroplated from an aqueous solution directly without the assistant of metal Ni. With increasing the molybdenum content, the deposited alloys tend to the amorphous state and an amorphous pattern appears when the content of molybdenum is over 20 at.%.^[77] A further increase in the molybdenum content causes crack in the deposited film. Hence, a molybdenum concentration of 20 at.% in the alloy is found optimal by tuning the deposition parameters (Figure 3.3a). After being treated by N_2 plasma for 15 min, the content of Mo increased to 60 at.% due to the removal of Ni atoms (Figure 3.3b).

Figure 3.4 Structural and composition characterization of NiMoN: (a) TEM image of NiMoN, inset of (a) is HRTEM image, (b) Elemental maps of Ni, Mo and N. (c) XRD patterns; XPS spectra of (d) Ni 2p, (e) Mo 3d and (f) N 1s-Mo 3p.

Further insight into the microstructure of NiMoN is provided by results of TEM examinations. In **Figure 3.4**, the TEM images show clearly the porous structure and lattice fringes with an interplanar distance of 0.246 nm, corresponding well to the (100) planes of Ni_{0.2}Mo_{0.8}N (JCPDS 29-0931) (inset of Figure 3.4a). The phase and composition of the NiMoN are examined by XRD, EDX and XPS. The uniform

distribution of Ni, Mo and N elements is exhibited by EDX elemental maps in Figure 3.4b. The XRD spectra in Figure 3.4c show the dominating $\text{Ni}_{0.2}\text{Mo}_{0.8}\text{N}$ phase after the N_2 plasma treatment, together with a small amount of Ni_3N . Figure 3.4d-f show the XPS core-level spectra of Ni 2p, Mo 3d and Mo 3p-N 1s, respectively. The selected position of each peak for fitting is calibrated on the basis of the position of C 1s. For the high resolution spectrum of Ni 2p (Figure 3.4d), the observed binding energies at 856.5 eV and 874.0 eV are both attributed to the Ni-N bond, corresponding to the +3 valences of Ni ions.^[78] For the spectrum of the Mo 3d (Figure 3.4e), the fitting reveals three oxidation states (+3, +4, and +6) for Mo on the surface of NiMoN with a relative concentration of 3.6:2.0:1.0. The Mo^{3+} in the metal nitride is thought to be active for HER, while Mo^{4+} and Mo^{6+} species are attributed to the surface oxidization of Mo^{3+} upon air exposure.^[79] In Figure 3.4f, the peaks at 395.2 eV and 397.8 eV correspond to Mo 3p_{3/2} and N 1s respectively. The latter one is a characteristic peak for a metal nitride material.^[79, 80]

For comparison, two control samples were also prepared: porous Ni_3N on carbon cloth (**Figure 3.5**), and N-doped MoO_2 (MoON) on carbon cloth (**Figure 3.6**). Via electro-deposition method, the Ni metal is covered on the carbon fiber uniformly (Figure 3.5a and b). After being N_2 plasma treated for 5 min, the dense Ni film converts into 3D porous structure (Figure 3.5c and d) and pure Ni_3N is produced and confirmed by HRTEM

Figure 3.5 SEM images of (a, b) electrodeposited Ni, (c, d) Ni_3N and (e, f) TEM images of Ni_3N under 5 min N_2 plasma activation.

Figure 3.6 SEM images of (a) electrodeposited MoO_2 , (b) MoON (MoO_2 after 15 min N_2 plasma treatment.)

As for the MoON , without the assistance of Ni component, MoO_2 instead of Mo metal is acquired directly during the deposition process. The microstructure of MoO_2 is featureless (Figure 3.6a) and a typical of amorphous phase confirmed by the XRD (Figure 3.7a). After being treated with N_2 plasma at 450 °C for 15 min, no porous structure is formed (Figure 3.6b) and four broad XRD peaks indexed to MoO_2 appear

(JPCDS 32–0671), implying that MoO₂ is not converted into molybdenum nitride. For reference, MoO₂ is annealed under Ar at 450 °C for 1 h (red line). According to the XPS spectra shown in Figure 3.7b-d, the surface of MoO₂ is doped with nitrogen.

Figure 3.7 (a) XRD patterns of carbon cloth, MoO₂ precursor, annealed MoO₂ at 450 °C under Ar for 1 h and MoON; the XPS spectra of (b) Mo 3d, (c) N 1s-Mo 3p and (d) O 1s

To investigate their HER activities, NiMoN, Ni₃N and MoON were investigated in a 1 M KOH solution using a typical three electrode system (**Figure 3.8**). Figure 3.8a shows the linear-sweep voltammograms (LSVs) at a scan rate of 5 mV s⁻¹ after iR-correction for all the as-fabricated catalysts. Bare carbon cloth and commercial Pt/C were also tested for comparison. As well-known, Pt/C shows a high activity for HER with onset overpotential (η_{onset}) nearly 0 V. Nevertheless, the carbon cloth substrate exhibits an insignificant HER activity performance. Among the three as-synthesized

catalysts, the NiMoN exhibits the smallest η_{onset} of ~ 50 mV compared to MoON (~ 95 mV) and Ni₃N (~ 161 mV), beyond which the current density increases sharply. As the determination of onset potential is rather arbitrary, a more meaningful practice is to compare the required overpotential for driving the current density of 10 mA cm^{-2} (η_{10}). As can be seen from Figure 3.8a, the overpotential η_{10} for NiMoN is 109 mV, much lower than those of MoON (146 mV) and Ni₃N (208 mV). In addition, the current density of NiMoN is higher than those of the MoON and Ni₃N in the whole potential region.

Figure 3.8 (a) Polarization curves, (b) Tafel slopes of various catalysts.

For further insight into the HER activity, Tafel plots of NiMoN, MoON, Ni₃N and Pt/C derived from the polarization curves at 1 mV s^{-1} are shown in Figure 3.8b. The fitted Tafel plot for NiMoN shows a Tafel slope of 95 mV/dec , which is smaller than that of MoON (101 mV dec^{-1}) and Ni₃N (123 mV dec^{-1}). The exchange current densities, j_0 (the current density at zero overpotential), are determined from the Tafel plots. NiMoN exhibits highest j_0 (0.92 mA cm^{-2}), which is higher than that of the MoON (0.22 mA cm^{-2}) and the Ni₃N (0.12 mA cm^{-2}).

Generally, the small Tafel slope value and high exchange current density

demonstrate the superior HER activity; which implies NiMoN has best HER activity among various catalysts investigated in this study. Compared with other recently reported metal nitride catalysts, our NiMoN catalyst shows an enhanced performance for HER activity, which is even comparable to other noble metal-free catalysts (**Table 3.1**).

Table 3.1 Comparison of HER activities for metal nitrides and recently reported noble metal-free catalysts.

Material	Electrolyte	<i>b</i> (mV/dec)	η_{10} (mV)	Loading (mg/cm ²)	Ref.
NiMoN	1 M KOH	95	109	~1.1	This work
MoON	1 M KOH	101	146	~1	This work
Ni ₃ N	1 M KOH	113	208	~1	This work
NiMoN _x /C	0.1 M HClO ₄	35.9	~300	0.25	[39]
Mo ₂ N	0.1 M HClO ₄	157	400	0.25	[39]
Mo ₂ N	1 M KOH	108	353	0.102	[81]
Mo ₂ N/CN T-GR	0.5 M H ₂ SO ₄	72	186	0.65	[82]
Ni ₃ N	1 M KOH	120	96	N.A	[83]
NiN _x	1 M KOH	N.A	N.A	N.A	[84]
Co _{0.6} Mo _{1.4} N ₂	0.1 M HClO ₄	N.A	200	0.24	[79]
CoP	1 M KOH	51	54	6.2	[85]
Mo ₂ C	0.1 M KOH	55	112	N.A	[86]
	0.5 M H ₂ SO ₄	62	172		
Co-Co ₃ O ₄	1 M KOH	44	~100	0.85	[87]
Ni-Co-P	1M KOH	71	167	0.286	[75]
CoTe ₂ NPs	0.5 M H ₂ SO ₄	41	246	1	[88]
MoC ₂ @C	0.5 M H ₂ SO ₄	41	78	0.25	[89]
Ni doped Graphene	0.5 M H ₂ SO ₄	45	150	N.A	[90]

Figure 3.9 (a) Nyquist plots and (b) Bode plots of NiMoN at three different applied overpotentials. Bode plots of (c) Ni₃N and (d) MoON at three different applied overpotentials

To gain a better understanding of the HER kinetics occurring at the electrode/electrolyte interface, EIS measurements were carried out from 100 kHz to 0.01 Hz at three selected values of the overpotential ($\eta_{\text{onset}}-50$ mV, η_{onset} , $\eta_{\text{onset}}+50$ mV) with an AC voltage of 10 mV. The corresponding Nyquist plots and Bode plots of NiMoN are shown in **Figure 3.9**. The Nyquist plots show clearly two frequency regimes, one in the low frequency and the other in the high frequency region. It has been confirmed previously that, for solid electrodes the radius of semicircle in high frequency region is related to the electronic transport; whereas the low-frequency semicircle R_{ct} (the polarization resistance or charge-transfer impedance) that varies with overpotential is associated with the HER kinetics.^[91] Log R_s (R_s representing the resistance from the solution) and log ($R_{\text{ct}}+R_s$) can be directly obtained from the

corresponding Bode plots at high and low frequencies (shown in Figure 3.9b).^[92] For comparison, Bode plots of Ni₃N and MoON are shown in Figure 3.9c and d. It is seen from **Table 3.2** that, with the increase of overpotential (η), the values of R_{ct} for all catalysts decrease quickly. Moreover, NiMoN presents the smallest R_{ct} (55 Ω) at onset potential compared to that of MoON (149 Ω) and Ni₃N (123 Ω), implying its high active HER kinetics.

Table 3.2 Charge-transfer impedances at different overpotentials for various catalysts

	R_{ct} (Ω)		
	$\eta_{onset}-50$ mV	η_{onset}	$\eta_{onset}+50$ mV
Ni ₃ N	596	123	52.5
MoON	625	149	30.5
NiMoN	302.4	55	26.4

Another critical factor to evaluate a HER catalyst is the long-term stability. To probe the durability of the NiMoN catalysts, the electrolysis tests were carried out at three constant current densities (10, 30 and 50 mA cm⁻²,) for up to 36 h (Figure 3.10a). The catalytic activity for NiMoN is stable over long-term testing. The violent activity of HER leads to serious fluctuation of voltage at 50 mA cm⁻². The photograph (inset of Figure 3.10a) show enormous small bubbles near the electrode at the current density of 30 mA cm⁻². The small bubbles indicate that the produced H₂ are easily released from the surface of catalyst. At constant current densities, the overpotential only increases a few micro-volts (7, 11, and 12 mV at 10, 30 and 50 mA cm⁻²) after 10 h electrolysis, which is partially due to the reduced active surface area caused by the physical

adsorption of the generated H_2 bubbles on the catalyst surface. In addition, after 36 h stability test, the LSV and SEM images were collected again for comparison (Figure 3.10b and c). It can be seen that the polarization curves of NiMoN before and after 36 h of electrolysis nearly overlap with each other, especially at the low overpotential region. The 3D hierarchical porous structure is also well preserved.

Figure 3.10 (a) Stability tests of the NiMoN electrode at current densities of 10, 30, and 50 mA cm^{-2} over 36 h (the inset photograph shows the bubble generation at 30 mA cm^{-2}). (b) Polarization curves before and after 36 h stability test. (c) SEM image of the electrode surface after 36 h electrolysis.

