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First-Row Transition Metal Sulfides and Phosphides as Competent Electrocatalysts for Water Splitting

Nan Jiang
Utah State University

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FIRST-ROW TRANSITION METAL SULFIDES AND PHOSPHIDES AS COMPETENT ELECTROCATALYSTS FOR WATER SPLITTING

by

Nan Jiang

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

Approved:

Yujie Sun, Ph.D. Major Professor	Lisa M. Berreau, Ph.D. Committee Member
Lance C. Seefeldt, Ph.D. Committee Member	Mark R. McLellan, Ph.D. Vice President for Research and Dean of the School of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2017

ABSTRACT

First-Row Transition Metal Sulfides and Phosphides as Competent Electrocatalysts for Water Splitting

by

Nan Jiang, Master of Science

Utah State University, 2017

Major Professor: Dr. Yujie Sun
Department: Chemistry and Biochemistry

Conversion of renewable energy resources (such as solar and wind) through water splitting to hydrogen and oxygen has attracted increasing attention. The sole product of hydrogen combustion is water, rendering a carbon-neutral energy cycle. Water splitting consists of two redox half reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Both of these two transformations involve multi-electron/proton movement and thus are kinetically sluggish. In order to accelerate the reaction rates for practical application, efficient catalysts are needed. State-of-the-art catalysts for water splitting are usually composed of noble metals, such as platinum, ruthenium, and iridium, whose scarcity and high cost limit their wide employment. Consequently, it is of critical importance to develop competent and non-precious catalysts via low-cost preparation.

Owing to the thermodynamic convenience and potential application in proton exchange membrane and alkaline electrolyzers, traditionally, most HER catalysts were developed under strongly acidic conditions while OER catalysts under strongly alkaline conditions. In order to accomplish overall water splitting, the coupling of HER and OER catalysts in the same electrolyte is mandatory. This thesis will summarize our recent efforts towards developing 1st-row transition metal-based sulfides and phosphides for electrocatalytic water splitting under ambient conditions.

(98 pages)

PUBLIC ABSTRACT

First-Row Transition Metal Sulfides and Phosphides as Competent Electrocatalysts for Water Splitting

Nan Jiang

Solar energy is a carbon-neutral and renewable energy resource. Its nature of intermittence and unequal distribution requires efficient solar energy capture, conversion, and storage. Solar-driven water splitting to produce hydrogen and oxygen is widely considered as an appealing approach to meet this goal, in which hydrogen acts as a green energy carrier. Water splitting consists of two redox half reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Both reactions involve the transfer of multiple electrons and protons and possess high energy barriers to proceed at appreciable rates, hence catalysts are needed.

A large number of HER and OER catalysts employ expensive metals, such as Pt, Ru, and Ir, but the associated scarce and cost prohibit their wide application. Solid-state catalysts employing earth-abundant elements have also been reported to show catalytic performance for water splitting under various conditions. Most research efforts have been devoted to developing non-precious HER and OER catalysts in acidic and basic media, respectively. The incompatibility of electrolytes makes it difficult to couple HER and OER catalysts to achieve overall water splitting. Taking into account of the vulnerability of most 1st-row transition metal-based OER catalysts in acidic solution and the much larger overpotential loss of OER than that of HER, we reasoned that developing bifunctional catalysts that operate in basic solution will be a promising strategy for

overall water splitting with high efficiency.

The research results presented in this thesis showcase our achievements in developing low-cost electrocatalyts for HER and OER. Our research particularly focused on the 1st-row transition metal-based sulfides and phosphides, which exhibited excellent activity and stability for electrocatalytic water splitting.

