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**MODULATING ELECTRONIC AND GEOMETRIC
STRUCTURE OF TRANSITION METAL COMPOUNDS FOR
EFFICIENT WATER SPLITTING**

TANG SHASHA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

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EFFICIENT WATER SPLITTING**

TANG SHASHA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as S. Tang, X. Wang, Y. Zhang, M. Court é H. J. Fan, and D. Fichou. Combining Co_3S_4 and $\text{Ni:Co}_3\text{S}_4$ nanowires as efficient catalysts for overall water splitting: an experimental and theoretical study. *Nanoscale* **11**, 2202-2210 (2019). DOI: 10.1039/c8nr07787h.

The contributions of the co-authors are as follows:

- I designed the study, conducted most of the laboratory work, and analyzed the data.
- I wrote the manuscript.
- All the co-authors had checked the manuscript before submitting.
- Dr Wang Xing provided the calculation of free energies.
- Dr Zhang Yongqi assisted in the preparation and analysis of electrochemical measurements.
- Dr Marc Court é helped to perform the X-ray diffraction and ICP-OES characterization.
- Prof Fan gave guidance in the discussion of the crystal growth process and other supplementary information.
- Prof Fichou provided the initial project direction and built a nice experimental environment.

Chapter 3 is published as S. Tang, M. Court é J. Peng, D. Fichou, Oxygen-deficient WO_3 via high-temperature two-step annealing for enhanced and highly stable water splitting. *ChemComm* **55**, 7958-7961 (2019). DOI: 10.1039/C9CC03621K.

The contributions of the co-authors are as follows:

- I designed the study, carried out most of the laboratory work, and analyzed the data.
- I prepared the manuscript drafts.

- All the co-authors had checked the manuscript before submitting.
- Dr Marc Court éhelped to perform the of X-ray diffraction measurements.
- Dr Peng Jingjing assisted in the collection of XPS results.
- Prof Fichou provided the initial project direction and built a nice experimental environment.

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Abstract

Traditional fossil fuels, such as coal, oil, and natural gas, represent more than 85% of the global energy consumption. The excessive use of these traditional fossil fuels has brought environmental problems, such as air pollution and greenhouse effect. Hence, the search of sustainable and renewable energy is of significant importance. In view of the inexhaustible supply of water, hydrogen generation by water electrolysis is a promising strategy to provide sustainable energy source. One of the important factors that constrains the mass production of water electrolysis is lack of efficient and cost-effective catalysts. Thus, developing high efficiency, stable and low cost catalysts is highly desirable for the commercial H₂ production from electrochemical/photoelectrochemical water splitting.

In order to minimize the cost, non-noble metal based materials are substituting the costly and scarce noble metal materials. In this Thesis, we have investigated different types of transition metal based catalysts for water electrolysis/photoelectrolysis. The synthesis techniques, materials characterizations, and electrochemical/photoelectrochemical performance evaluation of the catalysts are presented in details. Four different catalysts are studied, which are (i) Co₃S₄ and Ni:Co₃S₄ nanowires, (ii) oxygen-deficient WO₃ microplates, (iii) CoMo₂S₄ cross-linked porous nanoflakes, and (iv) hierarchical Cu(OH)₂@Co(OH)₂ nanotrees.

We study the above catalysts from different aspects, from materials design, nanostructure engineering, to theoretic calculation. First, we start with transition metal oxide (Co₃O₄) nanowires and convert to Co₃S₄ for bifunctional electrocatalytic water splitting. Then we doped the nanowires with Ni elements to obtain Ni:Co₃S₄. In addition to systematic electrochemical characterization, DFT calculation is applied to determine the Gibbs free energy (ΔG) of the intermediates. It is found that the sulfur element reduces the ΔG of the intermediates and results in lower theoretic overpotential, leading to better HER and OER electrocatalytic performance

of the sulfides as compared to the oxides. Additionally, doping Ni also improves the HER performance because of a better intrinsic electrocatalytic activity of Ni as compared to Co.

Secondly, the oxygen-deficient WO_3 plates are synthesized by a combining technique of hydrothermal treatment and two-step annealing treatment. The commercial tungsten foil acts as the starting material and converts to normal WO_3 plates following a hydrothermal and a traditional annealing process. In order to increase the oxygen defects, the above WO_3 plates are twice annealed at higher temperature. Oxygen deficiency in WO_3 increases the donor density, leading to better charge carrier generation and separation, achieving enhanced the photoelectrochemical performance, such as higher photocurrent density and super stability.

Furthermore, the CoMoO_6 and CoMo_2S_4 cross-linked porous nanoflakes are investigated as bifunctional electrocatalysts for overall water electrolysis. The CoMoO_6 nanoflakes are synthesized and considered as the starting material. Subsequently, the CoMoO_6 sample undergoes an ion exchange reaction in additional hydrothermal process to obtain CoMo_2S_4 . The CoMo_2S_4 electrode shows a low OER/HER overpotential than that of CoMoO_6 electrode. The two-electrode electrolyzer cell ($\text{CoMo}_2\text{S}_4//\text{CoMo}_2\text{S}_4$) exhibits efficient overall water electrocatalytic ability and stability.

In addition, we present the hierarchical hybrid $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees as efficient OER electrocatalyst. It is found that forming such core-branch hierarchical nanostructures out of both catalytic active materials is an effective strategy to increase the catalytic active sites, reaction kinetics, and charge transport. Specifically, leaves-like ultrathin $\text{Co}(\text{OH})_2$ nanoflakes are grown on the branch-like $\text{Cu}(\text{OH})_2$ nanowires *via* an combined synthesis of an anodization process and a electrodeposition process. This hierarchical $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotree electrode shows a low OER overpotential and high stability with negligible degradation, taking advantages from the hierarchical hybrid nanotree structure.

Therefore, our material and nanostructure design are effective in improving the catalytic capability of the catalysts. The well-separated hierarchical nanostructure promotes the reaction kinetics and charge transport, facilitates the contact of solid-electrolyte interface and the release of gaseous product. In addition, these catalyst materials are directly grown on conductive substrate support, such as Ni foam, W foil, and Cu foil. This not only enhances the contact surface areas (thus more active sites), but also eliminates the usage of binders. The research in this Thesis provides new possibility of materials design towards low-cost and efficient water electrolysis/photoelectrocatalysis.

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2. **S. Tang**, X. Wang, Y. Zhang, M. Court H. J. Fan, and D. Fichou. Combining Co₃S₄ and Ni:Co₃S₄ nanowires as efficient catalysts for overall water splitting: an experimental and theoretical study. *Nanoscale*. **2019**, 11, 2202–2210.
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Chapter 1 Introduction

1.1 Background

Historically, traditional fossil fuels served as a main and stable energy source to meet society's ever-growing energy demands for a long time. However, due to the rapid development of global human civilization, the ever-growing energy demands become one of the biggest issues for our society.¹ Based on International Energy Association's 2017 statistics, traditional fossil fuels represent almost 85% of the global energy consumption.² The superfluous use of traditional fossil fuels is considered to cause aggravating greenhouse effects and environmental deterioration. The world energy-related carbon dioxide (CO₂) emissions maintained flat from the year 2014 to 2016, and rose again by 1.6% in 2017, indicating the severe situation of global energy crisis.³ More importantly, energy-related air pollution causes numberless deaths each year.

To meet the fast-growing energy demand and alleviate severe environmental crisis, it is in pressing need to fasten the development of effective technologies to produce both clean and sustainable energy spanning from solar to hydro energies.^{4, 5} Renewable energies can greatly enhance the diversity of energy supply, and also reduce global environmental impacts, which is beneficial to the security of long-term sustainable energy supply.⁶

Hydrogen (H₂) is promising as a sustainable energy source of the next generation with zero carbon emission of the combustion products.⁷ In addition, H₂ is the smallest molecule, which has a high energy density, low weight, and high abundance on earth.⁸ Nowadays, gaseous H₂ can be produced by different approaches, such as steam reforming method, biological production, electrochemical water splitting and photoelectrochemical water splitting.^{5, 9, 10}

1.2 Current methods for H₂ production

1.2.1 Thermochemical H₂ production

In the process of thermochemical H₂ production, heat and catalysts are utilized to promote chemical reactions in order to transform raw materials (for example, methanol, natural gas, and renewable sources) into H₂.¹¹ There are different thermochemical methods have been reported for H₂ generation, such as gasification and pyrolysis, partial oxidation reforming, and so on.¹¹

Currently, as the most widely used thermochemical H₂ production method, steam reforming *via* natural gas produces 50% of global gaseous H₂.¹² As shown in Figure 1.1, steam reforming method contains three main steps. In the first step, with the help of catalysts, raw materials (such as methane, methanol, ethanol, or natural gas) react with steam (H₂O) and generate a mixture of H₂ and other gases (such as CO, CO₂, or C₂H₄) under high temperature (673-1273 K).^{11, 13} This conversion of raw materials to H₂ is called the steam reforming step. Then, the product CO from above step, reacts with steam to produce additional H₂ and CO₂, which is called the water-gas shift reaction step. This step occurs at lower temperature (473-573 K). Due to the poisoning of noble-metal catalysts by CO, it is better to conduct the reaction in excess steam in order to cut down the generation of CO, and thus promoting the water-gas shift reaction.¹²

Figure 1.1 Scheme of the membrane-integrated methane steam reforming process.¹⁴

1.2.2 Photobiological H₂ production

Photosynthetic microorganisms (such as cyanobacteria and green algae) extract electrons from water/organic acids, and combine electron and protons to produce H₂ gas under light illumination (Figure 1.2) in the process of photobiological H₂ production.^{12, 15-17} In photobiological H₂ production, solar light acts as the energy source. As shown in Figure 1.3, solar light energy is absorbed by pigment molecules of photosynthetic microorganisms and then transferred to reaction centers of two multi-membrane protein complexes called Photosystem I (PSI) and Photosystem II (PSII).^{15, 16} Here, together with the simultaneous generation of oxidants and reductants, charge separation takes place in PSI and PSII. The strong oxidant produced by PSII can extract electrons from water with the release of oxygen and protons by-products. These electrons combine with some membrane-bound and soluble carriers to reduce PSI generated oxidant. At the same time, PSI produces reductants and eventually provides electrons to obtain reduced ferredoxin/ferredoxin-NADP oxidoreductase (denoted as FD/FNR). In the end, protons are combined with electrons and converted into H₂ gas through above reduced FD/FNR.¹⁶ The wide application of photobiological hydrogen production is hindered by the limited photosynthetic efficiency and hydrogenase/nitrogenase catalytic abilities.

Figure 1.2 Scheme of photobiological H₂ production and its application in a H₂ fuel cell.¹⁶

Figure 1.3 Scheme of photobiological H_2 production pathway in green algae (using FeFe-hydrogenase) and cyanobacteria (using NiFe-hydrogenase). PQ, FD, and FNR represent plastoquinone, ferredoxin, and ferredoxin-NADP oxidoreductase, respectively.¹⁶

1.2.3 Electrochemical H_2 production

In comparison with above method, H_2 production via the electrochemical water splitting supplied by fuel cells is proposed to be a more sustainable choice. Furthermore, H_2O is both the raw material and the only product.¹⁸ Water splitting is a strong uphill reaction with a theoretic decomposition voltage of 1.23 V. In the case of standard conditions (1 atm and 298 K), the increase of Gibbs free energy ($\Delta G = nFE^\circ$) in this uphill reaction is 237.1 kJ mol⁻¹, where E° is the theoretical decomposition voltage (1.23 V), n is the transferred electrons number ($n=2$), and F is the Faraday constant (96485 C mol⁻¹). In addition, the transportation of electron at the electrode/electrolyte interface leads to energy loss, and thus results in the sluggish kinetics of water splitting process. It requires a working voltage of 1.7–2.4 V to complete water decomposition in practice, which is significantly greater than the theoretical value, which hinders the H_2 production on a large scale.

In order to complete the electrochemical water splitting, there are several essential components, such as cathode, anode, and electrolyte (Figure 1.4). In the cathode, there is a hydrogen evolution reaction (denoted as HER). While in the anode, it is oxygen evolution reaction (denoted as OER). Those reactions require efficient catalysts to motivate sluggish kinetic processes and enhance catalytic efficiency. It is known that the most efficient electrocatalysts are platinum-based compounds and iridium/ruthenium oxide ($\text{IrO}_2/\text{RuO}_2$), respectively.^{7, 10} Nevertheless, the high cost of rare precious metals greatly impede the widespread practical application of water splitting.⁹ Hence, it is in urgent need to find superior catalytic ability and cost-effective catalysts for water splitting.

Figure 1.4 Diagram of the basic components of electrochemical water splitting.¹⁹

1.2.4 Photochemical and photoelectrochemical H_2 production

Water splitting under light illumination is an excellent energy conversion strategy to alleviate the energy crisis in a sustainable way, which owes to the efficient utilization of the inexhaustible water and solar energy as starting material and energy.²⁰⁻²³ In the early 1970s,

Honda and Fujishima investigated n-type semiconductor TiO_2 as the photocatalyst to splitting water which opens an avenue in the request for photo-assisted water splitting using appropriate semiconductors.^{24, 25} Figure 1.5 shows the schematic diagrams of photochemical and photoelectrochemical water splitting processes. It is highly visible that solar light and semiconductor photocatalysts are used to trigger the hydrogen/oxygen evolution reactions. The detailed mechanism and working principles will be demonstrated in Chapter 1.4.

Figure 1.5 (a) Schematic illustration of photochemical water splitting with semiconductor photocatalysts.²⁶ (b) Schematic diagram of basic components of photoelectrochemical water splitting.²⁷

1.3 Recent advances in electrochemical water splitting

1.3.1 Working principles

The overall reaction of electrochemical water splitting can be expressed as follows.

More precisely, there are reduction reactions that hydrogen cations combine electrons to generate H_2 occurs, which is the HER process and can be demonstrated as equation 1.2 and 1.3.²⁷

In acidic electrolytes, HER has two processes occurring on the surface of an electrode (Figure 1.6).^{28, 29} The first one is the discharge reaction (noted as Volmer reaction, which is in blue in Figure 1.6) (equation 1.4). In this process, an empty active site (*) is combining a proton and an electron to become an absorbed hydrogen atom (*H_(a)). Later on, the generation of H₂ can take place either by Heyrovsky reaction (equation 1.5) or by Tafel reaction (equation 1.6). In Heyrovsky reaction, a second proton together with another electron is coupled to the *H_(a) obtained from the Volmer reaction, thus leads to the formation of H₂ (in purple in Figure 1.6). As shown in red arrows in Figure 1.6, two *H_(a) are coupled to generate H₂ at the surface of electrode in the Tafel reaction.^{30, 31} In neutral and alkaline electrolytes, the proton source is changed from H⁺ to H₂O molecule due to the high pH value of electrolytes.

According to metal-hydrogen (M-H) binding, the Gibbs free energy of hydrogen adsorption (ΔG_{H}^*) is usually regarded as an effective parameter evaluating the HER intrinsic electrochemical ability of metal materials.³² The plot of ΔG_{H}^* against exchange current density has a volcano shape (Figure 1.7). Generally, a strong M-H bond can accelerate the combination among empty active sites, protons, and electrons to yield H_(a) in the Volmer reaction. Whereas a weaker M-H bond promotes the desorption of H_(a) into H₂ gas in the Heyrovsky/Tafel reaction. Then, the catalysts have a M-H bond around zero ΔG_{H}^* , exhibiting better HER activity. In Figure 1.7, noble metal Pt locates at the summit of the volcano, and its ΔG_{H}^* is close to zero, indicating an appropriate M-H bond and highest activity. On the left side of the volcano curve, the M-H bond is very strong, means that metals have strong binding with H atoms, which blocks the H_(a) to generate H₂. On the right side, the M-H bond is too weak to maintain the

stabilization of the intermediate state, and thus prevents the occurrence of any reaction. Quantum chemical calculations showed that ΔG_{H^*} can be applied in both pure metals and transition metal compounds to analyze the HER activity. ΔG_{H^*} can be calculated by equation 1.7.

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S \quad (1.7)$$

Where ΔE_{H^*} is the hydrogen chemisorption energy, ΔZPE is the difference in zero-point energy (ZPE) between the adsorbed and the gas phase, T is thermodynamic temperature, and ΔS is the entropy change of H^* . The ZPE of H atom in different state (gas and adsorbed state) are very similar, thus ΔZPE is close to zero. The entropy of H in adsorbed state is negligible, and $T\Delta S$ is calculated based on the H_2 entropy in the gas phase. $T\Delta S$ is determined to be -0.21 eV.

Figure 1.6 The mechanism of HER on the surface of an electrode in acidic solutions.²⁸

Figure 1.7 The volcano curve of experimentally measured exchange current density as a function of the DFT-calculated ΔG_{H^*} . The solid lines are derived from the simple kinetic model proposed by Nørskov et al.²⁸

In the OER process, there is generation of O_2 (oxidation reactions) at the anode, and electrons are transferred to the cathode. The OER process can be summarized by equation 1.8 and 1.9.

In comparison with HER, a widely accepted OER mechanism in acidic electrolytes contains below four reaction steps, every step involves an electron transfers to electrode and a proton transfers to water (equation 1.10 to 1.13, see Figure 1.8).³⁰ The intermediates of OER process are HO^* , O^* , and HOO^* . Usually, the four-step OER process with sluggish reaction kinetics and large overpotential is the rate-determining reaction in overall water splitting. The active site at the electrode surface is denoted as $*$. In standard conditions ($T = 298.15 \text{ K}$, $P = 1 \text{ bar}$, and $pH = 0$), U is the potential against normal hydrogen electrode (NHE), and it is equal to 0. Furthermore, density functional theory (DFT) calculations are used for calculating the free energy change of intermediates along the OER processes (ΔG_n , $n = 1-4$), where ΔG_n^0 is the

ΔG_n at the relative reaction when $U = 0$.³³ In addition, e is the electron charge ($1.602176634 \times 10^{-19}$ C), k_B is the Boltzmann constant (1.380649×10^{-23} J/K), α_{H^+} represents the activity of the protons, Then, eU represents the shift in electron energy when applying a bias of U , and $k_B T \ln \alpha_{H^+}$ represents the free energy changes of the proton relative to the NHE electrode at nonzero pH.

The energy of isolated molecules (H_2 , H_2O , O_2) is computed in an orthorhombic cell.

Based on the equation 1.14, the Gibbs free energy for whole OER process (G^{OER}) is the maximum Gibbs free energy among the four ΔG_n^0 . In addition, the corresponding step with maximum Gibbs free energy is the rate-determining step (RDS) of OER process. Thus, the theoretical overpotentials (η) for OER can be calculated using the equation 1.15.

$$G^{OER} = \max [\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0] \quad (1.14)$$

$$\eta^{OER} = (G^{OER}/e) - 1.23 \text{ V} \quad (1.15)$$

Figure 1.8 Standard OER free energy diagram of the ideal catalyst.³³

In general, the subtraction of operating potential and theoretical potential (1.23 V) is defined as OER overpotential (η). At the same time, the absolute value of HER operating potential is defined as HER overpotential. Importantly, onset potential is defined as the lowest of OER/HER potential, where the start point for the generation of O₂/H₂ gas. The electrocatalytic ability of catalysts is often assessed by a designated current density at a designated overpotential. For example, η at the current density of 10 mA cm⁻² (η_{10}) is one essential parameter. Lower overpotential means the faster generation of products, and the better electrocatalytic ability.

To further dwell on the water electrolysis reaction kinetics, Tafel plots are fitted by Tafel equation $\eta = a + b \cdot \log(j)$, where η , a , b , and j are the iR-compensated overpotential, Tafel constant, Tafel slope, and current density, respectively. The RDS of water reduction process can be recognized by the Tafel analysis. If the b is around 30, 40, or 120 mV dec⁻¹, revealing that the RDS is Tafel, Heyrovsky, or Volmer reaction, respectively.^{34, 35} In the ideal situation, the Tafel slope is determined by the intrinsic activity of the catalysts. However, some other reasons may also affect the Tafel slope. For instance, Pt electrode has a low Tafel slope of 30 mV dec⁻¹, indicating that the Tafel reaction is the RDS. When the applied voltage is increased, the surface of Pt electrode will be covered by almost a saturated adsorption of hydrogen atoms, leading to the expedited atom–atom recombination, and thus resulting in a higher Tafel slope and a different RDS.³⁶

1.3.2 H₂ evolution electrocatalysts

As the most effective catalyst, platinum-based materials have been frequently investigated in the water splitting for HER, but its rarity and high cost makes it questionable for large-scale H₂ production.^{8, 9} In order to have a lower platinum loading without compromising efficiency,

the investigation of high surface atomic ratio Pt catalysts is promising to promote the application of noble metal based materials.

