Cation exchange process on copper selenide for HER/OER catalyst

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**CATION EXCHANGE PROCESS ON COPPER SELENIDE FOR
HER/OER CATALYST**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

CATION EXCHANGE PROCESS ON COPPER SELENIDE FOR HER/OER CATALYST

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2019

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Yan Qingyu

Abstract

Although fossil fuels play a crucial role in modern society, the burning of fossil fuels will cause air pollution and emitter of carbon greenhouse gases such as carbon dioxide (CO_2). Meanwhile, the increasing demand for energy in today's society makes fossil energy insufficient. Therefore it's necessary and urgent demand for sustainable and environmental friendly energy supply. Hydrogen has attracted people's attention because of the outstanding conversion efficiency without generation of greenhouse gases. It can be produced by splitting of water with the help of electrocatalyst. Currently, high-efficiency catalysts are made of precious metals, for instance the platinum and iridium oxide for hydrogen evolution (HER) and oxygen evolution reaction (OER). However, the shortage and expensive prices prevent their widespread application in modern industry. Thus, developing a commercial catalyst with high efficiency to replace expensive precious metal-based catalysts and increase electrochemical reaction efficiency is an urgent thing.

Non-precious metal catalysts with two-dimensional nanosheets structure are the most commonly used in catalytic electrolysis in recent years due to the relatively large exposed active area and stability compared with other nanomaterials. Here CuSe was selected to synthesize CuSe-CoSe nanosheets through cation exchange (CE) reaction.

Firstly, we try to synthesize ultrathin CuSe nanosheet since traditional CuSe materials with poor HER and OER activity are rarely reported. It's believed that the relatively large exposed active area of the nanosheets structure material can faster the mass transfer rate and facilitate the gas generated by the reaction to rapidly escape from the surface of the electrode. And nanosheet is stable compared with other nano materials, which means it would be difficult to destroy the structure during violent electrochemical reaction. An environmentally friendly and economical organic solution phase method was adopted to fabricated CuSe nanosheet.

Secondly, cobalt will be introduced to CuSe precursor to enhance HER and OER performance of pure CuSe nanosheet by forming CuSe-CoSe nanosheets heterostructure.

In one hand, Co-based catalysts are still considered to be one of the most likely alternatives to noble metal electrode catalysts because of their excellent performances towards HER and OER. In the other hand, the synergistic effect between copper and cobalt in heterostructures can increase the activity. To preserve the morphology of former nanosheet structure of CuSe, cation exchange (CE) reaction was used here. In the article, the effects of temperatures and reaction times can be explored with varying preparing conditions.

Furthermore, the morphology and the phase were analyzed by Field Emission Scanning Electron Microscope (FESEM) and High-resolution transmission electron microscopy (HRTEM). Energy Dispersion X-ray (EDX) and X-ray diffraction (XRD) instrument would be used to determine the composition and element contents. Hydrogen and oxygen evolution performances were also tested for these materials to investigate whether the special heterostructure enhanced electrochemical properties comparing with pure copper selenide.

Lay Summary

Fossil fuels play a crucial role in global energy systems in the 20th century. However, burning of fossil fuels will cause air pollution and greenhouse effect. The ecological environment of the earth has become increasingly unsuitable for human habitation. To make matters worse, we are facing both energy crisis at the same time. The growing demand for energy in today's society makes fossil energy insufficient. Therefore it's necessary to find out other sustainable and environmental friendly energy supply.

Among numerous technology, hydrogen fuel cell has attracted scientists' interest owing to its outstanding energy efficiency and no emission of greenhouse gases. Hydrogen could be produced by splitting of water under the input of electricity, which is abundant on earth. Therefore, excess solar energy and wind energy could be harnessed to produce hydrogen. However the process is very difficult to proceed without the helping of catalysts. The common used efficient catalyst is made of the noble metal, which costs a lot. So we want to develop a commercial and efficient catalyst to replace these expensive catalysts.

The efficiency of catalysts is related to many factors. Firstly, we will prepare copper selenide with nanosheet structure, which provide more surface area and is stable. Besides copper is known for its conductivity and abundant reserve in nature. All these properties will be beneficial to its application on catalysts. Secondly, cobalt was introduced to the copper selenide precursor to further enhance the performance. As one of the first-period transition metal elements, cobalt is famous for the crucial role in driving water splitting process. The fabrication method was by using simple cation exchange reaction, which can preserve the origin nanosheet structure of precursor. The synthesized materials were tested as a catalyst for water splitting process.

No one has reported this materials yet. According to our outcomes, this materials achieved greatly improved performance compared with copper selenide precursor. The work paves the way for further cation exchange with other first-period transition metal elements such as nickel to enhance the property of original precursor.

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Figure 6.5 The nanoparticles morphology and the intraparticle frameworks were preserved well after cation exchange process. STEM-EDS images are shown for each population of particles.⁴

Abbreviations

HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
CE	Cation Exchange
1D	One Dimension
2D	Two Dimension
FESEM	Field Emission Scanning Electron Microscope
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction
TEM	Transmission Electron Microscopy
HRTEM	High-resolution Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
DFT	Density Functional Theory
RHE	Reversible Hydrogen Electrode
GCE	Glassy Carbon Electrode
LSV	Linear Sweep voltammetry
EDX	Energy Dispersive X-ray Spectroscopy
BSE	Backscattered Electrons
Z	Atomic Number
CP	Chronopotentiometry
NS	Nanosheet

Chapter 1

Introduction

The growing demand of clean and sustainable energy drives the attention to electrocatalysts for water splitting. In this chapter, research background of water electrolysis including the development history of water splitting and the current major bottlenecks of electrocatalysts will be firstly presented. Based on the background, the motivation and objectives of the project will be proposed. Finally, the expected outcomes will be provided in the report.

1.1 Background

Fossil fuels play a crucial role in global energy systems in the 20th century, which have driven the Industrial Revolution. However, burning of fossil fuels will cause air pollution and emitter of carbon greenhouse gases such as carbon dioxide (CO₂). Meanwhile, the increasing demand for energy in today's society makes fossil energy insufficient. Therefore it's necessary and urgent demand for sustainable and environmental friendly energy supply.¹ Scientists have spared no effort to solve this problem and made a great progress. Among numerous technology, hydrogen fuel cell has attracted people's interest owing to its outstanding energy transformation efficiency and no emission of greenhouse gases.²

Figure 1.1 The concept of a H₂ green energy system.⁴

Hydrogen could be produced by splitting of water with the help of electrocatalysts. This way sounds practical since water resource is abundant on earth. In 1888, the industrial method to synthesize hydrogen by splitting of water was provided by Dmitry Lachinov. In the 1920s, a high quantity of electrolytic cells have been designed and several factories was built around the world at the same time.³ Since then, hydrogen has gradually attracted

people's interest and become an effective way to solve the energy crisis. As an energy-intensive process, water electrolysis requires the input of electricity so as to obtain hydrogen and oxygen. Therefore, excess solar energy and wind energy could be harnessed to produce hydrogen as shown in Figure 2.1. The stored hydrogen will be used in fuel cells and converted into other energy sources once the renewable resources can meet the demand for supply.

Water splitting means the decomposition of water into H_2 and O_2 when applying an external source to provide energy. In a typical electrolytic cell, two electrodes connected to the energy supply were immersed in the solution. HER will occur at the negative electrode and OER at the positive electrode when a current provided is large enough in the device of water electrolysis.⁵ These reactions can also take place both in acidic and alkaline environment. And acidic and alkaline solution are often used instead of water during experiment due to the not ideal conductivity of the pure water. According to Nernst equation (1), the minimum necessary voltage required for water-splitting at standard temperature and pressure is 0 V for HER and 1.23 V for OER. In fact, the real potential voltage to drive the electrolysis of water is much higher than the theoretical value because of a variety of factors such as power loss. Actually, the voltage to start water electrolysis can be described as equation (2), where E_r is the theoretical voltage, E_{ir} is the overvoltage and E_{ohm} is the potential of ohmic loss, which is due to the resistance of electric circuit. In order to drive the chemical reaction forwards, additional energy should be applied to overcome the E_{ir} resulting from activating the reaction. To reduce the overvoltage and accelerate the reaction, highly active electrocatalysts is needed.

$$E = E_0 + \frac{RT}{nF} \times \ln \frac{[A_{oxidized}]}{[A_{reduced}]} \quad (1)$$

$$E = E_r + E_{ir} + E_{ohm} \quad (2)$$

Currently, highly efficient catalyst is made of noble metal such as platinum and iridium oxide for hydrogen and oxygen evolution reaction. However, the scarcity and expensive prices prevent their widespread application in modern industry. Therefore, the common way to get hydrogen today is still through steam reforming from hydrocarbons because of

the lower cost compared with electrocatalysis.⁶ Thus, the challenge researchers are facing is developing a commercial and efficient catalyst to replace expensive precious metal-based catalysts and increase electrochemical reaction efficiency at the same time.

It is known that non-precious metal catalysts with two-dimensional nanosheets structure are the most commonly used structures in catalytic electrolysis in recent years.^{7,8} The relatively large exposed active area of the nanosheets structure material can faster the mass transfer rate and facilitate the gas generated by the reaction to rapidly escape from the surface of the electrode. Nanosheets is stable compared with other nano materials, which means it would be difficult to destroyed the structure during violent electrochemical reaction.⁹ Here CuSe was selected to synthesize CuSe-CoSe nanosheets through cation exchange (CE) reaction. Firstly, it has been reported that Cu-based chalcogenides with various sizes and morphology could be routinely synthesized.¹⁰⁻¹¹ Since CuSe belongs to chalcogenides, the nanosheets structure CuSe can also be synthesized through similar way. Secondly, the high mobility of Cu^{2+} can facilitate cation exchange process with other cations. These features make it possible for different kinds of morphologies to introduce a large range of elements and interfaces in consecutive steps.¹² The goals of this thesis is to synthesize CuSe-CoSe nanosheets with special heterostructure as an highly efficient electrocatalyst for HER and OER performance.

1.2 Objectives and Scope

The present research is concerned with the synthesis of bimetal materials via cation exchange reaction to enhance their performance to provide deeper understanding for application in water splitting catalysts. Cation exchange reaction is an efficient and simple method for the synthesis of materials with heterostructure while maintaining the origin morphology.

The objectives and scope of this thesis are as follows:

1. To have a better understanding of water splitting process, the studying of hydrogen and oxygen evolution reaction should be the first thing to do. Including the mechanisms of the reaction and selection of electrocatalysts.
2. Investigate the method to environmentally friendly and economically fabricate ultrathin copper selenide nanosheets by using non-toxic, green, phosphorus-free and inexpensive reactants.
3. Studying the mechanisms and kinetics of cation exchange. Investigate the role of main influencing factors in this process by introducing cobalt into copper selenide in different temperature and reaction time.
4. Explore the application of this bimetal nanosheets in hydrogen and oxygen evolution reaction.

1.3 Dissertation Overview

The thesis addresses the synthesis of CuSe-CoSe nanosheets with special heterostructure via cation exchange reaction as an highly efficient electrocatalyst for HER and OER performance.

Chapter 1 provides a rationale for the research and outlines the goals and scope. This thesis describes and validates the fabrication of a material that delivers quantitatively superior performance in the domain sector.

Chapter 2 reviews the literature concerning the mechanisms of hydrogen and oxygen evolution reaction. The currently research progress on cobalt-based and copper-based electrode catalysts are also discussed. Since cation exchange is a novel and effective method to synthesize heterostructure materials, the mechanisms is highlighted here to have a better understanding on reaction procedure.

Chapter 3 provides the details of the experimental procedures. In the experiment, nanosheets copper selenide can be routinely achieved through organic solution phase method, which is environmentally friendly and economical compared to other processes. Cation exchange reaction is used as a simple and effective synthesis method for introducing cobalt into copper selenide while preserving the initial nanostructure. The fabricated materials will be tested according to typical characterization techniques and electrochemical performance.

Chapter 4 gives the outcomes including the morphology, compositions and HER/OER activities of ultrathin CuSe nanosheets. The prepared CuSe was found out to have an average lateral size of ~ 120 nm and thickness of ~ 6 nm. The applying of hydrated hydrazine can completely remove the organic solution attaching on the surface of the samples, improving the performance towards HER and OER.

Chapter 5 elaborates the major set of results including the morphology, compositions and HER/OER activities of CuSe-CoSe nanosheets. By comparing the SEM images and performances of prepared samples with different temperature, the best fabrication situation was decided. To further reveal the process of cation exchange, cobalt was introduced into copper selenide in different reaction time. The enhanced electrochemical properties of CuSe-CoSe nanosheets compared with CuSe also illustrated the successful cation exchange reaction.

Chapter 6 combines the over summary and conclusions, the future prospects of applying the concept of cation exchange reaction to other systems are proposed.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Demonstrated the ability to fabricate ultrathin copper selenide nanosheets with controlled morphology and thickness to a few nanometers through organic phase

solution method.

2. Discovered the effect of different temperatures and reaction times on cation exchange process.
3. Understanding the major composition transformation between copper component and cobalt component during the incoming of cobalt ion.
4. Measuring the properties of synthesized materials towards HER and OER performance. The greatly improved activity reveals the crucial role of heterostructures and cobalt component in driving water splitting.

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Chapter 2

Literature Review

In this section, introduction to hydrogen and oxygen evolution reaction is presented firstly. Then, the current research progress on cobalt-based and copper-based electrode catalysts are provided. The hydrogen and oxygen evolution performance of these materials are also discussed. After that, the approaches towards the synthesis of ultrathin copper chalcogenides nanomaterials are presented. Cation exchange reaction as an effective method to fabricate heterostructure materials is highlighted.

2.1 Introduction of Water Splitting

Water splitting means the decomposition of water into H_2 and O_2 when applying an external energy source. In a typical water splitting reaction, two electrodes connected to the energy supply were immersed in the solution. Hydrogen evolution will occur at the negative electrode and oxygen evolution at the positive electrode when the current provided is large. This reaction can also take place both in acidic and alkaline environment. However, the acidic and alkaline solution are often adopted instead of water during experiment due to the non-ideal conductivity of the pure water. The voltage required to start water splitting reaction is related to the electrocatalyst as mentioned above. In order to reduce the overvoltage and accelerate the reaction, highly active electrocatalysts is needed.

2.1.1 Hydrogen Evolution Reaction

Hydrogen has been raised as an attractive energy resource among scientists owing to its high energy density and producing less pollution. One mole of hydrogen could generate 286 kJ of energy when burned in oxygen.¹ The reaction between hydrogen and oxygen will produce water, which is a completely harmless by-product. Therefore the promising future of hydrogen economy has attracted enormous attention on HER, which can be utilized to produce hydrogen gas. Specially, using alkaline solution as electrolyte for alkaline electrolysis cell is the most widely developed and the lowest cost technique, which is currently widely used. In addition, non-precious metal electrodes can preserve relative stability and avoid decomposition in alkaline environment. This is very important because as-synthesized pure CuSe nanosheets and CuSe-CoSe nanosheets are found out dissolving in acidic electrolyte and the efficiency is very low. In the article, HER performance was done in alkaline electrolyte in experiments with regard to avoiding dissolution. However, the HER is more difficult to happen under alkaline conditions than under acidic conditions since hydrogen production in alkaline solutions requires hydrolysis step, which will introduce extra energy barriers that impede the overall reaction speed.² The thermodynamics and kinetics of the HER will be discussed subsequently.