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CHAPTER I

INTRODUCTION[a]

1-1. Background

The growing global energy demands, depletion of fossil fuel reserves, as well as increasing concerns about climate change resulting from fossil fuel combustion have urged the exploration of green and sustainable energy resources.[1] Solar energy is a promising candidate owing to its gigantic capacity. However, its diurnal and intermittent nature requires efficient capture and storage. In this respect, solar-driven water splitting to produce hydrogen and oxygen is an attractive means to store solar energy in chemical forms.[1] In addition, hydrogen is also an important chemical feedstock, playing a crucial role in petroleum refining and NH_3 synthesis for fertilizers.[2] Molecular hydrogen (H_2) produced from water splitting with renewable energy input, is an attractive energy carrier and fuel candidate, since water is the sole product of H_2 combustion. Water splitting consists of two redox half reactions: H_2 evolution reaction (HER) and O_2 evolution reaction (OER). Both reactions involve the transfer of multiple electrons and protons and possess high energy barriers to proceed at appreciable rates, hence catalysts are required.

For electrocatalytic HER, it is a two-electron two-proton process, which has been investigated for decades.[1] Depending on the different reaction conditions (acidic, neutral, or alkaline electrolytes), HER can proceed according to one of the following two

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[a] Adapted with permission from [Nan Jiang, Meili Sheng, Yujie Sun, Chapter 6 in Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation, Hybrid Molecular–Nanomaterial Assemblies for Water Splitting Catalysis, **ISBN** 978-1-84973-959-7.]. Copyright 2016. The Royal Society of Chemistry. Reproduced by permission of The Royal Society of Chemistry, http://pubs.rsc.org/en/conten t/chapter/bk9781 849739 597-00108/978-1-84973-959-7#!divabstract.

pathways.[3] In acidic electrolyte, the proton source is sufficient. The overall HER can proceed via equation 1. However, in alkaline electrolyte, free protons are deficient. The overall HER can be achieved through equation 2. For both acidic and alkaline conditions, the commonly accepted reaction mechanism involves two steps: (i) an initial electrochemical hydrogen adsorption reaction (Volmer step, equation 3 for acidic or equation 4 for alkaline); (ii) an electrochemical hydrogen desorption (Heyrovsky step, equation 5 for acidic or equation 6 for alkaline), or recombination reaction (Tafel step, equation 7 for both acidic and alkaline), where H* represents a hydrogen atom adsorbed on a catalytically active site on the electrode surface (M). Due to the low concentration of free protons under alkaline conditions, water dissociation is involved prior to the formation of M–H* in Volmer and Heyrovsky steps (equation 4 and equation 6).[4]

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \text{ (acidic)} \tag{1}$$

$$2H_2O_{(aq)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \text{ (alkaline)} \tag{2}$$

$$H^{+}_{(aq)} + M + e^{-} \rightarrow M\text{–}H^* \text{ (acidic)} \tag{3}$$

$$H_2O + M + e\text{-} \rightarrow M\text{–}H^* + OH^{-}_{(aq)} \text{ (alkaline)} \tag{4}$$

$$M\text{–}H^* + H^{+}_{(aq)} + e^{-} \rightarrow M + H_{2(g)} \text{ (acidic)} \tag{5}$$

$$M\text{–}H^* + H_2O + e^{-} \rightarrow M + OH^{-}_{(aq)} + H_{2(g)} \text{ (alkaline)} \tag{6}$$

$$2M\text{–}H^* \leftrightarrow 2M + H_{2(g)} \text{ (both acidic and alkaline)} \tag{7}$$

These reaction pathways are strongly dependent upon the inherent properties of the active sites. The standard reduction potential of HER is defined as 0 V *vs.* standard hydrogen electrode (SHE) at pH 0, which shifts −59 mV by every pH unit increase. This pH dependence can be avoided when the measured potential is referenced to the reversible hydrogen electrode (RHE). With a RHE scale, the observed potential always equals to the overpotential η (the difference between applied potential and thermodynamic potential), since the Nernstian potential of HER is 0 V *vs.* RHE regardless of pH. Under kinetic-controlled region, the correlation between catalytic current density and overpotential can be described by the Tafel equation (equation 8)[3]:

$$\eta = \frac{-2.3RT}{\alpha nF}\log j_0 + \frac{2.3RT}{\alpha nF}\log j = a + b\log j \tag{8}$$

where R is the ideal gas constant, F is the Faraday constant, T is the temperature, n is the number of electron transferred (n = 2 for HER), α is the charge transfer coefficient, j_0 is the exchange current density at $\eta = 0$ V, j is the current density, and b is the Tafel slope. Depending on the rate-limiting step, different Tafel slopes can be obtained: 29.5 (Tafel), 39 (Heyrovsky), or 118 (Volmer) mV/decade.