The high catalytic performance for the obtained 3D hierarchical porous NiMoN can be mainly attributed to the exposure of more active sites and their improved electronic/chemical properties, which are related to their unique porous structure. Firstly, the hierarchical porous structure not only endows a large electrode-electrolyte contact area but also facilitates sufficient transport of reactants and products. Secondly,

the intimate contact with substrate enables a good mechanical adhesion and electrical connection, which grants high stability during electrolysis reaction. Thirdly, the metallic NiMoN as a good electrical conductor favors fast electron transport during catalytic activity. Finally, bimetal nitrides generally exhibit superior electrocatalytic properties presumably because of a synergistic effect between bimetal atoms.^[17]

3.2.2 Synthesis of CoN Nanowire Arrays and Its OER Performance

Figure 3.11 (a) XRD pattern and (b) SEM of $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire arrays

The characterization of synthesized $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire arrays is shown in **Figure 3.11**. All peaks can be indexed to $\text{Co}_2(\text{OH})_2\text{CO}_3$ (JCPDS Card no. 29-1416) except three strong peaks attributed to Ni substrate. The starting material, $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires, have a diameter of around 50–100 nm (Figure 3.11b). Samples were annealed in furnace at 300 °C under Ar atmosphere for 1.5 h leading to the formation of Co_3O_4 . The RF-plasma discharge was conducted at 300 W and 13.56 MHz for different treatment time (30 s, 1 min and 3 min).

Figure 3.12 Conversion from Co_3O_4 to CoN . (a) XRD patterns of Co_3O_4 , CoN -30 s, CoN -1 min, and CoN -3 min. The dashed and solid lines indicate the peak positions of Co_3O_4 and CoN , respectively. XPS spectra of Co_3O_4 and CoN -1 min (b) Co 2p, (c) O 1s. (d) N 1s spectrum of CoN -1 min.

The phase and composition of these samples at different synthesis stages were studied by XRD (Figure 3.12a). Typically, the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires convert to Co_3O_4 after thermal annealing (300 °C in air for 1.5 h); Excluding three strong peaks attributed to the Ni foam substrate, all peaks (marked with $\blacklozenge$) can be indexed to the spinel phase Co_3O_4 (JCPDS 42-1467). The obtained Co_3O_4 nanowires were treated under N_2 RF plasma at room temperature for different durations, 30 s, 1 min, and 3 min, which are denoted as CoN -30s, CoN -1min and CoN -3min, respectively. After the N_2 plasma treatment, the peaks indexed to CoN phase (marked with $\heartsuit$) appear and those peaks for Co_3O_4 phase become weaker. In the pattern of CoN -30s sample, peaks for

Co₃O₄ and CoN coexist. The peak attributed to (311) plane of Co₃O₄ and (111) plane of CoN overlap at 36.5 ~36.8°. Increasing the duration to 1 min, only peaks indexed to CoN remain (solid line).^[93] There is no difference between the pattern of CoN-3min and that of CoN-1min, implying that pure CoN nanowire arrays were obtained after just 1 min N₂ plasma treatment.

The surface chemical states of Co₃O₄ and CoN-1min were further investigated by X-ray photoelectron spectroscopy (XPS) (Figure 3.12b-d). The selected position of each peak for fitting is calibrated on the basis of the position of C 1s. For the Co spectra (Figure 3.12b), the two dominating peaks, Co 2p_{3/2} and Co 2p_{1/2}, are in good agreement with Co₃O₄ in literature.^[94] Both peaks of the CoN-1min sample show a positive chemical shift by 0.5 eV compared with that of Co₃O₄, indicating a modulation of the surface electronic band bending of after N₂ plasma. The satellite peak at 787.5 eV is due to Co²⁺, which indicates the presence of cobalt oxide/hydroxide unavoidably formed on the surface during the preparation procedure and atmosphere exposure.^[54] This is consistent with the spectrum of O 1s shown in Figure 3.12c. Two intense peaks at 531.6 and 529.8 eV are clearly seen and are attributed to be adsorbed oxygen species and oxygen ions in crystal lattice, respectively. The intensity of the peak at 531.6 eV, corresponding to adsorbed oxygen species, has no obvious change after the N₂ plasma treatment. In contrast, the peak at 529.8 eV, derived from M-O, decreases significantly. This corroborates with the transformation to CoN and formation of a thin layer of oxides/hydroxides on the CoN surface when it exposed in air. For the N 1s spectrum in Figure 3.12d, the broad peak at 397.7 eV is assigned to the nitrogen in a metal nitride

environment.^[95]

Figure 3.13 SEM images of (a) Co_3O_4 , (b) CoN-30 s, (c) CoN-1 min, and (d) CoN-3 min.

Morphologies of the CoN nanowires at different fabrication stages are examined using electron micrographs (see **Figure 3.13**). After annealing, the Co_3O_4 nanowires were well maintained with a tapered morphology as shown in Figure 3.13a. SEM images of the CoN-30s, CoN-1min and CoN-3min samples are presented in Figure 3.13b-d. After 30 s treatment, the nanowire morphology was overall reserved except for slight twist and granulation of the tips. Increasing the treatment duration to 1 min causes more curvature and entanglement of the nanowires and more evident surface roughness (Figure 3.13c). Meanwhile, the nanowire arrays structure was kept very well. After 3 min plasma treatment, however, the nanowire arrays structure was nearly destroyed because of severe reaction with energetic ions (Figure 3.13d).

Figure 3.14 TEM images of (a) and (b) Co_3O_4 , (c) and (d) CoN-1 min .

Further insights into particle size and morphology of Co_3O_4 and CoN-1min were obtained from TEM images. It can be seen that the Co_3O_4 nanowire is composed of nanoparticles and the edge of nanowire is even (Figure 3.14a). The lattice fringes of 0.466 and 0.244 nm determined from the Figure 3.14b can be assigned to (111) and (311) planes of the spinel Co_3O_4 , respectively. After N_2 plasma treatment, the surface of CoN-1min nanowire became rougher compared with that of Co_3O_4 (Figure 3.14c). And the lattice fringes of 0.248 and 0.214 nm in Figure 3.14d can be indexed to (111) and (200) planes of the cubic CoN , respectively. These results are in agreement with the previous analysis of XRD.

The catalytic activities of all synthesized materials (Co_3O_4 , CoN-30s , CoN-1min and CoN-3min) in electrochemical water oxidation were evaluated in 1 M KOH solution using a standard three electrode system (see result in **Figure 3.15**). Before testing, electrodes were continuously activated between 0 V and 0.6 V vs Ag/AgCl at 50 mV s^{-1}

until repeatable and stable voltammograms were obtained. Potentials obtained in this study are all calibrated to reversible hydrogen electrode (RHE) reference. Figure 3.15a shows the linear-sweep voltammograms (LSVs) at a scan rate of 5 mV s^{-1} after iR-correction for all electrodes. The small oxidation peak before the onset of OER is mainly attributed to the Co(III) and Co(IV) redox couple. The CoN-1min exhibits highest catalytic activity (highest levels of current density) across the whole potential window. It only requires an overpotential of 290 mV for the CoN-1min to reach a current density of 10 mA cm^{-2} (η_{10}), which is lower than those of Co_3O_4 (339 mV), CoN-30s (304 mV) and CoN-3min (306 mV). Ni foam along was also tested for comparison. The poor OER activity of the Ni foam suggests that the high catalytic activity of these samples originates from the CoN nanowires.

Figure 3.15 Comparison of the OER performance of different electrodes. (a) iR-corrected polarization curves and (b) Tafel plots of Ni foam, Co_3O_4 , CoN-30 s, CoN-1 min, CoN-3 min. (c) Comparison of η_{10} (potentials required to reach 10 mA cm^{-2}) and Tafel slopes for all catalysts.

To gain further insight into the OER activity, Tafel slopes for all catalysts derived from the polarization curves at a slow scan rate (1 mV s^{-1}) are exhibited in Figure 3.15b. A smaller Tafel slope corresponds to a faster OER rate. The Tafel slope of the CoN-1min was 70 mV dec^{-1} , smaller than that of Co_3O_4 (82 mV dec^{-1}) and similar or same to that of CoN-30s (72 mV dec^{-1}) and CoN-3min (70 mV dec^{-1}). In addition, the Tafel slope versus the overpotentials (η_{10}) for all the studied catalysts is plotted in Figure 3.15c. This comparison shows clearly that the composition transformation of Co_3O_4 to CoN can significantly improve the catalytic activity (larger current density and faster OER rates). We compared with previous reported Co-related catalysts, such as Co_2B ,^[54] CoS ,^[96] CoP_2 ^[60, 97] and cobalt oxides/hydroxides,^[58, 98] our CoN nanowire arrays obtained by the ultrafast plasma treatment method outperform most of the samples as an OER catalyst (**Table 3.3**).

Table 3.3 Comparison of OER activity for CoN-1 min and recently reported Co-based catalysts.

Catalyst	Electrolyte	Overpotential @10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Substrate	Reference
CoN-1min	1 M KOH	290	70	Nickel foam	This work
Co_3O_4	1 M KOH	339	82	Nickel foam	This work
Co_4N	1 M KOH	257	44	Carbon cloth	[59]
Co_2B	0.1 M KOH	380	45	Carbon cloth	[54]
$\text{Co}(\text{OH})_2$	0.1 M KOH	510	65	Carbon cloth	
CoP_2/RGO	1 M KOH	330	96	Glassy carbon	[60]
CoS	1 M KOH	306	72	Carbon paper	[96]
CoP_2	1 M KOH	290	65	Nickel foam	[99]
Nanoporous CoP	1 M KOH	~300	65	Au	[97]

NiCo ₂ O ₄	1 M NaOH	320	47	Carbon cloth	[58]
Co nanoparticle	0.1 M KOH	390		Glassy carbon	[100]
CoNi(OH) _x	1 M KOH	280	77	Cu foil	[98]
Co ₃ O ₄ @cnt	0.1 M KOH	390	65	Glassy carbon	[101]

Figure 3.16 Cyclic voltamogram curves in double layer region at scan rates of 4, 8, 12, 16 and 20 mV s^{-1} of (a) Co₃O₄, (b) CoN-30 s, (c) CoN-1 min, and (d) CoN-3 min. (e) Current density as a function of the scan rate for all-prepared electrodes for an indication of the electrochemically active surface area.

Roughness factor, the ratio of effective ECSA to the geometric surface area of the

electrode, is an important parameter for catalysts. A higher roughness factor corresponds to larger active sites. The EASAs were estimated by using the electrochemical double-layer capacitance (C_{dl}) (**Figure 3.16**). After N_2 plasma, the ECSA increased slightly compared with pure Co_3O_4 , which may be attributed to the rougher surface achieved during plasma. However, it seems that ECSA has no obvious changes when the plasma treatment duration increased from 30 s to 3 min. So the larger current density of CoN-1min than that of CoN-3min implies that the structure and morphology of catalyst also play a vital role in catalytic performance when the EASAs are similar. The quasi-vertical alignment of nanowire arrays is generally favorable for the transport of reactants (H_2O) and products (O_2 and H_2).^[58] The above analyses lead to the conclusion that the CoN-1min is the most efficient electrocatalyst among the materials investigated herein.

Figure 3.17 OER performance of the CoN-1 min electrode. (a) Nyquist plots of Co_3O_4 and CoN-1 min electrodes. (b) Comparison of evolved oxygen volume with theoretical oxygen volume calculated based on the amount of consumed charges in the course of electrolysis.

EIS was carried out to study the kinetics occurring at the electrode/electrolyte surface under OER condition for the CoN-1min sample. The Nyquist plots in Figure

3.17a show that the charge transfer resistance of CoN-1min decreased significantly in comparison with Co₃O₄. This result suggests that CoN-1min has the faster charge transfer process. The Faradaic efficiency measurement at fixed current density (30 mA cm⁻²) was carried out to check whether the current was associated with water oxidation as shown in Figure 3.17b. The Faradaic efficiency was estimated using volumetric method. The evolved oxygen gas on CoN nanowire arrays electrode was collected in a 10 mL graduated tube, which was filled with electrolyte. Fixed current electrolysis was carried out at 10 mA for about 3.5 h under standard conditions (25 °C, 1 atm). The time points at each 1 mL of collected O₂ gas were recorded. The accumulated charge passing through the working electrode were calculated by the equation ($Q=It$). The coincidence of both values (near 100% of Faradaic efficiency) indicates that no side reaction happened during electrolysis.