2.1.1.1 Mechanisms

The chemical reaction of hydrogen evolution includes multi-process, which can be divided into two steps: adsorption, followed by desorption. The general reaction mechanisms in alkaline electrolyte for the HER can be concluded as follows:³⁻⁴

(1) Adsorption

(2) Desorption

The adsorption and desorption processes of atomic hydrogen on the surface of catalytic electrode (H_{ads}) are competitive, which strongly depend on the properties of the electrode such as element composition and conductivity. Therefore, the reactivity of the hydrogen electrode is directly related to the interaction between the electrode surface and hydrogen atoms. Given that hydrogen is too weakly adsorbed by the electrode surface, the adsorption process will limit the reaction speed. For another thing, if the H_{ads} is too tightly adsorbed by the electrode surface, then the following desorption process will limit the overall reaction speed. According to Sabatier principle, a favorable catalytic electrode is better to have an appropriately strong contact with the H_{ads} to promote the transformation of hydrogen, but it should also be weak enough to ensure that the linkage can be easily broke so the hydrogen can be released.⁵

Table 2.1 Relationship between Tafel slope and rate control steps in electrode reaction

Reaction Type	Tafel Slope ($\text{mV} \cdot \text{dec}^{-1}$)	Metal
Volmer	≥ 120	Zn, Cd, Hg, Pb
Heyrovsky	40~120	Ag, Ni, Co
Tafel	≤ 30	Pt, Pd, Rh

According to different rate-determining steps, the HER can follow the Volmer-Heyrovsky or the Volmer-Tafel processes. And which kind of process the electrode will choose depends on its intrinsic properties.⁶ Scientists can use the polarization curve and Tafel slope to determine the process, as shown in Table 2.1. Because the bond energy between noble metal (Pt, Pd, Rh) and the absorbed hydrogen is most suitable, the overpotential is generally very small for these metals. Therefore the reaction type belongs to Tafel reaction and they are excellent electrode materials for the hydrogen evolution.⁷ However, the scarcity and expensive prices prevent their widespread application in hydrogen evolution reaction. That's the reason why a commercial and efficient catalyst need to be fabricated to substitute noble-metal based electrodes. Compared with other non-noble metal materials, the Tafel slopes of Co and Ni are relatively small and the rate control step is Heyrovsky step. In recent years, Co and Ni are frequently used for water decomposition experiments.

2.1.1.2 Volcano Plot for the HER

First discussed by Sabatier, there must be appropriate interaction between the reactants and the catalyst⁸. If the interaction is too weak, the slow reaction of intermediates will influence the total reaction speed, but if the interaction is too powerful, the intermediates may occupy all accessible surface area and poison the reaction. It turns out that the speed of the whole process greatly relies on the free energy of hydrogen adsorption (ΔG_H). It has long been known that the relationship between the ΔG_H of metals and their HER exchange current density (j_0) demonstrated a “volcano” plot, which has been plotted by Greeley and co-workers through Density functional theory (DFT).⁹ The reaction rate will be affected once the interaction between the electrode and the adsorbed hydrogen is too strong or too weak. There must exist a site where the exchange current density is highest. Proposed by Parsons firstly, the favorable value would be located in the place near $\Delta G_H = 0$, the peak position of volcano plot.¹⁰

According to Figure 2.1, noble metals with small $|\Delta G_H|$ and high j_0 are located on the top of volcano plot, such as Pt and Pd. Compared with them, the performances of Co, Ni and

other non-precious metal materials are a little worse. However, some newly developed catalysts with different nanostructures and morphologies have exhibited excellent hydrogen evolution reactivity than conventional non-precious metal electrode materials. And some of them even show similar performances to noble metal electrode materials in recent years. With further research, it is believed that non-precious metal materials with great properties can substitute for noble metal catalysts for HER one day. In the experiment, Co was chosen to replace Cu in CuSe due to this reason.

Figure 1.1 Volcano plot for different pure metals towards hydrogen evolution reaction.⁹

2.1.2 Oxygen Evolution Reaction

The oxygen evolution reaction (OER) is a half reaction of water splitting that occurs on the anode. Today, electrodes made of alloys of nickel, iron and chromium are commonly used in the water splitting process. Currently, IrO_2 and RuO_2 are considered to be the most advanced OER catalysts and mostly used in industry. Although scientists are trying to develop low-cost alternatives to these oxygen evolution catalysts, the performances of most

non-precious metal catalysts are still lower than conventional catalysts. Oxygen evolution reaction can also take place in acidic condition even though alkaline condition is generally used as electrolyte. As mentioned above, using alkaline solution as electrolyte for alkaline electrolysis cell is the most widely developed and lowest cost technique. Non-precious metal electrodes can preserve relative stability and avoid decomposition in alkaline environment. Unlike HER, the OER is easier to happen under alkaline conditions than under acidic conditions, because no extra energy barriers that influence the overall reaction speed will be introduced. The thermodynamics and kinetics of the OER will be presented later.

2.1.2.1 Mechanisms

The oxygen evolution reaction process is much more complicated than the hydrogen evolution reaction. Therefore the reaction mechanism is also much more complicated. There is no absolute theory at present, but some mechanism processes are generally agreed. OER is an important oxygen electrode reaction, and the reaction mechanism varies in different electrolytes. In alkaline electrolyte, the mechanism can be concluded as follows:

According to the overall water splitting process, the oxidation reaction happens on positive electrode where two molecules of water were oxidized into one molecule of oxygen, releasing four protons and four electrons. While the reduction reaction takes place in negative electrode where two protons receive two electrons to form hydrogen. From a thermodynamic point of view, the reaction barrier that is required to hydrogen evolution is low compared with oxygen evolution. A large number of experimental and theoretical

analyses have shown that high-efficiency catalytic OER is very difficult from the perspective of thermodynamics and kinetics. Firstly, the oxidative half-reaction of water requires more energy than the reducing half-reaction. Secondly, the theory of mechanical collisions shows that the release of oxygen by the generation of O-O bonds is also a very difficult process. Therefore, the OER has become a bottleneck restricting the efficiency of the entire electrolysis reaction. Therefore, developing highly efficient OER catalysts has become a core issue in the field of electrolyzed water.

2.1.2.2 Volcano Plot for the OER

The theory of Sabatier has already introduced in volcano plot for the HER. Based on the previous experimental results, it has been able to obtain the volcano relationship diagram of HER, and initially summarize the interaction between different electrode materials and hydrogen adsorption. In addition to HER, similar volcano plots can be used for various electrochemical processes to evaluate the trend of electrochemical activity.

Figure 2.2 Volcano plot for different metal oxides towards oxygen evolution reaction.¹¹

Trasatti firstly reported on the OER volcano plot.¹² They used the transition of the metal in the metal oxide from the low oxidation state to the high oxidation state as a basis to analyze the electrocatalytic activity of the oxide electrode. The OER can be seen as a transition between two different configurations of surface coordination. If the intermediate is weakly adsorbed and the oxidized metal oxide is not very active, in which case the decomposition of water is a rate limiting step. On the other hand, if the intermediate is strongly adsorbed and the easily oxidized metal oxide is also not very active, the removing of oxygen from these electrodes is a rate controlling step. Therefore, the activity of the electrode is related to $(\Delta G_O^0 - \Delta G_{HO}^0)$.¹² Such volcano plot is commonly used for various oxide surfaces (Figure 2.2). Apparently, non-precious metal oxides such as Co_3O_4 and NiO are located in catalytically active tops on the volcano plot. They are even more active than some noble metals.

2.1.3 Selection of Electrochemical Catalysts

In general an excellent electrochemical catalyst needs to have the following properties:

First, the good electron transport capability, that is, good electrical conductivity. As an electrochemical catalyst, great electrical conductivity is a prerequisite for excellent catalytic activity. It's not only to ensure good electrical conductivity between the catalyst material and the electrode substrate, but also to provide rapid electrons and protons transfer between the catalyst and electrolyte.

Second, the high catalytic activity and selectivity. The high catalytic activity means to obtain the highest current density at low overpotential. And good selectivity should be ensured at the same time since the electrode reaction is often complicated. An excellent catalyst material can not only have high catalytic activity but also a certain selectivity to improve the efficiency of the electrochemical reaction.

Third, the high specific surface area or a great amount of active positions per unit area. Many of the reported materials are intentionally prepared into a hollow shape, which

enhances the connection between the active site and the electrolyte by increasing active sites of the catalysts, even facilitates the exchange of reaction products, such as the escape of bubbles during splitting of water.

Fourth, stability. Electrochemical reactions including oxidation and reduction processes tend to be very violent. Therefore, it's important to pay attention to changes in the electrode material itself while observing changes in reactants and products. A good catalyst is preferable to maintain catalytic activity for a long period of time without being oxidized or reduced and the change of the structure.

Through the above discussion, noble metals like Pt and Pd are ideal electrocatalysts for hydrogen evolution reaction. They have good electron transporting ability, small overpotential and strong acid and alkali resistance. However, the production of precious metals is scarce so the price is high, which directly restricts the development of noble metal electrode materials. In recent years, people have been looking for electrode materials that can replace precious metals.¹³⁻¹⁴ At present, transition metal such as Co-based¹⁵ and Ni-based¹⁶ materials, semiconductor materials similar to MoS₂¹⁷, and graphene-like¹⁸ materials are hot topics of recent research. Among them, transition metals have become the most widely studied inexpensive metal catalytic electrode because of their successful conductivity and relatively suitable ability to adsorb hydrogen.¹⁹

2.2 Co-based Electrode Catalyst

People are paying increasing attention to the development and utilization of sustainable new energy sources, with the energy crisis and environmental problems becoming more and more serious, especially by preparing clean hydrogen energy by decomposing abundant water in nature. However, a suitable catalyst is needed to lower the barrier of water decomposition reaction due to this reaction carried out not easily. In the past, efforts have been made to use precious metal to catalyze the decomposition of water. For example, Pt has been found to possess high efficiency in catalyzing the H₂ reduction reaction of water. And the Ru complex or IrO₂ is also a good water oxidation catalyst. Due to the high

cost of the precious metal catalysts themselves, they are greatly limited in practical applications. As a result, scientists are gradually turning their attention to less expensive metal electrodes, for instance the first-period transition metal elements, for instance the Mn, Co, Ni, Fe, and Cu. Compared with precious metal materials, these non-precious metal materials have obvious advantages: (1) Rich reserves and lower cost make them conducive to practical application; (2) good material stability; (3) simple preparation method, especially for metal oxides; (4) good catalytic performance. Therefore, in-depth research and development of efficient and stable non-precious metal materials used as catalysts for water decomposition is a hot spot in the current new energy field.

Cobalt, a commonly used non-precious metal, is richer than many transition metals in the earth's crust. Since Co-based catalysts have long been considered to be one of the most likely alternatives to precious metal catalysts, many studies have been done on them, such as the regulation of the morphologies of these Co-based catalysts. Special morphological structures can be used to improve the area of exposed active surface and increase conductivity by promoting the contact with the electrode substrate.²⁰⁻²¹ It can even further accelerate the reaction and improve the performance of the catalyst through controlling the way the gas escapes. In theory, the most active cobalt-based catalyst should be elemental cobalt metal. However, the metal element is relatively easy to be oxidized in the air, which will affect the catalytic activity. Therefore, many studies have focused on the composition and morphology of the cobalt metal catalyst. On one hand, some other elements are combined with cobalt metal to enhance the activity of the catalyst through the interaction between different metals. On the other hand, the non-metallic compound being stable in the air is combined with the cobalt metal to protect the elemental cobalt from oxidation.²² On this basis, there has been a lot of cobalt-based electrodes with different compositions and morphologies are reported.

2.2.1 Co-based Nanoparticles Electrode Catalyst

In order to increase the utilization of non-precious metals and also to reduce the cost of the HER reaction, a transition metal compound catalyst or a transition metal catalyst coated

with the carbon is generally designed. The energy conversion efficiency of the metal nanoparticle material per unit mass is high, but with the increasing of the amount of the catalyst, an agglomeration will be formed to affect the efficiency. For the purpose of avoiding the agglomeration of the nanoparticles and further enhancing the electron transporting ability, it is designed to coat graphene or carbon nanotube in the outside of the metal nanoparticles.²³

Figure 2.3 (a,b,c) TEM images and schematic illustration of CoNi@NC revealing the graphene outer casing and particles inside. (d,e) HER performance of LSV and Tafel slopes for prepared CoNi@NC at different temperatures.²⁵

Using carbon material to cover metal or alloy materials is an important direction for designing high-efficiency and stable catalysts. It is generally believed that the electron transfer between graphene and metal directly increases the electron density of graphene surface, which is beneficial for the reduction reaction on the surface.²⁴ Bao and his group

reported a uniform hierarchical structure CoNi nanoalloy consisting of ultrathin graphene shells (1-3 layers), which can enhance hydrogen evolution performance. Due to the increasing of the electrons on the surface, the graphene shells can not only reduce ΔG_H , but also improve the stability of the adsorbed H_{ads} . This catalyst displays high stability and activity in acidic media: the overpotential is almost zero v.s. the reversible hydrogen electrode (RHE) and this value just increases to 142 mV when the current density is $10 \text{ mA} \cdot \text{cm}^{-2}$. Notably, the performance is approaching to industrial 40% Pt/C catalyst (Figure 2.3).²⁵

Similarly, Yu et al. fabricated CoP particles covered by nitrogen doped graphene with hollow nanostructure as bifunctional electrodes, which showed outstanding efficiency and chemical-stability towards gas evolution. During electrochemical water splitting process, CoP_h/NG hybrids achieved a current density of 10 mA cm^{-2} around 1.58 V, favorably comparable to the comprehensive activity of commercial Pt/C and IrO_2 . This successful performance was resulting from the hollow structure and incorporation of N in graphene (Figure 2.4).²⁶

Figure 2.4 (a,b) TEM graphics of the CoP_h/NG hybrid composites. (c,d) The polarization and Tafel plots curves of as-prepared materials towards OER. (e,f) Linear sweep voltammetry and Tafel plots curves of samples towards HER.²⁶

2.2.2 Co-based One-dimensional Electrode Catalyst

High electrical conductivity and high active area are still the two main directions for scientists to pursue higher catalytic performance. However, in the process of water splitting, there are many methods for loading the catalyst on the electrode. The most commonly used method is directly dispensing, since synthesized catalyst can be quickly and conveniently loaded onto the electrode. But some catalysts do not adhere well to the surface of the electrode and will fall off as the reaction proceeding. In such situation, an adhesive might be required, for example the Nafion solution, which is often used in precious metal catalysts to help the catalyst tightly contact the electrode. However, the poor conductivity of the binder may affect the activity of the electrode.²⁷ Another solution is in-situ growth. The electrode and the catalyst can automatically connect together to be conductive and the catalyst is not easily dropped during electrochemical reaction.²⁸ Therefore, many of the catalysts for water splitting are obtained by this way.

Figure 2.5 (a) SEM results of CoP/CC. (b,c) TEM and High-resolution TEM images of CoP nanowire. (d,e) The LSV curves and Tafel plots of samples towards HER.²⁹

There have been many reports on in-situ growth of cobalt baseline array catalysts. Sun and coworker synthesized self-supported porous nanowire CoP arrange on carbon cloth forming CoP/CC via topotactic phosphidation at low temperature. As a catalyst for HER process, the CoP/CC displayed a small overpotential of 38 mV and a low Tafel slope of 51 mV dec⁻¹ with admirable stability and endurance (Figure 2.5).²⁹ The rapid electrons transfer from carbon cloth to CoP forms an adsorbed H_{ads} in metallic cobalt. P can promote desorption process of hydrogen by adsorption with hydroxyl groups. Besides, the high porosity of nanowires can not only increase active surface, but also accelerate the mass transfer process in the reaction. They together account for the excellent performance of CoP/CC.

2.2.3 Co-based Two-dimensional Electrode Catalyst

Two-dimensional non-precious metal catalyst is one of the most commonly used structures in the catalytic electrolysis water in recent years, due to its relatively large exposed active area and the faster mass transfer rate. This kind of structures can accelerate the generation and escape of gas from the electrode surface. Apart from this, materials with sheet structure are difficult to be destroyed during violent electrochemical reaction.³⁰ The preparation method of the two-dimensional electrode material can be divided into two ways: in-situ growth and non in-situ. The shape, thickness and element doping of the materials can be adjusted through non in-situ growth, which regulates the catalytic properties of the material from the original scale. While the two-dimensional materials fabricated by in-situ growth are more closely connected to the substrate, which is beneficial to the transmission of electrons.