Owing to the sluggish kinetics of HER, electrocatalysts are needed to decrease the overpotential for higher energy efficiency and accelerate the reaction rate. Billion years of evolution provided nature with hydrogenases to perform the H^+/H_2 inter-conversion with a remarkably high efficiency under ambient conditions. Hydrogenases are able to catalyze H_2 evolution near the thermodynamic potential and a turnover frequency (TOF) of ~ 9000 s^{-1} can be achieved at room temperature.[5] In order to mimic the catalytic fashion of hydrogenases, a large number of bioinspired molecular complexes containing the core structures of hydrogenase cofactors, including [Fe-Fe], [Ni-Fe], and [Fe], have been explored extensively.[6] Many delicate models have been synthesized and investigated. Those studies led to our deeper understanding in the catalytic mechanisms of hydrogenases, paving the way for designing improved biomimetic HER catalysts.

Owing to well-defined active sites and tunable properties of molecular HER catalysts via structural/electronic substituents, molecular complexes have attracted much attention in developing catalytic systems for water splitting. Traditionally, molecular HER catalysts were studied in organic solvents with the addition of an organic or inorganic proton source, owing to the limited solubility and/or stability of those catalysts in aqueous media.[7] In order to develop a catalytic system for water splitting at an industrial scale, it is more desirable to directly utilize water as the reaction medium. Although molecular catalysts might possess high intrinsic activity, their stability is usually inferior compared to solid-state heterogeneous catalysts, potentially due to undesirable inter-molecular collision of high-energy catalytic intermediates.[8]

Along with the rapid development of nanomaterials science over the last three decades, an ever increasing research focus has been shifted towards developing solid-state heterogeneous HER catalysts, which tend to possess better stability in aqueous media. Solid-state catalysts employing noble metals, such as Pt, have long been recognized as competent HER catalysts with low overpotential and great stability.[9] Unfortunately, the associated scarce and high cost limit their application on a large scale. It remains a great challenge to develop inexpensive HER catalysts exhibiting both high efficiency and strong robustness.[10] Recent years have witnessed the emergence of several promising solid-state HER catalysts composed of earth-abundant elements. For example, metal alloys,[11] metal oxides/hydroxides,[12] chalcogenides,[13] carbides,[14] phosphides,[15] and even metal-free nanomaterials[16] have been reported as potential HER catalysts. During the last decade, transition metal chalcogenides and phosphides have rapidly emerged as two popular groups of HER catalysts, largely owing to their earth abundance, low cost, rich redox chemistry, promising activity, and stability under a variety of conditions.[17]

It is known that all the cofactors in hydrogenases ubiquitously involve metal-sulfur interactions.[6] Inspired by the blueprints of hydrogenase active sites, increasing efforts have been devoted to exploring 1st-row transition metal chalcogenides, such as CoS_x,[18] $CoSe_2$,[19] FeS,[20] $FeSe_2$,[21] and NiS_x,[22] as potential HER catalysts. The success of 1st-row transition metal chalcogenides for HER application motivated researchers to explore other transition metal chalcogenides. More recent work showed that molybdenum sulfides with various morphologies and structures are active HER catalysts.[23] Due to its terrestrial abundance and involvement in [Ni-Fe] hydrogenases,[6] nickel has long been sought as a promising candidate for HER catalysis. Indeed, a variety of nickel-based catalysts have emerged for electrocatalytic H_2 production recently. Typical examples include nickel alloys,[24] sulfides,[25] selenides,[26] oxides/hydroxides,[27] and phosphides,[28] among which nickel sulfides are one of the most investigated because of their low cost, facile preparation, and high catalytic activity. In fact, many nickel sulfide-based HER catalysts of different crystal structures have been reported for H_2 evolution under acidic, neutral, or alkaline conditions. For instance, metal–organic framework-derived NiS nanoframes have been demonstrated as HER catalysts in 1.0 M KOH.[25] Similarly, NiS_2 of various nanostructures was reported to exhibit remarkable HER catalytic performance in strongly acidic electrolytes.[29] Recently, we reported an electrodeposited Ni-S film with active and robust HER activity not only in neutral buffer but also in natural water.[22] A suite of characterization techniques, including X-ray absorption spectroscopy, were conducted to probe the catalyst and the main composition of the Ni-S film was revealed to be Ni_3S_2. This was the first time that Ni_3S_2 was found to be a competent HER catalyst. Details of preparation, characterization, and catalytic performance of Ni-S film are presented in Chapter II.