In addition to the activity, stability is another important parameter to evaluate an electrocatalyst. To assess the durability of CoN-1min nanowire arrays for OER in alkaline electrolyte, electrolysis at three current densities (10, 30, and 50 mA cm⁻²) was conducted sequentially for over 30 h (Figure 3.18a). The corresponding overpotential remains stable at around 290, 318 and 325 mV for over 10 h each. The SEM image collected after 30 h stability test (Figure 3.18b) show that the original nanowire arrays structure is well preserved. In addition, the C_{dl} was tested again and there was nearly no change after the 30 h electrolysis (Figure 3.18c). These mean that the CoN nanowire arrays are quite stable as OER catalyst.

Figure 3.18 (a) Stability tests of the CoN-1 min catalyst at current densities of 10, 30, and 50 mA cm⁻² over 30 h. (b) SEM image of CoN-1 min after 30 h electrolysis; (c) corresponding current density as a function of the scan rate for CoN-1 min after 30 h electrolysis

To better understand the superior performance of CoN nanowire arrays, the catalytic mechanism of CoN was studied via cyclic voltammetry (CV) measurement, and XPS and TEM after electrolysis (**Figure 3.19**). The widely accepted mechanism for oxygen evolution on transition metal oxides in alkaline electrolytes is proposed as follow:^[102]

Figure 3.19 CoN-1 min catalyst: (a) The CV curve at the scan rate of 1 mV s^{-1} . The XPS spectra before and after electrolysis: Co 2p (b) and O 1s (c). (d) TEM image of the nanowire surface after OER electrolysis.

It has been reported that the essentially active sites of non-oxide metal-based catalysts (metal nitride, phosphide and boride and so on) for the electrochemical oxidation of water are the thin layer of oxide/hydroxide formed on the surface.^[54] In our case, CoN has the similar catalytic mechanism to that of proposed above for metal oxide based catalysts in alkaline electrolytes. A layer of CoOOH is expected to form on the surface prior to the OER process as the active sites. As shown in Figure 3.19a, the CV curve tested at 1 mV s^{-1} shows an anodic peak at around 1.39 V and a corresponding cathodic peak, attributed to the redox couples of $\text{Co}^{3+}/\text{Co}^{4+}$. The Co 2p spectrum after electrolysis coincides with that of Co_3O_4 , indicating that the Co atoms have the same chemical environment (Figure 3.19b). The O 1s XPS spectra in Figure 3.19c show that the peak attributed to oxygen ions in crystal lattice increase enormously after water

electrolysis, in accordance to the proposed formation of cobalt oxide on the surface of CoN nanowire arrays during the electrolysis. The TEM images of CoN (Figure 3.19d) after electrolysis confirmed that a layer of cobalt oxide around 10 nm formed on the surface of CoN nanowire. Hence, the core (CoN)/shell (Co_3O_4) structure formed during the water oxidation process contributes to the high OER activity of the CoN catalyst.

3.2.3 Overall water splitting of the NiMoN || CoN electrolyzer

Figure 3.20 Overall water splitting. NiMoN nanodendrite is the HER electrode and CoN nanowire is the OER electrode. (a) The iR -corrected polarization curve of water electrolysis at a scan rate of 5 mV s^{-1} . (b) Stability test at 30 mA cm^{-2} for 120 h.

Finally, the overall water splitting is conducted in a two-electrode configuration by employing the CoN nanowire as the OER and 3D porous NiMoN arrays as the HER catalysts in 1 M KOH. As shown in Figure 3.21a, the NiMoN || CoN electrolyzer affords a current density of 10 mA cm^{-2} at the operating potential of 1.63 V, representing a combined overpotential of 400 mV for overall water oxidation and reduction. This voltage is comparable to that of previously reported electrocatalysts for overall water splitting in alkaline media (Table 3.4). More importantly, this combined electrolyzer also maintained an excellent stability (see Figure 3.21b): The operating

voltage remained stable at around 1.7 V at a fixed current density of 30 mA cm⁻² for 120 h of continuous electrolysis. The representative photograph (inset in Figure 3.21b) exhibit the obvious production of H₂ and O₂ gas of this configuration during overall water electrolysis.

Table 3.4 Comparison of the bifunctional water splitting activity of the NiMoN || CoN with recently reported bifunctional electrolyzers in basic solutions

Catalyst	electrolyte	Voltage@10 mA cm ⁻² (V)	Reference
NiMoN CoN	1 M KOH	1.63	This work
PNC/Co	1 M KOH	1.64	[103]
CoNi(OH) _x NiN _x	1 M KOH	~1.65	[98]
CoP ₂ /RGO	1 M KOH	1.56	[60]
CP/CTs/CoS	1 M KOH	1.74	[96]
TiN@Ni ₃ N	1 M KOH	1.64	[104]
CoMnO@CN	1 M KOH	~1.5	[105]
CoP-MNA	1 M KOH	1.62	[99]
NiSe	1 M KOH	1.63	[106]
Ni ₅ P ₄	1 M KOH	1.70	[107]
Ni ₂ P	1 M KOH	1.63	[108]

3.3 Conclusion

In summary, we demonstrated a new and efficient method by N₂ RF plasma to convert metal precursors (metal or metal oxides) into corresponding metal nitrides. This method is environmental friendly, efficient and safe. And compared to common ammonia annealing method, it has the following advantages: i) the N₂ is taken as Nitrogen source, which is abundant and environmental friendly, ii) shorter treatment duration (a few minutes) and relatively lower reaction temperature (room temperature to a few hundred centigrade). 3D hierarchical porous nickel molybdenum nitride on

carbon cloth as HER catalyst and cobalt nitride arrays as OER catalyst have been prepared successfully, for the first time, by N₂ plasma method. Owing to the high roughness factor, superior mass and electron transport, and possibly a synergistic effect of the Ni, Mo and N, the obtained NiMoN catalyst exhibits outstanding HER performance with a small overpotential of around 109 mV to acquire the current density of 10 mA cm⁻² with an outstanding durability at different current densities. Owing to the better conductivity and the reserved large surface area, the obtained CoN nanowire arrays on nickel foam exhibit outstanding OER performance with a small overpotential of around 290 mV to acquire the current density of 10 mA cm⁻² and with an outstanding durability at different current densities. The overall water splitting performance of the NiMoN||CoN electrolyzer confirms that metal nitrides are one class of promising noble metal-free catalysts. This new method presented in this Chapter may be extended to the fabrication of a wide range of metal nitrides with tailored nanostructures.

Chapter 4 Pre-reduction of Metal Oxides via Carbon Plasma as Catalysts for Hydrogen Evolution Reaction

In addition to N₂ plasma, C-plasma could also apply to modify the electrode materials. Transitional metal oxides, as a large and important class of chemical compounds, are easily available materials with various nanostructures, which endows them large specific surface area. Unfortunately, most of them fail to play an important role in electrocatalytic hydrogen evolution due to their low electrical conductivity, sluggish catalytic kinetics and poor long-term stability. In addition to convert into corresponding nitrides as shown in chapter 3, pre-reduction is another feasible method to improve their catalytic activity. In this chapter, taking NiMoO₄ nanowire arrays as example, we demonstrate a novel and efficient carbon plasma method to pre-reduce metal oxides and make them more efficient and robust HER catalysts. Compared with traditional H₂ annealing reduction method, the carbon plasma treatment has a “One stone, two birds” effect - It not only creates lower-valence Ni₄Mo alloy nanoclusters by surface reduction, but also deposits a thin graphitic carbon shell simultaneously. This carbon shell protects the surface from re-oxidation and can maintain catalytic activity for long time.

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4.1 Introduction

Transitional metal oxides are easily available compound materials with a wide variety of nanostructures with high specific surface area.^[27] However, most of them fail to play an important role in hydrogen evolution due to their low electrical conductivity, sluggish catalytic kinetics and poor long-term stability. In this regard, it is highly desirable to improve the HER performance of transition metal oxides. Recently, there has been a few reports that modulation of the local atomic structure via introducing oxygen vacancy could improve the HER activity for certain metal oxides^{[28] [30]}. For example, Yang et. al. reported that the commercial WO₃ nanoparticles can show enhanced HER activity after annealing under H₂ atmosphere.^[30] In addition, we found that metal oxides (herein, NiMoO₄, Co₃O₄ and NiO) show a self-activation effect during the continuous hydrogen evolution process (**Figure 4.1**). The activity improvement is probably due to the surface reduction of metal oxides by the highly active hydrogen atoms that are produced on their surface during the HER process. This phenomenon is similar to the surface oxidation of some non-oxide catalysts during oxygen evolution reaction (OER) process.^[72] However, this *in-situ* improvement by self-activation is slow (takes a few hours), transient, and extremely unstable; the catalytic activity degrades quickly when the H₂ evolution is interrupted (Figure 4.1d). The CV curves clearly show that the improved catalytic activity during constant hydrogen production degenerated quickly under the intermittent operation condition (There were almost no hydrogen produced in the voltage range of -0.2 V – 0 V). So pre-reduction of metal oxides should be a more feasible and efficient strategy to

improve their HER catalytic activity. H_2 annealing is a commonly employed for pre-reduction of metal oxides. Unfortunately, the high temperature and long annealing time may destroy the nanostructure. And the reduction is still unstable and obvious degradation of HER catalytic activity is observed for the H_2 -annealed $NiMoO_4$, Co_3O_4 and NiO (see Figure 4.1c). Therefore, it is necessary that the modification to the transition metal oxides should simultaneously improve the catalytic activity and stability, and maintain the nanostructures.

Figure 4.1. a) Metal oxides; b) Corresponding metal oxides annealing under H_2 ; c) the stability test of metal oxides and after H_2 annealing at 10 $mA\ cm^{-2}$ in 1 M KOH; d) CV curves of metal oxides tested directly after stability test.

In this chapter, we report a more efficient method to boost the HER catalytic activity

of metal oxides with more stable performance via carbon plasma modification. We take NiMoO₄ nanowire arrays on carbon cloth as a case study. The carbon plasma (C-plasma) treated NiMoO₄ nanowire electrode displayed a low overpotential of 76 mV to reach 10 mA cm⁻² in 1 M KOH and superior duration in intermittent operation condition. This strategy is generic and effective for Co₃O₄ nanowire arrays. Our work offers a feasible plasma-assisted strategy towards activation and stabilization of transition metal oxide based electrocatalysts.

4.2 Results and Discussion

4.2.1 Pre-reduction of NiMoO₄ nanowire arrays and their HER performance

Figure 4.2 Electron micrographs of C-30s: (a) SEM, (b-d) TEM and (e) STEM image and EDS elemental mapping.

Figure 4.2 shows the detailed morphological structures of the C-30s. The morphology of nanowire arrays was preserved and many nanoparticles with the diameter of 5-10 nm were separated out on the surface of nanowires (Figure 4.2a and b). In the high magnified transmission electron micrograph (TEM) images (Figure 4.2c and d), *d*-spacing of 0.208 nm and 0.180 nm were measured for the nanoparticles, which corresponds to the (211) and (130) plane of the Ni₄Mo alloy (PDF# 65-5480). This indicates that Ni₄Mo alloy could be separated under the reductive atmosphere, which is in agreement with previous reports.^[110] About 1-2 layers of carbon were coated on the surface of nanowire. By their nature of catalytic decomposition of ethanol, Ni₄Mo nanoparticles have a thicker carbon shell, which is around 2 nm, corresponding to 5 graphitic layers. Furthermore, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image further confirmed that the metal nanoparticles decorated nanowires were formed (Figure 4.2e). As presented in the corresponding energy-dispersive X-ray (EDX) mappings, the Mo, O and C elements were homogeneously distributed throughout the whole nanowire, while the Ni element was distributed granularly on the surface with distinguishable particle boundaries.

The morphology of samples at different treatment times are presented and compared in Figure 4.3. First, the original NiMoO₄ nanowires show a smooth surface and clear crystal lattice (Figure 4.3a and a'). After treatment for 15 s, some nanoparticles are formed on the surface of nanowire (Figure 4.3b and b'). Increasing the treatment duration to 30 s, more nanoparticles are separated out (Figure 4.3c and c'). After 60 s

treatment, many carbon nanoflakes grow on the surface of nanowires (Figure 4.3d and d'). More detailed information is presented in magnified TEM images. For C-15s, MoO_2 is observed around the Ni_4Mo nanoparticles and NiMoO_4 phase is still observed partially (Figure 4.3b''). For C-60s, the carbon shells on Ni_4Mo nanoparticles grow longer to be hollow nanoflakes (Figure 4.3d'').