Solvothermal method is commonly used as a non in-situ growth of two-dimensional materials. Gao et al. reported a highly efficient catalyst for HER, which was fabricated by growing MoS₂ on the face of CoSe₂ nanobelt substrate (Figure 2.6 a,b,c). MoS₂/CoSe₂ was found achieving fast HER rate with a small onset voltage of -11 mV and a low Tafel plot of 36 mV dec⁻¹. The electrocatalytic synergism between MoS₂ and CoSe₂ and the high active area can account for its excellent performance, which is even fairly near to industrial

Pt/C catalyst (Figure 2.6 d,e).³¹ However, the binder such as Nafion solution is required for tightly contact, which will cause the poor conductivity of the electrode to affect the reaction activity.

Figure 2.6 (a) TEM image of MoS₂/CoSe₂ hybrid. (b,c) HRTEM results of MoS₂/CoSe₂ composite material are distinguished with the microstructures of MoS₂ and CoSe₂. (d,e) HER performances of the samples.³¹

Therefore, many scientists choose to synthesize nanosheets by in-situ growth on the substrate. The close connection between electrode and the catalyst can accelerate the electron transfer on the electrode and improve the stability. It is ensured that the catalyst will not easily fall off the surface of the electrode in the case of vigorous gas generation. Fang and his group synthesized a porous CoSe₂ on carbon cloth through in-situ growth on a Co-based metal organic framework template.³² This porous CoSe₂ materials exhibited a lower overpotential of 1.48 V (vs. RHE) towards OER owing to the increased catalytic area and excellent conductivity (Figure 2.7 d,e).

Figure 2.7 (a,b,c) SEM, TEM, HRTEM, and SAED results of prepared porous CoSe₂, respectively. (d,e) Linear sweep voltammetry and Tafel slopes curves of the as-formed materials towards OER in 1 M KOH.³²

2.3 Ultrathin Copper Chalcogenides Nanomaterials

Ultrathin nanostructures are believed to have at least 1D size close to few crystal unit cells, usually less than 5 nanometers.³³⁻³⁴ Due to the development of graphene, strong research attention in other ultra-thin nanomaterials has recently ignited.³⁵ In particular, ultrathin metal chalcogenides nanomaterials display many special advantages, and are therefore potential materials for widespread applications. What's more, the simple preparation and processability of these nanostructures are becoming the most important things, making them a promising building block for widespread application.

In order to efficiently synthesize such ultra-thin nanostructures by colloidal chemical synthesis, fine handling of the interplay between the nucleus and the ligand molecule is essential, which enables growing of the crystals anisotropically along a particular orientation. To date, many ultrathin metal-based chalcogenides nanomaterials have been fabricated by organometallic or organic solutions method.

2.3.1 Ultrathin Copper Sulfide Nanomaterials

Copper sulfide, the semiconductor, is widely studied and typically used for solar cells.³⁶ Scientists have already fabricated some ultrathin copper sulfide nanostructures, since ultrathin metal sulfide nanocrystals have attracted great interest owing to their special performance, which resulting from the quantum size effects. With well-defined morphology and size, copper sulfide nanostructures will be able to bring new applications and improve the properties of present photoelectric devices.

Much of the attention have already focused on the evolution of novel synthesis methods for the fabrication of inorganic nanowires with small diameters and high aspect ratios. Liu et al. reported a uncomplicated solution phase technique for fabricating ultrathin nanowires of hexagonal Cu_2S with high aspect ratio.³⁷ Controllable Cu_2S nanowires can be obtained with sizes less than 2.5 nm and lengths up to tens of microns (Figure 2.8). Furthermore, by carefully choosing the parameters, the resulting Cu_2S nanostructures can be selectively controlled to have nanowires, nanorods and nanoparticles structures. Therefore, the method also offers an effective way for synthesizing Cu_2S nanostructures with different shapes and sizes.

Figure 2.8 (a) Low magnification and (b) high magnification TEM images of as-prepared Cu_2S nanowire bundles. (c) HRTEM images of Cu_2S nanowire.³⁷

Besides, Zhang and his group gave a simple and versatile technique to achieve monodisperse, ultra-thin, single-crystal CuS nanosheets based on a soft template strategy.³⁸ According to their work, a large number of hexagonal CuS nanosheets have been

synthesized with a thickness up to 3.2 nm and a plane size up to 453 nm (aspect ratio ~ 150), as shown in Figure 2.9. Based on a soft template strategy, this technique has several benefits over traditional fabrication of ultra-thin copper sulfide nanocrystals. First of all, it is environmentally friendly and economical compared to organometallic thermal decomposition and chemical vapor deposition processes, since the reactants are non-toxic, green, phosphorus-free and inexpensive. Besides, it is capable of fabricating large scale and high yield of uniform ultra-thin CuS nanostructures through one-step reaction at comparatively low cost. Furthermore, this method could be applied to synthesis of other types of ultra-thin metal sulfide nanocrystals.

Figure 2.9 (a,b,c) FESEM images of ultrathin copper sulphide nanosheets. (d,e) TEM images of ultrathin copper sulphide nanosheets with lying flat and standing on the TEM grids. (f,g) HRTEM images of a specific copper sulphide sheet lying flat and several stacked copper sulphide sheets standing on the TEM grids.³⁸

2.3.2 Ultrathin Copper Selenide Nanomaterials

2D nanomaterials have attracted huge interest due to their extraordinary characteristics resulting from the thin size and two-dimension morphology. Especially, 2-D transition metal chalcogenide nanomaterials are already be widely proceeded and employed in various applications.³⁹⁻⁴¹ Copper selenide is an important anisotropic p-type semiconductor with many phases including stoichiometric and non-stoichiometric phase. It also grows as cubic with high thermodynamic stability and other crystalline phases such as hexagonal, orthorhombic and monoclinic.⁴²⁻⁴³ For instance, stoichiometry hexagonal CuSe is stable at room temperature, while non-stoichiometry Cu_{2-x}Se usually shows a cubic structure and is commonly used for solar-cell.⁴⁴⁻⁴⁵ However, the fabrication of ultrathin CuSe nanomaterials has rarely been reported.

Figure 2.10 (a,b) TEM images of precursor CdSe nanosheets with 1.6 nm thickness. (c,d) TEM results of Cu_{2-x}Se nanosheets with same thickness as CdSe after cation exchange reaction. Inset images in (a) and (c) are the lattice-resolved TEM graphics of the edge of CdSe and Cu_{2-x}Se nanosheets. The top and bottom inset images in (b) and (d) are the lattice-resolved basal plane TEM and overall SAED pictures.⁴⁶

Wang et al. successfully fabricated Cu_{2-x}Se nanosheets with controllable thickness through CE reaction beginning with CdSe nanosheets.⁴⁶ By gently adding a Cu^+ salt in methanol to a suspensions of prepared cadmium selenide nanosheets, ultrathin Cu_{2-x}Se nanosheets were obtained after centrifuging. The as-prepared ultrathin Cu_{2-x}Se nanosheets (1.6 nm) were also stable when exposed to air. Notably, through cation exchange reaction, the original morphology and crystal structure of the CdSe can be reserved due to the maintaining of parent anion sublattice.

While Zhang and the group synthesized 2-dimensional ultrathin copper selenide nanosheets (thickness ~ 5 nm) through an organic solutions phase method at low temperature, which avoided using a poison, pyrophoric, and high cost alkyl phosphine.⁴⁷ Without a morphology change, the as-synthesized microscale, phase-pure hexagonal copper selenide nanosheets can be even converted to cubic Cu_{2-x}Se nanosheets through simple heat treatment (Figure 2.11 a,c).

Figure 2.11 FESEM and TEM results of as-formed (a,b) CuSe nanosheets and (c, d) Cu_{2-x}Se nanosheets (e,f) HRTEM results of a small area of CuSe nanosheet with orientation perpendicular to the [001] region axis (e) and the folded edge of a CuSe nanosheet (f). (g,h) HRTEM results of a small area of a Cu_{2-x}Se nanosheet with orientation perpendicular to the [111] region axis (g) and the folded edge of a Cu_{2-x}Se nanosheet (h).⁴⁷

2.3.3 Copper Selenide Catalyst

In recent years, non-precious metal materials have been researched and developed very rapidly in the field of electrocatalytic water decomposition, in view of expensive cost of the precious metal catalysts. As a result, scientists are gradually turning their attention to the first-period transition metal elements, for instance the Mn, Co, Ni, Fe, and Cu. Representative materials such as Co, Ni and Fe, and their alloys, oxides, hydroxides, phosphides, etc., have been used for applications in water decomposition. Compared with them, there are few studies about Cu-based materials on electrocatalytic water splitting. However, Copper-based materials have many unique advantages over the cobalt, nickel, and iron-based materials discussed above. First of all, the conductivity of copper is second only to that of precious metal silver in nature, and its cost is far less than silver, which makes it widely used in the field of electrode materials. Second, copper-based materials have obvious advantages in terms of earth reserves, material costs and redox properties. Third, Cu(II) itself has a prominent advantage in coordination chemistry, which can be reduced to Cu(0) or Cu(I), or be oxidized to Cu(III) or even Cu(IV). However, at present, the research on electrocatalytic water decomposition of copper-based materials is far less than that of cobalt, nickel and iron-based materials. Therefore, in-depth study of the potential of copper-based materials in electrocatalytic water oxidation and water reduction is of great importance for the using of inexpensive materials in the field of catalytic water splitting.

Initially, it was studied that bimetallic Cu complexes were used as molecular catalysts in electrocatalytic water reduction.⁴⁸⁻⁴⁹ Until 2014, Liu et al. reported the first Cu metal mononuclear complex that can be used for electrocatalytic water reduction to produce hydrogen.⁵⁰ Subsequently, many mononuclear copper complexes were found to have certain effects on electrocatalytic water splitting.⁵¹⁻⁵² However, whether it is a single-core or a dual-core Cu metal complex, they have very obvious defects in the electrocatalytic water splitting, that is, low catalytic efficiency, high overpotential, etc., which greatly limit their widespread application.

Figure 2.12 (a) SEM graphic of Cu_{2-x}Se nanostructure. (b) TEM result of as-prepared Cu_{2-x}Se material. (c) High-resolution TEM image of one Cu_{2-x}Se nanosheet. (d,e) HER activity and corresponding Tafel plots curves of synthesized Cu_{2-x}Se/Cu foam with hierarchical structure in 0.5 M H₂SO₄.⁵⁶

Later, it was found that Copper nanomaterials with higher specific surface area have better property in HER. Ganguli and the coworker obtained copper nanoparticles (4-6nm) through thermal decomposition of copper oxalate nanorods, showing highly enhanced efficiencies and stability toward HER.⁵³ In addition to Cu(0) materials, copper-based composite materials such as Cu₃P and Cu₂MoS₄ are also determined to effectively catalyze water reduction to produce hydrogen.⁵⁴⁻⁵⁵ Yuan and the group used the anion exchange method to fabricate hierarchical nanomaterials composing of ultrathin Cu_{2-x}Se nanosheet.⁵⁶ This nano Cu_{2-x}Se/Cu foam catalyst obtained improved hydrogen evolution activity with a small overpotential of 313 mV around -100 mA cm⁻² current density (Figure 2.12 d). Resulting from its special structure, the promoted mass transfer properties can account for the great improvement of water splitting performance for Cu_{2-x}Se/Cu foam. This broadens the research ideas of copper-based materials in the field of electrocatalytic hydrogen production, and provides the possibility for people to further develop new copper-based materials.

2.4 Cation Exchange Reaction

Recent years witnessed an increasing concern about the heterostructures formed by different semiconductors, which play an important role in modern industry and have been widely applied. Depending on the different architectures of the heterostructures, the fabrication methods vary. Here, partial transformation through cation exchange reaction is demonstrated, since it allows for increased complexity in the fabrication of nanocrystals.⁵⁷⁻⁵⁸ As for ionic crystals, origin metal ions can substitute with other cations through a rapid, simple and reversible CE, changing the component of the nanocrystals yet maintaining their nanostructure morphology. Particularly, this is frequently used in transition metal chalcogenide.⁵⁹⁻⁶⁰ Through cation exchange reaction, the anionic framework and the compositional interface between constituents can be reserved and utilized for fabricating nanoheterostructures. This will greatly expand the field of CE to design of even more complex nanostructures.

Cation exchange is a technique for chemically converting liquids or extending solids by replacing cations with other kinds of cations in an ionic materials with long history. Because of the emergence of high-quality nanocrystals, the technology is undergoing a major renaissance: currently scientists have the ability to overcome the limitations of bulk materials and make full use of CE process for material fabrication through solid-state fast low-temperature conversion. Briefly, by exposing the precursor crystals to other cation, CE occurs with the replacement of the metal ions in the previous material while the anionic backbone being unchanged. When the previous metal ions spread out of the crystals, new cation will enter the parent crystal. CE could happen in both isovalent (i.e. $\text{Cu}^+ \leftrightarrow \text{Ag}^+$) and non-isovalent (i.e. $\text{Cu}^{2+} \leftrightarrow \text{Ag}^+$) situation. The overall cation exchange reaction is as equation showing in Figure 2.13. Here M is the in going cation, C and A are the original crystal ions. The thermodynamic driving forces are decided by concluding the influence of lattice energy, surface tension, solvation effect, dislocation and dissociation energy. These factors mentioned above are of great importance for CE (Figure 2.13).⁶¹ This thermodynamic information helps to predict the possibility of an CE process. Furthermore, it even provide significant knowledge about the critical point of the CE process. And the

conditions that must be performed are different for each CE reaction, since they all have a unique thermodynamic fingerprint.

Figure 2.13 Principals for achieving cation exchange reaction.⁶¹

Although the kinetics of CE can be accelerated by elevated temperatures, material stability or manufacturability would usually be affected. Actually, CE reaction in solids typically is a compromise between kinetics stability and thermal stability. Previously, it requires a long reaction time for a solid to complete a CE reaction at a temperature of 100-800 °C, sometimes even for many days. Such long processing time greatly limits the using of CE method for bulk materials. What's more, any further temperature increasing is also limited by material stability. The basic barriers for cation exchange in solid state scale mentioned above are alleviated in nanocrystals, in view of the promoting specific surface area and low atomic number, which make significant acceleration of transformation possible. For nanocrystal CE reactions, it's reported that room temperature and sub-second reaction times are up to one hundred times quicker than bulk materials in the example of silver ion exchange in cadmium selenide, which can even be described as a molecular reaction.⁶²

2.4.1 Cation Exchange in Nanocrystals

Because the reaction barrier for nucleation and interfacial strain can be greatly reduced on the nanometer scale, there is no doubt that exchange kinetics can vary widely depending on the morphology and composition of the materials. Besides, the energy of CE process is also regulated by the size of the nanocrystals, as the surface energy begins to have a more and more significant effect on the lattice energy with decreasing size of the nanocrystals. From a mechanical point of view, the great surface area of nanocrystals can realize the fabrication of special phases and decrease required energy. Plus, the reaction direction can be slightly altered to achieve an almost completely reversible CE reaction because of the reducing activation barrier.⁶³⁻⁶⁴ For nanocrystals, both a great amount of ingoing cations and favorable solubility of the origin metal ions are enough to initiate the reaction at low temperature. This can also be utilized to change CE reaction. A typical example is the cation exchange between Cu^+ and Cd^{2+} : the CE reaction from Cd^{2+} to Cu^+ is particularly easy to achieve through differential solvation,⁶⁵ and the opposite CE reaction from Cu^+ to Cd^{2+} can be driven by using a large excess of Cd^{2+} at room temperature.

In recent years, CE process have increasingly been used as a synthesis tool to acquire unique materials because the typical CE process is very simple. Besides this, nanoscale CE reactions generally display outstanding morphological retention, fast reaction speeds and adjustable thermodynamics, making them especially attractive method. Cadmium chalcogenides CdX ($X = \text{S}, \text{Se}, \text{Te}$) as typical template for cation exchange are widely investigated. Nanocrystals of Zn, Cu, Ag, Pb and Hg chalcogenides can be fabricated starting from nanocrystals CdX ($X = \text{S}, \text{Se}, \text{Te}$) through cation exchange method.^{63,66-67} CE process allows scientists making other nanocrystals using established cadmium chalcogenide chemistry, which may not be easily directly achieved with similar morphology through other methods. The ability of materials with nanostructures undergoing fast CE process at low temperature broadens a wide range of applications on nanoscale than we can see in bulk materials.