Analogous to the case of chalcogenides, transition metal phosphides have long been used for catalysis. The HER application of phosphides has also benefited from the inspiration of hydrogenase. In 2005, Rodriguez *et al.* reported density functional theory (DFT) calculation results suggesting promising HER activities of Ni_2P (001) as the dilution effect of phosphorous would make Ni_2P (001) behave more like hydrogenases rather than pure metal.[30] It was suggested that the negatively charged phosphorous atoms and isolated nickel atoms could function as proton and hydride acceptor sites, respectively. Although it was not until 2013 that transition metal phosphides started to attract wide attention as promising HER catalysts,[31] currently phosphides are among the most active category of HER catalysts, whose catalytic performance are quickly approaching those of benchmark platinum groups. Parallel to the rapid development of nickel phosphides for electrocatalytic H_2 generation, a roughly equal amount of efforts have been devoted to exploring cobalt phosphides[32] and molybdenum phosphides[33] as potential HER catalysts.

As a four-electron/four-proton process, O_2 evolution from water bears a high activation barrier and has to go through multiple intermediate states. Nature evolved a delicate biological machinery to convert solar energy, water, and CO_2 into carbohydrates via a process named photosynthesis. There are mainly two components involved in photosynthesis: photosystem I and photosystem II. The most chemically challenging step occurs at the O_2 evolution center of photosystem II, where water oxidation to O_2 takes place. Recently, the crystal structure of the O_2 evolution center, which contains a Mn_4CaO_5 cluster, was obtained with a 1.9 Å resolution.[34] The cubane-type Mn_4CaO_5 cluster has been an inspiration source for many scientists aiming at developing competent O_2 evolution catalysts. Inspired, but not constrained, by nature, a large library of molecular catalysts has been reported,[35] ranging from early focus on ruthenium and iridium complexes to more recent efforts on earth-abundant transition metals, like manganese, iron, cobalt, nickel, and copper species.[36]

Owing to thermodynamic convenience and potential application in proton-exchange membrane, most HER catalysts were developed under strongly acidic conditions. Since most OER catalysts are vulnerable in acidic media, such a prevailing approach in the development of HER and OER catalysts often result in their incompatible integration to accomplish overall water splitting in the same electrolyte. As the overpotential loss of OER is usually much larger than that of HER, it’s more economically viable to explore bifunctional electrocatalysts active for both HER and OER in strongly alkaline electrolytes. Such a new type bifunctional electrocatalyst will not only avoid the incompatibility issue of the HER and OER catalysts working in the same electrolyte, but also offer time-saving preparation and hence reduce the total cost of water electrolyzers. Recently, transition metal oxides/hydroxides and phosphides have been reported as bifunctional catalysts.[37] For example, H_2–CoCat, metallic cobalt coated with a cobalt-oxo/hydroxo-phosphate layer can be prepared via electrodeposition in a phosphate buffer containing cobalt salts.[37b] It is able to mediate H_2 evolution in aqueous solution. Remarkably, it can be converted via anodic equilibration into the amorphous cobalt oxide film (O_2–CoCat or CoPi) catalysing O_2 evolution. The switch between the two catalytic forms is fully reversible and corresponds to a local interconversion between two morphologies and compositions at the surface of the electrode. Based on the above factors, H_2–CoCat functions as a robust, bifunctional, and switchable catalyst for overall water splitting albeit with mediocre performance. Last year, we reported that an electrodeposited Co-P film (10% phosphorous doped in metallic cobalt) could act as a bifunctional and competent electrocatalyst for both HER and OER under strongly alkaline condition (1.0 M KOH).[32] Details of preparation, characterization, and catalytic performance of Co-P film are presented in Chapter III.