Chen *et al.* synthesized nearly monolayer platinum grown on tungsten monocarbide (WC) support for H₂ generation to investigate the limitation of mass loading without compromising the catalytic efficiency.⁹ Owing to similar electronic structures, low-cost WC has “platinum-like” catalytic properties with great adhesion between the WC and the platinum. WC acts as the substrate to support monolayer platinum, resulting in a lower platinum loading catalyst with very high HER activity, which accompanies with the huge reduction in cost of whole electrode. In addition, utilizing chemical reduction method, carbon-supported electroactive Pt and Pd nanoparticles are synthesized by Grigoriev *et al.*¹⁰ This catalyst has a much lower metal loading of 0.7 mg cm⁻², while metal-black usually has a higher metal loading of 2 mg cm⁻². Catalytic properties of carbon-supported Pd catalysts are slightly lower than those obtained with carbon-supported Pt catalysts, which means that Pd is a promising candidate as the HER catalysts in electrochemical water splitting. Furthermore, carbon-supported noble-metal catalysts fabricated in this method, have a much lower cost compared with bulk noble-metal catalysts.

In the past decades, the investigation of metal alloys based on the volcano plot has gained tremendous attention as the most convenient and straightforward approach to produce highly catalytic HER catalysts.^{8, 37-42} For example, Ni-Mo alloy are considered as the highest activity non-noble metal alloy catalyst for HER.^{43, 44} However, Ni-Mo alloys show poor stability in HER process, especially under strong pH condition. Introducing the third component (metal or non-metal elements) is a feasible method to enhance the catalytic performance. Zhang *et al.* prepared porous nickel molybdenum nitride by N₂ plasma, which combines weak M-H bond (Ni) with a strong bond (Mo) to obtain a synergistic effect for HER.⁴⁵

In addition, materials on the basis of earth-abundant transition metals have so far been developed as promising HER catalysts. Especially, either totally or partially replacing the O

atoms by other non-metal atoms (N, C, S, B, or P) is an efficient method to enhance the electrocatalytic capability. Compared with transition metal oxides, these composites are reported to exhibit better conductivity and higher chemical/physical stability.^{38, 41, 42} Their electronic structures are controlled by the introduction of non-metal atoms, accompanying with the improvement of catalytic activity. Xu *et al.* reported the effects of oxygen and copper co-doping in CoP nanowires (O,Cu-CoP nanowires).⁴⁶ This combination of metal and non-metal co-doping dramatically promotes the catalytic activity of pure CoP nanowires, opening a new avenue to improve HER catalysts.

Carbonaceous materials (graphene, carbon nanotube and g-C₃N₄) are important metal-free catalysts for HER application. Both experimental and theoretical studies have proved that chemical doping with N, S, B, or P can effectively improve the HER catalytic ability of carbon materials.^{47, 48} Shinde *et al.* introduced a small amount of phosphorus in the porous graphene sheets, and then integrated with g-C₃N₄.⁴⁷ This phosphorus doped composites exhibit a high overpotential of 340 mV, a Tafel slope of 90 mV dec⁻¹, and high long-term stability, offering competitiveness to those reported metal electrocatalysts. Ito *et al.* introduced a small amount of nitrogen and sulfur in porous graphene, which proves that the doping of nitrogen and sulfur shows a synergistic effect and improves the HER performance.⁴⁸ However, compared with high catalytic activity metal based catalysts, metal-free catalysts still need further improvement.

1.3.3 O₂ evolution electrocatalysts

The most viable and efficient electrocatalysts for water oxidation are noble metal materials, such as IrO₂ and RuO₂.^{49, 50} Nevertheless, the scarcity and high cost of these noble metals remarkably hinder their practical applications. Preparing nanostructured material and using low-cost conductive support materials are useful approaches to reduce noble metal loading and improve catalytically active surface area.⁹

To date, non-noble metal-based materials are thoroughly studied as substituted electrocatalysts for OER application. Single metal-based materials with different nanostructures attract tremendous attention as efficient OER catalysts by experimentally and theoretically investigation.^{30, 51} For example, Li *et al.* investigated the CoS nanoflakes *via* a template-directed technique. The two-electrode electrolyzer of CoS nanoflakes shows a voltage of 1.72 V to deliver 10 mA cm⁻².⁵² Jin *et al.* presented porous MoO₂ nanosheets having bifunctional catalytic ability for overall water electrolysis, requiring a voltage of 1.53 V to deliver 10 mA cm⁻².⁵³

In addition, researchers also found that the multi metal-based materials show superior electrocatalytic properties as OER catalysts due to the electronic structure modulation and synergistic effect. Kuznetsov *et al.* and Tong *et al.* fabricated bimetallic Co-Mo alkoxide and oxygen-deficient Co₃O₄ quantum dots as efficient electrocatalysts to enhance the oxygen evolution electrolysis, respectively.^{54, 55} Cao *et al.* reported the investigation of Cu-Ni sulfide nanowires for improving the water oxidation efficiency.⁵⁶ Chen *et al.* fabricated Cu-Co(OH)₂ nanosheets having superior electrocatalytic activity with an OER overpotential of 300 mV at 10 mA cm⁻².⁵⁷ Nguyen *et al.* described that the direct growth of binary FeCoOOH nanosheet structure leads to a high electrical conductivity, and thus resulting in the high bifunctional electrocatalytic ability for overall water splitting.⁵⁸

In the view of electronic structure regulation, doping other metal atoms (such as Ni, Mn, and Fe) in the catalysts can further enhance the OER performance. For example, Wu *et al.* synthesized Ni_xCo_{3-x}O₄ on Ti foils, exhibiting improved catalytic performance.⁵⁹ Furthermore, replacing O by non-metal atoms like N, S, C, and P is another meaningful approach to adjust the electronic structures and enhance the catalytic performance of catalysts.^{46, 60, 61} Moreover, it has been proposed that the active materials of transition metal oxide electrocatalysts are the

corresponding hydroxides/oxyhydroxides.^{57, 62, 63} Zhang *et al.* prepared CNTs@FeOOH showing an outstanding OER performance of an overpotential of 250 mV at 10 mA cm⁻².⁶⁴

Besides, the development of non-metal carbon-based materials open a new avenue towards the OER application. For example, N-doped graphene and g-C₃N₄ hybrid composites show high OER electrocatalytic activity because of the highly active centers, rich porosity and conductive networks.⁶⁵

1.4 Recent advances in photoelectrochemical water splitting

1.4.1 Working principles

As indicated in Figure 1.5b, the photoelectrochemical water splitting process has three main steps. Solar light and semiconductor photocatalysts are used to trigger the photolysis process of water. First, the semiconductor absorbs the photons those with higher energy exceeding the bandgap under solar light illumination, and then charge carriers (e⁻ and h⁺) are excited and generated in the semiconductor. Subsequently, those photo-induced charge carriers are separated and diffused to the surface active sites. Finally, photoexcited electrons diffuse to the surface of cathode and lead to the generation of H₂, indicating the reduction reaction of water. Meanwhile, photoexcited holes diffuse to the surface of anode to produce O₂, which is the oxidation reaction process of water. More importantly, accompanying with the charge separation and diffusion, recombination of the charge carrier occurs concurrently. Hence, the lifetime of charge carriers depends on the charge recombination. In order to obtain successful photolysis of water, it is important to modify the surface with co-catalysts and buffer layers and promote the charge separation and diffusion.

In order to realize the photolysis reduction to obtain H₂, the bottom of photocatalysts conduction band should be more negative than the H₂O reduction potential, while the

maximum of valence band ought to be more positive than H₂O oxidation potential to realize the generation of O₂. In the meantime, the bandgap of photocatalysts should be as narrow as possible to trigger the visible light absorption, demonstrating that the theoretical bandgap of photocatalysts is around 1.23 eV. Nevertheless, it is quite difficult for a semiconductor to meet the above standards. Then, there are three types of PEC water splitting systems, which are all based on the different roles of semiconductor photocatalysts (Figure 1.9).

Taking into account the mechanism of PEC water splitting process and the requirements of semiconductor photocatalysts, there are two main factors to achieve PEC water splitting with high efficiency. First, the semiconductor photocatalysts should have appropriate bandgap to absorb enough light and facilitate the water oxidation/reduction. Second, the photoexcited electrons and holes can separate, migrate, and then combine with the active sites rapidly, instead of charge carriers' recombination. Importantly, adding co-catalysts to the semiconductor can trigger the water photocatalysis through multiphoton processes.

Figure 1.9 Energy diagrams of three different configurations for PEC water splitting.²²

1.4.2 Photoanode for O₂ evolution

Titanium dioxide is earth-abundant and environment-friendly, which has been investigated as the catalysts for photocatalytic and photovoltaic application for a long time (as shown in

Figure 1.10).⁶⁶ In the early 1970s, Honda and Fujishima investigated n-type rutile TiO₂ as the photoanode and Pt as the counter electrode to decompose water into O₂ and H₂ (similar as the configuration in Figure 1.9a).^{24, 25} However, TiO₂ contains a large bandgap of 3.0-3.2 eV that hampers the absorption of visible light, together with high charge carrier recombination rate, which is challenged on the large-scale application of PEC water splitting. Since then, extensive reports have been published on TiO₂ with improved photocatalytic performance. Wang *et al.* has illustrated the preparation of hydrogen-treated TiO₂ nanowires as efficient photocatalysts for PEC water catalysis.⁶⁷ The hydrogen-treated TiO₂ sample shows a photocurrent density of 1.97 mA cm⁻² (at -0.6 V vs. Ag/AgCl), owing to the improved charge separation/migration *via* the hydrogen treatment. Han *et al.* prepared α -Fe₂O₃/TiO₂ 3D hierarchical nanostructures to improve the performance, such as the light absorption and photocatalytic activity.⁶⁸ Under the adjustment of Fe precursor and specific parameters, α -Fe₂O₃ nanoflakes or nanorods are perpendicularly deposited on the surface of TiO₂. These 3D hierarchical composites provide a twofold increase in the photocatalytic activity than that of bare TiO₂.

Figure 1.10 Band positions of several semiconductors in acidic electrolyte (pH 1).⁵

ZnO is another typical n-type semiconductor, having a bandgap around 3.2 eV with a suitable band energy structure, which has been intensively investigated as promising photocatalytic and photovoltaic catalyst.⁶⁹⁻⁷¹ Fichou *et al.* proposed the idea that doping ZnO by 3d cations (Co^{3+} , Mn^{2+} , Fe^{3+} , and Ni^{2+}) substantially extends its photoresponse into the visible range, thus resulting in improved solar light conversion into electricity.^{69, 71} Furthermore, ZnO with different nanostructures, especially ZnO nanowires, have large surface area and efficient transport pathway for charge carriers, which are investigated as cost-effective and efficient photoanode materials for water oxidation.

Being an n-type semiconductor, bismuth vanadate (BiVO_4) has a suitable bandgap (2.4 eV), and the maximum of valence band is more positive than the H_2O oxidation potential. Zhao *et al.* focused on the influence of W doping in BiVO_4 thin films as the photoanode for water

oxidation.⁷² Here, W doping improves the charge transportation by reducing the charge transfer resistance, and facilitates the charge separation by forming V atoms as reactive sites. Afterward, this group also reported on the influence of W-Ti co-doping in BiVO₄ photoanode for PEC water oxidation.⁷³ They discovered that W-Ti co-doping reduces the static dielectric constant of BiVO₄, and leads to a higher hole mobility and dramatically high efficiency in charge separation (79% at 1.23 V_{RHE}). Additionally, this co-doping introduces more active sites due to the presence of Ti. Creating a p-n junction is another strategy to enlarge the solar light absorption and promote the photocatalytic performance. Ye *et al.* combined BiVO₄ with a p-type semiconductor BiOI, the electrons in BiVO₄ transfer and fill the holes in the BiOI to form the p-n junction.⁷⁴ This BiOI-BiVO₄ p-n junction photoanode contains a light absorption range to 600 nm, together with higher charge carrier separation efficiency.

Hematite (α -Fe₂O₃) is considered as a suitable photocatalyst having a narrow bandgap of 2.1 eV, which make better utilization of the visible light than the TiO₂ and BiVO₄ semiconductor. However, the short charge carrier lifetime and inferior oxygen evolution reaction kinetics hinder the application of α -Fe₂O₃ as an efficient photoanode.⁷⁵ Liu *et al.* prepared 10 nm α -Fe₂O₃ film via atomic layer deposition (ALD), and coated a 1-2 nm layer of Ni(OH)₂ nanosheet by hydrothermal process.⁷⁵ The ultrathin nanostructures facilitate the diffusion of charge carriers within the lifetime, while the amorphous Ni(OH)₂ nanosheets show large specific surface area acting as hole storage layers. These lead to the enhanced photocurrent density and ultrahigh durability of Ni(OH)₂/ α -Fe₂O₃ films. Furthermore, Lim *et al.* incorporated cerium (Ce) in Ni precursor solution to obtain the NiCeO_x co-catalyst on α -Fe₂O₃ photoanode in order to overcome the photoinduced reaction between Ni²⁺ and Ni³⁺.⁷⁶ This composites show a 200 mV cathodic shift of the onset potential and 1.5 times higher photocurrent.

Among the promising semiconductors, inexpensive non-toxic tungsten trioxide (WO_3) are also favorable as the catalysts in PEC application.^{77, 78} First of all, WO_3 is an n-type semiconductor having a bandgap of 2.6 eV suitable for the solar light absorption.⁷⁹ In addition, WO_3 can serve as the photoanode showing an appropriate valence band edge for water oxidation. Furthermore, WO_3 is stable in the acidic solution (<pH 4).⁷⁸ Nevertheless, the practical use of WO_3 is still blocked by their high electron-hole recombination rate (inferior charge separation) and limited light absorption ability. Different strategies are proposed to improve the photocatalytic ability of WO_3 in PEC application. Metal-doping is helpful to reduce the WO_3 bandgap, enhancing visible light absorption and thus improving the photocatalytic performance.^{78, 80-83} Besides, some groups utilize all kinds of nanostructures or modified WO_3 surface to enhance the photocatalytic capability.^{77, 84, 85} Moreover, facilitating the charge separation by different kinds of hybrid heterojunctions or p/n junctions is another strategy to improve the photocatalytic capability, such as $\text{WO}_3/\text{g-C}_3\text{N}_4$,⁸⁶ $\text{CuWO}_4/\text{WO}_3$,⁸⁷ $\text{WO}_3/\text{BiVO}_4$,^{88, 89} and $\text{WO}_3/\text{Cu}_2\text{O}$.⁹⁰

1.4.3 Photocathode for H_2 evolution

When n-type semiconductors are investigated as the photoanodes, p-type semiconductors are developed as the photocathodes for PEC water splitting. The p-type semiconductor cuprous oxide (Cu_2O) shows a bandgap of 2.0-2.2 eV with a suitable hydrogen reduction potential and high absorption efficiency, which is deemed as a promising photocathode material for solar hydrogen generation (similar as the configuration in Figure 1.9b).⁹¹ However, the severe photocorrosion of Cu_2O materials hampers its practical application as the photocathode. Coating a protect layer is an important method to overcome the photocorrosion problem of Cu_2O materials. Ignacio *et al.* coated a 10-50 nm layer of Cu_2S on the Cu_2O nanowires via ion exchange reaction.^{92, 93} In comparison with bare Cu_2O nanostructures, these $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$

composites exhibit improved photocatalytic activity as the photoanode for solar hydrogen reduction. Qi *et al.* utilized NiFe-layered double hydroxide (NiFe-LDH) as the co-catalyst to facilitate the photocatalytic ability of Cu₂O via a facile two-step electrodeposition technique.⁹⁴ Morales-Guio *et al.* deposited a layer of amorphous MoS_{2+x} films to protect Cu₂O and showed improved stability in PEC hydrogen reduction in acidic electrolytes.⁹⁵

The bandgap of silicon (Si) is around 1.1 eV, much narrower than that of metal oxides, together with the high solar light absorption efficiency, leading to its intensive investigation in photovoltaic electronics. Even though the intrinsic optical properties of Si is remarkable, the durability of Si in aqueous solutions is rather poor and hinders the application as efficient photocathode. Oh *et al.* utilized nanoporous black Si photocathode with extremely low reflection and high surface area, indicating remarkable solar light absorption and superior charge carrier transportation, which leads to the highly-efficient PEC water splitting.⁹⁶ Ji *et al.* demonstrated a directly growth of a layer of SrTiO₃ on Si (001) by molecular beam epitaxy technique, this Si-based photocathode exhibited a rather high photocurrent density of 35 mA cm⁻² and high durability in acidic solution.⁹⁷ Here, the band alignment and lattice match facilitate the transportation of photoexcited electrons between single-crystalline SrTiO₃ and Si, and thus leads to the efficient and stable PEC water splitting process. Sim *et al.* prepared the nitrogen doped monolayer graphene/silicon photocathode by N₂ plasma treatment.⁹⁸ The induced nitrogen atoms and numerous defects are considered as active sites to improve the photocurrent density and activity of hydrogen reduction process. Additionally, monolayer graphene passivates the surface and reduces the surface oxidation of Si, resulting in the high chemical stability of Si-based photocathode.

1.5 Motivation and objective of this Thesis

In theory, water splitting is a highly economical and almost limitless process. Nevertheless, in practice, the inferior intrinsic properties of catalysts greatly hinder the large-scale H_2 production, such as high overpotentials, inferior stability of materials, large bandgap, and high recombination rate. As discussed above, viable catalysts used in large-scale water splitting applications are precious metal material, such as Pt, Ir, Ru, *etc.*. Nevertheless, the high cost, scarcity, and poisoning effect of these catalysts have hindered their application and commercialization. Therefore, the investigation of cost-effective and high-durability catalysts is both technologically and academically important. In this Thesis, different strategies are utilized to improve the electrochemical and photoelectrochemical performance of catalysts in water splitting application.

First, we devote in the research of exploring cost-effective non-noble metal based catalysts with good activity and stability during all process in water splitting in the same electrolyte in Chapter 2. Based on the OER volcano plot, we choose the non-noble metal oxide (Co_3O_4) as the starting catalyst. In order to enhance the catalytic reactivity of Co_3O_4 , we modify Co_3O_4 by introducing with Ni and S elements to reduce the intrinsic Gibbs free energy on the surface active site, leads to the enhancement of catalytic ability of $Co_3S_4/Ni:Co_3S_4$. On the other hand, we synthesize the nanostructured catalyst with high surface area to increase the position of active site. Additionally, Ni foam support is utilized to increase the contact with the catalysts.

In addition, we change the dopant from Ni to Mo atoms and increase the amount of dopant, which may affect the electrocatalytic properties accordingly. In Chapter 3, investigate the $CoMoO_6$ and $CoMo_2S_4$ interconnected porous nanoflakes as bifunctional catalysts for overall water electrolysis. The efficient catalytic performance of $CoMo_2S_4$ could be ascribed to the material and nanostructure design, leading to the increased active sites and meanwhile enhanced charge transport capability. The two-electrode electrolyzer cell with above

bifunctional catalysts maintains a voltage of 1.65 V to achieve 10 mA cm⁻² for at least 10 hours, suggesting high electrocatalytic ability and stability.

According to the proposed concept of surface reconstruction during OER process, oxyhydroxide is generated on the surface of the catalysts. Moreover, to further reduce the cost of the catalytic system, we use earth-abundant Cu element to substitute part of the expensive Co element. Herein, we have investigated the hierarchical hybrid Cu(OH)₂@Co(OH)₂ nanotrees as efficient OER electrocatalyst in Chapter 4. Following an combined synthesis of an anodization process and a electrodeposition process, leaves-like ultrathin Co(OH)₂ nanoflakes are grown on the branch-like Cu(OH)₂ nanowires. The as-prepared electrode shows improved OER electrocatalytic capability and stability. This hybrid has high number of catalytic active sites, fast reaction kinetics, and better charge transport capability, indicating that it is an effective strategy to design three dimensional hierarchical nanostructure together with decorating the main catalysts surface with co-catalytic metal compounds. Therefore, our material and nanostructure design, are effective in benefitting the catalytic capability of the catalysts.

PEC water splitting with the energy supply of solar energy and electricity is also an important technique towards hydrogen production, which increases the solar conversion efficiency. In Chapter 5, a combined synthesis of a hydrothermal process and a two-step annealing process are proposed to obtain oxygen-deficient WO₃. Oxygen deficiency increases the donor density of WO₃ leading to better charge carrier generation and separation. Owing to the two-step annealing, the WO₃ samples exhibit a higher photocurrent that is twice as high as that of one-step annealed WO₃ samples. The two-step annealed WO₃ shows so extremely high durability that the photocurrents remain 98% stable over 24 hours, even reaching to 48 hours.

All these strategies are able to modulate the electronic and geometric structure of the transition metal compounds, leading to the improved electrochemical and

photoelectrochemical performance of catalysts. For example, in the Chapter 2, Ni element doping is used to regulate the electronic structure and reduce the ΔG of the intermediates. In addition, introducing oxygen deficiency is another method to adjust the electronic structure and achieve better performance. Besides, the regulating of geometric structure is studied in our Thesis too. We found that the well-separated hierarchical nanostructures increase the surface area with higher active site density, facilitate the contact of solid-electrolyte interface and the release of gaseous product. In view of this fact, hierarchical nanostructures with high porosity are generally favorable in designing high-performance catalyst electrodes. Additionally, these catalysts are directly grown on conductive substrates, which avoids the use of binders and minimizes the intrinsic resistance. Hence, it is recommended to utilize various conductive and chemically stable substrates, such as carbon cloth/papers and copper foam/foil.

In Chapter 6, we make a conclusion about all the presented works, and give a summary about the future work.