2.4.2 Cation Exchange in Heterostructures

Recent years, multicomponent nanocrystals with heterostructures have attracted particular interest and are widely investigated for the applications such as photovoltaic cells. Post-synthetic conversion of nanocrystals has become a powerful method for making complex nanomaterials with controlled structures or compositions. Among them, the cation exchange (CE) reaction in solution has been increasingly used as an effective synthesis method for preparing nanoheterojunctions, or even a metastable material with a unique composition and morphology. The partial exchange of cation allows for increased complexity in the synthesis of nanocrystals, which can be classified as "homogeneous" or "heterogeneous".⁶⁸

For "homogeneous" cation exchange, a solid solution will be obtained, for example, nanocrystals doped with foreign cations (i.e. CuInZnS nanocrystals).⁶⁹ By cation exchange reaction, doping can be realized with suitable driving forces at room temperature.⁷⁰ Currently, doping of chalcogenide nanocrystals is generally realized through introducing a dopant precursor in a hot-injection step. Unfortunately, the technique requires the stability of materials at high temperature and provides poor crystallographic stoichiometric control. While stoichiometry can be ensured by "homogeneous" CE with strong thermodynamic driving forces at mild temperature environment. Compared with traditional hot-injection method, the CE is also more flexible and easy to handle.

"Heterogeneous" cation exchange usually happens when the new phase nucleates on the surface and then grows towards the interior of the nanocrystals. Such partial cation exchange process might introduce sharp interfaces or heterojunctions into nanocrystals. For instance, core shell heterostructure PbSe/CdSe was formed by exchange PbSe with Cd²⁺ through CE.⁷¹ The resulting materials exhibited enhanced quantum yield excitonic emission and increased stability due to the limitation of electron and hole carriers within the lower band-gap lead selenide. Other unique nanoscale attributes such as asymmetry and anisotropy are also possibly introduced during cation exchange process. In the cation exchange CdS nanorods with Cu⁺, the replacement was selectively beginning with the end

faces such that Cu₂S grew inwards from the ends.⁷² Due to the unity of the anion skeleton, partial transformations and preservation of nanocrystal size/shape can be ensured during cation exchange as mentioned above. Apart from the size and shape of nanocrystals, the composition interface within heterostructures is also preserved with high fidelity, which may also propose a new idea that heterostructure nanocrystals can also be used as templates.^{46,73}

Cation exchange has been able to generate a variety of heterogeneous structures, and the number of other complex structures that can be achieved is not limited. It's a powerful tool to synthesize covalent phases, metastable nanomaterials, multi-component alloys, and doped nanocrystals with morphological well-defined nanocrystals, which will be inaccessible via direct fabrication.⁷⁴

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Chapter 3

Experimental Methodology

In this chapter, the reason for the selection of materials and the goal are illustrated first. The experimental methods for the synthesis of CuSe nanosheets and CuSe-CoSe heterostructures are described. And the characterization techniques together with electrochemical studies are also presented. For characterization machines such as FESEM et al, the physical principles of techniques are also described.

3.1 Rationale for selection

The goal of this article is to synthesize CuSe-CoSe nanosheets with special heterostructure as an efficient electrocatalyst for HER and OER. Here, the preparation of CuSe-CoSe nanosheet heterostructures used cation exchange method beginning with CuSe. The reasons for the selection of method and materials are as follow.

Firstly, it is known that non-precious metal catalysts with two-dimensional nanosheets structure are the most commonly used structures in catalytic electrolysis in recent years.¹⁻² The relatively large exposed active area of the nanosheets structure material can faster the mass transfer rate and facilitate the gas generated by the reaction to rapidly escape from the surface of the electrode. Nanosheets are stable compared with other nanomaterials, which means it would be difficult to destroy the structure during violent electrochemical reaction.³ There are already many reports about the synthesis of nanosheets CuSe. In the experiment, nanosheets CuSe can be routinely achieved with CuCl₂ reagent through organic solution phase method, which is environmentally friendly and economical compared to organometallic thermal decomposition and chemical vapor deposition processes, since the reactants are non-toxic, green, phosphorus-free and inexpensive.

Secondly, heterostructures formed by different semiconductors play an important role in modern industry. Cobalt will be introduced to CuSe precursor to form CuSe-CoSe nanosheets heterostructure since the HER and OER performances for traditional CuSe are not good. To achieve this, cation exchange reaction in solution was used as an effective synthesis method for preparing materials with heterostructure due to the simplicity and the preservation of former nanocrystal size and shape.⁴⁻⁷ Besides, the high mobility of Cu²⁺ can facilitate exchange process with other cations during cation exchange reaction. These features make it possible for different kinds of morphologies to introduce a rich set of nanomaterials and interfaces in following processes.

3.2 Synthesis of CuSe Nanosheets

3.2.1 Chemicals

Oleylamine [OA, technical grade, 70%, Sigma-Aldrich], 1-dodecanethiol [DDT, >98%, Sigma-Aldrich], Copper (II) chloride [CuCl_2 , 99.99%, Sigma-Aldrich], Selenium powder [Se, 99.99%, Sigma-Aldrich], Hydroxylamine hydrochloride [$\text{NH}_2\text{OH}\cdot\text{HCl}$, 99%, Sigma-Aldrich], Hydrated hydrazine [$\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 80%, Sigma-Aldrich]. All chemicals were used without further purification.

3.2.2 Method

A typical organic solution phase procedure was employed to synthesize CuSe nanosheets. 0.5 mmol of CuCl_2 and 10 mL OA were added in a 3-necked flask (50mL) at room temperature. In order to remove water and oxygen, the slurry was heated in a temperature-controlled electromantle with vigorous magnetic stirring at 120°C under vacuum for 30 minutes to get a deep blue solution. Then the temperature was lower to 80°C in an oil bath until the temperature of the solution was stable. After 30 minutes, 1 mmol of $\text{NH}_2\text{OH}\cdot\text{HCl}$ powder was added into the solution for the reduction of copper (II) to copper (I). The resulting mixture will become slight yellowish and transparent after about 3 minutes and finally to deep green solution about 5 minutes. Then 1 mmol of Se powder together with 1 mL OA and 0.5 mL DDT were mixed by ultra-sonication at room temperature to form Se dispersion. After that, the dispersion was immediately injected into the previous liquid at 80°C . The resulting solution became dark when it was kept for 3 hours at 80°C . In order to study the effect of the increasing reaction time and temperature on the fabrication of hexagonal sheet structure, the resulting solution was also kept for 5 hours at 80°C and 3 hours at 120°C .

After cooling down to room temperature, the synthesized CuSe was precipitated through addition of absolute ethanol and hexane to the mixture. In order to completely remove the remaining Se precursor (can be easily oxidized to Se powder), the precipitate was washed

by the mixture of 6 mL of OM and 1 mL of DDT and ultra-sonication for 30 minutes. Finally, the nanosheet materials were washed by hexane for several times to remove other organic solution and collected by centrifugation at 8,000 r.p.m. for 5 minutes. The as-prepared CuSe nanosheets can be well-dispersed and stored in hexane before using for the next step. This CuSe nanosheet was named CuSe-Before.

Figure 3.1 Experimental device for the synthesis of CuSe.

Organic solution such as OA can be difficult to remove totally and will influence the electrochemical activity by decreasing the conductivity. Therefore, in order to completely remove OA for testing CuSe, 30 μL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 2 mL of absolute ethanol were added to approximate 10 mg CuSe, followed by ultrasonic dispersion for 10 minutes. Then the centrifugation and resuspension processes were further repeated three times for each sample by adding 1:1 absolute ethanol:hexane mixture before the final product was

suspended in hexane for characterization. The CuSe with the treatment of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was named CuSe-After. Following characterization and electrochemical studies will reveal the function of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ by comparing CuSe-After with CuSe-Before.

Figure 3.2 The picture of laboratory centrifuge.

3.3 Cation Exchange Reaction on CuSe

3.3.1 Chemicals

The as-formed Copper selenide nanosheets. Oleylamine [OA, technical grade, 70%, Sigma-Aldrich], Cobalt chloride [CoCl_2 , 99.99%, Sigma-Aldrich], Hydrated hydrazine [$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%, Sigma-Aldrich]. All chemicals were used without further purification.

3.3.2 Preparation at Different Temperatures

CuSe – CoSe Nanosheets were synthesized through cation exchange reaction. A total of 35.5 mg of the as-formed copper selenide nanosheets were dispersed in 5 mL oleylamine to form CuSe/OA slurry at room temperature for further use. In a typical cation exchange

reaction with Co^{2+} at 140°C , 5 mL of OA were added in a 50 mL three-necked flask and the temperature was elevated to 120°C to remove water and oxygen with vigorous magnetic stirring under vacuum for 30 minutes in a temperature-controlled electromantle. Then the temperature was slowly increased to 140°C . When the temperature was stable, 1 mL of CuSe/OA and 0.05 mmol of CoCl_2 were added to the solution. After cation exchange reaction for 30 minutes the three-necked flask was quickly cooled down by being immersed in cool water. The product was isolated through addition of 1:1 absolute ethanol:hexane mixture, followed by subsequent centrifugation and resuspension in hexane. The centrifugation and resuspension processes were repeated twice for each sample. The whole experiment was repeated for other cation exchange reaction temperature including 160°C , 180°C , 200°C and 220°C .

Figure 3.3 Experimental device for cation exchange reaction.

Same to the synthesis of copper selenide nanosheets, in order to completely remove oleylamine, 30 μL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 2 mL of absolute ethanol were added to each sample, followed by ultrasonic dispersion for 10 minutes. Then the centrifugation and resuspension processes were further repeated three times for each sample by adding 1:1 absolute ethanol:hexane mixture before the final product was suspended in hexane for characterization. The prepared materials were recorded as Co-CuSe 140°C, Co-CuSe 160°C, Co-CuSe 180°C, Co-CuSe 200°C and Co-CuSe 220°C.

3.3.3 Preparation at Different Reaction Times

CuSe – CoSe Nanosheets were synthesized through cation exchange reaction. A total of 21.3 mg of the as-formed copper selenide nanosheets were dispersed in 3 mL oleylamine to form CuSe/OA slurry at room temperature for further use. In a typical cation exchange reactions with Co^{2+} , 15 mL of OA were added in a 50 mL three-necked flask and the temperature was elevated to 120°C to remove water and oxygen with vigorous magnetic stirring under vacuum for 30 minutes in a temperature-controlled electromantle. After that the temperature was slowly increased to 180°C. When the temperature was stable, 3 mL of CuSe/OA and 0.15 mmol of CoCl_2 were added to the solution. Took 3.6 mL of sample each time after 5 minutes, 15 minutes, 30 minutes, 60 minutes and 120 minutes. The product was isolated through addition of 1:1 absolute ethanol:hexane mixture, followed by subsequent centrifugation and resuspension in hexane. The centrifugation and resuspension processes were repeated twice for each sample.

To completely remove oleylamine, 30 μL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 2 mL of absolute ethanol were added to each sample, followed by ultrasonic dispersion for 10 minutes. Then the centrifugation and resuspension processes were further repeated three times for each sample by adding 1:1 absolute ethanol:hexane mixture before the final product was suspended in hexane for characterization. The prepared materials were recorded as Co-CuSe 5 min, Co-CuSe 15 min, Co-CuSe 30 min, Co-CuSe 60 min and Co-CuSe 120 min.

3.4 Characterization Techniques

The size and morphology of the prepared CuSe NSs and CuSe – CoSe NSs were analyzed by a Field Emission Scanning Electron Microscope (FESEM) JEOL, JSM-7600F at 15.0 kV, coupled with Energy Dispersion X-ray (EDX) detector, which was used to determine the composition and element of the nanosheets.

The morphology and composition of synthesized materials were also characterized through the using of transmission electron microscopy (TEM), JEOL, 2100F microscope at an acceleration of 200 kV. To prepare the samples, CuSe NSs and Co-CuSe 30 min were separately dispersed in ethanol followed by ultrasonic dispersion. Then dropped one or two drops of prepared aqueous solution onto carbon-coated copper grids.

The phase and the crystallographic structure of the nanomaterials were examined using Bruker-AXS D8 Advance X-ray diffraction (XRD) instrument with tube voltage of 40 kV and tube current of 40 mA with filtered Cu-K α radiation ($\lambda=1.541874$ Å). Under ambient condition, diffraction patterns were recorded at a step width of 0.05° with 2θ ranging from 10° to 70° . The measurement was done in 14 minutes for each sample.

3.4.1 Scanning Electron Microscope

Scanning electron microscope is one kind of tools that produce images of invisible microspace and nanospace. SEM can show details and complexity not available with optical microscopy through a focussed beam of electrons, which will react with atoms when hitting the sample. Various outcomes such as back scattering electron, secondary electrons and alternatively X-rays will be generated during the interaction process. Figure 3.4 displays the reaction between electron beams and the sample, which is known as interaction diagram of SEM. These signals are utilized as the information containing the topography and composition of the sample.

The most common mode of image formation used in the scanning electron microscope makes use of low energy secondary electrons that can only escape (and therefore be detected) from near surface features. The efficiency of secondary electron emission is known as the secondary electron coefficient and increases markedly as a function of angle of tilt (θ) of the specimen surface (Figure 3.5). As a result of their low energy, secondary electrons can only escape from depths less than 10nm.⁹

Figure 3.4 The interaction between electron beams and sample.⁸

Figure 3.5 Angular dependence of secondary electron emission.¹⁰

Backscattered electrons (BSE) are produced through elastic. As for a flat specimen with regions of different chemical constitution, electron backscattering efficiency is primarily controlled by the average atomic number.⁹ Thus, in an image of a multiphase sample formed by backscattered electrons, regions of high signal intensity correspond to the highest atomic number elements and low signal to low atomic number elements. Since backscatter contrast is adjusted so that the highest atomic number regions appear white, the intermediate atomic numbers as shades of grey, and the lowest Z, black.

Figure 3.6 Backscattered electron co-efficient (θ) as a function of atomic number.

The size and morphology of the prepared CuSe NSs and CuSe – CoSe NSs were analyzed by a Field Emission Scanning Electron Microscope (FESEM) JEOL, JSM-7600F at 15.0 Kv. SEM images can reveal the change between CuSe before and after $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ treating, such as the shape and size of copper selenide. It's a direct method to show how morphology change when cation exchange reaction takes place at different temperatures. Most importantly, the process of cation exchange will be explored by examining samples varied in reaction times. The details of materials' shape, size and thickness are crucial points to justify the maintaining of initial nanocrystal structure while introducing the cobalt.

Figure 3.7 FESEM, JEOL, JSM-7600F.¹¹

3.4.2 Energy Dispersion X-ray

Typically, an energy dispersion X-ray systems are integrated into either an SEM or TEM instrument. It is an analytical technology used for elemental or chemical characterization of prepared materials. EDX is achieved by resolving the characteristic X-ray wavelength and intensity of the element emitted by the sample, and deciding the element contained in the sample based on the difference in X-ray wavelengths of the different elemental features. The quantity of the elements in the material could be determined through contrasting the

high of peaks of different elements. Usually EDX is applied in conjunction with an electron microscope to perform micro-component examination of the sample.