In the following chapters, I will first summarize my research results in developing electrodeposited Ni-S films for electrocatalytic H_2 generation. Subsequently, a novel type of bifunctional Co-P electrocatalyst for overall water splitting under strongly alkaline conditions will be introduced, where the OER catalysts are formed from HER catalysts under *in situ* electrocatalytic conditions.

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CHAPTER II

NICKEL SULFIDES AS EFFICIENT ELECTROCATALYSTS FOR HYDROGEN EVOLUTION FROM WATER[b]

1-1. Introduction

Nature evolves hydrogenases to catalyze the conversion between proton and hydrogen in neutral aqueous media at nearly zero overpotential with turnover frequencies of 100 to 10,000 per second.[1] Nevertheless, the large size and relative instability of hydrogenases under aerobic conditions limit their practical applications. Three types of hydrogenase cofactors, binuclear iron/iron, iron/nickel, and mononuclear iron, have been identified.[2] All of these cofactors ubiquitously involve metal-sulfur interactions. Inspired by the core structures and active elements of hydrogenases, metal chalcogenides composed of earth-abundant elements have been investigated to catalyze HER in various reaction systems.

Early in 1970s, Bennett *et al.* studied the electrocatalytic HER activity of bulk MoS_2.[3] Subsequently, molybdenum sulfides of varying morphologies have been reported to be active HER catalysts in strong acidic solution. In 2005, Nørskov *et al.* predicted that Mo (1010) edge of nanostructured MoS_2 materials possessed promising HER activity via density functional theory (DFT) calculation.[4] Later, Chorkendoff *et al.* experimentally confirmed that the electrocatalytic HER performance of MoS_2 was indeed correlated with

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the number of its edge sites.[5] Besides those crystalline MoS_2 species, various amorphous molybdenum sulfides have also been reported as competent HER catalysts. For instance, Hu *et al.* prepared MoS_x films on conductive substrates via electrodeposition and the resulting MoS_x films demonstrated excellent HER performance in acidic electrolytes.[6] Inspired by the blueprints of hydrogenase active sites and encouraged by the success of 2nd-row transition metal chalcogenides in HER electrocatalysis, increasing efforts have been devoted to exploring 1st-row transition metal chalcogenides. For instance, electrodeposited Co-S films on fluorine-doped tin oxide (FTO) were reported to act as efficient and robust catalysts for electrochemical and photoelectrochemical H_2 generation in neutral aqueous media.[7] The amorphous Co-S film exhibited porous morphology, low catalytic onset overpotential (43 mV), small Tafel slope (93 mV/dec), near 100% Faradaic efficiency, and robust stability. Recently, bio-inspired FeS nanoparticles were also reported as HER electrocatalysts in neutral water.[8] Despite its much lower catalytic activity than that of CoS, FeS possessed attractive stability showing no structural decomposition or activity decrease for at least six days. Continuous research in elucidating the catalytic performance of NiS will undoubtedly provide more insights and guidelines in designing and developing novel nickel-based HER catalysts.

Herein, we describe that a slightly modified electrodeposition method enabled us to generate amorphous nickel-sulfide (Ni-S) films as well. Electrochemical experiments under various conditions demonstrate that the Ni-S films are very active HER catalysts in water over a wide range of pH values. The Ni-S film maintained its catalytic activity over 100 h in pH 7 phosphate buffer with a Tafel slope of 77 mV/dec and a Faradaic efficiency of 100%. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) results revealed that the major composition of the Ni-S film is Ni_3S_2.