Chapter 2 Co₃S₄ and Ni:Co₃S₄ nanowires for overall water splitting

In the quest for mass production of H₂ from water electrolysis, to develop highly efficient, stable and low-cost catalysts is still the central challenge. When designing a novel catalyst, it is necessary to optimize the exposure and accessibility of its active sites as well as the reaction kinetics. This can be realized by combining an appropriate chemical composition of the material, including doping with metal elements, and a properly nanostructured morphology offering a high surface contact. We report here on the design and performances of cobalt-based oxide and sulfide nanowires as catalysts for both HER and OER in the alkaline electrolyte. Meanwhile, DFT calculations show that the free energy of the intermediates has been reduced after the introduction of sulfur and nickel atoms, which have smaller overpotentials and corresponding enhanced electrocatalytic performance.

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2.1 Introduction

Currently, the most viable and effective catalysts for HER and OER are noble metal-based materials such as platinum or iridium/ruthenium oxide ($\text{IrO}_2/\text{RuO}_2$).^{7, 8, 10, 64} However, the rarity and high cost of these materials considerably limit their large-scale application and commercialization.⁹ Furthermore and most importantly, HER catalysts are efficient in acidic electrolytes, while most OER catalysts are reported to have an optimized catalytic ability in alkaline electrolytes. Therefore, if not totally incompatible the integration of the two types of catalysts into the same electrolyte results in inferior performance in overall water electrolysis. Thus it is mandatory to prepare novel low-cost catalysts that are efficient for both HER and OER while being in the same electrolyte.

With cobalt being an earth-abundant metal, cobalt-based catalysts attract tremendous attention for oxygen evolution reactions.^{61, 99-104} The catalytic properties of Co_3O_4 with different nanostructures have been investigated both theoretically and experimentally.^{30, 51, 59, 105-107} These studies demonstrate that the electrocatalytic reactivity is controlled by the engineering of the electronic structure of the cobalt-based catalysts. Replacing either totally or partially the oxygen atoms by other non-metal atoms such as N, C, S, B, or P is another important strategy for improving the catalytic activity of cobalt-based catalysts.¹⁰⁸⁻¹¹¹ The performances of Co_3O_4 can be further improved by doping with another 3d-metal element such as Ni, Mn, or Fe. Subbaraman *et al.* systematically studied these metals and found that the binding strength of the M–OH bond (M=Mn, Fe, Co and Ni) plays a key role in governing the catalytic activity, which increases in the order: $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni}$.⁷ The introduction of metallic 3d atoms into the lattice structure of the host catalyst allows the tuning of its electronic properties toward an optimal activity. For example, the carbon cloth-supported NiCo_2S_4 of Liu *et al.* delivers a cell voltage of 1.68 V to achieve a current density of 10 mA cm^{-2} .¹¹²

We propose here a new strategy to design cost-effective cobalt-based catalysts deposited on Ni-foam that exhibit good catalytic activity for overall water splitting in the same electrolyte. This strategy consists in manipulating the electronic structure of the Co_3O_4 by the introduction of S and Ni atoms to improve the catalytic performance. We start from Co_3O_4 as the basic OER catalyst and convert it into Co_3S_4 to achieve higher OER catalytic ability. Most importantly, Co_3S_4 can also be used as a HER catalyst in the same electrolyte as for OER. Then, we introduce a small amount of nickel into the Co_3S_4 lattice in order to form bimetallic catalytic sites that will reduce the active energy of the reaction and decrease the HER overpotential. The synthesis of nickel-doped Co_3O_4 ($\text{Ni}:\text{Co}_3\text{O}_4$) and Co_3S_4 ($\text{Ni}:\text{Co}_3\text{S}_4$) proceed via a hydrothermal technique by adding a Ni-precursor to the starting material. In addition, the Ni-foam supports are used to enhance the adhesion between the substrate and the electrocatalyst, as well as the whole electronic conductivity. This experimental protocol affords a high surface area nanostructure made of well-separated nanowires that greatly increase the number of catalytic active sites per specific area. We demonstrate that these Co_3S_4 (OER) and $\text{Ni}:\text{Co}_3\text{S}_4$ (HER) electrodes operate as efficient catalysts when introduced into a compatible electrolyte to finally deliver an operating voltage as low as 1.70 V at 10 mA cm^{-2} over 40 hours. Later on, the DFT calculations are employed to investigate the Gibbs free energy of hydrogen adsorption in the HER process and other intermediates in the OER process.^{9, 30, 33, 109, 113} Following sulfuration and Ni-doping, the Gibbs free energies are decreased, indicating that the two catalysts have smaller overpotentials and better catalytic performance.

2.2 Synthesis of cobalt-based materials

As shown in Figure 2.1, the Co_3O_4 nanowire was synthesized on commercial nickel foam by hydrothermal method. A piece of pressed Ni foam was sonication cleaned with de-ionized water and ethanol. Polytetrafluoroethylene tape was utilized to protect the backside of Ni foam

from solution contamination. Afterward, the Ni foam was immersed in Teflon liners containing 60 mL de-ionized water of 2 mmol cobalt nitrate, 4 mmol ammonium fluoride, 10 mmol urea. Then, the Teflon liners were put in the stainless steel autoclave and maintained at 120°C for 4 hours. After hydrothermal reaction, the sample was rinsed with de-ionized water and ethanol several times. The dark grey Ni foam turned pink, suggesting the formation of cobalt-based material. Subsequently, the sample was annealed at 300°C for 1 hour in air. This turned the pink Ni foam black, suggesting the conversion from cobalt-based precursor to Co_3O_4 . The average mass loading of Co_3O_4 is 2.5 mg cm^{-2} .

Figure 2.1 Preparation scheme of as-grown cobalt-based materials.

To synthesize Co_3S_4 , the above Co_3O_4 sample underwent an ion exchange reaction in another hydrothermal treatment. The backside of the above sample was again covered with polytetrafluoroethylene tape and then sealed in Teflon-lined stainless steel autoclave liners containing 60 mL of deionized water of 300 mg $\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$. The autoclave was heated at 160°C for 6 hours. After cooling down naturally, the sample was rinsed several times with deionized water and ethanol.

To obtain nickel doped cobalt-based materials, 0.1 mmol nickel nitrate was added in the first hydrothermal process. Other heat treatment and sulfuration process were the same as above. Also, we collected the precipitated pink powders after the first hydrothermal reaction and washed them with de-ionized water and ethanol by centrifugation. After drying at 60°C for 5 hours, the powder sample was annealed under above conditions and collected as $\text{Ni}:\text{Co}_3\text{O}_4$.

powder. After drying at 60 °C for 5 hours, the powders were annealed at 300 °C for 1 hour in air. Then, these Ni:Co₃O₄ powders were converted to Ni:Co₃S₄ under the similar ion exchange condition as above. The Ni:Co₃O₄ and Ni:Co₃S₄ powders are completely dissolved in pure nitrate acid and used to perform the ICP-OES characterizations.

2.3 Characterization of cobalt-based materials

As shown in Figure 2.2a, the chemical composition and phase of cobalt-based materials are confirmed by X-ray diffraction (XRD, 6000 Shimadzu). For all the samples, there are two strong diffraction peaks at $2\theta = 44.5^\circ$ and 51.8° pertaining to the nickel metal (JCPDS 04-0850), which is derived from the Ni foam substrate. Except these two peaks, for Co₃O₄ and Ni:Co₃O₄, all characteristic peaks are identical to the spinel phase Co₃O₄ (JCPDS 42-1467) and no major second phase is observed. In the pattern of Co₃S₄ sample, the peaks of Ni foam are still existing, while other characteristic peaks are in good agreement with Co₃S₄ (JCPDS 19-0367) indicating the conversion of sulfides from oxides after sulfuration. In addition, there is a weak peak located at 29° pertaining to a small amount of CoS (JCPDS 70-2864), which can be ascribed to the unstable condition of sulfuration. Compared the XRD patterns of undoped and doped cobalt-based oxides, there are not much difference between Ni:Co₃O₄ and Co₃O₄. This can be derived from the similar electronic structure between Ni and Co. Ni ions have a little bit larger diameter than Co ions. When doping a small amount of Ni ions into Co₃O₄, the structure stability of Co₃O₄ will not be affected too much. So, the XRD patterns of Co₃O₄ and Ni:Co₃O₄ are quite similar. The same phenomenon can also be found in Co₃S₄ and Ni:Co₃S₄.

Figure 2.2 Bulk and surface chemical composition of our cobalt-based materials. (a) XRD patterns of Co₃O₄ (blue line), Co₃S₄ (red line), Ni:Co₃O₄ (pink line), and Ni:Co₃S₄ (black line) grown on Ni foam. ◆ denotes the peaks corresponding to the spinel phase Co₃O₄ (JCPDS 42-1467), while ♣ corresponds to Co₃S₄ (JCPDS 19-0367), and ♠ can be indexed to the CoS (JCPDS 70-2864). XPS full survey results of the Co₃S₄ (b) and Ni:Co₃S₄ (c) samples. (d-f) High resolution XPS spectra of cobalt sulfide samples: (d) Co 2p spectrum of Co₃S₄ and Ni:Co₃S₄, (e) S 2p spectrum of Co₃S₄ and Ni:Co₃S₄, and (f) Ni 2p spectrum of Ni:Co₃S₄.

Table 2.1 Atomic ratio of Ni:Co₃O₄ and Ni:Co₃S₄ determined by ICP-OES measurements.

Material	Ni:Co ₃ O ₄		Ni:Co ₃ S ₄	
Element	Ni	Co	Ni	Co
Units	ppm	ppm	ppm	ppm
Average	0.3085	3.069	0.0700	0.6880
Average atom ration of Ni:Co	10.05%		10.17%	

Furthermore, the surface chemical states of Co₃S₄ and Ni:Co₃S₄ are analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5700). All the peaks of other elements are calibrated based on the peak position of C 1s. In Figure 2.2b and c, XPS full survey spectrum of Co₃S₄ and Ni: Co₃S₄ prove the existence of Co element and S element in Co₃S₄ and Ni:Co₃S₄, and the

presence of Ni element in Ni:Co₃S₄. Importantly, the presence of Ni in Co₃S₄ very likely originates from the Ni substrate. In the high resolution Co 2p spectrum (Figure 2.2d), there are two dominating peaks with binding energy at 782.1 and 797.4 eV are observed, indexing to the Co 2p_{3/2} and Co 2p_{1/2} spin orbit, validating that the oxidation states of Co are Co²⁺ and Co³⁺. This is in good agreement with some reported cobalt-based materials.¹¹⁴ In addition, two peaks around 786.8 and 804.4 eV are the satellite peaks of Co 2p_{3/2} and Co 2p_{1/2} spin orbit, respectively. For the high resolution S 2p spectrum (Figure 2.2e), the peak locating at 163.4 eV is assigned to the S species in the metal sulfide bond, which demonstrates the formation of Co-S bond. And the peak at 162.7 eV is attributed to the sulfur ions in low coordination state at the surface.^{112, 115, 116} Comparing the Co 2p spectrum and S 2p spectrum with pure Co₃S₄ sample, Ni:Co₃S₄ sample has very similar Co 2p spectrum and S 2p spectrum, which is consistent with XRD measurement. The high resolution spectrum of Ni species of Ni:Co₃S₄ is displayed in Figure 2.2f. Two peaks at 856.6 and 874.2 eV are pertaining to the Ni 2p_{3/2} and Ni 2p_{1/2} spin-orbit, corresponding to the +3 valence of Ni in nickel cobalt sulfides.^{112, 115-118} Note that the two small peaks at 858.2 and 876.6 eV might originate from the multiplet-splitting of Ni³⁺.¹¹⁹⁻¹²² XPS characterization is a surface-sensitive and semi-quantitative analysis technique, the testing depth of XPS is lower than 10nm, so the Ni:Co atomic ratio (1:2) tested by XPS can only represent the surface of Ni:Co₃S₄. Probably most of Ni atoms are located at the surface, thus resulting into the high atomic ratio of 1:2. In order to determine more accurately the Ni and Co ratio, we conducted Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) characterization with a Thermo Fischer iCAP 6000 series spectrometer. We did not use the samples scraped from the Ni substrate in order to avoid increasing the Ni ratio. Instead, we collected the precipitated powders after hydrothermal process and dissolved in pure nitrate acid and tested by ICP-OES. The average Ni and Co ratio in Ni:Co₃O₄ and Ni:Co₃S₄ are 10.05% and 10.17%, respectively (Table 2.1).

Scanning electron microscopy (SEM, FEI SIRION) and transmission electron microscopy (TEM, JEOL-2010 HR & UHR and JEOL-2100F with UHR Configuration) are utilized to characterize the morphology and microstructure of cobalt-based samples. First, the morphology of cobalt-based precursor after solvothermal treatment, are checked using SEM (Figure 2.3). The Ni-foam substrate is fully covered by cobalt-based precursor⁶¹ nanowires with a diameter in the range 50-100 nm. After annealing for 1 hour, the precursor transforms into Co_3O_4 nanowires with similar diameter (Figure 2.4a and b). Following the sulfuration process of Co_3O_4 , the Co_3S_4 nanowires morphology is preserved although the diameter of nanowires becomes slightly larger (100-150 nm; Figure 2.4c and d). Besides, Figure 2.4e and f shows that the morphology of $\text{Ni}:\text{Co}_3\text{O}_4$ is similar to that of the undoped oxide, in particular with an average nanowire diameter in the range 50-100 nm. This can be ascribed to the similar size and electronic structure of Ni and Co atoms. After sulfuration, the $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires become hollow, which is clearly visible in the high resolution SEM (Figure 2.4g and h) and TEM (Figure 2.5c and d) images. In addition, the diameter of $\text{Ni}:\text{Co}_3\text{S}_4$ becomes slightly larger (100-150 nm) than that of $\text{Ni}:\text{Co}_3\text{O}_4$.

Figure 2.3 SEM images of the Co_3O_4 precursor after the first hydrothermal method.

Figure 2.4 SEM images revealing morphological differences between (a,b) Co_3O_4 , (c,d) Co_3S_4 , (e,f) $\text{Ni}:\text{Co}_3\text{O}_4$, and (g,h) $\text{Ni}:\text{Co}_3\text{S}_4$. In particular, the diameter of the nanowires increases when going from oxides ($\phi=50\text{-}100\text{ nm}$) to sulfides ($\phi=100\text{-}150\text{ nm}$).

Figure 2.5 TEM images of (a, b) Co_3O_4 , (c, d) Co_3S_4 , (e, f) $\text{Ni}:\text{Co}_3\text{O}_4$, and (g, h) $\text{Ni}:\text{Co}_3\text{S}_4$. The nanowires are made of thousands of compacted nanoparticles, each particle having a diameter of $\approx 15\text{ nm}$. Images g, h clearly show that the $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires have a darker outer contrast (see arrows) suggesting that they are hollow nanowires (or nanotubes).

Figure 2.6 (a-e) Elemental mapping images of Co, Ni, and O elements in $\text{Ni:Co}_3\text{O}_4$ samples. Co, Ni, and O are in green, yellow and red color, respectively. (f-j) Elemental mapping images of $\text{Ni:Co}_3\text{S}_4$ samples.

Meanwhile, high resolution TEM images clearly show the microstructure of the above samples. In Figure 2.5a and b, it is seen that Co_3O_4 nanowires consist of numerous small particles rather than a single crystal. There is a distinct void in-between the particles. The average diameter of these small particles is estimated to be ≈ 15 nm. The morphology of Co_3S_4 (Figure 2.5c and d) and $\text{Ni:Co}_3\text{O}_4$ (Figure 2.5e and f) is highly similar with Co_3O_4 nanowires. They are also constituted of small particles. However, when introducing sulfur into $\text{Ni:Co}_3\text{O}_4$ nanowires, the nanowires become hollow due to the Kirkendall effect^{123, 124} (Figure 2.5g and h). More precisely, the diffusion rates of Ni and Co being different, their respective ion exchange rates with S atoms will also be different on the surface, thus leading to the hollow

structure of the nanowires. TEM images show that the diameter of the Ni:Co₃S₄ hollow nanowires is in the 50-100 nm range and that the wall thickness of the Ni:Co₃S₄ hollow nanowires is ~10 nm. Furthermore, the lattice fringes of four materials are measured and shown in the high-resolution TEM images (Figure 2.5b, d, f and h). The lattice fringes separated by 0.466 and 0.283 nm are indexed to the (111) plane of Co₃O₄ and the (311) plane of Co₃S₄ respectively (Figure 2.5 b and d). These results are in good agreement with the XRD results. It is worth noting that the lattice fringe of Ni:Co₃O₄ (0.470 nm) and Ni:Co₃S₄ (0.286 nm) are slightly larger than those of Co₃O₄ and Ni:Co₃S₄. To further confirm the distribution of the Ni, Co, O, and S, elemental mapping images of Ni:Co₃O₄ and Ni:Co₃S₄ are provided in Figure 2.6. It is highly visible that all the elements are evenly distributed in the nanowires for both Ni:Co₃O₄ and Ni:Co₃S₄ materials.

2.4 Electrochemical measurements of cobalt-based materials

2.4.1 Electrochemical measurements parameters

Electrochemical testing was conducted in a three-electrode glass configuration via a Zahner-Zennium electrochemical workstation. The samples grown on Ni foam were used as working electrodes, a platinum foil/carbon rod as the counter electrode, and an Ag/AgCl (3.0 M KCl) electrode as the reference. All electrodes were immersed into the 1 M KOH electrolyte, and the electrolyte was bubbled with high purity O₂ gas for 15 min before the test. All the tests were conducted at room temperature. Before any measurements were performed, cyclic voltammetry from 0 to 0.8 V at 50 mV s⁻¹ were carried out 20 cycles, which is an activation process to stabilize the current and detach any impurity formed on the surface of the electrode. Then, the linear sweep voltammetry (LSV) tests were performed at 2 mV s⁻¹ for the polarization curves. All data were dealt with iR-compensation by the current-interrupt method. The main point of this method is to consider uncompensated cell resistance (R). Generally, the obtained

potential is corrected by subtracting ohmic drop (iR), where i is the current related to the potential. Tafel plots were derived from the above LSV curves by fitting the data to the equation $\eta = a + b \log(j)$, where η is the iR -compensated overpotential, a is the Tafel constant, b is the Tafel slope, and j is the current density. The stability was investigated at fixed current densities (10, 30, and 50 mA cm^{-2}) by chronopotentiometry. The electrochemical impedance spectroscopy (EIS) of the catalysts was tested under a current density of 1 mA cm^{-2} in the frequency range from 100 Hz to 100 kHz. The current density was calculated based on the geometric area of the electrode. The Faradaic efficiency was estimated using the volumetric method. In all measurements, Ag/AgCl (3.0 M KCl) electrode was used as the reference, which has the potential of 0.210 V *vs.* RHE. Potentials obtained in this study were calibrated against the reversible hydrogen electrode (RHE) reference by the following equation: $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.059 \text{ pH} + E (\text{Ag/AgCl vs. RHE})$. In our study, η_{10} is the iR -compensated overpotential which can achieve a current density of 10 mA cm^{-2} .

2.4.2 OER and HER performance

We first evaluate the catalytic performances of our materials using the overpotential (here denoted η_{10}) that is necessary to achieve a current density of 10 mA cm^{-2} . Figure 2.7a shows the linear sweep voltammogram (LSV) after compensation by the ohmic drop (noted iR) at a scan rate of 2 mV s^{-1} for all electrodes. In these LSV curves, all the cobalt-based catalysts show a small oxidation peak before the onset of OER, which is mainly associated with the transition from Co(III) to Co(IV). In the OER part, the required η_{10} of pure Co_3O_4 catalysts is 371 mV, which is quite high. After Ni doping of pure Co_3O_4 , the required η_{10} of $\text{Ni}:\text{Co}_3\text{O}_4$ decreases down to 348 mV. Based on literature, Ni has higher catalytic activity than Co.⁷ This means that Ni doping may reduce the free energy of the intermediates adsorbed on Co_3O_4 , which is investigated by DFT calculations in the following paragraphs. In addition, after conducting the

sulfuration step, the required η_{10} of Ni:Co₃S₄ is 293 mV which is much lower than that of Ni:Co₃O₄. We observe a similar trend in the Co₃S₄/Co₃O₄ system where a lower overpotential of 283 mV is needed for Co₃S₄ to reach a current density of 10 mA cm⁻², as compared with Co₃O₄ (371 mV). The above trend reveals that the sulfide catalysts exhibit lower overpotential than their oxide counterparts, suggesting that sulfides possess a higher catalytic activity. This can be due to the lower free energy of the adsorbed intermediates in sulfides, which is investigated by DFT calculations later. Furthermore, the current density of the sulfides is obviously much higher than that of oxides, revealing the higher reaction kinetics of the cobalt-based sulfides. However, the η_{10} of Co₃S₄ is 10 mV lower than that of Ni:Co₃S₄, indicating the highest catalytic activity.

The overpotential of our catalysts is comparable to most of the reported catalysts in alkaline electrolyte (Table 2.2). In the HER process, the required η_{10} (222 mV) of Ni:Co₃O₄ is very close to that of Co₃O₄ (221 mV). In the curves of cobalt-based sulfide catalysts, Ni:Co₃S₄ have the smallest η_{10} (199 mV), while undoped Co₃S₄ needs 218 mV to reach a current density of 10 mA cm⁻². Our results show that the sulfides have lower HER overpotentials compared with the oxides, and the introduction of nickel also can decrease the overpotential in the low current density range.