Figure 3.8 Principal of energy dispersion X-ray.¹²

The principal of EDX is as follows: An inner electron is excited to create a hole, causing the whole atomic system to become an unsteady excited condition, and will spontaneously transit from a high energy state to a low energy state. When the outer layer of electrons transition to a hole, the liberated energy is then absorbed within the atom and ejected from another external photoelectron of the outer layer, which is called the Auger effect. And the secondary optoelectronics kicked out is called Auger electron. Its energy is identity and irrelevant to the energy of the incident radiation. When the energy released by the outer layer of electrons into the inner layer of holes is not assimilated in the atom, but is transmitted as a mode of X-ray fluorescence, the energy of which is equal to the energy difference between the two layers. Therefore, the energy or wavelength of X-ray fluorescence is identity and maintains a one-to-one relationship with the elements. H. G. Moseley found that the wavelength (λ) of the X-ray is relevant to the atomic number (Z) of the element. The mathematical relationship is known as Mosley's law:

$$\lambda = K(Zs)^{-2}$$

Where K and S are constants, hence as long as the wavelength of the X-ray is calculated, the type of the element can be studied. This is the basis for qualitative analysis of the X-ray fluorescent. Furthermore, the intensity of the X-ray fluorescent has a certain relevance with the amount of the corresponding elements, and quantitative analysis of the elements will be carried out according to this.

For cation exchange experiment, characterization techniques such as energy dispersion X-ray (EDX) is necessary and useful. It can directly judge whether cobalt enters copper selenide after cation exchange while observing the morphology. Sometimes X-ray diffraction (XRD) is unable to detect the phase of cobalt selenide if the cobalt content of prepared materials is very low. However, EDX can easily finish this job and provide the dispersion of cobalt in the sample. What's more, the content ratio between different elements is offered through quantitative analysis. In the experiment, the content ratio of cobalt and copper in each sample will be examined to explore the cation exchange reaction process.

3.4.3 X-ray Diffraction

Figure 3.9 The wave-train is reflected by series of lattice planes.¹³

X-rays are optical radiation generated by the transition of atomic inner electrons under the impact of high-speed moving electrons, mainly including continuous X-rays and characteristic X-rays. XRD is an X-ray diffraction method. By using XRD, the diffraction pattern is analyzed to obtain information on crystalline content and phases of materials. Due to the highly sensitivity of XRD, it can even be applied to identify preferential ordering and epitaxial growth of crystallites.

Figure 3.10 Bruker-AXS D8 Advance.¹⁴

Crystals can be used as gratings for X-rays. When a monochromatic X-ray interacts with the large numbers of particles (atoms, ions, or molecules) in crystal, each particle that collides with the beam will produce an interference pattern, as shown in Figure 3.9. The patterns will interfere with each other causing the intensity of the scattered X-rays to increase or decrease. Due to the superposition of a large number of scattered waves of particles, the beams that interfere with each other to produce maximum intensity are called X-ray diffraction lines, which will happen only at specific distances and angles. This relationship is known as Bragg's law and the form is shown below. Here, λ is the wavelength of X-ray, θ is diffraction angle and d is the internal spacing between planes.

$$\lambda = 2d\sin\theta$$

The phase and the crystallographic structure of the nanomaterials were examined using Bruker-AXS D8 Advance X-ray diffraction (XRD) instrument. Diffraction patterns were recorded at a step width of 0.05° with 2θ ranging from 10° to 80° . The measurement was done in 14 minutes for each sample. Elemental mapping can only show the element content and distribution of the samples without revealing the phase of synthesized materials. Therefore XRD characterization is necessary to find out phase formation and change during cation exchange reaction by comparing the resulting spectrum of samples.

3.4.4 Transmission Electron Microscopy

Figure 3.11 The interaction between electron beams and TEM sample.¹⁵

Transmission electron microscopy projects an accelerated and concentrated electron beam onto a very thin sample that collides with atoms in the material to alter direction, causing solid angle scattering. The size of the scattering angle is concerning with the density and

thickness of the material, so the graphics with distinct brightness and darkness can be formed. Since De Broglie wavelength of the electron is very short, the resolution of the transmission electron microscope is much higher than that of the optical microscope, and can reach 0.1 to 0.2 nm. Therefore, transmission electron microscopy can be used to scrutinize the fine morphology of the material, and is even able to examine the construction of only one column of atoms, which is tens of thousands times smaller than the smallest structure that can be observed with an optical microscopy.

Figure 3.12 TEM, JEOL, 2100F.¹⁶

The imaging theory of transmission electron microscopy can be divided into three cases:

1. Absorption image. When electrons are projected into high mass and high density materials, the main phase forming effect will be scattering. The scattering angle of the electrons becomes larger as the mass thickness on the sample increases. Therefore the number of electrons passing through the sample is reduced, resulting in darkening of the image. Early TEM was designed according to this principle.

2. Diffraction image. Due to the different diffraction capabilities of each portion of the crystal, the diffraction wave amplitude distribution at different locations will correspond to different portions of the crystal as the electron beam is diffracted by the test material. When a defect occurs in the crystal, the diffraction ability of the defective portion will be different from the other intact region. Hence, the distribution of crystal defects is reflected by the amplitude of the diffraction wave which is unevenly distributed.
3. Phase image. When the thickness of sample is less than 100 Å, electrons can pass through the sample and the amplitude of the wave changes can be negligible. To this basis, the imaging reason originate from the phase change.

During TEM characterization, the morphology of CuSe and CuSe-Co 30 min would be showed. Particularly, the observation of lattice fringe is of great important in order to determine the new phase generated during the cation exchange process. To prepare the samples, CuSe NSs and Co-CuSe 30 min were separately dispersed in ethanol followed by ultrasonic dispersion. Then dropped one or two drops of prepared aqueous solution onto carbon-coated copper grids.

3.5 Electrochemical Studies

The working electrode was prepared through the following procedure: firstly, a glassy carbon electrode (GCE) substrate was fully washed twice with ethanol and water for 5 minutes each time after manually polished. A uniform suspension, including 1 mg sample, 250 µg super P, 250 µL isopropanol and 25 µL Nafion dispersion (5 wt%, Sigma-Alrich) was prepared by ultra-sonication for at least 30 minutes for homogeneous dispersion. 6 µL of the prepared solution were dropped on the top of the GCE and left over night for drying.

All electrochemical performances of the materials as electrocatalyst of water were conducted by Solartron Analytical 1470E electrochemistry workstation at room temperature. A classical three-electrode cell consisting of a working electrode (GCE with

catalyst layer, 0.07 cm² surface area), reference electrodes (Ag/AgCl electrode, sat. KCl for HER and Hg/Hg₂Cl₂, sat. KCl for OER) and a carbon counter electrode was used.

Figure 3.13 Solartron Analytical 1470E electrochemistry workstation.

Catalytic activity of HER in alkaline solution was examined by conducting Linear Sweep Voltammetry (LSV) at a scan rate of 5 mV/s and 10 mV/s. For the purpose of activating the catalyst surface, removing possible pollution and stabilizing the electrochemical currents, cyclic voltammetry (CV) was performed in the voltage range of -0.8~ -1.8 V at a scan rate of 50 mV/s for 30 cycles in the alkaline electrolyte in advance of analysis. All examinations were carried out in 1 M KOH solution. Besides, the voltages were measured v.s. the Ag/AgCl reference electrode and which need to be converted to the reversible hydrogen electrode (RHE) scale using the equation below.

$$E_{(\text{RHE})} = E_v + 0.0592 \text{ pH} + E^0_{(\text{Ag}/\text{AgCl})}.$$

Where E_v is the origin result potential, $E^0_{(\text{Ag}/\text{AgCl})}$ is the reference electrode potential and here is 0.197, $E_{(\text{RHE})}$ is the final potential after the conversion to RHE.

Figure 3.14 A three-electrode cell consisting of a working electrode (GCE), reference electrodes (Ag/AgCl electrode, sat. KCl for HER and Hg/Hg₂Cl₂, sat. KCl for OER) and a carbon counter electrode.

Catalytic activity of OER was also measured in alkaline solution. Before electrochemical testing, cyclic voltammetry (CV) was conducted in the voltage range of -0.1~ -0.7 V at a scan rate of 100 mV/s for 20 cycles in the alkaline electrolyte in advance of analysis, in order to activate the catalyst surface, remove possible pollution and stabilize the electrochemical currents. Electrochemical performance was assessed by performing Linear Sweep Voltammetry (LSV) at a scan rate of 10 mV/s. The testing was done in 1 M KOH solution. Moreover, the voltages were calculated v.s. the Hg/Hg₂Cl₂ reference electrode and

which need to be converted to the reversible hydrogen electrode (RHE) scale based on the equation below.

$$E_{(\text{RHE})} = E_v + 0.0592 \text{ pH} + E^0_{(\text{Hg}/\text{Hg}_2\text{Cl}_2)}.$$

Where E_v is the origin result potential, $E^0_{(\text{Hg}/\text{Hg}_2\text{Cl}_2)}$ is the reference electrode potential and here is 0.2415, $E_{(\text{RHE})}$ is the final potential after the conversion to RHE.

Stability tests of CuSe-CoSe prepared at 180°C for 30 minutes was evaluated by chronopotentiometry (CP) at 10 mA cm⁻² for 20 hours in 1 M KOH for both HER and OER.

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Chapter 4

Results for CuSe Nanosheets

The goal of this chapter is showing the results and discussing these outcomes. Firstly, the morphologies and compositions of CuSe nanosheets before and after hydrated hydrazine treatment are demonstrated. Then the LSV and Tafel plots of prepared samples towards HER and OER activity are discussed. By comparing the morphology and performances, the influence of hydrated hydrazine treatment can be revealed.

4.1 Introduction

In recent years, non-precious metal materials have been researched and developed very rapidly in the domain of electrocatalytic water splitting, resulting from the expensive cost of the precious metal catalysts. As a result, scientists are gradually turning their attention to the first-period transition metal elements, such as Mn, Co, Ni, Fe, and Cu. It's known that Co-based catalysts have long been considered to be one of the most likely alternatives to precious metal catalysts and many studies have been done on them, while there are few studies about Cu-based materials. However, Cu-based materials have many unique advantages over the cobalt, nickel, and iron-based materials such as the conductivity.

Copper selenide is an important anisotropic p-type semiconductor with many phases including stoichiometric and non-stoichiometric phase. It also grows as cubic with high thermodynamic stability and other crystalline phases such as hexagonal, orthorhombic and monoclinic.¹⁻² There are already some reports about the synthesis of ultrathin nanosheet CuSe, since the relatively large exposed active area of the nanosheets structure can faster the mass transfer rate and facilitate the generated to rapidly escape from the surface of the electrode during HER and OER. Besides, the stability of nanosheet structure can avoid being destroyed during violent electrochemical reaction.³

In order to efficiently synthesize such ultra-thin nanostructures by colloidal chemical synthesis, fine handling of the interplay between the nucleus and the ligand molecule is essential, which enables growing of the crystals anisotropically along a particular orientation. To date, many ultrathin metal-based chalcogenides nanomaterials have been fabricated by organometallic or organic solutions method. However, the organic solution such as oleylamine will tightly attached to the sample and difficult to be removed totally. As a result, the HER and OER performances will be affected. Thereby, hydrated hydrazine was used to wash the sample completely. In this section, not only the morphology, composition and electrochemical activity of ultrathin CuSe nanosheets will be discussed, but also the comparison between CuSe-Before and CuSe-After.

4.2 Characterization Results for CuSe Nanosheets

The strategy to synthesize CuSe nanosheets involved a typical organic solution phase procedure. The temperature of slurry including OA and CuCl₂ was elevated to 120°C to remove water and oxygen. Then the temperature was lower to 80°C in an oil bath and NH₂OH·HCl powder was added into the solution for the reduction of copper (II) to copper (I). After that Se dispersion formed by ultra-sonication of Se powder in the mixture of oleylamine and 1-dodecanethiol at room temperature was added to the mixture solution. After the solution was maintained at 80°C for 3 hours, it became dark, which was the synthesized CuSe. The as-formed CuSe nanosheets stored in hexane exhibited slight reflection due to the existing of nanosheets. The mole ratio of CuCl₂ and Se contributes a considerable effect in the fabrication of CuSe. Insufficient reagent of Se powder will cause the formation of Cu_{2-x}Se while the excess Se powder will cause the formation of CuSe₂.

Figure 4.1 XRD image of CuSe nanosheets.

X-ray diffraction (XRD) experiment was first utilized to analyze the as-prepared CuSe. XRD result (Figure 4.1) shows the diffraction peaks of as-prepared CuSe-Before and CuSe-After could both be perfectly assigned to the hexagonal CuSe (PDF#34-0171, space group P63/mmc). The diffraction angles of nanosheets CuSe loaded at $2\theta = 26.642, 28.133, 30.468, 31.109, 45.403, 46.088, 50.044$ and 56.6511° correspond to the (101), (102), (103), (006), (107), (110), (108) and (116) crystal planes of CuSe respectively. The peaks of (103) and (006) planes are too close and the limited resolution during XRD characterization, causing the merged of these two peaks in the final diagram. By comparing the diffraction spectrum between the samples, it's clearly that the peaks of CuSe-After is sharper, for instance the intensity of peaks at (006) and (110), due to the influence of hydrated hydrazine which can totally remove the oleylamine attached in copper selenide nanosheets. The higher intensity of marked peak at $2\theta = 31.109^\circ$ in CuSe-After compared with reference PDF card corresponds to the (006) planes, which illustrates the successfully fabrication of CuSe nanosheet.

Figure 4.2 FESEM images of (a,b) CuSe-Before and (c,d) CuSe-After.

The morphologies of the as-prepared samples are explored with Field Emission Scanning Electron Microscope (FESEM) JEOL, JSM-7600F at 15.0 kV. There is something wrapping synthesized copper selenide according Figure 4.2 (a) and (b). The translucent substance around the boundary of CuSe-Before is believed to be oleylamine, which obviously affects the conductivity of the samples, as a result the morphology of copper selenide is difficult to identify. Oleylamine is still exist after washing with ethanol and hexane several times, that's the reason why hydrated hydrazine will be applied. SEM images of as-prepared CuSe-After (Figure 4.2 (c) and (d)) show no presence of oleylamine and the morphology can be observed clearly ultrathin nanosheet structure. However, it's obvious the size of CuSe nanosheets is not uniform, varied from 100 nanometers to 200 nanometers. Furthermore, the FESEM image reveals that the shape of these nanosheets contains round and irregular shapes, revealing that the prepared CuSe NSs has not yet grown to the hexagonal structure as the reference copper selenide during XRD characterization.

Figure 4.3 SEM images of copper selenide prepared at 120°C for 3 hours (a,b), and 80°C for 5 hours (b,c).

The increasing reaction time and temperature might be helpful for the fabrication of hexagonal sheet structure according to Figure 4.3. The morphology of copper selenide prepared at 120°C for 3 hours and 80°C for 5 hours appeared edges and corners in the structure. However, the thickness and size range of copper selenide will also increase. According to (e,f), the samples achieved a thickness around 100 nm. This confirmed that higher temperature and longer reaction times are beneficial for the growing of copper selenide, which induce the dissolution of small sheets and growth of large sheets.

The visible information provided by EDX elemental mappings (Figure 4.4) displays the uniform distributions of copper and selenium in the copper selenide. And the measured Cu/Se atomic ratio is 47.39:52.61, which is about 1:1, in agreement with the stoichiometric ratio of copper selenide.

Figure 4.4 FESEM-EDX element mapping for copper and selenium in CuSe nanosheets after washed by hydrated hydrazine.

The detailed microstructure of CuSe-After was further analyzed by high-resolution transmission electron microscopy (HRTEM). According to Figure 4.5 (a,b,c), the observation clearly reveals the nanosheet structure with the average lateral size of ~ 120 nm, agreeable with the above SEM results. The high-resolution transmission electron microscopy result of the thickness is shown in (d), every copper selenide nanosheet obtains a thickness of ~6 nm. Moreover, the lattice fringes 0.3397 and 0.3180 ascribing from Figure 4.5 (e) and (f) respectively can be assigned to the (101) and (102) planes of hexagonal CuSe, further confirming the analyzed consequent on X-ray diffraction experiment ($d_{(101)} = 0.3346$, $d_{(102)} = 0.3172$ in PDF#34-0171).

Figure 4.5 High resolution TEM images of CuSe-After nanosheets.