Figure 4.3 SEM and TEM images of the NiMoO_4 nanowires before and after C-plasma treatment for different time: a) no treatment, b) C-15s, c) C-30s and d) C-60s.

Figure 4.4 Full XPS spectra of all samples

The surface chemical composition and valence states of samples were further characterized by X-ray photoelectron spectroscopy (XPS). Four elements including Ni, Mo, O and C were identified from the XPS spectra (**Figure 4.4**), consistent with EDX mapping results. With the increasing treatment duration, the peak intensities of Ni, Mo and O became weaker, while the peak intensities of C became stronger. For C-60s, the layer of carbon was too thick to detect the signal of Ni, Mo and O.

Figure 4.5 High-resolution XPS for NiMoO₄ and C-30s (a) Ni 2p_{3/2}; (b) O 1s; (c) Mo 3d, and (d) C 1s.

The high-resolution spectra of C-30s and NiMoO₄ were presented in **Figure 4.5**. For Ni 2p (Figure 4.5a), the peak at 855.6 eV and its broad satellite peak at 861.8 eV belongs to Ni²⁺. After 30 s C-plasma treatment, the new peak at 852.4 is indexed to metallic Ni.^[111] The partial reduction of NiMoO₄ under C-plasma treatment could also be seen from the O 1s spectra (Figure 4.5b). As exhibited, the intensity of the peak at 530.7 eV, corresponding to the O²⁻ ions in the crystal line of NiMoO₄, decreased for the C-30s sample.^[72] A new peak from the surface groups of carbon shell appeared at 531.8 eV. The Mo 3d spectra in Figure 4.5c displays a new peak at low binding energy at 229.4 eV after C-plasma treatment, which attributes to low valence Mo^{δ+} species (δ=0, 1, 2, 3).^[112] The percentage of Mo^{δ+} in C-30s is 40.2%, which is higher than that of C-15s (12.7%). The C 1s spectra in Figure 4.5d only manifest the graphitic carbon at 284.3 eV, and no carbide peak (lower binding energy, ≈282.7 eV) was observed.

Figure 4.6 Electrochemical test of all samples: (a) LSV curves; (b) Tafel slopes; (c) Comparison of η_{10} values and Tafel slopes for all catalysts; (d) Nyquist plots at 10 mA

cm^{-2} .

The electrocatalytic activity of all samples for HER were evaluated by a three-electrode system in 1 M KOH (**Figure 4.6**) and compared to the state-of-the-art Pt/C electrocatalysts. Carbon rod was used as the counter electrode to avoid the possible contamination of Pt. The polarization curves at a sweep rate of 5 mV s^{-1} after iR-correction show an increase in the HER activity in the following order: NiMoO₄, C-15s, C-60s, C-30s and Pt/C. The η_{10} of C-30s sample is only 76 mV, which is slightly higher than that of Pt/C (45 mV) and obviously lower than that of NiMoO₄ (406 mV), C-15s (135 mV) and C-60s (152 mV). The inferior HER activity of C-60s attributes to the thicker and hollow carbon shell, which blocks the active sites from electrolyte. Tafel slope, as one of the experimental descriptor to study the HER kinetics, were obtained by plotting the overpotential versus the logarithm of current density (Figure 4.6b). The Tafel slope of C-30s (78 mV dec^{-1}) is smaller than those of NiMoO₄ (130 mV dec^{-1}), C-15s (106 mV dec^{-1}) and C-60s (103 mV dec^{-1}). The comparison of Tafel slope versus η_{10} value for all of the studied catalysts in Figure 4.6c has clearly shown that the C-plasma treated NiMoO₄ had significantly improve the HER performance. To better understand the superior HER activity of C-plasma treated NiMoO₄, their electrochemical impedance spectroscopies (EIS) were carried out. The typical Nyquist plots in Figure 4.6d depict the diameter of the semicircles decreased in the following order: NiMoO₄, C-15s, C-60s and C-30s, indicating that C-30s has the fastest electron transfer and HER activation.

Figure 4.7 Stability test. (a) Pristine NiMoO₄ nanowire, and C-30s sample, as well as another sample after H₂ treatment. (b) LSV curves of the C-30s electrode under different HER test stage. (c) C-30s at different overpotentials (without iR-correction).

The C-30s sample also exhibits an excellent long-term electrochemical stability. As shown in **Figure 4.7**, Electrolysis at 10, 30 and 50 mA cm⁻² were carried out sequentially over 36 h (Figure 4.7a). The overpotentials at different current densities show a relatively small fluctuation after each 12 h electrolysis (-4, 8 and 17 mV at 10, 30 and 50 mA cm⁻², respectively). The slight decrease of overpotential at 10 mA cm⁻² was probably due to the penetration of electrolyte to expose more active sites. The physical adsorption of the generated H₂ led to the degradation at 30 and 50 mA cm⁻². As shown in Figure 4.7b, the linear sweep voltammetry (LSV) curves after electrolysis at different current densities almost overlap with the original one. In addition, a multistep chronoamperometric curve was recorded in a wide overpotential range (from 50 mV to

500 mV) with an increment of 50 mV (Figure 4.7c). The response current densities remain constant at each step, implying the excellent mass transportation, conductivity, and mechanical robustness of the C-30s electrode.

Figure 4.8. C-30s sample after stability test. a) SEM, b) TEM, c) Ni $2p_{3/2}$ XPS spectra, and d) Mo $3d$ XPS spectra

The electrode also maintains its morphology and chemical composition after the 36 h stability test (**Figure 4.8**). The nanowire array morphology and the layer of carbon shell were well preserved, as shown by SEM and TEM images in Figure 4.8a and b. The Ni_4Mo nanoparticles are clearly observed in nanowires, owing to the protection provided by the carbon shell. We also compare the XPS spectra of Ni and Mo before and after stability test (Figure 4.8c and d). The peaks due to both Ni^0 and $\text{Mo}^{\delta+}$, which act as the active sites, remain except for slight decrease in their intensities. This verifies that the C-30s sample is a highly active and a very stable electrocatalyst for HER in

alkaline medium.

Figure 4.9. Effect of H_2 treatment of the $NiMoO_4$ (H_2 -1h): a, b) Morphology of the nanowires after annealing in an H_2/Ar (2%) ambient at $450^\circ C$ for 1 h. c) LSV curves of the H_2 -annealed $NiMoO_4$ nanowire sample, and after 30 min soaking in the electrolyte. XPS spectra of H_2 -1h and H_2 -1h after 12 h stability test at 10 mA cm^{-2} : e) Mo 3d and f) Ni $2p_{3/2}$.

To verify the contribution of C shell, we intentionally synthesized a hydrogen-reduced $NiMoO_4$ nanowires film in gas ambient (H_2 -1h) and investigated its catalytic enhancement and stability. Surface treatment of the $NiMoO_4$ nanowires in a

H₂ gas ambient can also improve the catalyst activity, but cannot solve instability problem. The synthetic and structural details of H₂-1h were presented in the Experimental Section and **Figure 4.9**. The SEM (Figure 4.9a) and TEM images (Figure 4.9b) confirmed that indeed Ni₄Mo nanoparticles were formed on the surface of nanowires, similar to carbon-plasma reduction. Furthermore, the surface chemical composition and valence states of H₂-1h were the same as those of C-30s (XPS of Ni and Mo in Figure 4.9d and e). A current density of 10 mA cm⁻² was achieved with an overpotential of only 60 mV in 1 M KOH, which was better than that of C-30s (76 mV) (Figure 4.9c). However, it is quite unstable. After 1-2 h stability test at 10 mA cm⁻², the overpotential of H₂-1h was higher than that of C-30s (Figure 4.7a). If soaking the H₂-1h in electrolyte for only 30 min, the η_{10} would sharply increase to ~223 mV (Figure 4.9c). The XPS spectra of Ni and Mo, after the 30 min soaking (Figure 4.9d and e), showed that both peaks for Ni⁰ and Mo ^{δ^+} disappeared.

To further check their chemical stability, the NiMoO₄, H₂-1h and C-30s samples were immersed in 1 M KOH solution for 12 h (without electrochemical measurement). We found the nanowire arrays of the NiMoO₄ and H₂-1h samples almost disappeared, but not the C-30s (**Figure 4.10**). This indicates that the carbon shell effectively protects the active materials from dissolution in KOH solution.

Figure 4.10. A summary of the chemical stability of NiMoO_4 nanowires under different treatments. (a) As-grown NiMoO_4 nanowires on carbon fiber. (b) after soaking sample in a 1 M KOH solution for 12 h. (c) H_2 -treated sample after soaking in a 1 M KOH solution for 12 h. (d) C-plasma treated sample after soaking in a 1 M KOH solution for 12 h. It indicates that the carbon coating after C-30s treatment effectively protects the nanowires from dissolution in KOH.

4.2.2 Pre-reduction of Co_3O_4 nanowire arrays and their HER

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Finally, to further demonstrate the versatility of our fabrication strategy, we also used C-plasma to treat Co_3O_4 nanowire arrays (**Figure 4.11**). After the C-plasma treatment, the nanowire morphology was retained and lower valence CoO phase was generated. Similarly, a thin layer of graphitic carbon shell formed on the CoO nanowire surface. Compared with H_2 annealing, the pre-reduction of Co_3O_4 via C-plasma treatment not only improve the HER catalytic activity but also the longtime stability.

Figure 4.11 C-plasma treatment of Co_3O_4 nanowires. SEM of (a) as-grown Co_3O_4 nanowires on nickel foam and (b) the sample after C-30s plasma treatment. TEM of (c) one Co_3O_4 nanowire and (d) one CoO nanowire. Inset shows the surface of nanowire. (e) XRD spectra show the conversion from Co_3O_4 to CoO . (f) Stability tests of Co_3O_4 , Co_3O_4 - H_2 annealing and Co_3O_4 -C30s at 10 mA cm^{-2} . Co_3O_4 -C30s shows a better stability compared with Co_3O_4 - H_2 annealing

4.3 Conclusion

In summary, we have demonstrated that pre-reduction of transition metal oxides is an efficient method to greatly improve their catalytic activity for hydrogen evolution. Compared with the common H_2 annealing, the C-plasma treatment not only has a

reduction reaction function, but also leads to a concurrent encapsulation of the whole nanowire with a thin layer of graphitic carbon. Benefiting from the protection of carbon shell, the modified metal oxide exhibits outstanding physical and chemical stability under longtime and intermittent operation for hydrogen evolution. We show that this strategy is generic and effective to other metal oxides (such as Co_3O_4), which paves a new way to exploit transition metal oxide materials as highly activity and stable HER catalysts to compete against precious metals.

Chapter 5 Ultrafine metal nanoparticles/N-doped porous carbon hybrids coated on carbon fibers as flexible and binder-free water splitting catalysts

Bimetal-based catalysts of two proper transition metals are generally more active than individual constituents for HER and/or OER. In Chapter 3 and 4, we also found that the NiMo based materials deliver high catalytic activity. In addition, N-doped carbon materials are not only an excellent catalyst supporter but also an effective catalyst for electrolysis. Until now, there are only few catalysts combining the bimetal material and N-doped carbon material together. The available few reports are in powder form and need polymer binders, which are not favorable for the test.

In this chapter, we achieved a series of ultrafine transition metal-based nanoparticles embedded in N-doped carbon layers on carbon cloth for both HER and OER catalysts. The synthesis was realized by employing an in-situ reduction of metal precursor and an interesting metal-assisted carbon etching process. We demonstrate Ni-Mo and Ni-Fe embedded in N-doped carbon (NiMo-PVP and NiFe-PVP) as highly efficient electrocatalysts for HER and OER, respectively. Then overall water splitting is also realized based on the couple of NiMo-PVP||NiFe-PVP catalyzer.