To gain further insight into the OER and HER kinetics of above catalysts, Tafel plots are fitted the data to the Tafel equation. As shown in Figure 2.7b, the OER Tafel slope of the Co₃S₄ and Ni:Co₃S₄ catalysts is 66 and 65 mV dec⁻¹, respectively, lower than that of Co₃O₄ (69 mV dec⁻¹) and Ni:Co₃O₄ (74 mV dec⁻¹), suggesting the favourable OER kinetics and faster OER rates for cobalt-based sulfides. This comparison shows clearly that the composition transformation of cobalt-based oxides to cobalt-based sulfides can improve the OER kinetics. In addition, the Ni:Co₃S₄ catalysts exhibit the lowest HER Tafel slope (91 mV dec⁻¹), compared with Co₃O₄ (110 mV dec⁻¹), Co₃S₄ (134 mV dec⁻¹), and Ni:Co₃O₄ (93 mV dec⁻¹). As introduced

in Chapter 1.3.1, the rate-determining step (RDS) for the whole HER process could be identified by the Tafel analysis. When the Tafel slope is 120, 40, or 30 mV dec^{-1} , suggesting that the rate-determining step is Volmer, Heyrovsky, or Tafel reaction, respectively.^{34, 35, 125, 126} In this work, Tafel slopes locate within the range of 40 to 120 mV dec^{-1} , revealing that the hydrogen evolution on Co_3O_4 , $\text{Ni:Co}_3\text{O}_4$, and $\text{Ni:Co}_3\text{S}_4$ surfaces are related to a Volmer-Heyrovsky mechanism.

Figure 2.7 Oxygen and hydrogen evolution of different cobalt-based electrodes in a three-electrode system with 1.0 M KOH as the electrolyte. (a) Current-voltage curves of water electrolysis after iR-compensation (scan rate = 5 mV s^{-1}). (b) Corresponding Tafel plots with associated linear fits. (c) Stability tests under a constant current density of 10 mA cm^{-2} for 10 hours. (d) Comparison of η_{10} and Tafel slopes for all electrodes used here.

Table 2.2 Comparison of the OER performance of as-prepared our catalysts and reported Co-related catalysts.

Catalyst	Overpotential @10mA/cm ² (mV)	Tafel slope (mV dec ⁻¹)	Substrate	Electrolyte
Co ₃ S ₄ (our work)	283	66	Ni foam	1.0 M KOH
Ni: Co ₃ S ₄ (our work)	293	65	Ni foam	1.0 M KOH
CoN ⁶¹	290	70	Ni foam	1.0 M KOH
Co ₄ N ¹²⁷	257	44	Carbon cloth	1.0 M KOH
Co ₂ B ¹²⁸	380	45	Powder	3.0 M KOH
CoS ¹²⁹	306	72	Carbon paper	1.0 M KOH
NiCo ₂ S ₄ ¹¹⁵	260	40	Ni foam	1.0 M KOH
IrO ₂ ¹¹⁵	340	72.5	Ni foam	1.0 M KOH
S-Co/CNS ¹⁰⁹	320	52.3	Powder	1.0 M KOH

Stability in strong alkaline electrolyte is crucial to assess the catalytic ability of electrodes. To this end, catalysts are tested at a constant current density of 10 mA cm⁻² for 10 hours. As shown in Figure 2.7c, the pure Co₃O₄ shows OER overpotential (η) of 374 mV, which is the largest among four catalysts. After doping with nickel atoms, the η of Ni:Co₃O₄ decreases to 334 mV, showing 40 mV lower than that of pure Co₃O₄. When we proceed to the sulfuration of Ni:Co₃O₄, the η of Ni:Co₃S₄ is as low as 300 mV. However, a potential of 295 mV is required for Co₃S₄ after 10 hours of stability test, which is the lowest overpotential among the four catalysts, whereas these catalysts show negligible degradation over 10 hours of continuous testing. In the HER stability test, we observe that the overpotential of Ni:Co₃S₄ is 190 mV after 10 hours. Meanwhile, Co₃S₄, Co₃O₄, and Ni:Co₃O₄ display a potential of 213, 234, and 244 mV, respectively. Interestingly, all catalysts show decreased HER overpotential in the initial one or two hours, which can be ascribed to the activation process during the stability tests. This phenomenon may be caused by an oxidation process, which happens at a very slow rate and gradually reaches to a limit. This may help to create additional active sites and refresh the

boundaries of the interconnected particles, which slightly increases the activity. Also, the gas evolution can blow off surface residues from the testing, and contributes to the increased activity.¹³⁰⁻¹³²

To further investigate the kinetics, the impedance of the catalysts are tested under a current density of 1 mA cm^{-2} in the frequency range from 100 Hz to 100 kHz. In general, the semicircle in the low-frequency region refers to charge-transfer resistance of electrodes. The semicircles of oxides are larger than those of sulfides, indicating that the charge-transfer resistance is larger at the oxide/electrolyte interface (Figure 2.8). In addition, a larger charge-transfer resistance results in a slower charge transfer kinetics and reaction rates, pointing that cobalt sulfide materials have better kinetics in strong alkaline electrolyte as compared to cobalt oxides. Combining the results of η_{10} , Tafel slopes and impedance (Figure 2.7d and Figure 2.8), reveal that the sulfuration of cobalt oxide into cobalt sulfide significantly enhances both OER and HER activity leading to lower overpotentials and faster reaction rates while nickel doping further improves the HER catalytic activity.

Figure 2.8 Nyquist plots of cobalt-based catalysts in the frequency range from 100 kHz to 100 H. Impedance tests are performed in a three-electrode glass configuration in 1.0 M KOH electrolyte. These catalysts are used as working electrodes, a platinum foil as counter electrode, and an Ag/AgCl (3.0 M KCl) electrode as the reference electrode.

2.4.3 Overall water splitting tests

Prompted by these promising results we proceeded to overall water splitting tests in a two-electrode configuration with 1.0 M KOH as the electrolyte, where Co_3S_4 acts as the OER electrode and $\text{Ni}:\text{Co}_3\text{S}_4$ as the HER electrode (denoted as $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$) (Figure 2.9). This electrolyzer cell delivers a current density of 10 mA cm^{-2} at an operating potential of 1.706 V, thus indicating a combined overpotential of 476 mV for an overall water splitting process (Figure 2.9a).

Figure 2.9 Comparative experiments of overall water electrolysis of two systems: $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ and $\text{Ni}//\text{Ni}$ systems in 1.0 M KOH electrolyte. In $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ system, Co_3S_4 acts as the OER electrode and $\text{Ni}:\text{Co}_3\text{S}_4$ acts as the HER electrode. In $\text{Ni}//\text{Ni}$ system, two pure Ni foams act as OER and HER electrode. Current-voltage curves of overall water electrolysis of $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ (a) and $\text{Ni}//\text{Ni}$ (b) after iR-compensation (scan rate = 5 mV s^{-1}). The curve in black is tested before stability test. The curves in blue and red are tested after 20 and 40 hours stability test, respectively. (c, d) Stability tests of $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ and $\text{Ni}//\text{Ni}$ under a constant current density of 10 mA cm^{-2} , respectively. Electrolyte is replaced every 20 hours in $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$, causing the sudden drop in the curve. (e) Stability tests of $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ under 30 mA cm^{-2} for 20 hours. (f) Scheme of overall water splitting tests in the $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ configuration in 1.0 M KOH electrolyte.

Table 2.3 Summary of the electrochemical activities of the catalytic electrodes for overall water splitting.

Catalyst	V _{total} @10mA cm ⁻²	Durability	Substrate	Electrolyte
Co ₃ S ₄ // Ni:Co ₃ S ₄ (our work)	1.70 V	40 h	Ni foam	1.0 M KOH
Co ₂ B // Co ₂ B ¹²⁸	1.81 V	-	Powder	3.0 M KOH
Co-S // Co-S ¹²⁹	1.74 V	2 h	Carbon paper	1.0 M KOH
NiCo ₂ S ₄ // NiCo ₂ S ₄ ¹¹⁵	1.63 V	50 h	Ni foam	1.0 M KOH
Ni ₃ S ₄ // Ni ₃ S ₄ ¹¹⁵	1.73 V	-	Ni foam	1.0 M KOH
NiS // NiS ¹³³	1.64 V	35 h	Ni foam	1.0 M KOH
NiCo ₂ S ₄ // NiCo ₂ S ₄ ¹¹²	1.68 V	10 h	Carbon cloth	1.0 M KOH
NiCo ₂ O ₄ // NiCo ₂ O ₄ ¹¹²	1.98 V	-	Carbon cloth	1.0 M KOH
CoNi(OH) _x // NiN _x ¹³⁴	1.65 V	-	Cu foil	1.0 M KOH

In comparison with previous reported catalysts for overall water splitting, the overpotential of our electrolyzer cell is comparable to most of the catalysts in alkaline electrolyte (Table 2.3). Comparative experiments of Ni//Ni system are also conducted in the same electrolyte. As Figure 2.9b shows, the Ni//Ni system only delivers a very small current density of 0.1 mA cm⁻² at operating potential of 1.8 V, while the current density can reach to 30 mA cm⁻² in the Co₃S₄//Ni:Co₃S₄ system.

Additionally, the Co₃S₄//Ni:Co₃S₄ electrolyzer cell shows superior stability (Figure 2.9c). The operating voltage remains stable at ~1.70 V with negligible degradation, even after continuous electrolysis at constant current density of 10 mA cm⁻² for at least 40 hours. The voltage drop after 20 hours is due to the replacement of electrolyte. In Figure 2.9d, the Ni//Ni system needs a quite high operating potential of more than 2.2 V to deliver a current density of 10 mA cm⁻², which is 0.5 V higher than that of Co₃S₄//Ni:Co₃S₄ system. This shows that our system has a better performance compared with Ni//Ni system. Increasing the current density up to 30 mA cm⁻², the Co₃S₄//Ni:Co₃S₄ system requires an operating voltage of 1.86 V to maintain the water splitting process even after 20 hours (Figure 2.9e).

2.4.4 Characterization after electrochemical tests

SEM images and XRD patterns recorded after 20 hours of stability test (Figure 2.10 and 2.11) show that the original morphology and chemical composition of Ni:Co₃S₄ are almost preserved. However, the morphology and crystal structure of Co₃S₄ exhibit some changes as compared to fresh Co₃S₄ catalysts. More precisely, a few Co₃S₄ nanowires may be damaged by the generated oxygen gas and then cracked in the long-term tests (Figure 2.10). Also, some Co₃S₄ nanowires agglomerate together during the stability test. A similar phenomenon can be found in other publications.^{135, 136} The reason is not clearly understood yet. This may be due to the recrystallization and growth of Co₃S₄, which also leads to an additional (400) peak of Co₃S₄ (Figure 2.11). In this process, the CoS peak disappears, indicating that the CoS are converted into Co₃S₄ and also leads to stronger peak intensity of Co₃S₄ compared with fresh Co₃S₄.

Figure 2.10 SEM images of the morphology of (a-b) Co₃S₄ nanowires (act as the OER electrode) and (c-d) Ni:Co₃S₄ nanotubes (act as the HER electrode) after stability test for overall water splitting in 1.0 M KOH electrolyte under a constant current density of 30 mA cm⁻² for 20 hours.

Figure 2.11 XRD patterns of Co_3S_4 (red line) and $\text{Ni}:\text{Co}_3\text{S}_4$ (blue line) after stability test for overall water splitting in 1.0 M KOH under 30 mA cm^{-2} for 20 hours. ♣ denotes the peaks corresponding to the Co_3S_4 (JCPDS 19-0367), and ♠ is indexed to the CoS (JCPDS 70-2864).

2.5 Theoretical study via DFT calculation

2.5.1 Computational models and methods

Spin-polarized density functional theory (DFT) calculations have been performed using the full-potential all-electron code FHI-aims¹³⁷ at the level of the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) parameterization.¹³⁸ A pre-constructed high-accuracy all-electron basis set of numerical atomic orbitals was employed, as provided by the FHI-aims default option. Structural optimization was performed with a tolerance of $10^{-3} \text{ eV/\AA}$. All geometries and energies reported herein correspond to the optimal spin state for each system. Co_3O_4 adopts the normal spinel structure with Co^{2+} (Co^{3+}) ions located in the tetrahedral (octahedral) sites of the face centered cubic lattice formed by O^{2-} anions. The effects of the coverage on the catalytic activities have been discussed by Garc á-Mota *et al.*¹³⁹ and Zhang *et al.*¹⁴⁰ for the cobalt oxide systems. Surfaces with coverage of O/OH are reported to be more active than the clean surface. Therefore, half-monolayer OH covered

surface model is used for the oxygen-poor A termination. For the oxygen-rich B termination, a clean surface model is used.

In this study, the adsorption energy (ΔE_{ads}) for H^* , OOH^* , O^* , and OH^* were calculated by the following equations:

$$\Delta E_{\text{H}^*} = E(\text{H}^*) - E(*) - 1/2E_{\text{H}_2} \quad (2.1)$$

$$\Delta E_{\text{OOH}^*} = E(\text{OOH}^*) - E(*) - (2E_{\text{H}_2\text{O}} - 3/2E_{\text{H}_2}) \quad (2.2)$$

$$\Delta E_{\text{O}^*} = E(\text{O}^*) - E(*) - (E_{\text{H}_2\text{O}} - E_{\text{H}_2}) \quad (2.3)$$

$$\Delta E_{\text{OH}^*} = E(\text{OH}^*) - E(*) - (E_{\text{H}_2\text{O}} - 1/2E_{\text{H}_2}) \quad (2.4)$$

Where $*$ and X^* denotes surfaces and adsorbed X species, respectively. The energies of isolated molecules (H_2 , H_2O , O_2) were computed in an orthorhombic cell of dimensions $10 \text{ \AA} \times 11 \text{ \AA} \times 12 \text{ \AA}$. The OER energy profile were constructed based on the model developed by Nørskov.¹⁴¹ In the scheme, the OER is assumed to involve four elementary reaction steps and each step involves electron transfer of an electron to the electrode and a proton to water, the reaction equation 1.10–1.13. Based on the computational hydrogen electrode model,¹⁴¹ the free energy change along the OER processes (ΔG_n , $n = 1-4$) at standard conditions can be derived as:

$$\Delta G_1 = \Delta G_{\text{OH}^*} \quad (2.5)$$

$$\Delta G_2 = \Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*} \quad (2.6)$$

$$\Delta G_3 = \Delta G_{\text{OOH}^*} - \Delta G_{\text{O}^*} \quad (2.7)$$

$$\Delta G_4 = 4.92 - \Delta G_{\text{OOH}^*} \quad (2.8)$$

Then the theoretical overpotentials (η) for OER can be calculated using the equation 1.14 and equation 1.15.

The adsorption energy of a single H atom (ΔG_{H^*}) is usually considered as an effective descriptor for evaluating the hydrogen evolution reaction (HER) activity over a given system.²⁹ Generally, the smaller (ΔG_{H^*}) absolute value, the better the HER activity. ΔG_{H^*} can be

calculated by equation 1.7 ($\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$). Here, ΔE_{H^*} is the binding energy, ΔZPE is the zero-point energy (ZPE) difference and ΔS is the entropy change of H^* . The ZPE of H atom in different state (gas and adsorbed state) are very similar, thus ΔZPE is close to zero. The entropy of hydrogen in adsorbed state is negligible, and $T\Delta S$ is calculated based on the entropy of H_2 in the gas phase. $T\Delta S$ is determined to be -0.21 eV.

2.5.2 Calculation results and discussion

From the above results, the introduction of S and Ni atoms can improve the electrocatalytic performance of pure cobalt oxides. To obtain a better understanding on this phenomenon, we utilized DFT calculations to determine the binding energy of four key species (H^* , OH^* , O^* and OOH^*) adsorbed on the corresponding catalysts (Co_3O_4 , $Ni:Co_3O_4$, Co_3S_4 and $Ni:Co_3S_4$).

The energetically favourable (110) surface was used to explore the catalytic performance.¹⁴²⁻

¹⁴⁴ This surface has two different terminations, usually denoted as A (Co_4O_4) and B (Co_2O_4).

Here, the A termination exposes two Co^{2+} (three-fold Co_{3c}), two Co^{3+} (four-fold Co_{4c}), and four oxygen atoms (three-fold O_{3c}) per surface unit cell in the Co_3O_4 (110) surface. The B termination exposes two Co^{3+} , and two O_{2c} and two O_{3c} per surface unit cell. The structure of A and B termination of $Ni:Co_3O_4$ (110) surface is displayed in Figure 2.12(a, b) and Figure 2.13(a, b), respectively. The $Ni:Co_3X_4$ (110) ($X=O$ and S) surface is modeled by replacing one of the Co^{3+} with Ni atom, based on that Ni^{3+} is found in our experiment by XPS characterization.

It has been known that the free energy of the adsorbed intermediates (ΔG) is a good descriptor for the electrocatalytic activity of a catalyst.^{29, 145, 146} In the case of HER process, free energy of hydrogen adsorption (ΔG_{H^*}) is used to investigate the hydrogen evolution activity. Additionally, to ensure a reasonable intermediates (H^*) binding step as well as a fast hydrogen release process, ΔG_{H^*} should have a compromise between these two limits, indicating that the optimum value is a small absolute value which closes to zero.^{32, 147, 148}

Figure 2.12 (a) Side view and (b) top view of the A termination of Ni:Co₃O₄ (110) surface. In the top view of the structure, the atoms at the top layer are illustrated by ball-and-stick models, and the rest of the atoms are given by line models. Co³⁺, Co²⁺, Ni, and O atoms are shown in pink, blue, green and red, respectively. (c) Calculated free energy diagram for the HER process on the A termination of four catalysts. Calculated free energy diagram for the OER process on the A termination of Co₃O₄ (d), Ni:Co₃O₄ (e), Co₃S₄ (f), and Ni:Co₃S₄ (g) and the corresponding theoretical overpotential.

As shown in Figure 2.12c, for single Ni doping, the ΔG_{H^*} of Ni:Co₃O₄(110)-A termination is -0.13 eV. When replacing oxygen atoms with sulfur atoms, the ΔG_{H^*} of Co₃O₄ is changed from -0.21 eV to -0.14 eV, which is closer to zero. If we continue with the introduction of nickel atoms, the ΔG_{H^*} of Ni:Co₃S₄ changes to 0.08 eV. In the B termination (Figure 2.13c), the ΔG_{H^*} of Co₃S₄ (-0.12 eV) is also closer to zero than Co₃O₄ (-0.15 eV). Remarkably, after Ni doping, Ni:Co₃S₄ has a rather favorable ΔG_{H^*} of -0.10 eV. For both A and B terminations, the ΔG_{H^*} of Ni:Co₃S₄ is closest to zero, indicating that the introduction of sulfur and nickel atoms can decrease the free energy of hydrogen adsorption. This also suggests that Ni:Co₃S₄ can provide the best HER activity among all the four catalysts, which matches well with the experimental results.

For the OER processes, four elementary reaction steps have been considered. Figure 2.12(d-g) show the calculated free energy profiles along the OER pathway for the A termination of the four systems. For Co₃O₄, Co₃S₄ and Ni:Co₃S₄ systems, the conversion of OH* to O* process is the RDS, and the corresponding theoretical overpotentials (η) of above three systems are 0.82 V, 0.44 V and 0.52 V respectively. However, the RDS for Ni:Co₃O₄ is the conversion of OOH* to O₂ process, corresponding to a η of 0.71 V. In the A termination, the overpotential of the four systems decreases in sequence of Co₃O₄, Ni:Co₃O₄, Ni:Co₃S₄ and Co₃S₄, suggesting that the introduction of sulfur and nickel atoms is effective in reducing the free energy barrier of OER process and the corresponding overpotential. Also, Co₃S₄ has the smallest overpotential among four systems, revealing that it has a better OER catalytic activity, which in good agreement with the experimental results. As shown in Figure 2.13(d-g), for the B termination of Co₃O₄ and Ni:Co₃O₄ systems, the conversion of OH* to O* process has the largest reaction free energy, and it is the RDS. When it comes to Co₃S₄ and Ni:Co₃S₄ systems, the conversion of O* to OOH* process is the RDS. Contrary to that of A termination, B

termination of Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ show a very similar overpotential of 0.46 and 0.44 V, respectively.

Figure 2.13 (a) Side view and (b) top view of the B termination of $\text{Ni}:\text{Co}_3\text{O}_4$ (110) surface. Co^{3+} , Co^{2+} , Ni, and O atoms are shown in pink, blue, green and red, respectively. (c) Calculated free energy diagram for the HER process on the B termination of four catalysts. Calculated free energy diagram for the OER process on the B termination of Co_3O_4 (d), $\text{Ni}:\text{Co}_3\text{O}_4$ (e), Co_3S_4 (f), and $\text{Ni}:\text{Co}_3\text{S}_4$ (g) and the corresponding theoretical overpotential.