4.3 Electrochemical Performance on CuSe Nanosheets

To investigate the hydrogen evolution activity of CuSe NSs catalyst towards HER and OER, corresponding electrochemical analyses were accessed in 1 M KOH alkaline solution. However, as mentioned in the beginning, Cu-based catalysts have obvious defects in the electrocatalytic water splitting, that is, low catalytic efficiency, high overpotential.

According to Figure 4.6, for HER performance, the prepared materials achieved a large overpotential of 599 mV for CuSe-Before and 577 mV for CuSe-After at a geometric current density of -10 mA cm^{-2} at a scan rate of 10 mV/s. There was only a little decrease of overpotential after the treatment of hydrated hydrazine. But during OER measurement, it's clearly the CuSe-After achieved a much lower overpotential compared with that of CuSe-Before (Figure 4.7). The HER activity of copper selenide fabricated at 80°C for 5 hours was also examined, and the sample had an overpotential of 627 mV at -10 mA cm^{-2} . It can be known from SEM images that the size of nanosheets in CuSe prepared at 3 hours

is much smaller than 5 hours. So the enhanced HER activity of CuSe-After can be ascribed to the relatively small sheet structure, in other words, the larger exposed active area, which fasters the mass transfer rate and facilitates the generated gas to rapidly escape from the surface of the electrode.

Figure 4.6 LSV curves of prepared CuSe nanosheets towards HER in 1 M KOH at a scan rate of 5 mV/s.

Figure 4.7 LSV curves of prepared CuSe nanosheets towards OER in 1 M KOH at a scan rate of 10 mV/s.

4.4 Conclusions

Through organic phase solution reaction, the ultrathin CuSe nanosheet was successfully fabricated with controlled average lateral size of ~ 120 nm and thickness of ~ 6 nm according to high-resolution transmission electron microscopy images. The high peak in the XRD image at $2\theta = 31.109^\circ$ corresponds to the (006) planes of hexagonal CuSe. EDX elemental mappings display the uniform distributions of copper and selenium in the copper selenide. And the measured Cu/Se atomic ratio is about 1:1, in agreement with the stoichiometric ration of copper selenide.

The applying of hydrated hydrazine can completely remove the organic solution attaching on the surface of the samples, improving the performances towards HER and OER. However, the prepared ultrathin CuSe nanosheets still exhibit poor electrochemical activity, waiting to be further improved by introducing cobalt through cation exchange process.

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Chapter 5

Cation Exchange Process on CuSe Nanosheets

The purpose of this chapter is to reveal the effect of temperature and reaction time during cation exchange process. In the beginning, the temperature influence on cation exchange are demonstrated, including the morphologies, compositions and electrochemical aspect. Secondly, the reaction process was examined by comparing samples synthesized with different reaction times. Finally, the stability tests of CuSe-CoSe prepared at 180°C for 30 minutes was evaluated for both HER and OER.

5.1 Introduction

Multicomponent nanocrystals with heterostructures have attracted particular interest and are widely investigated. Depending on the different architectures of the heterostructures, the fabrication methods vary. In this project, CuSe-CoSe nanosheets heterostructure is developed through partial cation exchange method by introducing cobalt to CuSe precursor, which is believed to enhance HER and OER performance of pure CuSe.

Cation exchange reaction may be a desired technique for preparing heterostructure materials due to the simplicity and the preservation of size and shape of the nanostructure.¹⁻⁴ As for ionic crystals, origin metal ions can be substituted with other cations, changing the component of the nanocrystals yet maintaining anionic framework. Particularly, this is frequently used in transition metal chalcogenide.⁵⁻⁶ Generally, each cation exchange reaction will be performed under different conditions because they all have unique thermodynamic kinetics. In most cases, the speed of cation exchange can be accelerated with elevated temperatures. However this is greatly limited by material stability and manufacturability. For example, the as-prepared CuSe NSs is found out to decompose in the solution of oleylamine when the temperature was higher than 160°C. Replacing oleylamine with other solution such as 1-octadecene will extend the reaction time at the same degree of exchange. Besides, the kinetic is also related to the mobility of cations and the surface area of materials. This is a significant reason why copper selenide was adopted as the precursor for cation exchange reaction. Due to the higher mobility of Cu and greater exposure surface of nanosheets, the required energy for reaction could be decreased.

In this thesis, CuSe-CoSe nanosheets with different cobalt content can be synthesized with varying temperature and reaction time. By comparing the samples themselves, the effect of temperature and process on cation exchange reaction can be discussed. Hydrogen and oxygen evolution performance will also be tested for these materials to investigate whether the special structure enhance electrochemical property comparing with pure copper selenide.

5.2 Cation Exchange process at Different Temperatures

5.2.1 Characterization Results

The CuSe-CoSe NSs were synthesized through cation exchange reaction. The procedure was simply through exposing pre-synthesized CuSe nanosheets to Co^{2+} by adding cobalt chloride in oleylamine solution. After the removal of water and oxygen with vigorous magnetic stirring under vacuum, the cation exchange reaction was initiated when the temperature of the whole mixture was increased to 180°C . And the cation exchange reaction was stopped after 30 minutes. CuSe-CoSe NSs with different cobalt content can be synthesized with varying reaction temperatures. In the experiment, the temperature was controlled at 140°C , 160°C , 180°C , 200°C and 220°C . The as-prepared samples were recorded as CuSe-Co 140°C , CuSe-Co 160°C , CuSe-Co 180°C , CuSe-Co 200°C and CuSe-Co 220°C , respectively. Notably, in order to completely remove oleylamine, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was used for each sample.

According to X-ray diffraction (XRD) experiment results (Figure 5.1), the diffraction angles of as-prepared samples loaded at $2\theta = 28.1326$, 31.1087 , 46.0880 and 50.0438° correspond to the (102), (006), (110) and (108) crystal planes of hexagonal CuSe (PDF#34-0171, space group $\text{P}6_3/\text{mmc}$) respectively, loaded at $2\theta = 26.874$, 44.601 and 52.842° correspond to the (111), (220) and (311) crystal planes of cubic $\text{Cu}_{1.78}\text{Se}$ (PDF#10-6041, space group $\text{Fm-}3\text{m}$) respectively, loaded at $2\theta = 28.354$, 29.643 and 49.383° correspond to the (311), (222) and (440) crystal planes of cubic Co_9Se_8 (PDF#89-4180, space group $\text{Fm-}3\text{m}$) respectively, loaded at $2\theta = 29.554$, 33.001 and 36.236° correspond to the (200), (210) and (211) crystal planes of cubic $(\text{Cu},\text{Co})\text{Se}_2$ (PDF#25-0309, space group $\text{Pa-}3$) respectively, and loaded at $2\theta = 31.137$ and 47.568° correspond to the (211) and (122) crystal planes of rhombohedral Se (PDF#32-0992, space group $\text{R-}3$). All these components above are not present in the same sample at the same time. Firstly, CuSe-Co 140°C and CuSe-Co 160°C only contain the CuSe, $\text{Cu}_{1.78}\text{Se}$ and some Se, without detection of any cobalt composition, which means the temperature was still low to induce cation exchange reaction, only resulting the change from hexagonal CuSe to cubic $\text{Cu}_{1.78}\text{Se}$. Here, Cu^{2+} was

reduced to Cu^+ , and Se^{2-} loses electrons to become Se. At the elevated temperature such as 180°C , cobalt started to appear as a component of $(\text{Cu},\text{Co})\text{Se}_2$. The complete transform from hexagonal CuSe to cubic $\text{Cu}_{1.78}\text{Se}$ will be beneficial for the later cation exchange process since $(\text{Cu},\text{Co})\text{Se}_2$ also maintains a cubic nanocrystal structure. The peaks marked as “?” might correspond to the crystal planes of monoclinic Cu_2Se (PDF#27-1131, space group P), which is not detected at higher temperature. When the temperature was 200°C , cobalt still exists as the cubic $(\text{Cu},\text{Co})\text{Se}_2$. For CuSe-Co 220°C , cobalt component shows as cubic Co_9Se_8 and some cubic $(\text{Cu},\text{Co})\text{Se}_2$. To this basis, the higher thermal energy is conducive to the growing of cubic Co_9Se_8 .

Figure 5.1 X-ray diffraction image of CuSe-CoSe nanosheets at different reaction temperatures of 140°C , 160°C , 180°C , 200°C and 220°C for 30 minutes.

Figure 5.2 (a,b) FESEM images of CuSe nanosheets. FESEM images of CuSe-CoSe nanosheets heterostructures prepared at different reaction temperatures (c,d) 140°C, (e,f) 160°C, (g,h) 180°C, (i,j) 200°C and (k,l) 220°C for 30 minutes.

The morphologies of the as-prepared samples were explored with FESEM (JEOL, JSM-7600F at 15.0 kV). Figure 5.2 (c)-(l) show the morphologies of CuSe-CoSe NSs prepared at 140°C, 160°C, 180°C, 200°C and 220°C, respectively. Compared with Figure 5.2 (a), the pure CuSe NSs, it's clearly all the CuSe-CoSe samples still maintain an ultrathin nanosheet structure. The surface of CuSe-Co 140°C and CuSe-Co 160°C are smooth, while the CuSe-Co 180°C, CuSe-Co 200°C and CuSe-Co 220°C exhibit an uneven surface with many small

particles on it. Interestingly, the size of nanosheets was increased without the change of thickness. Combined with the outcome from XRD, these small particles can be attributed to the coming of cobalt, forming the phases of $(\text{Cu},\text{Co})\text{Se}_2$ and Co_9Se_8 . Materials with entire hexagonal shape start to appear at 140°C and 160°C , as shown in (c) to (f). When temperature was above 160°C , the nanosheet structural deformation at corner sites was observed, resulting the round shape structure in CuSe-Co 180°C and CuSe-Co 200°C (Figure 5.2 (g-j)). The materials even exhibit irregular shape when prepared at 220°C . In addition, the size range of as-synthesized samples is also increase compared with pure CuSe NSs due to the transform from CuSe to $\text{Cu}_{1.78}\text{Se}$ according to XRD. As mentioned in chapter 4, higher temperature and longer reaction times can induce the growth of copper selenide. Cation exchange experiment was done in oleylamine solution which is the same as the previous synthesis of copper selenide precursor. Even without the adding of copper chloride and selenium, the materials can still become large through the dissolution of small sheets and growth of large sheets during the transformation process.

Table 5.1 Atomic content between Cu, Co and Se in different samples prepared at different temperatures.

Samples	Cu At %	Co At %	Se At %	Cu /Co
<u>CuSe</u>	47.39	/	52.61	/
140°C	51.23	1.46	47.32	35.1
160°C	53.65	2.12	44.23	25.3
180°C	49.45	8.08	42.48	6.1
200°C	48.86	9.24	41.90	5.3
220°C	46.28	15.42	38.29	3.0

Corresponding EDX elemental mappings display the uniform distributions of copper, cobalt and selenium in the CuSe-CoSe NSs (Figure 5.3). In the light of XRD and SEM results, these images demonstrate that Co successfully merged into CuSe nanosheets to form CuSe-CoSe heterostructures. However, the signal of Cobalt in CuSe-Co 140°C and CuSe-Co 160°C are difficult to recognize compared with other samples. As the cation exchange reaction temperature elevated, the content of Cu gradually decreases while the

content of Co gradually increases (Table 5.1). Besides that, atomic content outcome also indicates the higher of Cu/Se ratio compared with pure CuSe, demonstrating that CuSe will firstly transform into $\text{Cu}_{1.78}\text{Se}$ once cation exchange process begins.

Figure 5.3 FESEM-EDX element mapping for copper, cobalt and selenium in CuSe-CoSe nanosheets heterostructures with different CE reaction temperatures.

The detailed microstructure of CuSe-Co 180°C was further analyzed by high-resolution transmission electron microscopy (HRTEM). According to Figure 5.4, the observation clearly reveals the ultrathin nanosheet structure with the increased range of lateral size. Apart from this, the nanosheet appears structural deformation at corner sites and is

decorated by some nanoparticles compared with pure CuSe, agreeable with the above SEM results. In the light of XRD and TEM consequent, the nanoparticles should be the new composition of (Cu,Co)Se₂.

Figure 5.4 High-resolution transmission electron microscopy (HRTEM) images of (a) CuSe-CoSe prepared at 180°C for 30 minutes and (b) decorated (Cu,Co)Se₂ nanoparticles.

5.2.2 Electrochemical Performance Discussion

To investigate the hydrogen and oxygen evolution activity of CuSe-CoSe heterostructures catalyst, the corresponding electrochemical analysis were accessed in 1 M KOH alkaline solution. For this purpose, CuSe NSs and CuSe-CoSe NSs fabricated under different temperatures were supported on super p to prepare catalysts. A three-electrode setup was used with Ag/AgCl (filled with sat. KCl) for HER, Hg/Hg₂Cl₂ (filled with sat. KCl) for OER) and a carbon rod as a reference and a counter electrode, respectively.

Compared with pure CuSe NSs, CuSe-CoSe samples exhibit smaller onset HER potential. According to Figure 5.5, CuSe-CoSe achieves lower overpotential of 462 mV, 432 mV, 322 mV, 370 mV and 388 mV at a geometric current density of -10 mA cm^{-2} (scan rate at 10 mV/s) for CuSe-Co 140°C, 160°C, 180°C, 200°C and 220°C respectively, whereas

overpotential for CuSe-After is 577 mV. It is clearly that the electrocatalytic properties of CuSe-CoSe prepared above 180°C have been enhanced greatly towards HER compared with CuSe-Co 140°C and CuSe-Co 160°C, indicating the significant role of cobalt and heterostructures. Among them, the linear sweep voltammetry performance for CuSe-Co 180°C is the best. According to the above XRD and EDX characterization, CuSe-Co 200°C and CuSe-Co 220°C have similar atomic content of Cu, Co and Se. Whereas the cobalt component in CuSe-Co 220°C is composed of $(\text{Cu,Co})\text{Se}_2$ and Co_9Se_8 , CuSe-Co 200°C is only composed of $(\text{Cu,Co})\text{Se}_2$, revealing its relatively high composition of $(\text{Cu,Co})\text{Se}_2$. Thereby the highly increased activity might be attributed to the existence of $(\text{Cu,Co})\text{Se}_2$ driving HER.

Figure 5.5 LSV curves of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at different reaction temperatures for 30 minutes towards HER in 1 M KOH at a scan rate of 5 mV/s.

The intrinsic reaction procedures of hydrogen evolution can be reflected in the Tafel plots.⁷ A Tafel slope of 167 mV dec⁻¹ for CuSe nanosheets acquired from voltammetry data was described in Figure 5.6. In addition, the Tafel slopes for CuSe-Co 140°C, 160°C, 180°C,

200°C and 220°C electrode are 188 mV dec^{-1} , 202 mV dec^{-1} , 248 mV dec^{-1} , 244 mV dec^{-1} and 233 mV dec^{-1} , respectively. On the basis of the classical principle about HER dynamics, the Volmer-Heyrovsky mechanism may be in charge of the hydrogen evolution reaction by CuSe-CoSe heterostructures electrode. So the adsorption step is limiting the reaction speed. The relatively small Tafel slope is superior since it will result in rapid increase in the hydrogen evolution rate as the potential increases. However, after cation exchange process, CuSe-CoSe samples have relatively higher Tafel slope compared with pure CuSe nanosheets. It's known that weakly adsorption of H_2O will influence hydrogen evolution reaction. The increasing later size of nanosheets with the decreasing of active sites on the surface probably accounts for this phenomenon. On the basis of even poor Tafel slope of CuSe-Co180°C compared with 200°C and 220°C, the good adsorption ability of Co_9Se_2 also make a difference. Even though with relatively higher Tafel slope, the advantage of reducing the overpotential in CuSe-CoSe nanosheets after cation exchange process is still unparalleled.

Figure 5.6 Tafel plots of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at different reaction temperatures for 30 minutes towards HER in 1 M KOH at a scan rate of 5 mV/s.