1-2. Preparation of the Ni-S film

In a typical preparation of a Ni-S film, two FTO electrodes were used as the working and counter electrodes, respectively, with a Ag/AgCl (sat.) electrode as the reference electrode. Prior to electrodeposition, the FTO electrodes were sonicated in acetone, water, and ethanol, consecutively. Each sonication was conducted for at least 15 min. Subsequently, the FTO electrodes were dried and stored under vacuum at room temperature. Scotch tape was used to cover the working FTO electrode with only a circular area of diameter of 7 mm exposed to the deposition solution (5 mM $NiSO_4$ and 0.5 M thiourea in water). Nitrogen was bubbled through the electrolyte solution for at least 20 min before deposition and maintained during the entire deposition process. The

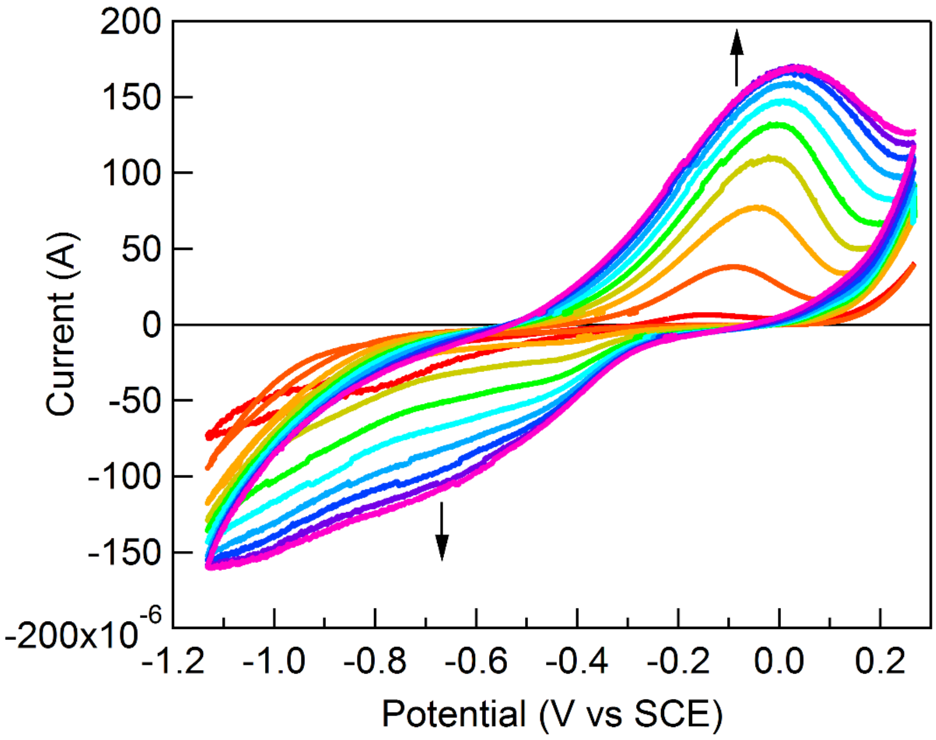

Figure 2-1. A typical potentiodynamic deposition for the preparation of Ni-S films on FTO.

potential of consecutive linear scans was cycled between −1.2 and 0.2 V *vs.* Ag/AgCl (sat.) at a scan rate of 5 mV/s under stirring. Figure 2-1 shows typical cyclic voltammograms of the deposition of a Ni-S film on FTO. Along the deposition process, the area of the FTO working electrode exposed to the electrolyte solution gradually turned black and a uniform film formed on the surface. After deposition, the Ni-S/FTO electrode was removed from the deposition bath and rinsed with copious water gently. Ni-S/FTO was dried under vacuum at room temperature overnight, followed by annealing at 300 °C for 4 h under nitrogen, which was found to strengthen the mechanic stability of the deposited film attached to FTO. The prepared Ni-S/FTO electrodes were always stored under vacuum at room temperature prior to electrochemical experiments.