In our study, the tested OER overpotential of Co_3S_4 is smaller than that of $\text{Ni}:\text{Co}_3\text{S}_4$, which coincides with the calculated data in the A termination, suggesting that A termination might be the main existing surface in our catalysts. In addition, no matter A or B termination, the free energy of the intermediates in both HER and OER process decrease after the introduction of sulfur and nickel atoms, which means that electrocatalytic activity of cobalt-based catalysts can be enhanced through sulfuration and nickel doping.

2.6 Conclusion

In summary, cobalt-based catalysts such as Co_3O_4 , $\text{Ni}:\text{Co}_3\text{O}_4$, Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ deposited on Ni foam have been prepared by hydrothermal method. Their catalytic performance for both OER and HER have been evaluated in 1.0 M KOH. Co_3S_4 shows improved OER catalytic performance with a low overpotential $\eta=283$ mV to deliver a constant current density of 10 mA cm^{-2} , while $\text{Ni}:\text{Co}_3\text{S}_4$ shows a HER overpotential $\eta=199$ mV. These catalysts are used in two-electrode electrolyzer cells having an operating voltage of 1.70 V at a constant current density of 10 mA cm^{-2} for at least 40 hours, thus demonstrating high catalytic activity and stability. Additionally, the free energy of adsorbed intermediates for both HER and OER process are studied by DFT calculations. It is shown that the presence of sulfur in cobalt-based catalysts decreases the free adsorption energy and leads to the lower theoretic overpotential, corresponding to the improved HER and OER catalytic performance of the sulfides than that of the oxides. Furthermore, the HER catalytic performance is also enhanced by Ni-doping due to the better catalytic activity of Ni compared with Co. The superior catalytic activity and stability of our Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires open new avenues towards overall water splitting and other practical applications as efficient noble-metal-free catalysts.

Chapter 3 CoMo₂S₄ interconnected porous nanoflakes as bifunctional electrocatalyst

Driven by the excessive use of fossil fuels and rapid aggravation of environmental pollution, it is vital to focus on the development of sustainable and green energy. In considering of the inexhaustible supply of water, H₂ generation by water electrolysis is a promising strategy to solve the environmental problems. As compared to binary metal oxides, ternary metal oxides contains additional active sites due to the specific metal bonding. In addition, their ternary metal sulfides shows better electrocatalytic performance with increased active sites and enhanced charge transport.

3.1 Introduction

The emergence of bifunctional catalysts provides a new possibility for the widespread application and commercialization of overall water splitting.^{112, 115, 129, 132, 149-151} Bifunctional catalysts have a dual electrocatalytic capability for HER and OER in the same electrolyte without the problem in the incompatibility of electrolyte. This simplifies the water electrolysis device and further reduces the costs. Nguyen *et al.* described that the direct growth of binary FeCoOOH nanosheet structure leads to a high electrical conductivity, and thus resulting in the high bifunctional electrocatalytic ability for overall water splitting.⁵⁸ Jin *et al.* presented porous MoO₂ nanosheets having bifunctional catalytic ability for overall water electrolysis, requiring a voltage of 1.53 V to deliver 10 mA cm⁻².⁵³ Li *et al.* investigated the CoS nanoflakes *via* a template-directed technique. The two-electrode electrolyzer of CoS nanoflakes shows a voltage of 1.72 V to reach 10 mA cm⁻².⁵² These bifunctional catalysts have high concentration catalytic active sites and superior charge-transfer kinetics, together with the advantages of nanostructure morphology, resulting in the enhanced catalytic performance of bifunctional catalysts.

As an earth-abundant transition metal, molybdenum and its compounds are extensively studied as promising catalysts for water electrolysis, such as MoO₂,⁵³ Mo_xC,¹⁵² CoO/MoO_x,¹⁵³ CoMoS₄,^{154, 155} CoMoS₄/Ni₃S₂.¹⁵⁶ Jin *et al.* developed template-free and binder-free porous MoO₂ nanosheets on nickel foam, which needs a voltage of 1.53 V to complete water electrolysis.⁵³ Sun *et al.* fabricated amorphous CoMoS₄ by hydrothermal method and investigated the electrocatalytic properties.¹⁵⁴ The related two-electrode electrolyzer cell shows a voltage of 1.72 V to reach 10 mA cm⁻².

Herein, we report CoMoO₆ and CoMo₂S₄ interconnected porous nanoflakes grown on nickel foam substrate that exhibiting good bifunctional electrocatalytic capability for overall water electrolysis in the alkaline electrolyte. The bimetallic catalytic sites between Co and Mo could tune the electron structure and facilitate the hydrogen adsorption, and thus promotes the release

of gaseous product. Being converted to CoMo_2S_4 also introduces high concentration of active sites, and make it possible to obtain highly-efficient catalysts. Additionally, the CoMoO_6 and CoMo_2S_4 catalysts show the nanoflake structure with high surface area, resulting in the increased amount of active site position. This study could make it a new avenue for the design and development of promising catalysts for overall water electrolysis.

3.2 Experimental section

3.2.1 Synthesis of CoMoO_6 and CoMo_2S_4 materials

A combining technique of hydrothermal process and annealing process is used to synthesize the CoMoO_6 interconnected porous nanoflakes. First, the pressed commercial nickel foam was sonication cleaned with deionized water (DI water) and ethanol. After drying with a nitrogen gas gun, the backside of nickel foam was protected by polytetrafluoroethylene tape from solution contamination. Afterward, the nickel foam was immersed in a Teflon-lined stainless steel autoclave containing 60 mL DI water of 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 mmol $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 4 mmol NH_4F , and 10 mmol urea. Subsequently, the autoclave was heated at 120°C for 4 hours. After hydrothermal t, the samples were cleaned with DI water and ethanol. Later on, the sample was annealed at 300°C for 1 hour in air. The average mass loading of CoMoO_6 is 0.7 mg cm^{-2} . Additionally, the precipitated powders generated during the hydrothermal step were washed and annealed following the same process, and finally CoMoO_6 powders were yielded.

In order to synthesize CoMo_2S_4 , the above CoMoO_6 sample underwent an ion exchange reaction in additional hydrothermal treatment. The backside of the above sample was again covered with polytetrafluoroethylene tape and then immersed in the autoclave having 60 mL of $\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$ (300mg) aqueous solution. The autoclave was maintained at 160°C for 6 hours. After cooling down naturally, CoMo_2S_4 was cleaned several times with DI water and ethanol.

The collected CoMoO₆ powders were also treated with the same ion exchange reaction process to obtain the CoMo₂S₄ powders.

3.2.2 Material characterization

A scanning electron microscopy (SEM, JEOL JSM-6700F) and a transmission electron microscopy (TEM, JEOL-2100PLUS) were utilized to detect the morphology and microstructure. The chemical composition was confirmed through X-ray diffraction (XRD, Bruker D2 Phaser). The chemical valence states were characterized by X-ray photoelectron spectroscopy (XPS) with a Thermo Fisher ESCALAB 250Xi machine.

3.2.3 Electrochemical characterization

Electrochemical testing was conducted with a three-electrode glass configuration via a CHI electrochemical workstation. The samples grown on Ni foam and a platinum foil/carbon rod were used as working and counter electrode, respectively, taking an Ag/AgCl (saturated KCl) electrode as the reference. All electrodes were immersed into the 1.0 M KOH electrolyte, and the electrolyte was bubbled with high purity O₂ gas for 15 min before the OER test. All the tests were conducted at room temperature. Before testing, we conducted cyclic voltammetry in the range of 0-0.7 V under 50 mV s⁻¹ for 20 cycles, which is an activation process to stabilize the current and detach any impurity formed on the surface of the electrode. Then, the current-voltage curves were measured at 5 mV s⁻¹. All data were dealt with iR-compensation by the current-interrupt method. Generally, the obtained overpotential is calibrated by subtracting ohmic drop (iR), where *i* is the current related to the overpotential and *R* is the uncompensated cell resistance. Tafel plots were calculated from the above current-voltage curves by fitting the data to the equation $\eta = a + b \log(j)$, with η , *a*, *b* and *j* being the iR-compensated overpotential, Tafel constant, Tafel slope, and current density, respectively. The stability was investigated at

a constant current density 10 mA cm^{-2} by chronopotentiometry method. The electrochemical impedance spectroscopy (EIS) is used to measure the Nyquist plots in the frequency range from 100 kHz to 100 mHz. The current density was calculated based on the geometric area of the electrodes. Potentials obtained in this study were calibrated against the reversible hydrogen electrode (RHE) reference by the following equation: $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.059 \text{ pH} + E (\text{Ag/AgCl vs. RHE})$.

3.3 Results and discussion

The CoMoO_6 nanoflakes are directly grown on Ni foam via a combining technique of hydrothermal and annealing process. Due to the low mass loading and crystallinity, it is difficult to detect the existence of CoMoO_6 and CoMo_2S_4 on the Ni foam. Alternatively, we collect the precipitated powders generated during the first hydrothermal step.

In order to obtain CoMoO_6 , the precursor undergoes an annealing process at 300°C for 1 hour in air. The CoMoO_6 can be converted to CoMo_2S_4 through an ion exchange reaction in an additional hydrothermal process. Additionally, the precipitated powders are treated with the same method as the samples grown on Ni foam, and then studied by XRD to analyze the composition (Figure 3.1). The diffraction peaks of these powders match well with the CoMoO_6 (JCPDS 14-0086) and CoMo_2S_4 (JCPDS 24-0332), respectively. The weak diffraction peak intensity of the samples indicates that CoMoO_6 and CoMo_2S_4 are low crystalline and amorphous. Exclude the peaks related to CoMoO_6 and CoMo_2S_4 , no more diffraction peaks are detected, indicating that no second phase exists in the samples.

The morphology of the samples is examined using SEM (Figure 3.2). Figure 3.2a shows that the CoMoO_6 sample are uniformly covered by numerous interconnected nanoflakes. From the high magnification SEM image (Figure 3.2b), it is seen that the thickness of the nanoflakes is less than 10 nm. Following a second hydrothermal process, the interconnected nanoflakes

morphology of CoMo_2S_4 is almost preserved (Figure 3.2c,d), while the thickness of nanoflakes is slightly increased as compared to CoMoO_6 .

Figure 3.1 XRD patterns of the powders for CoMo_2S_4 (blue line) and CoMoO_6 (red line). ◆ can be indexed to the CoMo_2S_4 (JCPDS 24-0332), and ▲ corresponds to the CoMoO_6 (JCPDS 14-0086).

Figure 3.2 SEM images of (a,b) CoMoO_6 and (c,d) CoMo_2S_4 interconnected nanoflakes grown on Ni foam.

Meanwhile, the microstructure are characterized using TEM (Figure 3.3). In Figure 3.3a,b, it is clearly visible that CoMoO_6 interconnected nanoflakes consist of numerous small particles with diameters in the range 2-5nm, and there are apparent voids in-between those particles. Concerning CoMo_2S_4 sample, the high resolution TEM images (Figure 3.3c,d) also provide clearly evidence of the porous nanoflake microstructure, which is similar as CoMoO_6 . The constituted small particles have a diameter in the range of 2-5 nm. In CoMoO_6 , the lattice spacing of 0.152 and 0.212 nm can be ascribed to diffraction peak (20) of 60.7° and 43.3° , respectively. As for CoMo_2S_4 , the lattice fringes separated by 0.202 and 0.210 nm could be associated with the (402) and (204) plane, respectively. These results are matched well with the XRD results. Furthermore, elemental mapping images show the elemental distribution in CoMoO_6 and CoMo_2S_4 nanoflakes (Figure 3.3e-l). The Co, Mo, O, or S elements are evenly distributed in CoMoO_6 and CoMo_2S_4 .

Figure 3.3 TEM images of (a,b) CoMoO_6 and (c,d) CoMo_2S_4 nanoflakes. Elemental mapping images of Co, Mo, O, and S elements in (e-h) CoMoO_6 and (i-l) CoMo_2S_4 samples.

The surface chemical states of CoMoO_6 and CoMo_2S_4 nanoflakes are investigated by XPS (Figure 3.4,3.5). All the spectra are corrected according to the C 1s spectrum. The full survey spectra provide the evidence of the characteristic peaks of Co 2p, Mo 3d, O 1s and S 2p, indicating the presence of Co, Mo, O and S elements (Figure 3.4). In the Co 2p spectrum of CoMoO_6 (Figure 3.5a), two main peaks (782.0 and 797.5 eV) are observed, associating with the Co $2p_{3/2}$ and Co $2p_{1/2}$ spin orbit, giving strong evidence that the oxidation states of Co are Co^{2+} and Co^{3+} .^{55, 60} In addition, two peaks at 787.1 and 804.2 eV are the satellite peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ spin orbits, respectively. In the Mo 3d spectrum (Figure 3.5c), the peaks at 232.1 and 235.5 eV are associated with the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ spin-orbits, revealing the existence of Mo on the surface of CoMoO_6 . In the O 1s spectrum (Figure 3.5e), we can observe one main peak at 530.4 eV, ascribed to the O species in the metal oxide bond. The 531.8 eV peak may originate from the oxygen defects in the sample. Concerning the Co 2p spectrum of CoMo_2S_4 nanoflakes (Figure 3.5b), the position of the peaks are almost the same as those of CoMoO_6 . However, the peak intensity become much weaker, indicating the low crystallinity and bonding of CoMo_2S_4 . More clearly, the Mo 3d spectrum of CoMo_2S_4 is extremely noisy with low intensity (Figure 3.5d). In the S 2p spectrum (Figure 3.5f), the peaks locate at 162.7 and 163.4 eV validate the S species in the metal sulfide bond.

Figure 3.4 Full survey XPS spectra of (a,) CoMoO_6 and (b,) CoMo_2S_4 .

Figure 3.5 High resolution XPS spectra of (a,c,e) CoMoO_6 and (b,d,f) CoMo_2S_4 : (a,b) Co 2p spectrum, (c,d) Mo 3d spectrum, (e) O 1s spectrum, and (f) S 2p spectrum

The OER and HER electrochemical properties of CoMoO_6 and CoMo_2S_4 nanoflakes are evaluated by the current-voltage curves (Figure 3.6a). In the current-voltage curves, two catalysts exhibit a small oxidation peak before the onset of OER, which can be ascribed to the conversion from Co(III) to Co(IV). The CoMoO_6 electrode shows an OER overpotential (η) of 316 mV to reach 10 mA cm^{-2} . Following the ion exchange reaction, the OER η decreases to 306 mV at 10 mA cm^{-2} for the CoMo_2S_4 electrode. In the HER part, the CoMo_2S_4 electrode

needs an overpotential of 162 mV at 10 mA cm^{-2} , much lower than that of CoMoO_6 electrode (249 mV). It is known that the lower overpotential means the superior electrocatalytic activity. The improved catalytic performance of CoMo_2S_4 electrode can be attributed to the synergistic effect of the Co-Mo-S bond. The catalytic activity of host catalysts can be enhanced by doping or replacing by another metal/non-metal element due to the synergistic effect.^{7, 60, 150, 154}

Figure 3.6 (a) The iR -compensated current-voltage curves of CoMoO_6 and CoMo_2S_4 electrodes for OER and HER process. The scan rate is 5 mV s^{-1} . (b) Linear fitted Tafel plots based on current-voltage curves. (c) Stability tests under 10 mA cm^{-2} for 10 hours. (d) Nyquist plots in the frequency range from 100 kHz to 100 mHz. The black lines are the corresponding fittings to the equivalent circuits.

To gain in-depth insight into the kinetics of the electrodes, the Tafel plots are studied (Figure 3.6b). In Figure 6b, the OER Tafel slope of the CoMo_2S_4 electrode is 66 mV dec^{-1} , lower than that of CoMoO_6 (71 mV dec^{-1}), hinting the superior kinetics and faster reaction rates of OER

process for CoMo₂S₄. This manifests that the composition change from oxide into sulphide could greatly enhance the OER kinetics. Meanwhile, the HER Tafel slope of the CoMo₂S₄ catalyst is as low as 116 mV dec⁻¹, compared with CoMoO₆ (132 mV dec⁻¹). It has been reported that the rate-determining step of HER is based on the analysis of Tafel slopes.^{28, 29} The Tafel slopes of 30, 40, or 120 mV dec⁻¹ can be indexed to the rate-determining step of Tafel, Heyrovsky, or Volmer reaction, respectively.^{34, 35, 126} According to the Tafel slopes in our work, the hydrogen evolution on CoMoO₆ and CoMo₂S₄ electrode surfaces could be ascribed to a Volmer and Volmer-Heyrovsky mechanism, respectively.

The durability is another crucial parameter to access the electrocatalytic properties of electrodes. In Figure 3.6c, an initial OER η of 312 mV is required for CoMoO₆ to deliver 10 mA cm⁻². The η gradually increases to 325 mV after 10 hours test. When we proceed to the sulfurized catalyst, the η of CoMo₂S₄ decreases from 310 mV to 282 mV after 10 hours stability measurements, showing 43 mV lower than that of CoMoO₆. In the HER stability measurement, the initial η of CoMoO₆ and CoMo₂S₄ are 251 and 170 mV, respectively. After 10 hours tests, their overpotentials change to 222 and 195 mV, respectively. The η of the stability tests are matched well with the results in the current-voltage curves. Here, the decrease of the η absolute value at the beginning of the test, may be caused by the so-called activation process, which could be an oxidation process occurring at a rather sluggish rate and gradually reaching to a steady status. This process may produce new boundaries in the interconnected particles, leading to the generation of additional active sites. Usually this process could slightly increase the catalytic capability. In addition, the gaseous products from the testing could blow away the residues at the interface, which is beneficial to enhance the electrocatalytic ability.¹³⁰⁻¹³²

The EIS results are used to further investigate the kinetics of the catalysts (Figure 3.6d), which are fitted with an equivalent circuit of two resistors having a parallel constant phase element. The resistor at high frequency region is associated with surface porosity (R_p), the

resistor at low frequency is associated with charge transfer resistance (R_{ct}). Based on the equivalent circuit, the R_{ct} of CoMo_2S_4 (63.5 Ω) is smaller than that of CoMoO_6 (102.2 Ω), revealing that the charge-diffusion resistance of CoMo_2S_4 is smaller at the interface. This could leads to faster charge diffusion kinetics and higher reaction rates of CoMo_2S_4 . Combining with results of overpotential and Tafel slopes, it reveals that both the OER and HER activity of CoMoO_6 could be remarkably improved by the sulfuration treatment.

Figure 3.7 Overall water electrolysis of $\text{CoMo}_2\text{S}_4//\text{CoMo}_2\text{S}_4$ system in 1.0 M KOH. Two CoMo_2S_4 electrode act as OER and HER electrode. (a) The iR -compensated current-voltage curves of $\text{CoMo}_2\text{S}_4//\text{CoMo}_2\text{S}_4$ system with a scan rate of 5 mV s^{-1} . (b) Stability tests of $\text{CoMo}_2\text{S}_4//\text{CoMo}_2\text{S}_4$ system under 10 mA cm^{-2} for 10 hours.

Figure 3.8 SEM images of (a) tested CoMoO_6 electrode and (b) tested CoMo_2S_4 electrode.

In Figure 3.7, the overall water electrolysis tests are measured in a two-electrode cell with the electrolyte of 1.0 M KOH. Here, two CoMo_2S_4 electrodes work as the HER and OER

electrode (denoted as CoMo₂S₄//CoMo₂S₄). As shown in Figure 3.8a, this cell requires a potential of 1.65 V to reach 10 mA cm⁻² current density, thus revealing a combined overpotential of 420 mV to complete the overall water electrolysis. Furthermore, this cell exhibits high stability (Figure 3.7b). The initial operating voltage is around 1.65 V, and slightly decreases to 1.61 V after 10 hours. As shown in Figure 3.8, it is highly visible that tested samples have much thicker nanoflakes than that of pristine samples. In addition, the contrast of the image is quite low, indicating that the conductivity of tested sample is inferior. It may have surface reconstruction during the measurements. This indicates that the structure stability of the hydroxide samples is inferior, which may result in the inferior stability of the catalysts.

3.5 Conclusion

CoMoO₆ and CoMo₂S₄ interconnected porous nanoflakes are investigated as bifunctional catalysts. The obtained CoMo₂S₄ electrode shows a low OER/HER overpotential of 306/162 mV to reach 10 mA cm⁻². Here, the material and nanostructure design, are effective in increasing the concentration of active sites and promoting the charge transport capability. Additionally, the well-separated nanostructure promotes the contact of solid-electrolyte interface and the release of gaseous product. These advantages benefit the catalytic capability of the catalysts. The two-electrode electrolyzer cell with above bifunctional catalysts maintains a voltage of 1.65 V to reach 10 mA cm⁻² for at least 10 hours, suggesting high electrocatalytic capability and stability. This work is both technologically and academically important for the mass production of H₂ from splitting water.