As for OER, CuSe-CoSe samples also display smaller onset potential, and CuSe-Co 180°C still has an undoubtedly improving electrocatalytic activity at elevated potentials. According to Figure 5.7, CuSe-CoSe achieves lower overpotential of 474 mV, 437 mV, 356 mV, 375 mV and 396 mV at a geometric current density of -10 mA cm^{-2} (scan rate 10 mV/s) for CuSe-Co 140°C, 160°C, 180°C, 200°C and 220°C respectively, whereas overpotentials for CuSe-After is too large to detect. It is clearly that the electrocatalytic properties of CuSe-CoSe have also been enhanced greatly towards OER, indicating the signification role of cobalt and heterostructures. The best performance for CuSe-Co 180°C and 200°C can be ascribed to the effect of $(\text{Cu},\text{Co})\text{Se}_2$ component in driving OER, based on the discussion above.

Figure 5.7 LSV curves of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at different reaction temperatures for 30 minutes towards OER in 1 M KOH at a scan rate of 10 mV/s.

However, Tafel plots reflect a completely different law in OER comparing with HER. A Tafel slope cannot be measured for CuSe nanosheets due to the poor activity. In addition, the Tafel slopes for CuSe-Co 140°C, 160°C, 180°C, 200°C and 220°C electrode are 136

mV dec^{-1} , 132 mV dec^{-1} , 94 mV dec^{-1} , 110 mV dec^{-1} and 110 mV dec^{-1} , respectively. The relatively little Tafel slope is superior since it will result in rapid increase in the oxygen evolution rate as the potential increasing. After cation exchange process, CuSe-CoSe samples have relatively reduced Tafel slope compared with pure CuSe nanosheets. Different from the adsorption process of HER in alkaline environment, OER is required to adsorb OH^- . In view of this, cobalt compound such as $(\text{Cu},\text{Co})\text{Se}_2$ and Co_9Se_8 have outstanding adsorption ability.

Figure 5.8 Tafel plots of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at different reaction temperatures for 30 minutes towards OER in 1 M KOH at a scan rate of 10 mV/s.

5.2.3 Summary

In conclusion, there is no doubt that the performance of CuSe-Co 180°C is the best, mainly due to the existence of (Cu,Co)Se₂ component, followed by CuSe-Co 200°C and CuSe-Co 220°C. In addition to (Cu,Co)Se₂, Co₉Se₈ can also improve the electrochemical activity. Besides, the properties of CuSe-Co 140°C and CuSe-Co 160°C is also enhanced compared to pure CuSe nanosheets. Although the presence of cobalt compound was not detected in XRD, EDX showed that some cobalt and copper were successfully exchanged. Therefore, cobalt have a great effect on hydrogen and oxygen production.

It is obviously that the cation exchange reaction rate is related to temperature. Higher temperatures help to carry out the exchange reaction, but at the same time it will cause the breakage of hexagonal sheet structure. It might be possible to produce (Cu,Co)Se₂ phase at a lower temperature with extended reaction time, but this will consume a lot of energy. In addition, the sheet will also affect the catalytic performance by growing larger with reduced active site. As a result, fabrication at the temperature of 180°C is selected for a two-hour cation exchange process. The cation exchange process can be better exposed by sampling and analyzing at successive time intervals.

5.3 Cation Exchange process at Different Times

5.3.1 Characterization Results

The CuSe-CoSe NSs were synthesized through cation exchange reaction. The procedure was simply by exposing pre-synthesized CuSe nanosheets to Co²⁺ by adding cobalt chloride in oleylamine solution. After the removal of water and oxygen with vigorous magnetic stirring under vacuum, the cation exchange reaction was initiated when the temperature of the whole mixture was increased to 180°C. CuSe-CoSe nanosheets intermediates with different cobalt content can be synthesized with varying reaction time. In the experiment, reaction time was controlled at 5 minutes, 15 minutes, 30 minutes, 1 hour and 2 hours. The as-prepared samples were recorded as CuSe-Co 5min, CuSe-CoSe

15min, CuSe-CoSe 30min, CuSe-CoSe 60min and CuSe-CoSe 120min, respectively. Notably, in order to completely remove oleylamine, $N_2H_4 \cdot H_2O$ was used for each sample.

Figure 5.9 X-ray diffraction image of CuSe-CoSe nanosheets intermediates at 180°C with different reaction times for 5 minutes, 15 minutes, 30 minutes, 60 minutes and 120 minutes.

According to X-ray diffraction (XRD) experiment results (Figure 5.9), the diffraction angles of as-prepared samples loaded at $2\theta = 28.1326, 31.1087, 46.0880$ and 50.0438° correspond to the (102), (006), (110) and (108) crystal planes of hexagonal CuSe (PDF#34-

0171, space group P63/mmc) respectively, loaded at $2\theta = 26.874, 44.601$ and 52.842° correspond to the (111), (220) and (311) crystal planes of cubic $\text{Cu}_{1.78}\text{Se}$ (PDF#10-6041, space group Fm-3m) respectively, loaded at $2\theta = 29.554, 33.001$ and 36.236° correspond to the (200), (210) and (211) crystal planes of cubic $(\text{Cu},\text{Co})\text{Se}_2$ (PDF#25-0309, space group Pa-3) respectively, and loaded at $2\theta = 31.137$ and 47.568° correspond to the (211) and (122) crystal planes of rhombohedral Se (PDF#32-0992, space group R-3). All these components above are not present in the same sample at the same time. Firstly, CuSe-Co 5min and 15min only contain the CuSe, $\text{Cu}_{1.78}\text{Se}$ and Se, without detection of any cobalt composition, which means the cation exchange reaction began with the transformation from hexagonal CuSe to cubic $\text{Cu}_{1.78}\text{Se}$. This might be beneficial for the later cation exchange process since $(\text{Cu},\text{Co})\text{Se}_2$ also maintains a cubic nanocrystal structure. As time went by, cobalt started to appear as a component of cubic $(\text{Cu},\text{Co})\text{Se}_2$ in the intermediates of 30 minutes. Besides, the hexagonal CuSe was completely changed into cubic $\text{Cu}_{1.78}\text{Se}$. After 60 minutes, only the phase of $\text{Cu}_{1.78}\text{Se}$ and $(\text{Cu},\text{Co})\text{Se}_2$ were detected. XRD shows no detection of Co_9Se_8 phase even after two hours, revealing the lack of energy for the synthesis of Co_9Se_8 . The detection of Se from the beginning of the cation exchange process can be explained by the oxidation of Se^{2-} due to the reduction of Cu^{2+} to Cu^+ . Interestingly, the Se disappears after 30 minutes, which means selenium was involved in the cation exchange reaction again. Here, the reducing electrons involved in the reduction of selenium are provided by oleylamine. Among all the peaks in the diffraction result, the intensity of (006) planes of CuSe and (200) planes of $(\text{Cu},\text{Co})\text{Se}_2$ are comparatively higher, indicating the well preserving of sheet structure during CE process.

The morphologies of the as-prepared samples are explored with FESEM (JEOL, JSM-7600F at 15.0 kV). Figure 5.10 (c)-(l) show the morphologies of CuSe-CoSe NSs prepared for 5 minutes, 15 minutes, 30 minutes, 60 minutes and 120 minutes, respectively. Compared with Figure 5.10 (a), the pure CuSe NSs, it's clearly all the CuSe-CoSe samples still maintain an ultrathin nanosheet structure. As mentioned before, the nanosheet structural deformation at corner sites appeared when temperature was above 160°C , resulting in the round shape structure. Since the reaction took place at 180°C , all the samples show certain decomposition, which is even serious for CuSe-Co 120min. Notably, the size

of nanosheets was increased without the change of thickness. In addition, the size range of as-synthesized samples was also increase compared with pure CuSe NSs due to the transformation from CuSe to $\text{Cu}_{1.78}\text{Se}$ according to XRD. The nanosheets can become large through the dissolution of small sheets and the growth of large sheets, evidenced by the Figure 5.10 (d) showing the small sheets on the surface of large sheet and entire hexagonal shape. After 30 minutes, the materials exhibits an uneven surface with many nanoparticles on it (Figure 5.10 (h)). According to XRD, these small particles are ascribed to the phases of $(\text{Cu},\text{Co})\text{Se}_2$ and maybe will finally change into Co_9Se_8 if the reaction time is long enough.

Figure 5.10 (a,b) FESEM images of CuSe nanosheets. FESEM imagers of CuSe-CoSe nanosheets heterostructures prepared at 180°C for different reaction times (c,d) 5 minutes, (e,f) 15 minutes, (g,h) 30 minutes, (i,j) 1 hour and (k,l) 2 hours.

Figure 5.11 FESEM-EDX element mapping for copper, cobalt and selenium in CuSe-CoSe nanosheets heterostructures with different CE reaction times.

Corresponding EDX elemental mappings display the uniform distributions of copper, cobalt and selenium in the CuSe-CoSe NSs (Figure 5.11). In the light of XRD and SEM results, these images demonstrate that Co successfully merged into CuSe nanosheets to form CuSe-CoSe heterostructures. As the cation exchange reaction proceeded, the content of Co gradually increased (Table 5.2). Atomic content outcome also indicates the decreasing ratio of Cu/Co, demonstrating that cobalt took the site of copper in nanocrystals. Interestingly, there is already a 6.24 At% content of cobalt after 5 minutes, but no detection

of cobalt compound according to XRD. Even though cobalt went into the crystal, the new bond between Co and Se was still not generated due to the lack of energy. After 30 minutes, the atomic content ratio between Cu/Se gradually decreased, also revealing the change from $\text{Cu}_{1.78}\text{Se}$ ($\text{Cu/Se} = 1.78$) to $(\text{Cu,Co})\text{Se}_2$ ($\text{Cu/Se} = 0.5$). Besides, the atomic content ratio between Co/Se is almost unchanged from 30 minutes to 60 minutes. Combined with the increased cobalt content, cobalt component was only existed as $(\text{Cu,Co})\text{Se}_2$ phase here. But in 120 minutes intermediate, the sudden reduced in the atomic content ratio between Co/Se is speculated for the appearance of other new cobalt components not shown in the XRD outcome due to the low content.

Table 5.2 Atomic content between Cu, Co and Se in different samples prepared at different times.

Samples	Cu At %	Co At %	Se At %	Cu /Co
<u>CuSe</u>	47.39	/	52.61	/
5 min	42.64	6.24	51.13	6.8
15 min	44.15	7.05	48.80	6.3
30 min	49.45	8.08	42.48	6.2
60 min	45.77	8.68	45.54	5.3
120 min	42.02	8.44	49.53	5.0

5.3.2 Electrochemical Performance Discussion

To investigate the hydrogen and oxygen evolution activity of CuSe-CoSe heterostructures catalyst, corresponding electrochemical analyses were accessed in 1 M KOH alkaline solution. For this purpose, CuSe NSs and CuSe-CoSe NSs fabricated at 180°C for different reaction times were supported on super p to prepare catalysts. A three-electrode setup was used with Ag/AgCl (filled with sat. KCl) for HER, Hg/Hg₂Cl₂ (filled with sat. KCl) for OER) and a carbon rod as a reference and a counter electrode, respectively.

Compared with pure CuSe NSs, CuSe-CoSe samples display smaller onset HER potential. According to Figure 5.12, CuSe-CoSe NSs achieve lower overpotential of 398 mV, 366

mV, 322 mV, 382 mV and 456 mV at a geometric current density of -10 mA cm^{-2} (scan rate 10 mV/s) for CuSe-Co 5min, 15min, 30min, 60min and 120min respectively, whereas overpotentials for CuSe-After is 577 mV. It is clearly that the electrocatalytic properties of CuSe-CoSe prepared at 180°C have been enhanced greatly towards HER compared with pure CuSe, indicating the signification role of cobalt. However, it's known that CuSe-Co 120min had more cobalt content than CuSe-Co 5min and CuSe-Co 15min according to XRD and EDX. Therefore the higher onset potential of CuSe-Co 120min can be attributed to the structural deformation during long cation exchange process. Among them, linear sweep voltammetry performance for CuSe-Co 30min are the best, followed by the intermediates of 15 minutes and 60 minutes. According to XRD and EDX characterization, above intermediates have similar atomic content of cobalt. The cobalt component of CuSe-Co 30min and 60min is $(\text{Cu},\text{Co})\text{Se}_2$, whereas CuSe-Co 15min shows no cobalt component, which means the amount of $(\text{Cu},\text{Co})\text{Se}_2$ is not the only factor that determines the level of activity.

Figure 5.12 LSV curves of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at 180°C for different reaction times towards HER in 1 M KOH at a scan rate of 5 mV/s .

Figure 5.13 Tafel plots of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at 180°C for different reaction times towards HER in 1 M KOH at a scan rate of 5 mV/s.

The intrinsic reaction procedures of hydrogen evolution can be reflected by the Tafel plots.⁷ A Tafel slope of 167 mV dec^{-1} for CuSe nanosheets acquire from voltammetry data was described in Figure 5.12. In addition, the Tafel slopes for CuSe-Co 5min, 15min, 30min, 60min and 120min electrode are 250 mV dec^{-1} , 294 mV dec^{-1} , 248 mV dec^{-1} , 246 mV dec^{-1} and 157 mV dec^{-1} , respectively. On the basis of the classical principle about HER dynamics, the Volmer-Heyrovsky mechanism may be in charge of the hydrogen evolution reaction by CuSe-CoSe heterostructures electrode. So the adsorption step is limiting the reaction speed. The relatively little Tafel slope is superior since it will result in rapid increase in the hydrogen evolution rate as the potential increasing. However, after cation exchange process, CuSe-CoSe samples have relatively higher Tafel slope compared with pure CuSe nanosheets except for CuSe-Co 120min. It's known that weakly adsorption of H_2O will influence hydrogen evolution reaction. According to the discussion on the effect

of temperature, the increasing later size of nanosheets with the decreasing of active sites mainly accounts for this phenomenon. By comparing intermediates of 30 minutes with 15 minutes, the smaller Tafel slope indicating the enhanced adsorption ability of $(\text{Cu},\text{Co})\text{Se}_2$, since CuSe-Co 30min contains much more $(\text{Cu},\text{Co})\text{Se}_2$ component. Besides, the almost unchanged Tafel slope for CuSe-Co 60min and even decreased Tafel slope for CuSe-Co 120min also show the enhanced adsorption ability of $(\text{Cu},\text{Co})\text{Se}_2$. Since these samples actually have smaller active sites resulting by highly growing as cation exchange process proceeded when compared with other CuSe-CoSe samples (Figure 5.10). The Tafel slope should have grown higher due to the increasing later size if which is the only factor.

Figure 5.14 LSV curves of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at 180°C for different reaction times towards OER in 1 M KOH at a scan rate of 10 mV/s.

As for oxygen evolution performance, CuSe-CoSe samples also display smaller onset potential, and CuSe-Co 30min still has an undoubtedly improving electrocatalytic activity at elevated potentials. According to Figure 5.13, CuSe-CoSe NSs achieve lower

overpotential of 446 mV, 384 mV, 356 mV, 404 mV and 451 mV at a geometric current density of -10 mA cm^{-2} (scan rate 10 mV/s) for CuSe-Co 5min, 15min, 30min, 60min and 120min respectively, whereas overpotentials for CuSe-After is too large to detect. It is clearly that the electrocatalytic properties of CuSe-CoSe have also been enhanced greatly towards OER, indicating the signification role of cobalt and heterostructures. The best performance for CuSe-Co 30min can be ascribed to the effect of $(\text{Cu,Co})\text{Se}_2$ component in driving OER and well maintain nanosheet structure, based on the discussion above. As a result of growing of nanosheets and structural deformation, CuSe-Co 60min and CuSe-Co 120min with more $(\text{Cu,Co})\text{Se}_2$ content exhibit higher onset potential than the intermediate of 30 minutes.

Figure 5.15 Tafel plots of pure CuSe nanosheets and CuSe-CoSe nanosheets prepared at 180°C for different reaction times towards OER in 1 M KOH at a scan rate of 10 mV/s .