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5.1 Introduction

Based on the theoretical and experimental investigations, combining two proper transition metal elements to form bimetal-based catalysts are significantly more active for HER or OER than each of single metal-based catalysts. According to the M-H bond strength of the optimal HER catalyst —Pt in the volcano plot, Ni, Co, Fe show weaker M-H bonds and W, Mo exhibit stronger M-H bonds.^[39] It is believed that moderate bond strength could be achieved via choosing two proper metal elements.^[23, 38, 39, 73] Porous nickel-molybdenum nitride has been successfully prepared in chapter 3 exhibiting better HER catalytic performance than single metal nitrides.^[73] It is also noted that NiFe bimetal-based catalyst is significantly active for OER than either single Ni or Fe, which is considered as the most promising candidate of non-noble metal OER catalysts.^[114, 115] Low-overpotential of ~230 mV at 10 mA cm⁻² has been reported for electrodeposited Ni-Fe films, which is even better than that of IrO₂ film.^[114]

In addition, growing transition metal-based material on porous doped carbon is another confirmed efficient method to improve the activity of transition metal-based catalysts.^[24] First, the carbon materials have porosity, great electron conductivity and strong corrosion resistance both in acidic and basic solutions, which make them ideal scaffolds to expose more active sites in constructing catalysts. Second, heteroatom dopants, take N element for example, can induce a charge rearrangement on the carbon materials and consequently create new catalytic centers. At last, the synergistic effect of the heteroatoms and metal-based nanoparticles can promote the catalytic process. MoC₂ modified N-doped carbon vesicle encapsulating Ni nanoparticles reported by

Wang' group exhibits high efficient HER catalytic performance both in basic (~ 129 mV at 10 mA cm^{-2}) and acidic solution (~ 75 mV at 10 mA cm^{-2}).^[24] N-doped porous carbon nanosheet/CoNi alloy-encapsulated carbon nanotubes demonstrated promising application in OER and oxygen reduction reaction (ORR).^[116] Thus transition metal-based nanoparticles composited with heteroatoms doped carbon materials can be excellent catalysts for water splitting. Despite great progress has been achieved in heteroatom-doped carbon supported transition metal-based powder catalysts; powder catalysts have several drawbacks, such as extra interfacial resistance and the loss of active sites. Integrated thin film catalysts are able to overcome above drawbacks commendably. So it is meaningful to explore a facile and high-efficient approach to fabricate hybrid catalysts of bimetal-based nanoparticles and doped carbon film for water splitting.

Herein, a series of metal-based nanoparticles/N-doped porous carbon hybrid films on carbon cloth were successfully prepared via cost-effective dip coating method. Ultrafine nanoparticles with a diameter of around 2 nm embed in the N-doped porous carbon randomly to form the above porous hybrid films. The ultrafine size of nanoparticles and the porous structure provide high density of active sites at specific area. In addition, the hybrid film structure avoids the aggregation of active material and improves the conductivity of electrodes. Ni/MoC₂@N-doped porous carbon (NiMo-PVP) produces a low HER overpotential of 130 mV at a current density of 10 mA cm^{-2} . When NiFe@N-doped carbon on carbon cloth (NiFe-PVP) applied as a catalyst for OER, a 297 mV overpotential is required to achieve the current density of

10 mA cm⁻². The overall water splitting of electrolyzer (NiMo-PVP || NiFe-PVP) is also studied, which affords a current density of 10 mA cm⁻² at the operating potential of 1.66 V, representing a combined overpotential of ~430 mV.

5.2 Results and Discussion

Figure 5.1 Schematics of metal-based nanoparticles/N-doped porous carbon hybrid catalysts. (a) Fabrication process; (b) Cross section view of the interface.

The general preparation process of ultrafine metal-based nanoparticles embedded in N-doped porous carbon hybrid films on carbon cloth is shown schematically in **Figure 5.1**. Carbon cloth is used as a substrate, which offers high specific surface area, excellent electrical conductivity, mechanical robustness and strong tolerance to acid/alkaline environment. A thin film of homogeneous precursor of metal salts (Ni, Fe, Mo) and nitro-organic compound (polyvinylpyrrolidone, shorted as PVP), is covered on cleaned carbon cloth via dip-coating method. After annealing precursors at 1000 °C under the protection of Ar atmosphere, PVP and metal salts are eventually converted into N-doped carbon and metal-based nanoparticles respectively. Due to the

confinement of the PVP and the thin film structure of precursor, the growth of metal-based crystals is restricted in a small area, resulting in the formation of ultrafine nanoparticles. In this process, PVP has the following functions: 1) provides the N source, 2) coheres with the metal precursor and 3) restrains the growth of metal-based catalysts, to form uniform ultrafine nanoparticles. Meanwhile, the carbon cloth is etched via metal nanoparticles to form porous structure.^[117]

5.2.1 Characterization of NiMo-PVP and its HER performance

Figure 5.2 SEM images of NiMo-PVP precursor: (a) top view image (low-magnification SEM image in inset); (b) cross-sectional image (high-magnification SEM magnification in inset).

As shown in **Figure 5.2**, a thin film of precursor (PVP, Ni and Mo metal salts) evenly covers on carbon cloth after dip coating and the textile structure of carbon cloth is well reserved.

Figure 5.3 Synthesis and characterization of NiMo-PVP. (a-b) top view and cross-sectional SEM images, respectively. Insets are low-magnification images. (c) low- and (d) high-magnification TEM images. (e) HAADF-STEM image and the corresponding EDX maps for C, Ni, Mo, N and their combine image.

After annealing (**Figure 5.3**), the surface of carbon cloth becomes porous (Figure 5.3a). The thickness of this porous layer is around 200 nm based on the cross-section SEM image (Figure 5.3b). The porous hybrid material can be identified by the strong contrast difference in the TEM image (Figure 5.3c). However, no visible interlayer gaps

are observed in NiMo-PVP, implying a good anchor-hold between NiMo hybrid catalysts and carbon cloth. According to the results of high resolution transmission electron microscopy (HRTEM), two kinds of crystalline particles (metallic Ni and γ -MoC₂) with a nearly identical diameter of around 2 nm are clearly embedded in the surface of carbon fibers (Figure 5.3d), which can efficiently prevent the aggregation and excessive growth of nanoparticles. The high crystallinity of nanoparticles is confirmed by clear lattice fringes. Moreover, the distributions of the exiting elements in NiMo-PVP were measured via the high-angle annular dark-field scanning transition electron microscopy (HAADF-STEM) and corresponding EDX mappings (Figure 5.3e). The edge part is brighter compared with the bottom of sample due to the metal elements (Ni and Mo). As shown in the EDX mappings, Ni and Mo elements were distributed homogeneously over the layer of hybrid film. For C element, the density is weaker in the edge part. On contrary, the density of N element is stronger in edge part.

Figure 5.4 Water contact angle measurement for (a) NiMo-PVP and (b) carbon cloth.

In addition, the NiMo-PVP is highly hydrophilic with a small contact angle of 8°, in contrast to 130° for the carbon cloth (Figure 5.4). This feature facilitates the access of electrolyte to catalyst active surface and the detachment of bubbles during

Figure 5.5 Structural and composition characterization of NiMo-PVP: (a) XRD patterns; XPS spectra of (b) Ni 2p, (c) Mo 3d, and (e) N 1s.

The phase and composition of NiMo-PVP are characterized by XRD and high-resolution XPS and shown in **Figure 5.5**. In agreement with the above HRTEM results, the diffraction peaks of NiMo-PVP (Figure 5.5a) could be well indexed to the metallic Ni (JCPDS Card No. 03-1051) and γ -Mo₂C (JCPDS Card No. 01-1188), respectively. The chemical states of Ni, Mo, and N species on the surface are shown in Figure 5.5b-d. Ni 2p XPS spectrum of NiMo-PVP samples (Figure 5.5b) shows that Ni mainly exists in the form of Ni⁰ and Ni²⁺. Ni²⁺ originates from the surface oxidation of Ni nanoparticles upon air exposure. In the spectrum of Mo 3d (Figure 5.5c), three oxidation states (+2, +4 and +6) of Mo exist on the surface. The peak at 229.5 eV is attributed to Mo₂C. Similarly, due to the consequence of surface oxidation, peak at

232.9 eV is indexed to MoO_2 and peaks at 231.8 and 235.9 eV are assignable to MoO_3 , both of them are considered to be inactive in HER process.^[73] The deconvolution of N 1s energy level signals shows two peaks at 398.7 eV and 401.5 eV, which are originated from the pyridinic and graphitic N (Figure 5.5d), respectively.^[63]

Figure 5.6 Top view and cross-sectional SEM images of all comparison samples

For comparison, a series of control samples were also prepared: Ni/ Mo_2C @porous carbon (NiMo-PEG), Mo_2C @N-doped porous carbon (Mo-PVP), Ni@N-doped porous carbon (Ni-PVP) and N-doped porous carbon (PVP). Similar to NiMo-PVP, all above

samples are showing the uniform porous morphologies (**Figure 5.6**). However, from the cross-section views, these samples with Ni element show a thicker thickness (~200 nm) of porous hybrid film, than that of samples without Ni (Mo-PVP and PVP) (~50 nm). This phenomenon is probably due to the etching of Ni for carbon at high temperature.^[117] In this way, the specific surface area of sample is increased, indicating that more active sites expose in the electrolyte. XRD patterns of these control samples are presented in **Figure 5.7** to identify their material phases.

Figure 5.7 XRD patterns for (a) NiMo-PEG, (b) Ni-PVP, (c) Mo-PVP, and (d) PVP

Figure 5.8 HER catalytic characterizations of all obtained catalysts: (a) polarization curves, (b) Tafel slopes

To investigate their HER activities, all samples were evaluated in a three-electrode system in 1 M KOH (**Figure 5.8**). Without specific justification, all potentials in this work are referred to RHE. The corresponding linear sweep voltammograms (LSVs) at 5 mV s⁻¹ after iR-correction are shown in Figure 5.8a. Commercial Pt/C and carbon cloth substrate were also tested for comparison. As expected, commercial 20% Pt/C shows the highest electrocatalytic activity with a small onset overpotential of nearly 0 V and pure carbon cloth exhibits far inactive HER performance. Among all samples, the NiMo-PVP exhibits the highest catalytic activity (highest current density) across the whole potential windows. In general, the potential value at current density of 10 mA cm⁻² (η_{10}) is chose as the benchmark of HER catalysts because solar-light-coupled HER apparatuses usually operate at 10-20 mA cm⁻² under standard conditions (1 sun, AM 1.5)^[119]. For NiMo-PVP, an overpotentail of only ~130 mV is required to reach the current density of 10 mA cm⁻², which is lower than those of Mo-PVP (181 mV), Ni-PVP (205 mV), NiMo-PEG (191 mV), and PVP (410 mV).

For further insight into the HER activity, Tafel plots were fitted to Tafel equation ($\eta =$

$b \log(j) + a$, where η is the overpotential, b is the Tafel slope, and j is the current density) in Figure 5.8b. The Tafel slope of Pt/C is 44 mV dec^{-1} , which is in agreement with the reported value.^[120] Under the same condition, NiMo-PVP exhibited a Tafel slope of 84 mV dec^{-1} , indicating a Volmer-Heyrovsky mechanism.^[111] For comparison, the Tafel slope of NiMo-PEG (103 mV dec^{-1}) is much larger than that of NiMo-PVP, suggesting that the N-doped carbon leads to the improved HER activity. It is noted that the Tafel slope of Mo-PVP (70 mV dec^{-1}) is even smaller than that of NiMo-PVP. This phenomenon may be due to the uneven distribution of Ni and Mo elements. Although the diameter of metal-based particles is ultrafine in our samples, two phases are still existed. It has been confirmed that the combination of Ni and Mo in atomic level facilitates the HER activity.^[24, 39, 73] It is speculated that some sites in the interface of two different phases are active at relative low overpotential. With the increase of overpotential, more and more sites become active. However, for Mo-PVP samples, all sites become active at a narrow overpotential window, so its Tafel slope is relative smaller. The HER performance is subject to Tafel slope only at small current density. So NiMo-PVP samples still show the largest current density at across potential window.