Chapter 4 Hierarchical Cu(OH)₂@Co(OH)₂ nanotrees for water oxidation

The accelerated development of human civilization has triggered the urgency of investigating novel cost-effective and high-efficiency energy conversion/storage systems to fulfil the ever-growing energy demands. H₂ generation from water electrolysis attracts tremendous attention as a sustainable technique to obtain energy. Considerable efforts are currently devoted to the development of water electrolysis. In order to increase the catalytic active sites, reaction kinetics, and charge transportation, an effective strategy is to design three dimensional hierarchical nanostructures. Herein, we have investigated the hierarchical hybrid Cu(OH)₂@Co(OH)₂ nanotrees as efficient OER electrocatalyst. This hierarchical nanotree structure is derived from the decoration with leaves-like ultrathin Co(OH)₂ nanoflakes on the surface of branch-like Cu(OH)₂ nanowires.

4.1 Introduction

Recently, 3d transition metal and their compounds are intensively investigated as efficient electrocatalysts due to their rich source and special d electronic configuration.^{46, 54, 55, 60, 61, 64, 157-159} Among all these promising catalysts, earth-abundant Cu and Co based materials are highly desired for OER. For example, Kuznetsov *et al.* and Tong *et al.* fabricated bimetallic Co-Mo alkoxide and oxygen-deficient Co₃O₄ quantum dots as efficient electrocatalysts to enhance the oxygen evolution electrolysis, respectively.^{54, 55} Cao *et al.* reported the investigation of Cu-Ni sulfide nanowires for improving the water oxidation efficiency.⁵⁶ Chen *et al.* fabricated Cu-Co(OH)₂ nanosheets having superior electrocatalytic activity with an OER overpotential of 300 mV at 10 mA cm⁻².⁵⁷

It has been confirmed that the active materials of transition metal oxide electrocatalysts are the corresponding hydroxides/oxyhydroxides.^{57, 62, 63} In considering of this fact, the development of transition metal hydroxides/oxyhydroxides electrocatalysts may provide a new avenue towards the water oxidation electrolysis.^{157, 160, 161} Specially, those transition metal hydroxides/oxyhydroxides with unique nanostructures show additional active sites and impressive charge transfer rates, which is beneficial for the high-efficient oxygen evolution. Zhang *et al.* prepared CNTs@FeOOH showing an outstanding OER performance of an overpotential of 250 mV at 10 mA cm⁻².⁶⁴ Liang *et al.* reported a high temperature/pressure hydrothermal synthesis of NiCo LDH nanoplates with an overpotential of 367 mV to reach 10 mA cm⁻².⁶³ Andronescu *et al.* investigated the OER catalytic capability of NiFe LDH in different alkaline electrolyte, and evaluated their durability at realistic conditions for industrial application.¹⁶²

Herein, we present a rapid preparation of hierarchical hybrid Cu(OH)₂@Co(OH)₂ nanotrees with superior catalytic ability towards water oxidation. This rapid synthesis involves a combined technique of an anodization process and an electrodeposition process. The

hierarchical $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees show several structural advantages. Firstly, the catalysts are directly grown on the conductive Cu foil substrate and no additional binder is required, and thus minimizing the resistance and gaining strong adhesion. Secondly, the hierarchical nanotree network structures consist of one dimensional nanowires and interconnected ultrathin nanoflakes, acting as interwoven electron highways, which provides a high electrolyte contact area and greatly enhances the charge transfer of the catalysts. Lastly, the combining of $\text{Cu}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ may enjoy the synergistic effect and show better OER catalytic activity. The electrochemical measurements prove that $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ shows a high OER catalytic ability with low onset potential, high OER activity, and excellent stability.

4.2 Experimental Section

4.2.1 Synthesis of $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ materials

An anodization technique is utilized to synthesize the of $\text{Cu}(\text{OH})_2$ nanowires. Following another electrodeposition process, $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees are obtained. In a typical process, Cu foil was used as the substrate and starting material in the growth of $\text{Cu}(\text{OH})_2$ nanowires. First, the compressed Cu foils were cut into standard pieces (1 cm $\times$ 1 cm). Then, washing the Cu foils in acetone, ethanol, and distilled water for 20 min separately. After drying with a N_2 gas gun, the backside of Cu foil was protected by polytetrafluoroethylene tape from solution contamination. Afterward, we conducted the anodization in a two-electrode system in 3.0 M KOH with a CHI 760d electrochemical workstation. Here, the Cu foil acts as the working electrode and platinum foil acts as the counter electrode. The anodizing current is 10 mA cm^{-2} , while the duration is 300s. After rinsing with distilled water, the blue $\text{Cu}(\text{OH})_2$ nanowires were obtained.

In order to prepare $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees, another electrodeposition process were performed in a three-electrode system in 0.05 M $\text{Co}(\text{NO}_3)_2$ solution. The as-prepared $\text{Cu}(\text{OH})_2$,

platinum foil, and Ag/AgCl act as the working electrode, counter electrode, and reference electrode, respectively. The operating potential of electrodeposition process is -0.9 V, while the operating duration is 300s. After rinsing with distilled water, the $\text{Cu(OH)}_2\text{@Co(OH)}_2$ nanotrees were obtained.

Additionally, pure Co(OH)_2 were electrodeposited on copper foil to study the composition of the nanoflakes. The electrodeposition duration was 300s. Moreover, Co(OH)_2 nanoflakes with different electrodeposition duration, such as 100 and 200s, were deposited on Cu(OH)_2 nanowires samples, and their Cu:Co atomic ratio were investigated.

4.2.2 Material characterization

The morphology and size of materials were confirmed using scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL-2100PLUS). The chemical composition was detected by X-ray diffraction (XRD, Bruker D2 Phaser) and a Thermo Fischer iCAP 6000 series inductively coupled plasma optical emission spectrometer (ICP-OES). The chemical valence states were characterized by X-ray photoelectron spectroscopy (XPS) with a Thermo Fisher ESCALAB 250Xi machine.

4.2.3 Electrochemical characterization

Electrochemical testing was conducted in a three-electrode glass configuration *via* a CHI electrochemical workstation. The samples grown on Cu foil were used as working electrodes, a platinum foil as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference. All electrodes were immersed into the 1.0 M KOH electrolyte, and the electrolyte was bubbled with high purity O_2 gas for 15 min before the test. All the tests were conducted at room temperature. Before any measurements were performed, cyclic voltammetry from 0 to 0.7 V at 50 mV s^{-1} were carried out 20 cycles, which is an activation process to stabilize the

current and detach any impurity formed on the surface of the electrode. Then, the linear sweep voltammetry (LSV) tests were performed at 5 mV s^{-1} . All data were dealt with iR -compensation by the current-interrupt method. The main point of this method is to consider uncompensated cell resistance (R). Generally, the obtained potential is corrected by subtracting ohmic drop (iR), where i is the current related to the potential. Tafel plots were derived from the above LSV curves by fitting the data to the equation $\eta = a + b \log(j)$, where η is the iR -compensated overpotential, a is the Tafel constant, b is the Tafel slope, and j is the current density. The stability was investigated at fixed current densities (10 , 20 , and 30 mA cm^{-2}) by chronopotentiometry. The current density was calculated based on the geometric area of the electrode. Potentials obtained in this study were calibrated against the reversible hydrogen electrode (RHE) reference by the following equation: $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.059 \text{ pH} + E (\text{Ag/AgCl vs. RHE})$. In our study, η_{10} is the iR -compensated overpotential which can achieve a current density of 10 mA cm^{-2} .

4.3 Results and discussion

In order to confirm the composition of the samples, X-ray diffraction (XRD) characterizations are performed. As shown in Figure 4.1a, three strong diffraction peaks at 43.3° , 50.4° , and 74.1° are assigned to the (111), (200), and (220) planes of Cu (JCPDS 04-0836), respectively, originating from the Cu foil substrate. After the anodization process, the XRD pattern confirms the crystallization of Cu(OH)_2 . More well-defined diffraction peaks appear after the anodization process, which in good agreement with the orthorhombic structure of Cu(OH)_2 (JCPDS 13-0420). After the Co(OH)_2 electrodeposition, no obvious additional peaks are observed from the XRD pattern, suggesting an extremely low crystallinity of Co(OH)_2 phase. Furthermore, we have prepared pure Co(OH)_2 nanoflakes. As shown in Figure 4.2a, exception the diffraction peaks from copper foil, the additional peaks correspond to the

Co(OH)_2 (JCPDS 51-1731). The SEM images also prove the nanoflake morphology of Co(OH)_2 (Figure 4.2b,c).

Figure 4.1 (a) XRD patterns of Cu foil (black line), Cu(OH)_2 (blue line), and $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ (red line). $\blacklozenge$ is indexed to the Cu (JCPDS 04-0836), and $\blackspade$ corresponds to the Cu(OH)_2 (JCPDS 13-0420). (b) Full survey of XPS spectrum of Cu(OH)_2 and $\text{Cu(OH)}_2@ \text{Co(OH)}_2$. (c) High resolution Cu 2p spectrum. (d) High resolution Co 2p spectrum.

Figure 4.2 (a) XRD patterns of pure Co(OH)_2 nanoflakes grown on copper foil. $\blacklozenge$ can be indexed to the Cu (JCPDS 04-0836), and $\clubsuit$ corresponds to the Co(OH)_2 (JCPDS 51-1731). (b,c) SEM images of Co(OH)_2 nanoflakes.

The X-ray photoelectron spectroscopy (XPS) analysis makes a further clarification about the composition and chemical state of the samples (Figure 4.1b-c). In the full survey of XPS spectrum, additional peaks in the range of 810-770 eV are indexed to the Co element, which has proven the deposition of Co(OH)_2 . The Cu 2p spectrum shows typical characteristics of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spin orbits with two corresponding satellite peaks, suggesting the existence of strong Cu^{2+} states, consistent with the XRD results. In the Co 2p spectrum, the dominating peaks around 782 and 798 eV are ascribed to the Co $2p_{3/2}$ and Co $2p_{1/2}$ spin orbits, respectively. Hence, the XRD together with XPS results manifest the generation of Cu(OH)_2 and Co(OH)_2 .

As shown in Figure 4.3a,b, the scanning electron microscopy (SEM) images clearly show that the Cu(OH)_2 nanowires densely grow on the Cu foil substrate, having a diameter around 100-150 nm and smooth surface. After electrodeposition with Co(OH)_2 , interconnected ultrathin nanoflakes deposit on the original nanowires (Figure 4.3e,f). Here, the nanowires can be regarded as the branches of trees, while the interconnected ultrathin nanoflakes act as the huge leaves of trees. The two samples are also characterized by transmission electron microscopy (TEM) to give further insight of the microstructures. Figure 4.3c confirms the nanowire morphology of Cu(OH)_2 , and the corresponding high-resolution TEM image (Figure 4.3d) shows well-defined lattice fringes with interplanar distances of 2.49 Å indexing to the (111) plane of Cu(OH)_2 . It is also highly visible that $\text{Cu(OH)}_2@\text{Co(OH)}_2$ are composed of ultrathin nanoflakes coated on the nanowires (Figure 4.3g), and this hierarchical nanotree structure is consistent with SEM result. In Figure 4.3h, the well-resolved fringes with distance of 2.70 Å matches well with the (101) plane of Co(OH)_2 . Interestingly, irregularly distributed small pores are present on surface of Co(OH)_2 nanoflakes, which may be created by the high-energetic electron beam of the electron microscopy.

Figure 4.3 (a-d) SEM and (e-h) TEM images of (a,b,e,f) Cu(OH)_2 nanowires and (c,d,g,h) $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees grown on copper foam.

Furthermore, $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees with different Co(OH)_2 electrodeposition duration are prepared and detected by the inductively coupled plasma optical emission spectrometer (ICP-OES). In Table 4.1, ICP-OES analysis further confirms the existence of Cu and Co elements and their distribution in the $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees. It is clearly seen

that the Co concentration is gradually increased when extending the electrodeposition duration from 100s to 300s. Concerning the $\text{Cu(OH)}_2\text{@Co(OH)}_2(300\text{s})$ sample, the atomic ratio of Co:Cu is 86.90%.

As shown in the SEM images (Figure 4.6), when the duration is shorter than 300s, the nanowires are not fully covered by the Co(OH)_2 nanoflakes. It is highly visible that the nanoflakes only cover the bottom part of the nanowires in the 100s sample, the middle and top of nanowires are still smooth. As for the 200s sample, some nanowires are already fully or half-fully covered by nanoflakes. If the duration increases more than 300s, the nanoflakes layer will be too thick. So we selected the $\text{Cu(OH)}_2\text{@Co(OH)}_2(300\text{s})$ sample as the main catalysts.

Figure 4.4 SEM images of (a) $\text{Cu(OH)}_2\text{@Co(OH)}_2(100\text{s})$ and (b) $\text{Cu(OH)}_2\text{@Co(OH)}_2(200\text{s})$ nanotrees grown on copper foam.

Table 4.1 Atomic ratio of Cu(OH)_2 and $\text{Cu(OH)}_2\text{@Co(OH)}_2$ materials determined by ICP-OES measurements.

Material	Cu(OH)_2		$\text{Cu(OH)}_2\text{@Co(OH)}_2$ (100s)		$\text{Cu(OH)}_2\text{@Co(OH)}_2$ (200s)		$\text{Cu(OH)}_2\text{@Co(OH)}_2$ (300s)	
Element	Cu	Co	Cu	Co	Cu	Co	Cu	Co
Concentration (ppm)	2.69	0.001	2.50	0.596	1.81	1.08	2.29	1.99
Atom ratio of Co:Cu	0		23.84%		59.67%		86.90%	

The electrocatalytic capability of the samples is first evaluated by linear sweep voltammetry (LSV) in O_2 -saturated 1.0 M KOH. In Figure 4.5a, the $\text{Cu(OH)}_2\text{@Co(OH)}_2$ electrode requires

an overpotential of 283 mV to reach the OER current density of 10 mA cm^{-2} , nearly 40 mV lower than that of Cu(OH)_2 electrode (320 mV). Tafel slope is another crucial parameter to evaluate the electrocatalytic performance of the electrodes. The Tafel slope of the $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees is as low as 48 mV dec^{-1} , as compared to Cu(OH)_2 nanowires (52 mV dec^{-1}), indicating the improved OER kinetics and faster reaction rates of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees (Figure 4.5b). Both LSV curves and Tafel plots prove that the hierarchical network structure of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees is beneficial to enhance the OER electrocatalytic activity.

To gain in-depth insight into the electrocatalytic performance of the electrodes, stability measurements are performed (Figure 4.5c). The overpotentials of the stability tests match well with the results in the LSV curves. In the initial of the tests, an overpotential of 325 mV is required for Cu(OH)_2 electrode to reach 10 mA cm^{-2} . The overpotential rapidly increases to 373 and 425 mV when changes the current density to 20 and 30 mA cm^{-2} , respectively. When we proceed to the $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees electrode, the overpotential is as low as 290, 340, and 370 mV under 10, 20, and 30 mA cm^{-2} , respectively. At the end of stability tests, the $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ electrode shows slightly increase of the overpotential (297 mV) compared with Cu(OH)_2 electrode (345 mV), when switching the current density back to 10 mA cm^{-2} . This suggesting the superior stability of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees electrode. After 20 hours stability tests, the LSV and Tafel results are collected and analyzed again (Figure 4.5 a,b,d). The required overpotentials of tested Cu(OH)_2 and $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ electrode are 331 and 292 mV to deliver 10 mA cm^{-2} , respectively, having corresponding Tafel slopes of 57 and 52 mV dec^{-1} .

Figure 4.5 Comparison of OER performances of Cu(OH)_2 and $\text{Cu(OH)}_2@\text{Co(OH)}_2$ electrodes in 1.0 M KOH electrolyte. (a) iR -compensated LSV curves of water electrolysis for pristine and tested electrode at a scan rate of 5 mV s^{-1} ; (b) Corresponding Tafel plots with associated linear fittings; (c) Stability test under different current densities for 20 hours; (d) Comparison of η_{10} and Tafel slopes for all the electrodes before and after stability tests; (e) Nyquist plots in the frequency range from 100 kHz to 100 mHz; (f) The linear relationship between the capacitive current and different scan rates in the potential range of 1.20-1.30 V vs. RHE.

To further study the kinetics of the electrodes, we recorded the electrochemical impedance spectroscopy (EIS) results and fitted with an equivalent circuit of two resistors having a parallel

constant phase element (Figure 4.5e). The resistor at high frequency region is associated with surface porosity (R_p), the resistor at low frequency is associated with charge transfer resistance (R_{ct}). The R_{ct} of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ (4.6 Ω) is smaller than that of Cu(OH)_2 (9.7 Ω), suggesting the smaller charge-diffusion resistance of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ at the interface, and thus resulting in the faster charge diffusion kinetics and higher reaction rates. Combining with overpotential and Tafel results, it reveals that the OER activity of Cu(OH)_2 nanowires are remarkably improved by the electrodeposition of Co(OH)_2 nanoflakes. In Figure 4.5f, the electrochemical double-layer capacitance (C_{dl}) is measured to discuss the active surface area of the two electrodes. The $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ electrode exhibits a C_{dl} of 144.4 mF cm^{-2} , which is 4.2 times as high as that of Cu(OH)_2 electrode (37.77 mF cm^{-2}), revealing a high active surface area of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ electrode. Hence, it can be concluded that this hierarchical hybrid structures not only enhances the electrical conductivity, but also maintains the high surface area, and thus leading to the improved electrocatalytic capability of $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ nanotrees.

As shown in Figure 4.6a, the XRD patterns recorded after stability measurements manifest that the monoclinic CuO phase (JCPDS 45-0937) is generated in two electrodes after the electrocatalytic measurements, and there is still no obvious peaks for Co element. For the XPS results (Figure 4.6b-d), the peaks of Cu 2p and Co 2p spectra maintain the same position compared with as-prepared samples, corresponding to the Cu^{2+} and Co^{2+} state. However, the peak intensity has changed a bit, which may due to the generation of CuO phase and occurrence of side reaction in the long-term stability tests. In the SEM images of tested Cu(OH)_2 (Figure 4.7a,b), it is highly visible that the morphology has greatly changed, almost cannot recognize the nanowire structure. Nevertheless, the tested $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ still preserve the nanowire morphology, while the cross-links ultrathin nanoflakes are disappeared (Figure 4.7c,d). These morphology changes may be caused by the generation of CuO phase, and the

$\text{Cu(OH)}_2@ \text{Co(OH)}_2$ may be a bit more stable by taking the advantages of the hierarchical hybrid nanotree structure.

Figure 4.6 (a) XRD patterns of Cu(OH)_2 (red line), and $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ (blue line) electrodes after 20 hours stability measurements. (b) Full survey of XPS spectrum of the tested $\text{Cu(OH)}_2@ \text{Co(OH)}_2$. (c) High resolution Cu 2p spectrum. (d) High resolution Co 2p spectrum.

Figure 4.7 SEM images of (a,b) Cu(OH)_2 and (c,d) $\text{Cu(OH)}_2@ \text{Co(OH)}_2$ electrodes after 20 hours stability measurements.

4.4 Conclusion

In summary, we have investigated the hierarchical hybrid $\text{Cu}(\text{OH})_2@ \text{Co}(\text{OH})_2$ nanotrees as efficient OER electrocatalyst. Following an combined synthesis of an anodization process and a electrodeposition process, leaves-like ultrathin $\text{Co}(\text{OH})_2$ nanoflakes are grown on the branch-like $\text{Cu}(\text{OH})_2$ nanowires. As evidenced by electrochemical characterization, the obtained electrode shows a low OER overpotential of 283 mV to reach a current density of 10 mA cm^{-2} . After 20 hours multi-current density stability test, the electrode shows negligible degradation with an overpotential of 290 mV to deliver 10 mA cm^{-2} , revealing high electrocatalytic capability and stability. It is also proven by other measurements that the reaction kinetics and charge transport capability is improved after forming the hierarchical hybrid nanotrees. Therefore, our material and nanostructure design, are effective in increasing the active sites exposure and promoting the charge transport capability. Additionally, the well-separated hierarchical nanostructure facilitates the contact of solid-electrolyte interface and the release of gaseous product. These advantages benefit the catalytic capability of the catalysts. This work is both technologically and academically important for the water oxidation application, providing new insights for enhancing the transition metal electrocatalysts to realize low-cost water oxidation in alkaline media.

Chapter 5 Oxygen-deficient WO₃ for efficient PEC water splitting

H₂ generation from PEC water splitting is a promising strategy to cope with the energy crisis in a sustainable way. Herein, we report on two-step annealed oxygen-deficient WO₃ plates grown on tungsten foil for PEC water splitting application. When grown according to the conventional one-step annealing process, WO₃ exhibits low photocurrent density and inferior photocurrent retention. In contrast, after a two-step annealing process, WO₃ contains a higher concentration of oxygen deficiency acting as shallow donors, thus leading to improved charge separation. Importantly, this results in a substantial photocurrent increase and higher material stability, two criteria that are of utmost importance for efficient photoelectrochemical water splitting.