However, Tafel plots reflect a completely different law in OER comparing with HER. A Tafel slope cannot be measured for CuSe nanosheets due to the poor activity. In addition,

the Tafel slopes for CuSe-Co 5min, 15min, 30min, 60min and 120min electrode are 210 mV dec^{-1} , 110 mV dec^{-1} , 94 mV dec^{-1} , 115 mV dec^{-1} and 127 mV dec^{-1} , respectively. The relatively little Tafel slope is superior since it will result in rapid increase in the oxygen evolution rate as the potential increasing. After cation exchange process, CuSe-CoSe samples have relatively reduced Tafel slope. Different from the adsorption process of HER in alkaline environment, OER is required to adsorb OH^- . In view of this, cobalt compound such as $(\text{Cu},\text{Co})\text{Se}_2$ has excellent adsorption ability so as to compensate for the influence of the decrease in surface active sites.

Stability tests of CuSe-Co 30 min was evaluated by chronopotentiometry (CP) at 10 mA cm^{-2} for 20 hours in 1 M KOH. The overpotentials of the samples underwent a smaller increase, indication the long-term stable hydrogen and oxygen evolution performance in alkaline solution. as the reaction time increases. This clearly reveals the excellent stability of prepared CuSe-Co 30 min. Besides, the overpotential gradually decreased over time during HER may be attributed to the forming of hydroxide active material on the surface of the testing sample.

Figure 5.16 Potential-time curves of CuSe-CoSe prepared at 180°C for 30 minutes was evaluated at a constant current density of 10 mA cm^{-2} for 20 hours.

5.2.3 Summary

In a two-hour cation exchange experiment, the generation of new phases and the disappearance of the old phase can be better exposed by sampling and analysis at intervals. Unlike the temperature experiment, the content of cobalt element did not change much throughout the reaction. There was a considerable cobalt content in the beginning of the reaction, after which the reaction was mainly the growing of (Cu,Co)Se₂ phase. According to the results of high temperature cation exchange process, the exchange rate was still restricted by the thermal energy.

Whether or not the exchange reaction was carried out at different temperatures or times, all materials initially underwent a conversion from hexagonal CuSe to cubic Cu_{1.78}Se. The Cu_{1.78}Se composition is a member of Cu_{2-x}Se. There is no Se-Se bond on the crystal structure of Cu_{2-x}Se, so the anion framework can be preserved without breaking the Se-Se bond to form Co-Se bond. The conversion to Cu_{1.78}Se started at the beginning of the reaction, which was advantageous for the subsequent entry of cobalt. Both the firstly formed (Cu,Co)Se₂ and Cu_{1.78}Se were actually cubic structures, greatly reducing lattice transformation energy during cation exchange process. When the CuSe was all changed into Cu_{1.78}Se, more exchange positions could be provided than the original CuSe, and cobalt existed in the form of (Cu,Co)Se₂. However, for more cobalt to enter the crystal, (Cu,Co)Se₂ component might eventually transformed into Co₉Se₈ according to temperature experiment. However, reaction time is not long enough to witness this process.

Unfortunately, due to the long-term high temperature reaction, the original copper selenide nanosheet structure was changed. The influence of morphology is also considered when studying the electrocatalytic performance, so it is difficult to directly reflect the role of the cobalt component. Although it is confirmed that cobalt has a great improvement in electrocatalytic activity, it's difficult to make sure whether the inferior performance of CuSe-Co 220°C compared with CuSe-Co 200°C is because the activity of Co₉Se₈ is not as good as (Cu,Co)Se₂ or morphology changed.

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Chapter 6

Conclusions and Future Work

In this chapter, the conclusion of this thesis studies is presented, including the high-yield fabrication of CuSe nanosheet, design and preparation of CuSe-CoSe heterostructures via cation exchange reaction. Furthermore, future work plan is also mentioned, including design and synthesis of CuSe-NiSe nanosheet.

6.1 Conclusions

The goals of this thesis is to synthesize CuSe-CoSe nanosheets with special heterostructure as an efficient electrocatalyst for hydrogen and oxygen evolution. Notably, the preparation of CuSe-CoSe nanosheet heterostructures used cation exchange method beginning with ultrathin CuSe nanosheet. And the effects of temperature and reaction on cation exchange process were also explored. Since there are already some reports about the synthesis of nanosheet CuSe and the adopting of cation exchange process for building heterostructures. CuSe-CoSe with special heterostructures can be achieved routinely. The conclusion will mainly be divided into two parts.

6.1.1 Synthesis of CuSe

To efficiently synthesize ultra-thin nanostructures by colloidal chemical synthesis, fine handling of the interplay between the nucleus and the ligand molecule is essential, enabling the growing of the crystals anisotropically along a particular orientation. In the experiment, organic solution phase method was adopted since it's environmentally friendly and economical without the using of toxic, phosphorus and expensive reactants.

According to the characterization results, the CuSe with ultrathin nanosheet structure was successfully fabricated firstly. The high peak in the XRD image at $2\theta = 31.109^\circ$ corresponding to the (006) planes of hexagonal CuSe and the FESEM results together illustrate the successfully fabrication of CuSe nanosheet. High-resolution transmission electron microscopy clearly reveals the nanosheet structure with the average lateral size of ~ 120 nm and thickness of ~ 6 nm. EDX elemental mappings display the uniform distributions of copper and selenium in the copper selenide. And the measured Cu/Se atomic ratio is about 1:1, in agreement with the stoichiometric ration of copper selenide. Besides, both the increase of temperature and reaction times will cause the larger lateral size and thickness. However, the prepared ultrathin CuSe nanosheets still exhibit poor electrochemical activity towards HER and OER performances.

6.1.2 Cation Exchange Process

By the using of cation exchange process, cobalt was introduced to CuSe precursor to form CuSe-CoSe nanosheets heterostructure, which is demonstrated by the compositions of Co_9Se_8 and $(\text{Cu},\text{Co})\text{Se}_2$ in XRD image and element mapping for cobalt in EDX images. To further revealing the reaction process, experiments on the effects of temperature and times were conducted separately.

As for temperature effect, CuSe-CoSe NSs with different cobalt content can be synthesized with varying reaction temperatures controlled at 140°C, 160°C, 180°C, 200°C and 220°C. It is obviously that the cation exchange reaction rate is related to temperature. Higher temperatures help to carry out the exchange reaction at the same time, but it will cause the breakage of hexagonal sheet structure, according to the outcome of EDX and FESEM. Among all the samples after CE process, the size of nanosheets was increased without the change of thickness. When the temperature was higher than 180°C, the sheet surface even became uneven with many small particles on it. These small particles were immediately confirmed to be the phases of $(\text{Cu},\text{Co})\text{Se}_2$ and Co_9Se_8 combining with the result from XRD. After testing the electrochemical performances, cobalt component showed crucial role in driving HER and OER. There is no doubt that the performance of CuSe-Co 180°C is the best, mainly due to the existence of $(\text{Cu},\text{Co})\text{Se}_2$

$(\text{Cu},\text{Co})\text{Se}_2$ is a composition appearing during the process of cation exchange, and will be transformed into Co_9Se_8 at elevated temperature. An entire cation exchange process was performed to explore the formation of $(\text{Cu},\text{Co})\text{Se}_2$. This composition was only detected in when temperature is higher than 180°C. It might be possible to produce $(\text{Cu},\text{Co})\text{Se}_2$ phase at 160°C with extended reaction time, but this will consume a lot of energy. In addition, the sheet will also affect the catalytic performances by growing larger to reduce the active site. Materials synthesized at 200°C shows more serious structural deformation than 180°C. As a result, 180°C was selected for a two-hour cation exchange process. The cation exchange process can be better exposed by sampling and analyzing at intervals, such as 5 minutes, 15 minutes, 30 minutes, 60 minutes and 120 minutes.

Unlike the temperature experiment, the content of cobalt element did not change much throughout the reaction. There was a considerable cobalt content at the beginning of the reaction, after which the reaction mainly underwent the growing of (Cu,Co)Se₂ phase. This component might eventually transformed into Co₉Se₈ according to temperature experiment. According to EDX and FESEM, even though all the samples after CE process still maintain sheet structure, the size of nanosheets is highly increased and structural deformation is worse as reaction proceeding. Besides, whether or not the exchange reaction was carried out at different temperatures or times, all materials initially went through a conversion from hexagonal CuSe to cubic Cu_{1.78}Se, reducing the lattice transformation energy during cation exchange process.

Figure 2.1 Schematic illustration of the cation exchange process on ultrathin CuSe nanosheets.

Electrochemical studies were also tested for these materials to investigate whether the special heterostructure enhanced electrochemical property comparing with pure copper selenide. When applied as a HER or OER electrode, the CuSe-CoSe NSs all achieved lower overpotential compared with pure CuSe nanosheets. Among them, the CuSe-CoSe prepared at 180°C for 30 minutes showed best electrocatalytic performance with an onset potential of 322 mV for HER and 356 mV for OER at the current density of -10 mA cm^{-2} in alkaline solution. The enhancing function of CuSe-CoSe nanosheets heterostructure can be ascribed to the following reasons. In one hand, the relatively large exposed active area of the nanosheets faster the mass transfer rate and facilitate the generated gas to rapidly escape from the surface of the electrode. In the other hand, the synergistic effect between copper and cobalt in CuSe-CoSe heterostructure significantly increases material properties.

Besides, the long-term stability result of CuSe-Co 30min also shows high stability of the nanosheet structure during violent electrochemical reaction.

Figure 6.2 Electrochemical performance of CuSe-CoSe heterostructures prepared at different temperatures and reaction times shows greatly enhanced activity towards HER and OER compared with pure CuSe.

Unfortunately, due to the long-term high temperature reaction, the original copper selenide nanosheet structure was changed. The influence of morphology is also considered when studying the electrocatalytic performances, so it is difficult to directly reflect the role of the cobalt component. For examples, it's difficult to decide whether the inferior performance of CuSe-Co 220°C compared with CuSe-Co 200°C is because the activity of Co_9Se_8 is not as good as $(\text{Cu},\text{Co})\text{Se}_2$ or morphology changed.

6.2 Future Work

The research findings and analyses described in this thesis have led to the further knowledge of cation exchange reaction process. It gives a brief insight to the effects of temperature and reaction times on CE process and also reveals the significant role of heterostructures in electrochemical performances. The work paves the way for further cation exchange with other first-period transition metal elements to enhance the property of original materials. However, there are still some outstanding issues remain to be solved. Hence, the following future work is recommended.

6.2.1 Maintaining of Structure during Cation Exchange Reaction

The as-prepared CuSe nanosheets was found out to decompose in the solution of oleylamine when the temperature was higher than 160°C. Replacing oleylamine with other solution such as 1-octadecene will extend the reaction time to the same degree of exchange. Besides, the materials became large through the dissolution of small sheets and growth of large sheets during cation exchange process. Thereby it's necessary to find out a way to keep morphology unchanged.

According to Jongsik Park's work, CTAC (cetyltrimethylammonium chloride) can be used as surface-stabilization agent to protect the structure of Cu_{2-x}S during cation exchange reaction.¹ The experiment also took place in the solution of oleylamine. However, there was still structural deformation at corner sites when the temperature was above 160 °C, because of the disappearance of CTAC (Figure 6.2). This surface-stabilization agent can be helpful if a long cation exchange reaction at lower temperature wanted to be conducted.

It's obvious that all the materials underwent the transformation from hexagonal CuSe to cubic $\text{Cu}_{1.78}\text{Se}$ once cation exchange began. This conversion will also result in the morphology change to some extent. Hence, if the cation exchange process is beginning with Cu_{2-x}Se nanosheets, this phenomenon could be avoided, which is beneficial for the preserve of initial structure.

Figure 6.2 TEM images of $\text{Pd}_{13}\text{Cu}_3\text{S}_7$ nanoparticles synthesized at different cation exchange reaction temperature from 80°C to 180°C.¹

Once the surface is stable during experiment, the influence of morphology can be removed when studying the electrocatalytic performances towards HER and OER. As result, it is able to directly compare the role of different cobalt components such as Co_9Se_8 and $(\text{Cu},\text{Co})\text{Se}_2$.

6.2.2 Organic Solution for Cation Exchange Process

On the basis of this thesis, temperature is the main effect on driving cation exchange reaction. Experiments done in lower temperature showed poor cobalt content in the materials. But once the reaction temperature exceeded 160°C, the decomposition of copper selenide happened. A key way to break this dilemma is altering previous organic solution.

In fact, there are some reports on cation exchange process using different solution environment. For examples, Zhang et al.² used pure 1-octadecene (ODE) for fabricating

CoSe₂-decorated NbSe₂. Tan et al.³ used ethylene-glycol to enable the transformation from CdS to Cu₂S and finally to Ag₂S. And Fenton et al.⁴ even introduced a series of tunable exchange reactions related to the solution including oleylamine, benzyl ether and trioctylphosphine (TOP). Above research outcomes are shown in Figure 6.3 and Figure 6.4. Therefore, finding a most suitable reaction solution for the cation exchange process on CuSe is still a long way to go.

Figure 6.3 (a) Schematic illustration of the cation exchange process on NbSe₂ nanosheets. (b) Detailed SEM image of CoSe₂-decorated NbSe₂. Inset: NbSe₂ precursor without cation exchange.² (c) Cation exchange process to form Cu₂S and Ag₂S nanowires. (d) EDS mapping for Cu₂S-Ag₂S superlattice nanowires fabricated after reacting Cu₂S with the Ag cation at room temperature.³

Figure 6.4 The nanoparticles morphology and the intraparticle frameworks were preserved well after cation exchange process. STEM-EDS images are shown for each population of particles.⁴

6.2.3 Reaction Mechanism

The reaction mechanism of cation exchange reaction between cobalt and copper in CuSe is of great importance. Regrettably, the process of cation exchange is too complex that the article only discusses the composition appeared and disappeared during the reaction. The research on the mechanism is necessary to conduct in future work.

For instance, cubic $\text{Cu}_{1.78}\text{Se}$ was found in the early stages of the reaction. The reason for this conversion is speculated because there is no Se-Se bond on the crystal structure of Cu_{2-x}Se , so the anion framework can be preserved without breaking the Se-Se bond to form Co-Se bond. And the similar cubic structure can reduce the lattice transformation energy during cation exchange process. However above explanation is only according to XRD, FESEM and EDX characterization, without measuring the exact bond length and lattice spacing between $\text{Cu}_{1.78}\text{Se}$ and other cobalt component. Further research is required.

It is recommended that HRTEM is utilized to in-depth study of the heterostructures and scrutinize the synthesized nanoparticles on the surface of CuSe precursor. A series of

HRTEM examinations of samples obtained after various reaction durations will allow us to follow the compositions involved in cation exchange reaction.

6.2.4 Cation Exchange with Other Metal Elements

First-period transition metal elements, such as Mn, Co, Ni, Fe, have long been considered to be the most likely alternatives to precious metal catalysts and many studies have been done on them. This is a crucial reason for selecting cobalt during cation exchange process. Exchanges between Mn, Co, Ni and Cu have already been realized with $\text{Cu}_{1.8}\text{S}$ precursor. Since they all belong to copper chalcogenides, the cation exchange with Mn and Ni can also happen in CuSe.

Although the electrocatalytic activity is still not enough and there are many things left to do, the work still provides a way to enhance materials properties by establishing heterostructure with other composition via simple cation exchange process. This work can even be extended to the forming of CuSe-NiSe, CuSe-MnSe and even the materials containing the elements of Mn, Co, Ni and Cu in the same time.

6.2.5 Practical Applications

The thesis introduces cation exchange on copper selenide for HER and OER performances. To test the properties of materials, only electrochemical activity was evaluated. However, during cyclic voltammetry (CV) process, there were high peaks of reduction and oxidation on CuSe and CuSe-CoSe. In other words, the as-prepared materials might have great potential in battery applications. For future work, the capacity and conductivity of the battery with the CuSe-CoSe electrode can be tested.

In other hand, CuSe materials are generally used for solar cell due to the excellent photoelectric properties. Therefore the property studies can be broadened to photoelectric studies so as to further widen the application range of CuSe-CoSe materials. Besides, stability of the materials is critical as an industrial production.

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