Figure 5.9 Nyquist plots for (a) NiMo-PVP at different overpotentials and (b) all HER samples at η_{10} .

Electrochemical impedance spectroscopy (EIS) analysis was then performed to gain further insight into the electrocatalytic activity (**Figure 5.9**). The corresponding Nyquist plots of NiMo-PVP for HER from 100 kHz to 0.05 Hz at three selected overpotential (η_0 , η_1 and η_{10}) are shown in Figure 5.9a. The plots were fitted by a model with two in parallel constant-phase elements: the one in high frequency region related to surface porosity (R_p), the other at low frequency related to charge transfer resistance (R_{ct}).^[121] The calculated value of R_{ct} decreases from 363 Ω at η_0 to 5.5 Ω at η_{10} , indicating that the charge transfer kinetics is significantly improved upon η increasing. Nyquist plots collected at η_{10} for all catalysts are shown in Figure 5.9b. NiMo-PVP exhibits the lowest charge transfer impedance value among all samples, which are in agreement with the superior HER activities. The eminent charge transfer kinetics and HER catalytic activity may result from the synergistic effect of Mo_2C , Ni and N-doped carbon.

Figure 5.10 Current density as a function of scan rate for various catalysts

As the water splitting process involved gas-liquid-solid three phases, the roughness factor, defined as the ratio of effective ECSA to the geometric surface area of the electrode, was also evaluated for further investigation into the different catalytic

performance. The electrochemical double layer capacitances (C_{dl}) can be measured to estimate the effective active area of catalysts via simple cyclic voltammetry method (**Figure 5.10**). The samples contain Ni element show a higher C_{dl} ($\sim 11 \text{ mF cm}^{-2}$), which is around two times larger than Mo-PVP and PVP (5 mF cm^{-2}) and five times larger than carbon cloth substrate (2 mF cm^{-2}). This indicates that the Ni element works as etch to make samples more porous so that more active sites expose to electrolyte and take part in the catalytic reaction.

Figure 5.11 Stability performance of the NiMo-PVP electrode: (a) stability tests at current densities of 10, 30 and 50 mA cm^{-2} over 60 h; (b) SEM after stability test.

Long-term stability is also critical for a practical HER catalyst. To assess the durability of the NiMo-PVP catalyst, the electrolysis tests were conducted at three different current densities (10, 30, and 50 mA cm^{-2}) for up to 60 h (Figure 5.11a). The time dependence of the overpotentials at different current densities show a slightly increase after a long period electrolysis. The required overpotentials to achieve current densities of 10, 30, and 50 mA cm^{-2} are merely increased 10, 8 and 8 mV, respectively, suggesting the excellent stability of NiMo-PVP as HER catalyst. The larger degradation at 10 mA cm^{-2} is probably due to the peeling off some catalysts that attached loosely on the surface. However, owing to the etching of carbon fibers, most of

the catalysts embed in the carbon cloth, which leads to more stable performance at higher current densities. The SEM images (Figure 5.11b) show the morphology of NiMo-PVP after 60 h stability test, indicating that the nanoporous structure is well preserved.

According to the above studies, the extraordinary properties of NiMo-PVP could be attributed to the following factors. First, γ -Mo₂C has been reported as an efficient non-noble metal catalyst for HER due to its unique Pt-like d-band electronic structure. Second, the introduction of Ni optimizes the M-H bond energy of Mo₂C based on the volcano-plots. Third, the pyridine N-dopants have been proven to synergistically increase the electron density on the carbon surface, which facilitates the HER catalytic process for these metal-based catalysts. Finally, the binder-free electrode improves its electron conductivity and benefits its long-term durability. The low overpotential and superior stability prove that it is an excellent candidate for HER catalyst.

5.2.2 Characterization of NiFe-PVP and its OER performance

For a practical water splitting electrolyzer, efficient HER and OER catalysts are both indispensable. In recent years, NiFe based materials are intensively studied for OER, such as NiFe layered double hydroxide (LDH),^[122] NiFe metal oxides,^[114] NiFe alloys^[115] and NiFe nitrides^[123]. Herein, ultrafine NiFe nanoparticles embedded N-doped porous carbon was successfully synthesized via the same method of NiMo-PVP, suggesting the generality of this method.

Figure 5.12 Synthesis and characterization of NiFe-PVP, (a,b) Top view and cross-sectional SEM images, respectively. Insets are the corresponding low-magnification image. (c) XRD pattern. (d) High-magnification TEM image. (e) HAADF-STEM image and the corresponding EDX maps for C, Ni, Fe, N and their combine image.

As shown in Figure 5.12a and b, NiFe-PVP shows the similar morphology as NiMo-PVP. Around 200 nm porous hybrid materials are formed on the outer of carbon fibers. Three XRD peaks at 43.9°, 51.2° and 75.4° (Figure 5.12c) are indexed to (111), (200) and (220) planes of NiFe alloy (JCPDS 12-0736), respectively. No peaks for Ni

or Fe phase are presented, indicating that pure NiFe alloy nanoparticles are synthesized without any impurity. In agreement with the results of XRD, HRTEM image (Figure 5.12d) shows that NiFe nanoparticles with a diameter of around 2 nm are randomly embedded in the surface of carbon fibers as the NiMo-PVP. The high crystallinity of nanoparticles is confirmed by clear lattice fringes.

Figure 5.13 (a) SEM images, (b) cross-section view and (c) XRD pattern for Fe-PVP

In addition, Ni and Fe elements were distributed homogenously over the layer of hybrid film (~ 200 nm). For comparison, Fe@N-doped porous carbon on carbon cloth (Fe-PVP) was also fabricated via the same method (**Figure 5.13**). The SEM image and cross-section view show that Fe-PVP has the same morphology and similar thickness of around 200 nm as NiFe-PVP, indicating that Fe element is also able to etch the carbon cloth as Ni element. The XRD pattern of Fe-PVP (Figure 5.13c) exhibits that pure Fe is

synthesized.

Figure 5.14 OER catalytic characterizations of NiFe-PVP and related catalysts: (a) polarization curves, (b) Current density as a function of scan rate for various catalysts, (c) The normalized polarization curves of NiFe-PVP, Fe-PVP and Ni-PVP by the electrochemical surface area of electrocatalysts, and (d) Tafel slopes

The OER catalytic performance of the NiFe-PVP, Ni-PVP and Fe-PVP were investigated in 1 M KOH solution via a typical three electrode system (**Figure 5.14**). The LSVs after iR-correction for all the as-fabricated catalysts are shown in Figure 5.14a. Among the three prepared catalysts, NiFe-PVP exhibits the smallest onset potential, and largest current density. Overpotential of 297 mV is required for NiFe-PVP to reach the current density of 10 mA cm^{-2} , which is much smaller than that of Fe-PVP (350 mV) and Ni-PVP (400 mV). The C_{dl} and OER LSV curves for all the samples normalized by the electrochemical surface area of electrocatalyst are shown in

Figure 5.14c and d. In this condition, NiFe-PVP still shows the highest specific current density, confirming that the catalytic activity of NiFe-PVP is indeed better than that of Ni-PVP and Fe-PVP. Linear fitting of the Tafel plot of NiFe-PVP shows a slope of 48 mV dec⁻¹ (Figure 5.14b), which is also lower than that of Fe-PVP (76 mV dec⁻¹) and Ni-PVP (75 mV dec⁻¹) and close to that of Ru-based catalysts (40 mV dec⁻¹)^[49]. The more negative overpotential and low Tafel slope confirm that NiFe-PVP is indeed promising OER electrocatalyst.

Figure 5.15 Nyquist plots of at different overpotentials. (d) polarization curves of initial, after 20 h electrolysis and after 60 h electrolysis test of the NiFe-PVP electrode. (e) Stability tests of the NiFe-PVP electrode at current densities of 10, 30 and 50 mA cm⁻² over 60 h.

EIS results in Figure 5.15a exhibit that NiFe-PVP has the smallest charge transfer resistance among the three catalysts, suggesting a much faster electron transfer rate during OER catalytic activity. The stability, as a crucial assessment parameter for

practical applications, was also tested and the results shown in Figure 5.15b and c. It is found that after 20 h bulk electrolysis at 10 mA cm^{-2} , NiFe-PVP shows an improved OER catalytic performance, higher current density at the same overpotential. As shown in Figure 5.15b, after 20 h bulk electrolysis at 10 mA cm^{-2} , η_{10} decreases 5 mV. After 60 h electrolysis, the LSV curve almost still overlaps with the pristine one. This is in agreement with the result shown in Figure 5.15c, the overpotential shows a slight decrease at the first 20 h at 10 mA cm^{-2} , and the required overpotential for 30 and 50 mA cm^{-2} almost keep constant at the following 40 h. These results confirm that NiFe-PVP have superior electrochemical durability.

5.3.3 Overall water splitting of NiMo-PVP||NiFe-PVP

Figure 5.16 Overall water splitting based on NiMo-PVP as the HER electrode and NiFe-PVP as the OER electrode. (a) The polarization curve. The inset is the photograph for overall water splitting reaction in a two-electrode configuration. (d) Coulombic efficiency: comparison of the amount O₂ and H₂ of the theoretically calculated and experimentally measured gas versus reaction time at a constant current density of 30 mA cm^{-2} . (c) The catalytic stability for 60 h at 30 mA cm^{-2} .

Encouraged by the superior catalytic performance of NiMo-PVP and NiFe-PVP as HER and OER catalysts respectively, the overall water splitting is further conducted in 1 M KOH via a two-electrode configuration, which is close to the practical device. As shown in **Figure 5.16**, application of the NiMo-PVP || NiFe-PVP electrolyzer cell affords a current density of 10 mA cm⁻² at the operating potential of 1.66 V, representing an overpotential of 430 mV for overall water splitting. This voltage is comparable to that of previously reported electrolyzer in alkaline media (**Table 5.1**).

Table 5.1 Comparison of the overall water splitting activity of the NiMo-PVP || NiFe-PVP with recently reported electrolyzers

Catalyst	Electrolyte	Volatege@10 mA cm ⁻² (V)	Reference
NiMo-PVP NiFe-PVP	1 M KOH	1.66	This work
NiMoN CoN	1 M KOH	1.63	[72]
CoNi(OH) _x NiN _x	1 M KOH	1.65	[98]
PNC/Co	1 M KOH	1.64	[60]
CP/CNs/CoS	1 M KOH	1.74	[96]
TiN@Ni ₃ N	1 M KOH	1.64	[104]
CoMnO@CN	1 M KOH	1.62	[99]
NiSe	1 M KOH	1.63	[106]
Ni ₅ P ₄	1 M KOH	1.70	[107]
Ni ₂ P	1 M KOH	1.63	[108]

The Faradic efficiency was calculated by comparing the experimentally produced gas volume with the theoretically calculated volume. Figure 5.16b shows that the amount of produced H₂ and O₂ are consistent with the calculated value, suggesting a ~100% Faradic efficiency. And the molar ratio of H₂ to O₂ is close to 2. In addition, this electrolyzer also presented an impressive long-term duration for the overall

water-splitting at 30 mA cm^{-2} as demonstrated in Figure 5.16c. There is a slightly increase of overpotential in the initial few hours, which may due to the physical adhesion of produced gas and the loss of some catalysts that attached loosely. Afterwards, the overpotential shows no obvious increase, indicating an impressive long-term duration.

5.3 Conclusion

In this chapter, we report the successful synthesis of a series of transition metal-based nanoparticles/N-doped porous carbon hybrid films on carbon cloth via a simple and economic method. Metal salts precursors uniformly covered on carbon fibers by dip coating are reduced into nano-size particles, which simultaneously catalyze etching of the carbon surface. The metal-assisted etching process induces both porosity and nitrogen doping in the carbon fiber surfaces. Owing to the superior electron transport, excellent hydrophilic property and the synergistic effect of Ni, Mo_2C and N-doped carbon, the as-prepared NiMo-PVP exhibits outstanding HER performance with a small overpotential of 130 mV to acquire a current density of 10 mA cm^{-2} and superior durability. The NiFe-PVP prepared in the same way shows a small overpotential of 297 mV to acquire a current density of 10 mA cm^{-2} as OER catalyst. The NiMo-PVP || NiFe-PVP couple in a two-electrode system delivers a current density of 10 mA cm^{-2} at 1.66 V and a Faradic efficiency of around 100% in 1 M KOH. Due to the facile synthetic method, abundant material availability and high catalytic property, these ultrafine metal-based nanoparticles embedded in N-doped carbon materials are

promising substitutes for noble metal catalysts toward high efficient and low cost water splitting.