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5.1 Introduction

Photoelectrochemical water splitting (PEC) is a promising strategy for hydrogen production because it has the inexhaustible supply of water and solar energy.^{92, 163} Among the promising visible-light photosensitive semiconductors, inexpensive and the non-toxic tungsten trioxide (WO_3) stands out as the catalysts in PEC application.^{77, 78} WO_3 is an n-type semiconductor with a bandgap around 2.6 eV for the visible light absorption and a suitable valence band edge for water oxidation as photoanode.⁷⁹ Furthermore, WO_3 is stable and resistant in the acidic solution (<pH 4).⁷⁸

Different approaches have been proposed to enhance the performance of WO_3 in PEC application. As reported, metal-doping is a useful technique to reduce the WO_3 bandgap, which leads to the enhancement of visible light absorption and thus improves the PEC performance.^{78, 83, 164} Some groups utilize different nanostructures or modified WO_3 surface to improve photocatalytic activity.^{77, 84, 85, 165} Promoting the charge separation at the interface by the formation of hybrid heterojunction structures or p/n junctions is another important method to enhance photocatalytic ability, such as $\text{WO}_3/\text{g-C}_3\text{N}_4$,^{86, 166} $\text{WO}_3/\text{BiVO}_4$,^{88, 89} and $\text{WO}_3/\text{Cu}_2\text{O}$.⁹⁰ However, the practical application of WO_3 is still suffering from their high electron-hole recombination rate (inferior charge separation).

Recently, oxygen-deficient catalysts have been employed to enhance the charge separation for water oxidation. Zhu *et al.* reported that air plasma treatment can introduce oxygen vacancies in ultrathin $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes, leading to a significant enhancement in the application of visible light PEC.¹⁶⁷ Lei *et al.* described oxygen-deficient In_2O_3 porous sheets with narrowed bandgap and improved carrier separation efficiency, thus promoting the photoelectrochemical water oxidation.¹⁶⁸ Yousaf *et al.* prepared a heterostructure photocatalysts of oxygen-deficient WO_{3-x} nanorods and $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ with efficient charge separation, and leads to highly efficient H_2 evolution rare.¹⁶⁹ Liu *et al.* investigated the surface

oxygen vacancy engineering of WO_3 by tuning the treatment time in H_2O_2 solution and applied it in the photocatalytic water splitting.¹⁷⁰ Also, there are some other meaningful research works about oxygen-deficient WO_3 in photoelectrochemical water oxidation application.¹⁷¹⁻¹⁷³ It has been discussed that oxygen deficiencies can work as the electron donors to improve the electrical conductivity and charge density, resulting in the better carrier transfer and separation efficiency, thus finally leading to better water splitting performance.^{169, 174, 175}

In this work, we propose a combined synthesis of a hydrothermal process and a two-step annealing process to obtain oxygen-deficient WO_3 . The presence of oxygen deficiency increases the donor density of WO_3 and leads to better charge carrier separation. Benefited from the two-step annealing, the WO_3 sample second treated at 700 °C for 1 hour shows improved photocurrent density of 0.66 mA cm^{-2} at 1.51 V vs. RHE. This is almost twice as high as that of one-step annealed WO_3 sample (0.32 mA cm^{-2} at 1.51 V vs. RHE). More importantly, after the second annealing process at 700 °C, the WO_3 photocurrents remain more than 98% stable over 24 hours, even reach to as many as 48 hours for some samples. These results indicate that the oxygen deficiency in WO_3 can be tuned through a two-step annealing method, which leads to the improved photocurrent density and super higher stability. This work offers a feasible strategy toward the enhancement of photocatalysts for efficient PEC water splitting.

5.2 Experimental section

5.2.1 Synthesis of WO_3 materials

The WO_3 plate was synthesized by a combining technique of hydrothermal treatment and two-step annealing treatment (Figure 5.1). First, the commercial tungsten foil was sonication cleaned with ethanol and de-ionized (DI) water for 15 min each. After drying with a nitrogen gas gun, the tungsten foil was immersed in a Teflon liner containing 50 mL DI water of 1.5 M

nitric acid and 80 mg ammonium fluoride. Then, the Teflon liner was put in the stainless steel autoclave and heated at 150°C for 3 hours. After cooling down naturally, the fabricated yellow precursor was washed with DI water and dried in an oven at 60°C for 5 hours.

Figure 5.1 Preparation scheme of as-grown and oxygen-deficient WO_3 samples.

In the first annealing treatment, the yellow precursor was heated up from room temperature to 550°C in 30 min and annealed at 550°C for different duration (1-6 hours) in air. This turned the yellow precursor blue, suggesting the formation of WO_3 . Here, we chose the sample annealed at 550°C for 3 hours and denoted it as $\text{WO}_3\text{-S0}$.

In order to obtain oxygen-deficient WO_3 , the above blue $\text{WO}_3\text{-S0}$ sample was annealed again in air. The heating rate was 3°C per minute for the second annealing process. The samples annealed again at 700°C for 60 min were denoted as $\text{WO}_3\text{-S1}$. After the second annealing treatment, the blue sample became olive yellow. Additionally, the samples twice-annealed at 670°C for 30 min, 700°C for 30 min, are denoted as $\text{WO}_3\text{-S2}$, and $\text{WO}_3\text{-S3}$, respectively.

5.2.2 Materials characterization

Field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL JEM-2100PLUS) was used to characterize the morphology of WO_3 samples. The sample chemical compositions were confirmed by X-ray diffraction (XRD, Bruker D2 Phaser). The chemical valence states and oxygen vacancies of

WO₃ samples were measured by X-ray photoelectron spectroscopy (XPS) with a Thermo Fisher ESCALAB 250Xi machine. Room temperature Raman measurements measurement were utilized to investigate the structure change and performed with a WITec CRM 200 system (an excitation laser with a wavelength of 532 nm). UV-visible spectrophotometer (UV-3600, Shimadzu) was used to record the diffuse reflectance spectra (DRS) of the WO₃ samples. In order to obtain the bandgap, Kubelka–Munk function ($F(R)=\frac{(1-R)^2}{2R}$, where R is the reflectance) is used to calculate the absorption coefficient F(R). After that, we can determine the Tauc Plots ($F(R) \cdot h\nu^{1/2}$ vs. $h\nu$) based on F(R). Then, the slope of the curves in Tauc Plots is the bandgap of WO₃. The WO₃ samples were characterized by photoluminescence (FluoroMAX-4, Horiba scientific).

5.2.3 Photoelectrochemical measurements

Photoelectrochemical measurements were performed by an Autolab electrochemical workstation coupled to a Newport solar simulator (AM 1.5) at room temperature. The WO₃ samples were used as working electrodes, a platinum foil as the counter electrode, and an Ag/AgCl (3.0 M KCl) electrode as the reference. All electrodes were immersed into the 0.5 M Na₂SO₄ electrolyte in a three-electrode quartz glass configuration. Then, linear sweep voltammetry (LSV) tests were performed at 10 mV s⁻¹ under incident chopped light (f = 0.1 Hz). The stability tests were investigated at constant voltage (1.51 V vs. RHE) by chronopotentiometry method. The short-term stability tests were recorded under incident chopped light (f = 0.05 Hz, AM 1.5) for 600s. Then, the above samples were used to perform the long-term stability tests with a chopped light (f = 0.05 Hz, AM 1.5) for 600s every 2 hours or 12 hours, and tested for 24 hours in total. The current density was calculated based on the geometric area of the electrode. The amount of evolved H₂ gas and the faradaic efficiency was measured with at the potential of 1.51 V vs. RHE for 60 min by a gas chromatography (Agilent

7890B with a TCD detector). The incident photon to current conversion efficiency (IPCE) was measured at 1.23 V *vs.* RHE via the electrochemical workstation coupled to the light source with band-pass filters. A Newport 1919-R optical power meter was used to record the monochromatic light intensity. IPCE is expressed by the equation: $IPCE = (1240 * I) / (\lambda * P)$, where I is the photocurrent density (mA cm^{-2}) under the monochromatic light, λ and P are the wavelength (nm) and intensity (mW cm^{-2}) of the light, respectively. Electrochemical impedance spectroscopy (EIS) was performed at the potential of 1.0 V *vs.* RHE with the AC amplitude of 10 mV under light illumination. The frequency range is from 0.1 Hz to 10 kHz. The applied bias photon-to-current efficiency (ABPE) was calculated following the equation: $ABPE (\%) = \frac{J_{ph} \times |1.23 - V_{app}|}{P_{total}} \times 100$, where J_{ph} and V_{app} are the photocurrent density (mA cm^{-2}) and applied bias (V) while P_{total} means the incident illumination power density (100 mW cm^{-2}). In all measurements, Ag/AgCl (3.0 M KCl) electrode was used as the reference, which has the potential of 0.210 V *vs.* RHE. The pH value of 0.5 M Na_2SO_4 electrolyte was 5.16 and double detected by both the pH Test Strip and the pH Meter (OHAUS-Starter 3100 Bench pH Meter). Potentials obtained in this study were calibrated against the reversible hydrogen electrode (RHE) reference by the following Nernst equation: $E (\text{V vs. RHE}) = E (\text{V vs. Ag/AgCl}) + 0.059 \text{ pH} + E (\text{Ag/AgCl vs. RHE})$. The catalytic area of our samples is 1 cm^2 .

Table 5.1: Light intensity for IPCE calculation

wavelength (nm)	300	310	320	330	340	350	360	370	380
light intensity (mW cm^{-2})	0.010	0.012	0.013	0.017	0.022	0.026	0.028	0.029	0.032
wavelength (nm)	390	400	410	420	430	440	450	460	470
light intensity (mW cm^{-2})	0.037	0.043	0.043	0.045	0.054	0.067	0.082	0.105	0.129
wavelength (nm)	480	490	500	520	540	560	580	600	
light intensity (mW cm^{-2})	0.118	0.120	0.118	0.119	0.122	0.121	0.122	0.116	

5.3 Results and discussion

The synthesis process is shown in Figure 5.1. Experimentally, W foil is used as the starting material and transformed into olive yellow precursor after hydrothermal process. Based on the conventional one-step annealing process, the precursors are first annealed at 550 °C for 3 hours (denoted as WO₃-S0). Afterward, the samples turn blue after cooling down, which is the usual color of as grown WO₃. In order to obtain oxygen-deficient WO₃, the samples are second annealed at 700 °C for 60 min and denoted as WO₃-S1. It is worth noting that the blue samples become yellow after the second annealing, which is attributed to the higher concentration of oxygen deficiency.

As shown in scanning electron microscopy (SEM) images (Figure 5.2a, b), the precursor is fully covered by numerous smooth plates with thickness in the range of 200-500 nm. Figure 5.2c shows X-ray diffraction (XRD) pattern of the precursor. Two strong diffraction peaks at 58 ° and 73 ° are matched well with tungsten metal (JCPDS 04-0806), which is pertaining to W foil substrate. Other diffraction peaks are indexed to H_{0.1}WO₃·1.6H₂O (JCPDS 40-0694) and WO₃·H₂O (JCPDS 43-0679).

Figure 5.2 Different magnification SEM images (a, b) and XRD pattern (c) of the WO₃ precursor after hydrothermal process.

When we perform a conventional one-step annealing process with the precursor at 550 °C for different duration, the morphology experiences a huge variation (Figure 5.3). It is visible that some smooth plates are ruptured after 1 and 2 hours annealing. When the heating time is

prolongated to 3 hours, more plates tend to rupture and small particles are formed on the surface. However, when the time exceeds 3 hours, the morphology is almost preserved and remains the same as the 3 hours sample. This is one reason why that the sample annealed at 550°C for 3 hours is chosen and denoted it as WO₃-S0. Due to the escape of H and O atoms caused by rapid heating rate in the first annealing, the smooth plates are ruptured and small particles are formed on the surface from 1 hour to 3 hours, and morphology preserves when exceeds 3 hours. Following a second annealing process, the plate-like morphology of WO₃-S1 does not show significant change (Figure 5.4a, b). TEM images (Figure 5.4c, d) confirm that both WO₃-S0 and WO₃-S1 possess a rough surface with numerous particles and distinct voids in-between those particles. The diameter of these particles is in the range 40-100nm. High resolution TEM images show that the lattice fringes separated by 0.254 and 0.365 nm belong to the (-122) and (200) planes of WO₃, respectively.

Figure 5.3 SEM images reveal morphological differences among the WO₃ samples annealed only once at 550 °C for different durations. (a) 1 hour, (b) 2 hours, (c) 3 hours, (d) 4 hours, (e) 5 hours, and (f) 6 hours, respectively. The inserts are the corresponding high magnification images of the samples.

Figure 5.4 SEM and TEM images of $\text{WO}_3\text{-S0}$ (a, c) and $\text{WO}_3\text{-S1}$ (b, d), respectively. The inserts are the corresponding high resolution images of the samples.

Figure 5.5a shows XRD patterns of WO_3 samples. It is highly visible that tungsten metal peaks of $\text{WO}_3\text{-S0}$ are quite strong. After annealing again at 700 °C for 60 min, $\text{WO}_3\text{-S1}$ do not show tungsten diffraction peaks, indicating that the residual tungsten metal has converted into WO_3 . Exclude tungsten peaks, all the diffraction peaks are indexed to monoclinic phase WO_3 (JCPDS 43-1035) and no second phase is observed. In Figure 5.5b, all the Raman bands originate from monoclinic WO_3 . More precisely, two main bands at 719(W-O bending (δ)) and 812(W-O stretching (γ)) cm^{-1} are typically coming from the symmetric bending and stretching vibrations of W and O atoms from $\gamma(\text{O-W-O})$ mode.¹⁷⁶⁻¹⁷⁸ The peaks at 276 and 330 cm^{-1} are belonging to the $\delta(\text{O-W-O})$ vibration mode.¹⁷⁸⁻¹⁸⁰ It is worth noting that the peak positions have no significant shift for $\text{WO}_3\text{-S0}$ and $\text{WO}_3\text{-S1}$, validating that the structure are not affected by the second annealing process. However, the intensity ratio of the 719 cm^{-1} and 812 cm^{-1} bands of $\text{WO}_3\text{-S0}$ is 0.6628, which is higher than the corresponding ratio of $\text{WO}_3\text{-S1}$ (0.5982). This

indicates that the high-temperature two-step annealing still have an influence on the vibrations between W and O atoms, that can be investigated in the future. More importantly, WO₃-S1 present a weak 620 cm⁻¹ band compared with WO₃-S0, which corresponds to the water absorption on oxygen deficiency.¹⁸¹ In Figure 5.5c, the UV-visible diffuse reflectance spectra show a typical optical feature of WO₃ with an absorption edge around 460 nm, which is associated with the literatures.⁷⁹ According to the Kubelka-Munk function and the Tauc Plots (F(R)•hv^{1/2} vs. hv)(Figure 5.5d), the calculated bandgaps are 2.80 and 2.82 eV for WO₃-S0 and WO₃-S1, respectively. The larger bandgap of WO₃-S1 indicates that the light absorption are not enhanced by the higher concentration of oxygen deficiency.

Figure 5.5 XRD patterns (a), room temperature Raman spectra (b), UV-vis diffuse reflectance spectra (c), and Tauc plots in terms of Kubelka–Munk function (d) of WO₃-S0 and WO₃-S1 samples. XPS O 1s and W 4f spectra of WO₃-S0 (e, g), WO₃-S1 (f, h), respectively.

X-ray photoelectron spectroscopy (XPS) is used to investigate surface chemical states of WO₃ samples. In the high resolution O 1s spectrum of WO₃-S0 (Figure 5.5e), one dominating peak with binding energy of 530.2 eV is observed, which is assigned to the O species in the metal oxide bond, validating the formation of W-O bonds.^{167, 182} The small peak at 531.8 eV originates from the oxygen defects in the sample.^{167, 182, 183} Concerning WO₃-S1 (Figure 5.5f), the peak intensity corresponding to oxygen defects is enhanced, suggesting that the second

annealing process leads to higher concentration of oxygen defects. For the high resolution W 4f spectrum (Figure 5.5g, h), there are two dominating peaks with binding energies of 35.4 and 37.7 eV, corresponding to the W 4f_{7/2} and W 4f_{5/2} spin-orbits, respectively. In Figure 5.6, WO₃-S1 sample exhibits stronger photoluminescence (PL) emission than that of WO₃-S0 sample, indicating that the presence of higher concentration of oxygen deficiencies in WO₃-S1.¹⁷⁵

Figure 5.6 Photoluminescence spectroscopy (PL) of WO₃-S0 and WO₃-S1 samples.

The photoelectrochemical performance of WO₃ can be evaluated by recording linear sweep voltammetry (LSV) curves. In Figure 5.7a, b, the WO₃ samples show extremely low current in the dark, and experience a dramatic increase when the light is on, indicating an evident photocurrent response feature under light illumination. WO₃-S0 delivers a low photocurrent of 0.37 mA cm⁻² at 1.51 V vs. RHE, which is only half of the WO₃-S1 (0.66 mA cm⁻²), revealing the significance of the second annealing process. It is interesting that the photocurrent of WO₃-S0 is decreased after 24h stability test, while it is opposite for WO₃-S1. Normally, the photocurrent will decrease during the long-term stability test because of the instability of catalysts. In WO₃-S1, the photocurrent increase may be attributed to the sufficient oxygen defects. These defects may not involve in the photoelectrochemical reaction at the beginning, and they will take part in the reaction during long-term test, and leads to the increase of photocurrent density.

Figure 5.7 LSV curves of WO₃-S0 (a) and WO₃-S1 (b) samples at 10 mV s⁻¹ under incident chopped light ($f = 0.1$ Hz, AM 1.5) with 0.5 M Na₂SO₄ as the electrolyte. Short-term and long-term stability tests of WO₃-S0 (c, e), and WO₃-S1 (d, f) samples at a constant voltage of 1.51 V vs. RHE for 600s and 24 hours, respectively. Short-term stability tests are measured under incident chopped light ($f = 0.05$ Hz, AM 1.5). Then, the above samples are used to perform the long-term stability tests with chopped light ($f = 0.05$ Hz, AM 1.5) for 600s every 2 hours or 12 hours, and tested for 24 hours in total.

From short-term stability tests (Figure 5.7c, d), it is observed that photocurrent density is increased from WO₃-S0 (0.32 mA cm⁻²) to WO₃-S1 (0.66 mA cm⁻²), which are consistent with LSV curves. In addition, there is negligible photocurrent loss over the 600s measurement for WO₃-S1, whereas WO₃-S0 has a small current loss, indicating that WO₃-S1 are more stable in short-term measurement. To gain further insight into the stability of samples, long-term tests are conducted for 24 hours (Figure 5.7e, f). At the first 600s, WO₃-S0 shows a photocurrent density of 0.32 mA cm⁻², which is the much lower than that of WO₃-S1 (0.70 mA cm⁻²). Then, the photocurrent density of WO₃-S0 is decreasing rapidly down to a photocurrent retention of 71.9% and 40.6% after 2 hours and 16 hours, respectively (Figure 5.7e). After that, photocurrent remains stable till the end of measurement (0.13 mA cm⁻²). For WO₃-S1 (Figure

5.7f), the photocurrent drop is negligible with a high retention of 98.5% after 16 hours and even until the end of test (0.69 mA cm^{-2}). In contrast with conventional one-step annealed $\text{WO}_3\text{-S0}$, high-temperature two-step annealed $\text{WO}_3\text{-S1}$ contains higher concentration of oxygen defects, leads to efficient charge generation, resulting in the improved photocurrent and higher stability.

After 24 hours stability tests, the LSV photocurrents at 1.51 V vs. RHE of $\text{WO}_3\text{-S0}$ is increased to 0.26 mA cm^{-2} , indicating that the photocurrent decrease in long-term test is a temporary phenomenon. This reversible decrease may originate from the inefficient charge separation of $\text{WO}_3\text{-S0}$, and the photocurrent recovers once you stop and start the measurement again later. While the irreversible photocurrent decrease should come from the instability of $\text{WO}_3\text{-S0}$. For $\text{WO}_3\text{-S1}$, the LSV photocurrent even reaches to 0.73 mA cm^{-2} . Benefited from the high-temperature two-step annealing, $\text{WO}_3\text{-S1}$ contains excessive oxygen defects, which may be not fully involved at the beginning of photoelectrochemical reaction, but it may take part in the reaction during long-term measurement. Then, this leads to the increase of photocurrent density in red LSV curves.

Furthermore, the average faradaic efficiency of WO_3 samples is above 90% (Figure 5.8a), indicating the sufficient usage of the charges. In Figure 5.8b, the $\text{WO}_3\text{-S1}$ shows a faster yield rate for H_2 , demonstrating the enhanced activity. In the incident light to electron conversion efficiency (IPCE) plots (Figure 5.8c), both samples exhibit increasing IPCE round 460 nm, corresponding with the bandgap of 2.8 eV. Furthermore, $\text{WO}_3\text{-S1}$ delivers higher IPCE than that of $\text{WO}_3\text{-S0}$ in the range of 300-460 nm, suggesting that $\text{WO}_3\text{-S1}$ has efficient charge separation and transportation, and matching with the photocurrent density results in Figure 5.7. The impedance of two electrodes are examined and fitted with an equivalent circuit (Figure 5.8d). The impedance of $\text{WO}_3\text{-S1}$ is smaller than that of $\text{WO}_3\text{-S0}$, indicating that $\text{WO}_3\text{-S1}$ has faster kinetics and improved interface charge transfer and separation efficiency after the introduction of oxygen deficiency. The applied bias photon-to-current efficiency (ABPE) of

WO₃-S1 is higher than that of WO₃-S0, indicating that the higher oxygen deficiencies in WO₃-S1 facilitates better solar energy conversion efficiency (Figure 5.9). In addition, we compared the PEC performance of as-prepared our catalyst and reported oxygen-deficient WO₃ and other photoanodes (Table 5.2), which indicates that our catalyst has superior photostability.