Chapter 6 Summary and Future Work

6.1 Conclusions

Considering that earth abundance of transition metals (Fe, Co, Ni and Mo, etc.), in this thesis, we focused on the rational design and facile synthesis of nanostructured transition metal based materials, which are one group of promising electrocatalysts. The major accomplishments of this thesis are three works finished in my past PhD research study.

In the chapter 3, we developed a novel and facial method to fabricated nanostructured metal nitrides via RF N₂ plasma and studied their superior electrochemical performances as catalysts for water splitting. In general, metal nitrides are prepared via annealing precursors under caustic and hazardous ammonia (NH₃) flow. Even worse, it requires long processing duration and high reaction temperature. In this method, earth abundant and nontoxic N₂ is used as nitrogen source and the processing duration is only a few minutes. We successfully converted dense NiMo alloy and Ni metal films into 3D porous NiMoN and Ni₃N, respectively. The as-prepared 3D porous NiMoN depicts outstanding HER performance due to the synergistic effect of Ni, Mo and N, high roughness factor and electron transport. In addition to dense metal precursors, nanostructured metal oxides can also be converted into corresponding nanostructured nitrides. Co₃O₄ nanowire arrays were converted in CoN nanowire arrays at room temperature in one min under N₂ plasma. It only requires a small overpotential ~290 mV to reach the current density of 10 mA cm⁻².

Based on this work, we provided a promising way to fabricate nanostructured metal nitrides. This method is new and should be applicable to a wide range of metal nitrides that can be useful in supercapacitors, Na-ion batteries, OER/HER, etc.

In chapter 4, C-plasma is applied to modify metal oxides as catalysts for HER. We found that pre-reducing of metal oxides is a feasible method to improve their catalytic activity. Metal oxides (NiMoO_4 , Co_3O_4 and NiO) were pre-reduced by H_2 and C-plasma, respectively. Compared with traditional H_2 annealing reduction method, the carbon plasma treatment has a “One stone, two birds” effect - it not only creates lower-valence active sites on the surface, but also deposits a thin graphitic carbon shell simultaneously. This carbon shell protects the surface from re-oxidation and can maintain catalytic activity for long time. Our C-plasma method opens a new door to make cheap metal oxides more catalytic efficient and stable for HER in harsh conditions.

In chapter 5, a series of ultrafine transition metal-based nanoparticles (Ni-Fe, Ni-Mo) embedded in N-doped carbon have been successfully fabricated as replacements for noble metal-based catalysts in electrolytic water splitting via dip-coating method and following in-situ annealing process. The diameter of metal-based nanoparticles is around 2 nm, which increases the availability of active sites for electrocatalysis. The as-prepared catalysts demonstrate outstanding catalytic activities rendered by the synergistic effect of bimetal elements and N-dopants, the improved electrical conductivity and hydrophilism. Ni/Mo₂C@N-doped porous carbon

(NiMo-PVP) and NiFe@N-doped carbon (NiFe-PVP) produce low overpotential of 130 and 297 mV at a current density of 10 mA cm⁻² as catalysts for HER and OER, respectively. In addition, the binder-free electrodes make them show long-term stability. Then overall water splitting is also realized based on the couple of NiMo-PVP||NiFe-PVP catalyzer.

6.2 Comments and future work

(1) Further develop the RF plasma technique in the fabrication and/or modification of electrode materials. Plasma-assisted processes are becoming unique and powerful tools for nanoscale fabrication and functionalization, as plasmas provide a complex, reactive and far from equilibrium chemical factory. High energy plasma process is a very powerful and versatile one in enhancing the efficiency of material synthesis, lowering the reaction temperature and shortens the reaction time. Lots of reactions that are difficult to achieve at lower temperatures become possible under high-energy plasma ambient. In chapter 3 and 4, we successfully applied C, N-plasma in the fabrication of electrode materials. However, before pushing the commercial application of RF plasma, there are still several challenges: (i) only a few kinds of plasma applied in the fabrication of electrode materials, such as H₂, C, N, P, O, Ar, etc.; (ii) the exact distribution of different plasma during reaction is still unclear. Therefore, we can develop RF plasma technology in the following aspects: i) exploit more reaction sources; ii) investigate the distribution and strength of plasma atmosphere under different temperature and power to make the fabrication more

controllable.

(2) *Ultrafine metal nanoparticles/N-doped porous carbon hybrids as flexible and binder-free water splitting catalysts.* In the obtained electrode materials in chapter 5, the diameter of metal-based nanoparticles is as small as to 2 nm. Due to the in-situ reduction and the protection of carbon substrate, aggregation is completely avoided. In this experiment, we only preliminary studied the effect of introduction of N and other metal element. To further improve their catalytic activity, we try to search for the optimal ratio of two metal elements, the processing temperature, and the content of dipping solution. In addition, single-atom materials have emerged as a group of promising catalysts.^[124] Our results maybe offer a feasible choice to fabricate single-atom catalysts.

(3) *To find out the catalytic mechanism in molecular level via theoretical calculation and in-situ observation of catalysts in electrochemical test.* Theoretical calculation is a popular technique in material science, which can predict some physical and chemical properties of designed materials. The electronic structure, ion adsorption free energy and band structure of catalysts can be calculated, which is essential for us to understand the function of each part of catalysts and further optimize catalysts. In addition, in-situ techniques,^[125] such as in-situ Raman and in-situ XRD, are probably usefully skills to detect the intermediate product during the catalytic process. Combing with calculation results, experimental strategy can be designed and then verified.

References

- [1] Huabin Zhang, Jianwei Nai, Le Yu, et al., *Joule* **2017**, *1*, 77-107.
- [2] Ahmed-Shams Forruque Ahmed, Khan-Mohammad Masud Kamal Khan, Amanullah-Amanullah Maung Than Oo, et al., *International Journal of Mechanical and Materials Engineering* **2014**, *9*, 14.
- [3] Ibrahim Dincer, *Renewable and Sustainable Energy Reviews* **2000**, *4*, 157-175.
- [4] Jing Qi, Wei Zhang, Rui Cao, *Advanced Energy Materials* **2018**, *8*, 1701620.
- [5] Marco-Tulio F Rodrigues, Ganguli Babu, Hemtej Gullapalli, et al., *Nature Energy* **2017**, *2*, nenergy2017108.
- [6] Jan Winsberg, Tino Hagemann, Tobias Janoschka, et al., *Angewandte Chemie International Edition* **2016**, *56*, 686-711.
- [7] M. A. Pellow, C. J. M. Emmott, C. J. Barnhart, et al., *Energy & Environmental Science* **2015**, *8*, 1938-1952.
- [8] Yan Jiao, Yao Zheng, Mietek Jaroniec, et al., *Chemical Society Reviews* **2015**, *44*, 2060-2086.
- [9] Zheng Bo, Shun Mao, Zhao Jun Han, et al., *Chemical Society Reviews* **2015**, *44*, 2108-2121.
- [10] Dong Jin Ham, Jae Sung Lee, *Energies* **2009**, *2*, 873-899.
- [11] Nian-Tzu Suen, Sung-Fu Hung, Quan Quan, et al., *Chemical Society Reviews* **2017**, *46*, 337-365.
- [12] Charles C. L. McCrory, Suho Jung, Jonas C. Peters, et al., *Journal of the American Chemical Society* **2013**, *135*, 16977-16987.

-
- [13]Jiong Wang, Hua Zhang, Xin Wang, *Small Methods* **2017**, *1*, 1700118.
- [14]Weijia Zhou, Jin Jia, Jia Lu, et al., *Nano Energy* **2016**, *28*, 29-43.
- [15]Zhu Luo, Ran Miao, Tran Doan Huan, et al., *Advanced Energy Materials* **2016**, *6*, 1600528.
- [16]Jian Zhang, Shaohua Liu, Haiwei Liang, et al., *Advanced Materials* **2015**, *27*, 7426-7431.
- [17]Sergio Trasatti, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1972**, *39*, 163-184.
- [18]Daniel V. Esposito, Sean T. Hunt, Alan L. Stottlemeyer, et al., *Angewandte Chemie International Edition* **2010**, *49*, 9859-9862.
- [19]Shan Wang, Guang Yang, Shengchun Yang, *The Journal of Physical Chemistry C* **2015**, *119*, 27938-27945.
- [20]Niancai Cheng, Samantha Stambula, Da Wang, et al., *Nature Communications* **2016**, *7*, 13638.
- [21]Yu-Yun Chen, Yun Zhang, Xing Zhang, et al., *Advanced Materials* **2017**, *29*, 1703311.
- [22]Yi Shen, Yongfang Zhou, Duo Wang, et al., *Advanced Energy Materials* **2017**, 1701759.
- [23]James R. McKone, Bryce F. Sadtler, Caroline A. Werlang, et al., *ACS Catalysis* **2013**, *3*, 166-169.
- [24]Shiping Wang, Jing Wang, Minglei Zhu, et al., *Journal of the American Chemical Society* **2015**, *137*, 15753-15759.

-
- [25] Anne-Marie Alexander, Justin S. J. Hargreaves, *Chemical Society Reviews* **2010**, 39, 4388-4401.
- [26] Sengeni Anantharaj, Sivasankara Rao Ede, Kuppan Sakthikumar, et al., *ACS Catalysis* **2016**, 6, 8069-8097.
- [27] Xinhui Xia, Yongqi Zhang, Dongliang Chao, et al., *Nanoscale* **2014**, 6, 5008-5048.
- [28] Jayashree Swaminathan, Ravichandran Subbiah, Vengatesan Singaram, *ACS Catalysis* **2016**, 6, 2222-2229.
- [29] Xiaodong Yan, Lihong Tian, James Murowchick, et al., *Journal of Materials Chemistry A* **2016**, 4, 3683-3688.
- [30] Yu Hang Li, Peng Fei Liu, Lin Feng Pan, et al., *Nature Communications* **2015**, 6, 8064.
- [31] Adriano Ambrosi, Zdenek Sofer, Martin Pumera, *Chemical Communications* **2015**, 51, 8450-8453.
- [32] Yindong Qu, Henry Medina, Sheng-Wen Wang, et al., *Advanced Materials* **2016**, 28, 1602697
- [33] Bin Liu, Yu-Fei Zhao, Hui-Qing Peng, et al., *Advanced Materials* **2017**, 29, 1606521.
- [34] Jesse D. Benck, Thomas R. Hellstern, Jakob Kibsgaard, et al., *ACS Catalysis* **2014**, 4, 3957-3971.
- [35] Hong Li, Charlie Tsai, Ai Leen Koh, et al., *Nature materials* **2016**, 15, 48-53.
- [36] Yu Zhong, Xinhui Xia, Fan Shi, et al., *Advanced Science* **2016**, 3, 1500286.
- [37] Cheng Wan, Yagya N. Regmi, Brian M. Leonard, *Angewandte Chemie*

International Edition **2014**, *53*, 6407-6410.

[38]Teng Wang, Xiaojuan Wang, Yang Liu, et al., *Nano Energy* **2016**, *22*, 111-119.

[39]Wei-Fu Chen, Kotaro Sasaki, Chao Ma, et al., *Angewandte Chemie International Edition* **2012**, *51*, 6131-6135.

[40]S. Ted Oyama, *Journal Of Catalysis* **2003**, *216*, 343-352.

[41]Yanmei Shi, Bin Zhang, *Chemical Society Reviews* **2016**, *45*, 1529-1541.

[42]Jingqi Tian, Qian Liu, Abdullah M Asiri, et al., *Journal of the American Chemical Society* **2014**, *136*, 7587-7590.

[43]Jingjing Duan, Sheng Chen, Mietek Jaroniec, et al., *ACS Nano* **2015**, *9*, 931-940.