Figure 5.8 The *i-t* curves and relative faradaic efficiency (a) and the amount of evolved H₂ production (b) of WO₃-S0 and WO₃-S1 samples at the potential of 1.51 V vs. RHE under illumination for 60 min. (c) The IPCE plots of WO₃-S0 and WO₃-S1 samples at 1.23 V vs. RHE from 300-600 nm. (d) EIS results of WO₃-S0 and WO₃-S1 samples at the potential of 1.0 V vs. RHE with the frequency range from 0.1 Hz to 10 kHz under illumination. The black lines are the corresponding fittings to the equivalent circuits.

Figure 5.9 The applied bias photon-to-current efficiency (ABPE) of the samples.

Table 5.2 Comparison of the PEC performance of as-prepared our catalysts and reported oxygen-deficient WO₃ and other photoanodes.

Photoanode	Photocurrent @1.23V vs. RHE	Photostability	ABPE @1.0V vs. RHE	Substrate	pH of Electrolyte	Light irradiation
WO ₃ -S1(This work)	0.54 mA cm ⁻²	24h	0.04%	W foil	0.5 M Na ₂ SO ₄ (pH= 5.16)	visible light (100 mW cm ⁻²)
Single-Crystalline WO ₃ Microplates(330 nm) ¹⁷¹	0.5 mA cm ⁻²	—	—	FTO	phosphate buffer (pH= 7)	visible light (100 mW cm ⁻²)
Single-crystalline WO ₃ microplates(470 nm) ¹⁷¹	0.9 mA cm ⁻²	—	—	FTO	phosphate buffer (pH= 7)	visible light (100 mW cm ⁻²)
Single-Crystalline WO ₃ Microplates(330 nm) ¹⁷¹	1.3 mA cm ⁻²	—	—	FTO	phosphate buffer (pH= 7)	UV-vis irradiation
Single-crystalline WO ₃ microplates(470 nm) ¹⁷¹	1.9 mA cm ⁻²	—	—	FTO	phosphate buffer (pH= 7)	UV-vis irradiation
WO _{3-x} nanorods supported Zn _{0.3} Cd _{0.7} S heterostructure ¹⁶⁹	0.05 mA cm ⁻²	—	—	Ti foil	0.1 M Na ₂ SO ₄	visible light (2.8 mW cm ⁻²)
WO _{3-x} @TiO _{2-x} core– shell nanosheets(15 nm) ¹⁷²	3.2 mA cm ⁻²	6h	—	FTO	0.5 M Na ₂ SO ₄ (pH= 6.8)	visible light (100 mW cm ⁻²)
WO ₃ plate-like films ¹⁷³	0.78 mA cm ⁻²	2h(15% loss)	—	FTO	0.5 M H ₂ SO ₄	visible light
WO ₃ nanotubes grown by FVD ¹⁸⁴	1.5 mA cm ⁻²	—	0.21%	—	0.5 M Na ₂ SO ₄	visible light (100 mW cm ⁻²)
WO ₃ /Fe ₂ O ₃ nanocomposites ¹⁸⁵	2 mA cm ⁻²	4h	0.45%	FTO	0.5 M Na ₂ SO ₄	visible light (100 mW cm ⁻²)
Nanostructured WO ₃ with triton surfactants ¹⁸⁶	2 mA cm ⁻²	—	0.6%	FTO	1 M H ₂ SO ₄ (pH = 0)	visible light (100 mW cm ⁻²)

After 24 performance tests, the morphology, XRD, and XPS patterns of tested WO₃ samples almost stay unchanged, still preserve particles covered plate-like morphology, same phase and chemical states (Figure 5.10, 5.11). Raman spectra show that monoclinic WO₃ structure also has negligible change after long-term tests (Figure 5.11g). Importantly, the intensity ratio of 719 to 812 cm⁻¹ band of tested WO₃-S0 decreases to 0.5993, while it increases to 0.6889 for tested WO₃-S1. It is interesting that these changes in the band ratio is the same as the

photocurrent changes. This may suggest that the symmetric bending (W-O bending (δ)) of W and O atoms may be beneficial for the charge generation and separation, and thus leads to the photocurrent increase after two-step annealing.

Figure 5.10 XRD patterns of $\text{WO}_3\text{-S1}$ before and after 24 hours stability test.

Figure 5.11 SEM images of the $\text{WO}_3\text{-S0}$ (a), and $\text{WO}_3\text{-S1}$ (b) after 24 hours stability test. The inserts are the corresponding high magnification images of above samples. O 1s (c, d) and W 4f (e, f) XPS spectra of the $\text{WO}_3\text{-S0}$ (c, e) and $\text{WO}_3\text{-S1}$ (d, f) samples after 24 hours stability test. (g) The room temperature Raman spectra of $\text{WO}_3\text{-S0}$ and $\text{WO}_3\text{-S1}$ samples after 24 hours stability tests. (h) The full survey spectra of XPS measurements of $\text{WO}_3\text{-S0}$ and $\text{WO}_3\text{-S1}$ after 24 hours stability tests.

5.4 Additional tests

Figure 5.12a-g show the LSV curves of WO_3 samples only experience conventional one-step annealing at 550 °C for different duration (3-6 hours). The samples annealed for 3 hours,

4 hours, 5 hours, and 6 hours deliver a photocurrent of 0.33, 0.19, 0.17, and 0.11 mA cm⁻² at 1.51 V vs. RHE, respectively. The photocurrent of above four samples is sequentially decreasing according to the first annealing duration. At the same time, the 3 hours sample has the highest photocurrent together with the highest photocurrent retention in comparison with other three samples during the short-term stability tests (Figure 5.12b-h). It can be concluded that the 3 hours sample exhibits the highest photocurrent and best stability. Here, this is another reason that sample annealed at 550°C for 3 hours is chosen as WO₃-S0 and make further treatment to obtain oxygen-deficient WO₃ (WO₃-S1).

Furthermore, the samples second annealed at 670°C for 30 min, 700°C for 30 min, are denoted as WO₃-S2 and WO₃-S3, respectively. After the second annealing process, the plate-like morphology of WO₃-S2 and WO₃-S3 do not show significant changes compared with WO₃-S0 and WO₃-S1 (Figure 5.13a, b). Both WO₃-S2 and WO₃-S3 plates contain rough surface and they are covered by particles. From TEM images (Figure 5.13c, d), it is confirmed again that numerous particles distribute on the surface and there are distinct voids in-between those particles. The diameter of the particles is in the range of 40-100nm. As shown in XRD patterns (Figure 5.13c), the diffraction peaks at 58 ° and 73 ° are indexed to the tungsten metal (JCPDS 04-0806), which is belonging to the W foil substrate. It is highly visible that the tungsten metal peaks of WO₃-S2 are quite weak. As the temperature increases to 700°C for 30 min, WO₃-S3 almost does not show the tungsten diffraction peaks. It can be concluded that the tungsten peaks are decreased and even vanished with higher temperature and longer duration of the second annealing process. Exclude the tungsten peaks, all the diffraction peaks are matched well with the monoclinic phase WO₃ (JCPDS 43-1035) and no second phase is observed.

Figure 5.12 LSV curves and stability tests of WO_3 photoanodes first annealed at 550°C for 3 hours (a, b), 4 hours (c, d), 5 hours (e, f), and 6 hours (h, g), respectively. The LSVs are tested at scan rate = 10 mV s^{-1} under incident chopped light ($f = 0.1 \text{ Hz}$). The stability tests are tested at 1.51 V vs. RHE under incident chopped light ($f = 0.05 \text{ Hz}$).

Figure 5.13 (a, b) SEM images about the WO_3 after a two-step annealing process. Here, the sample first annealed at 550°C for 3 hours, and then second annealed at 670°C for 30 min, and 700°C for 30 min, are denoted as $\text{WO}_3\text{-S2}$ (a) and $\text{WO}_3\text{-S3}$ (b), respectively. The inserts are the corresponding high magnification TEM images of above samples. (c) XRD patterns of the as-grown $\text{WO}_3\text{-S2}$ and $\text{WO}_3\text{-S3}$.

Compared with $\text{WO}_3\text{-S0}$, two-step annealed $\text{WO}_3\text{-S2}$ and $\text{WO}_3\text{-S3}$ also show higher photocurrent density (Figure 5.14). After the second annealed at 670°C for 0.5 hour, the LSV photocurrent density of $\text{WO}_3\text{-S2}$ at 1.51 V vs. RHE increases to 0.43 mA cm^{-2} . When we proceeds to 700°C for 0.5 hour, the photocurrent density of $\text{WO}_3\text{-S3}$ increases to 0.58 mA cm^{-2} . However, their photocurrents is lower than that of $\text{WO}_3\text{-S1}$ (700°C for 1 hour). This indicates that the increase of photocurrent density may be attributed to the two-step annealing process,

especially those treated in higher temperature and longer duration, leading to higher concentration of oxygen defects, and resulting in the higher charge generation. In the meantime, the short-term stability tests behave similar as WO₃-S0 and WO₃-S1, all the samples are stable in the short period. However, the photocurrent of WO₃-S2 decreases rapidly down to 0.08 mA cm⁻² after 24 hours long-term test. Interestingly, when the long-term test is over, and another LSV test is conducted, the photocurrent of WO₃-S2 recovers back to 0.37 mA cm⁻². This phenomenon also can be find in WO₃-So, which may due to the inefficient charge separation of samples. However, for higher temperature (700 °C) annealed WO₃-S1 and WO₃-S3, there is no such decrease and recovering changes in photocurrent. Although there is a photocurrent increase of both WO₃-S1 and WO₃-S3, originating from that excessive oxygen defects gradually get involved in the photoelectrochemical reaction during long-term tests.

We continue with another 600s short-term and a 24 hours long-term stability test on WO₃-S3 sample (the same device) (Figure 5.15). Here, the photocurrent of WO₃-S3 is as high as 0.61 mA cm⁻², and it almost has no photocurrent loss during these two measurements. It can be concluded that photocurrent is higher and much more stable with high temperature/long duration annealed WO₃ samples as compared to WO₃-S0 and WO₃-S2.

The morphologies of WO₃-S2 and WO₃-S3 after 24 hours stability tests are recorded in Figure 5.16. In comparison with as-grown samples, the tested samples almost stay unchanged, still preserve the plate-like structure and cover with particles. Additionally, the XPS patterns of tested WO₃-S2 and WO₃-S3 samples show that the surface chemical states do not change much after long-term tests.

Figure 5.14 (a) LSV curves of $\text{WO}_3\text{-S2}$ in a three-electrode quartz glass system with 0.5 M Na_2SO_4 as the electrolyte. LSV tests are performed at 10 mV s^{-1} under incident chopped light ($f = 0.1 \text{ Hz}$, AM 1.5). The curves in blue are tested before stability test. The curves in red are tested after 24 hours stability test. (b) Short-term and (c) long-term stability tests of $\text{WO}_3\text{-S2}$ sample at a constant voltage of 1.51 V vs. RHE for 600s and 24 hours, respectively. Short-term stability tests are measured under incident chopped light ($f = 0.05 \text{ Hz}$, AM 1.5). Then, the above samples are used to perform the long-term stability tests with chopped light ($f = 0.05 \text{ Hz}$, AM 1.5) for 600s every 2 hours or 12 hours, and tested for 24 hours in total. (d) LSV curves, short-term and (e), and long-term (f) stability tests of $\text{WO}_3\text{-S3}$ sample in the same condition as $\text{WO}_3\text{-S2}$ sample.

Figure 5.15 (a) Short-term stability test of $\text{WO}_3\text{-S3}$ sample for 600s after the first 24h stability test. (b) Another 24h long-term stability test of $\text{WO}_3\text{-S3}$ sample after the first 24h long-term and short-term stability tests. All the stability tests are measured at a constant voltage of 1.51 V vs. RHE under incident chopped light ($f = 0.05 \text{ Hz}$, AM 1.5).

Figure 5.16 SEM images of the $\text{WO}_3\text{-S2}$ (a), and $\text{WO}_3\text{-S3}$ (b) after 24 hours stability test. The inserts are the corresponding high magnification images of the above samples. The scale bar corresponds to 1 μm (big images) and 100 nm (insert images). O 1s (c, d) and W 4f (e, f) XPS spectra of the $\text{WO}_3\text{-S0}$ (c,e) and $\text{WO}_3\text{-S1}$ (d, f) samples after 24 hours stability test.

5.5 Conclusion

Oxygen-deficient plate-like WO_3 grown on tungsten foil have been investigated as catalysts for PEC applications. Compared with $\text{WO}_3\text{-S0}$, $\text{WO}_3\text{-S1}$ takes advantage from the high concentration of oxygen defects, thus leading to a better charge generation and separation, finally resulting in an improved photocurrent density and better stability. Here, the initial photocurrent density of $\text{WO}_3\text{-S0}$ as measured at 1.51 V vs. RHE is 0.32 mA cm^{-2} . Then this intensity decreases rapidly down to a photocurrent retention of 40.6% after 16 hours. As-grown $\text{WO}_3\text{-S1}$ catalyst has a much higher photocurrent density of 0.66 mA cm^{-2} , and the photocurrent retention is as high as 98.5% after 24 hours. The insight of this work may be extended to other catalysts in PEC application.

Chapter 6 Conclusions and future recommendations

6.1 Conclusions

In this Thesis, different types of transition metal based catalysts for efficient electrochemical/photoelectrochemical water splitting have been investigated. Specifically, four types of catalysts are studied, namely, Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires, oxygen-deficient WO_3 microplates, CoMo_2S_4 interconnected porous nanoflakes, and hierarchical $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees. The Thesis articulates the material design and nanostructure engineering, and detailed electrochemical/photoelectrochemical performance evaluation of the catalysts.

Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires for overall water electrolysis:

First, Co_3O_4 nanowires are chosen as the starting catalyst, and their electrocatalytic performance is studied for both HER and OER process. Then, we convert it to Co_3S_4 and further dope Co_3S_4 with Ni element to obtain $\text{Ni}:\text{Co}_3\text{S}_4$. Later on, systematic electrochemical measurements and DFT calculations are performed to evaluate the electrocatalytic activity and mechanism of these catalysts.

- It is proven that the Co_3S_4 nanowires show improved OER/HER electrocatalytic activity compared with pure Co_3O_4 .
- Because of the better intrinsic electrocatalytic activity of Ni, doping Co_3S_4 with Ni element shows improved HER electrocatalytic activity.
- Replacing O with S element and doping with Ni element are effective in reducing the intrinsic Gibbs free energy of the intermediates on the surface active site, which results in the lower theoretic overpotential, and thus leading to better OER/HER electrocatalytic performance.

- The Ni foam support are utilized to improve the contact with the catalysts, and the high surface area of nanowire structure increases the number of active sites.
- The superior electrocatalytic capability and stability of Co_3S_4 and $\text{Ni}:\text{Co}_3\text{S}_4$ nanowires provide new possibility towards overall water electrolysis.

Oxygen-deficient WO_3 microplates for PEC water oxidation:

A combining technique of hydrothermal process and two-step annealing process was utilized to prepare oxygen-deficient WO_3 microplates as photoelectrocatalyst for photoelectrocatalysis. In this case, we used commercial tungsten foil as the starting material. In addition to a traditional annealing method, oxygen-deficient WO_3 microplates were obtained after the second annealing process.

- These oxygen defects in WO_3 microplates can be roughly tuned by adjusting the temperature and duration of the multi-annealing technique.
- Oxygen defects in WO_3 can increase the donor density, leading to better charge carrier generation and separation, resulting in improved photoelectrocatalytic performance, such as higher photocurrent density and super higher stability.
- The utilization of tungsten foil helps to reduce the intrinsic resistance of the electrodes, which is favorable for increasing the electron conductivity.

CoMo_2S_4 interconnected porous nanoflakes as efficient bifunctional catalyst:

As compared to binary metal oxides, ternary metal oxides contains additional active sites due to the specific metal bonding. In addition, ternary metal sulfides shows better electrocatalytic performance with increased active sites and enhanced charge transport. We have also investigated CoMoO_6 and CoMo_2S_4 interconnected porous nanoflakes as bifunctional electrocatalysts for overall water electrolysis.

- Compared with CoMoO_6 , the efficient catalytic performance of CoMo_2S_4 could be ascribed to the material design that the sulfides show increased active sites and enhanced charge transport capability.
- The interconnected porous nanoflake structure is favorable for the release of gaseous products and the contact between catalyst and electrolyte.
- The utilization of conductive Ni foam support increases the surface area and active sites.

Hierarchical $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees as efficient water oxidation electrocatalyst:

Here, we designed three dimensional hierarchical nanostructure by decorating the main catalysts surface (branch-like $\text{Cu}(\text{OH})_2$ nanowires) with co-catalytic metal compounds (leaves-like ultrathin $\text{Co}(\text{OH})_2$ nanoflakes). This hierarchical hybrid $\text{Cu}(\text{OH})_2@\text{Co}(\text{OH})_2$ nanotrees were evaluated as efficient OER electrocatalyst.

- It is proven that the reaction kinetics and charge transport capability is improved after the formation of the hierarchical hybrid nanostructure.
- The hierarchical nanotrees with copper foil support facilitate the contact of solid-electrolyte interface and release of gaseous product.
- Our material design and nanostructure engineering lead to high electrocatalytic capability and stability, revealing that these designs are effective in achieving good catalytic performance of the catalysts.

6.2 Future recommendations

Looking into the future, I would like to suggest further studies in order to push the performance of noble-metal free electrocatalysts, including tuning of electronic-structure, fabrication techniques, and exploration of catalytic mechanisms using advanced characterization techniques.

(1) Electronic and geometric structure regulation:

It is proven that tuning electronic structure is an effective strategy to achieve highly-efficient catalysts for water splitting. There are different methods to tune electronic structures, such as alloying, doping, introducing oxygen deficiency, and edge-defect engineering. Generally, these methods can reduce the ΔG of the intermediates, provide additional active sites, and promote the charge transport, leading to improved catalytic performance of the catalysts. In this Thesis, the influences of doping, alloying, and introducing oxygen deficiency are preliminarily studied. It is shown that the electrochemical performance is strongly improved by these methods. In future, more studies should be conducted in order to understand the detailed mechanisms of the catalytic enhancement, for example, how the electronic structure is tailored by edge-defect engineering, or by a combination of two or three above mentioned methods.

Beyond the electronic structure, the engineering of geometric structure is also significantly important in increasing the active-site density and mass-transfer rates. In this Thesis, we found that the well-separated hierarchical nanostructures increase the surface area with higher active site density, facilitate the contact of solid-electrolyte interface and the release of gaseous product. In view of this fact, hierarchical nanostructures with high porosity are generally favorable in designing high-performance catalyst electrodes. Additionally, these catalysts are directly grown on conductive substrates, which avoids the use of binders and minimizes the intrinsic resistance. Hence, it is recommended to utilize various conductive and chemically stable substrates, such as carbon cloth/papers and copper foam/foil.

(2) Fabrication technique:

A few synthesis techniques are deployed in this Thesis study, such as hydrothermal treatment, annealing treatment, and electrodeposition method. They have pros and cons. For example, hydrothermal technique generally has a high reaction activity and thus can obtain

compounds that are hardly synthesized. Also, the composition and morphology of the products are controllable by tuning the solution concentration, heating temperature, and heating duration, etc. However, the presence and amount of defects are usually hard to control. Electrodeposition technique can provide good homogeneity of the deposited material, but the condition is quite thickness dependent. In general, a two-step fabrication method can result in better quality samples, especially for non-oxide materials. Thermal conversion from metal organic framework (MOF) or layered-double hydroxides (LDH) is a good example. Template assisted fabrication methods are also good choice when the alignment of the obtained low-dimensional materials (e.g., nanowires) is a concern.

(3) Catalytic mechanism understanding

Despite the large number of reports on experimental studies of efficient catalysts for water splitting, the fundamental understandings of the catalytic mechanism still lags far behind. DFT calculation is a robust tool to compute the adsorption free energies of intermediates which are useful to evaluating the reaction kinetics of the catalysts and the reaction pathways during water splitting process. Moreover, the electronic band structure (e.g., DOS) can also be determined which may give hints to the electronic transports at interface. For example, we calculated the ΔG of the intermediates for each step, and thus evaluating the reaction kinetics of $\text{Co}_3\text{S}_4/\text{Ni}:\text{Co}_3\text{S}_4$ nanowires in chapter 2. This makes better understanding of the catalyst mechanism and provides useful guideline to material selection and design of heterojunctions.

However, calculation alone is still insufficient since it is based on ideal models. More solid and direct evidences are still important to reveal the catalyst mechanisms. It is proven that in-situ characterization techniques,¹⁸⁷ such as in-situ Raman, XRD, synchrotron-based X-ray absorption, and STEM, can be useful to monitor the evolution of surface chemistry and atomic structure during the reactions. Under catalytic reaction conditions, key information of the

intermediates and their dynamic evolution can be effectively probed by these operando measurements. As a result, it is possible to build a clear correlation between structure/composition and activity, which lies in the focus of current research in photo/electrocatalysts.

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