[44]Zhi Yang, Zhen Yao, Guifa Li, et al., *ACS Nano* **2012**, *6*, 205-211.

[45]Hengcong Tao, Chao Yan, Alex W. Robertson, et al., *Chemical Communications* **2017**, *53*, 873-876.

[46]Yoshikazu Ito, Weitao Cong, Takeshi Fujita, et al., *Angewandte Chemie International Edition* **2015**, *54*, 2131-2136.

[47]E. Fabbri, A. Habereeder, K. Waltar, et al., *Catalysis Science & Technology* **2014**, *4*, 3800-3821.

[48]Isabela C. Man, Hai-Yan Su, Federico Calle-Vallejo, et al., *ChemCatChem* **2011**, *3*, 1159-1165.

[49]Tobias Reier, Mehtap Oezaslan, Peter Strasser, *ACS Catalysis* **2012**, *2*, 1765-1772.

[50]Youngmin Lee, Jin Suntivich, Kevin J. May, et al., *The Journal of Physical Chemistry Letters* **2012**, *3*, 399-404.

[51]Min Pang, Chuang Li, Ling Ding, et al., *Industrial & Engineering Chemistry*

Research **2010**, *49*, 4169-4174.

[52]Jin Suntivich, Kevin J May, Hubert A Gasteiger, et al., *Science* **2011**, *334*, 1383-1385.

[53]Y Matsumoto, S Yamada, T Nishida, et al., *Journal of the Electrochemical Society* **1980**, *127*, 2360-2364.

[54]Justus Masa, Philipp Weide, Daniel Peeters, et al., *Advanced Energy Materials* **2016**, *6*, 1502313.

[55]Dawei Su, Shixue Dou, Guoxiu Wang, *Scientific reports* **2014**, *4*, 5767.

[56]Yang Liu, Jing Li, Feng Li, et al., *Journal of Materials Chemistry A* **2016**, *4*, 4472-4478.

[57]Zhao-Qing Liu, Hui Cheng, Nan Li, et al., *Advanced Materials* **2016**, *28*, 3777-3784.

[58]Rong Chen, Hsin-Yi Wang, Jianwei Miao, et al., *Nano Energy* **2015**, *11*, 333-340.

[59]Pengzuo Chen, Kun Xu, Zhiwei Fang, et al., *Angewandte Chemie International Edition* **2015**, *54*, 14710-14714.

[60]Jianmei Wang, Wenrong Yang, Jingquan Liu, *Journal of Materials Chemistry A* **2016**, *4*, 4686-4690.

[61]Shuo Dou, Li Tao, Jia Huo, et al., *Energy & Environmental Science* **2016**.

[62]Abdelhamid M. El-Sawy, Islam M. Mosa, Dong Su, et al., *Advanced Energy Materials* **2016**, *6*, 1501966.

[63]Xiaowen Yu, Miao Zhang, Ji Chen, et al., *Advanced Energy Materials* **2016**, *6*, 1501492.

-
- [64]Stephanie-Angelika Wohlgemuth, Robin Jeremy White, Marc-Georg Willinger, et al., *Green Chemistry* **2012**, *14*, 1515-1523.
- [65]Tian Yi Ma, Sheng Dai, Mietek Jaroniec, et al., *Angewandte Chemie International Edition* **2014**, *53*, 7281-7285.
- [66]Sheng Chen, Jingjing Duan, Mietek Jaroniec, et al., *Advanced Materials* **2014**, *26*, 2925-2930.
- [67]Yong Zhao, Ryuhei Nakamura, Kazuhide Kamiya, et al., *Nature Communications* **2013**, *4*, 2390.
- [68]Tatsuya Shinagawa, Angel T. Garcia-Esparza, Kazuhiro Takanabe, *Scientific reports* **2015**, *5*, 13801.
- [69]Rawat Rajdeep Singh, *Ieee Transactions On Plasma Science* **2013**, *41*, 701-715.
- [70]RS Rawat, in *Journal of Physics: Conference Series, Vol. 591*, IOP Publishing, **2015**, p. 012021.
- [71]Xinhui Xia, Jiangping Tu, Yongqi Zhang, et al., *RSC Advances* **2012**, *2*, 1835-1841.
- [72]Yongqi Zhang, Bo Ouyang, Jing Xu, et al., *Angewandte Chemie International Edition* **2016**, *55*, 8670-8674.
- [73]Yongqi Zhang, Bo Ouyang, Jing Xu, et al., *Advanced Energy Materials* **2016**, *6*, 1600221.
- [74]Jingguang G. Chen, *Chemical Reviews* **1996**, *96*, 1477-1498.
- [75]Yi Feng, Xin-Yao Yu, Ungyu Paik, *Chemical Communications* **2016**, *52*, 1633-1636.

-
- [76]Milan M. Jaksic, *International Journal of Hydrogen Energy* **2001**, 26, 559-578.
- [77]A Marlot, P Kern, D Landolt, *Electrochimica Acta* **2002**, 48, 29-36.
- [78]Renu Dhunna, Chhagan Lal, DK Avasthi, et al., *Vacuum* **2009**, 83, 1448-1453.
- [79]Bingfei Cao, Gabriel M. Veith, Joerg C. Neuefeind, et al., *Journal of the American Chemical Society* **2013**, 135, 19186-19192.
- [80]Kenichiro Hada, Masatoshi Nagai, Shinzo Omi, *The Journal of Physical Chemistry B* **2001**, 105, 4084-4093.
- [81]Liang Ma, Louisa Rui Lin Ting, Valerio Molinari, et al., *Journal of Materials Chemistry A* **2015**, 3, 8361-8368.
- [82]Duck Hyun Youn, Suenghoon Han, Jae Young Kim, et al., *ACS Nano* **2014**, 8, 5164-5173.
- [83]Menny Shalom, Debora Ressnig, Xiaofei Yang, et al., *Journal of Materials Chemistry A* **2015**, 3, 8171-8177.
- [84]C. Hu, C. C. Lai, Q. Tao, et al., *Chemical Communications* **2015**, 51, 6560-6563.
- [85]Yun-Pei Zhu, Yu-Ping Liu, Tie-Zhen Ren, et al., *Advanced Functional Materials* **2015**, 25, 7337-7347.
- [86]Fei-Xiang Ma, Hao Bin Wu, Bao Yu Xia, et al., *Angewandte Chemie International Edition* **2015**, 54, 15395-15399.
- [87]Xiaodong Yan, Lihong Tian, Min He, et al., *Nano letters* **2015**, 15, 6015-6021.
- [88]Tzu-Hsiang Lu, Chih-Jung Chen, Mrinmoyee Basu, et al., *Chemical Communications* **2015**, 51, 17012-17015.
- [89]Wentian Gu, Alexandre Magasinski, Bogdan Zdyrko, et al., *Advanced Energy*

Materials **2015**, *5*, 1401148.

[90] H.-J. Qiu, Yoshikazu Ito, Weitao Cong, et al., *Angewandte Chemie International Edition* **2015**, *54*, 14031-14035.

[91] Chaoyun Tang, Wei Wang, Aokui Sun, et al., *ACS Catalysis* **2015**, *5*, 6956-6963.

[92] Su-Moon Park, Jung-Suk Yoo, *Analytical Chemistry* **2003**, *75*, 455 A-461 A.

[93] K Suzuki, T Kaneko, H Yoshida, et al., *Journal of Alloys And Compounds* **1995**, *224*, 232-236.

[94] Chunshuang Yan, Gang Chen, Xin Zhou, et al., *Advanced Functional Materials* **2016**, *26*, 1428-1436.

[95] Jun Liu, Shasha Tang, Yakun Lu, et al., *Energy & Environmental Science* **2013**, *6*, 2691-2697.

[96] Jun Wang, Hai-xia Zhong, Zhong-li Wang, et al., *ACS Nano* **2016**, *10*, 2342-2348.

[97] Yang Yang, Huilong Fei, Gedeng Ruan, et al., *Advanced Materials* **2015**, *27*, 3175-3180.

[98] Siwen Li, Yongcheng Wang, Sijia Peng, et al., *Advanced Energy Materials* **2016**, *6*, 1501661.

[99] Yun-Pei Zhu, Yu-Ping Liu, Tie-Zhen Ren, et al., *Advanced Functional Materials* **2015**, *25*, 7337-7347.

[100] Liheng Wu, Qing Li, Cheng Hao Wu, et al., *Journal of the American Chemical Society* **2015**, *137*, 7071-7074.

[101] Xunyu Lu, Chuan Zhao, *Journal of Materials Chemistry A* **2013**, *1*, 12053-12059.

-
- [102] Kun Xu, Pengzuo Chen, Xiuling Li, et al., *Journal of the American Chemical Society* **2015**, *137*, 4119-4125.
- [103] Xingyue Li, Zhiguo Niu, Jing Jiang, et al., *Journal of Materials Chemistry A* **2016**, *4*, 3204-3209.
- [104] Qiting Zhang, Yuhang Wang, Yongcheng Wang, et al., *Journal of Materials Chemistry A* **2016**, *4*, 5713-5718.
- [105] Jun Li, Yongcheng Wang, Tong Zhou, et al., *Journal of the American Chemical Society* **2015**, *137*, 14305-14312.
- [106] Chun Tang, Ningyan Cheng, Zonghua Pu, et al., *Angewandte Chemie International Edition* **2015**, *54*, 9351-9355.
- [107] M. Ledendecker, S. K. Calderon, C. Papp, et al., *Angewandte Chemie International Edition* **2015**, *54*, 12361-12365.
- [108] Lucas-Alexandre Stern, Ligang Feng, Fang Song, et al., *Energy & Environmental Science* **2015**, *8*, 2347-2351.
- [109] Yongqi Zhang, Bo Ouyang, Kun Xu, et al., *Small* **2018**, *14*, 1800340.
- [110] Jian Zhang, Tao Wang, Pan Liu, et al., *Nature Communications* **2017**, *8*, 15437.
- [111] Ming Gong, Wu Zhou, Mon-Che Tsai, et al., *Nature Communications* **2014**, *5*, 4695.
- [112] P. Reyes, I. Concha, G. Pecchi, et al., *Journal of Molecular Catalysis A: Chemical* **1998**, *129*, 269-278.
- [113] Yongqi Zhang, Xinhui Xia, Xun Cao, et al., *Advanced Energy Materials* **2017**, *7*, 1700220.

-
- [114] Mary W. Louie, Alexis T. Bell, *Journal of the American Chemical Society* **2013**, *135*, 12329-12337.
- [115] Zhengping Zhang, Yeshe Qin, Meiling Dou, et al., *Nano Energy* **2016**, *30*, 426-433.
- [116] Na Ma, Yi Jia, Xianfeng Yang, et al., *Journal of Materials Chemistry A* **2016**, *4*, 6376-6384.
- [117] Muhammad-Sadeeq Balogun, Weitao Qiu, Hao Yang, et al., *Energy & Environmental Science* **2016**, *9*, 3411-3416.
- [118] Rui Xu, Rui Wu, Yanmei Shi, et al., *Nano Energy* **2016**, *24*, 103-110.
- [119] Ji-Sen Li, Yu Wang, Chun-Hui Liu, et al., *Nature Communications* **2016**, *7*, 11204.
- [120] Xiaoshuang Chen, Guangbo Liu, Wei Zheng, et al., *Advanced Functional Materials* **2016**, *26*, 8537-8544.
- [121] Huanlei Lin, Zhangping Shi, Sina He, et al., *Chemical Science* **2016**, *7*, 3399-3405.
- [122] Lena Trotochaud, Samantha L. Young, James K. Ranney, et al., *Journal of the American Chemical Society* **2014**, *136*, 6744-6753.
- [123] Xiaodan Jia, Yufei Zhao, Guangbo Chen, et al., *Advanced Energy Materials* **2016**, *6*, 1502585.
- [124] Chongyi Ling, Li Shi, Yixin Ouyang, et al., *Nano letters* **2017**, *17*, 5133-5139.
- [125] Yilin Deng, Albertus D Handoko, Yonghua Du, et al., *ACS Catalysis* **2016**, *6*, 2473-2481.