1-3. Characterization of the Ni-S film

The scanning electron microscopy (SEM) image of a typical Ni-S/FTO electrode is displayed in Figure 2-2a, showing nearly complete coverage of the Ni-S film on FTO. No regular crystalline particles or aggregates were observed. The presence of nickel and

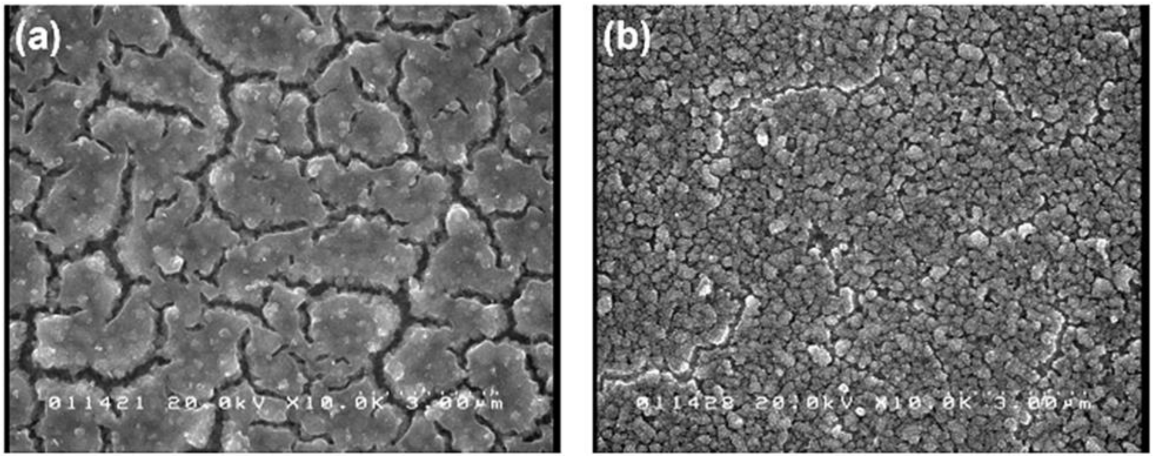

Figure 2-2. SEM images of the Ni-S films before (a) and after (b) a 1 h electrolysis in pH 7 phosphate buffer at –0.689 V *vs.* SHE. The post-electrolysis Ni-S film displays a rougher and more porous surface compared to the pre-electrolys.

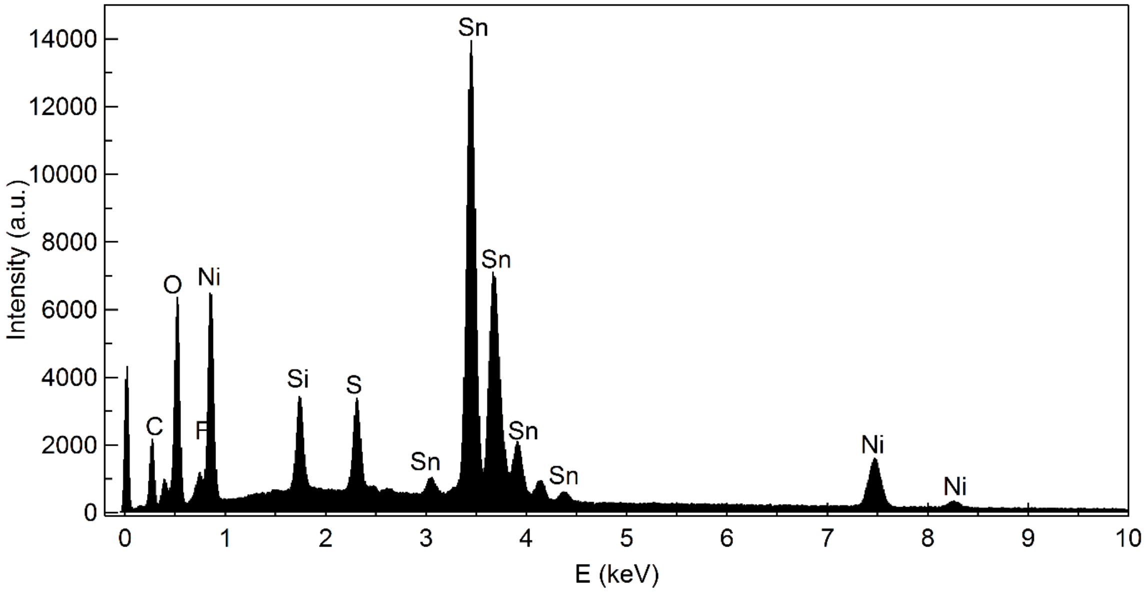

Figure 2-3. EDS of a Ni-S film deposited on FTO.

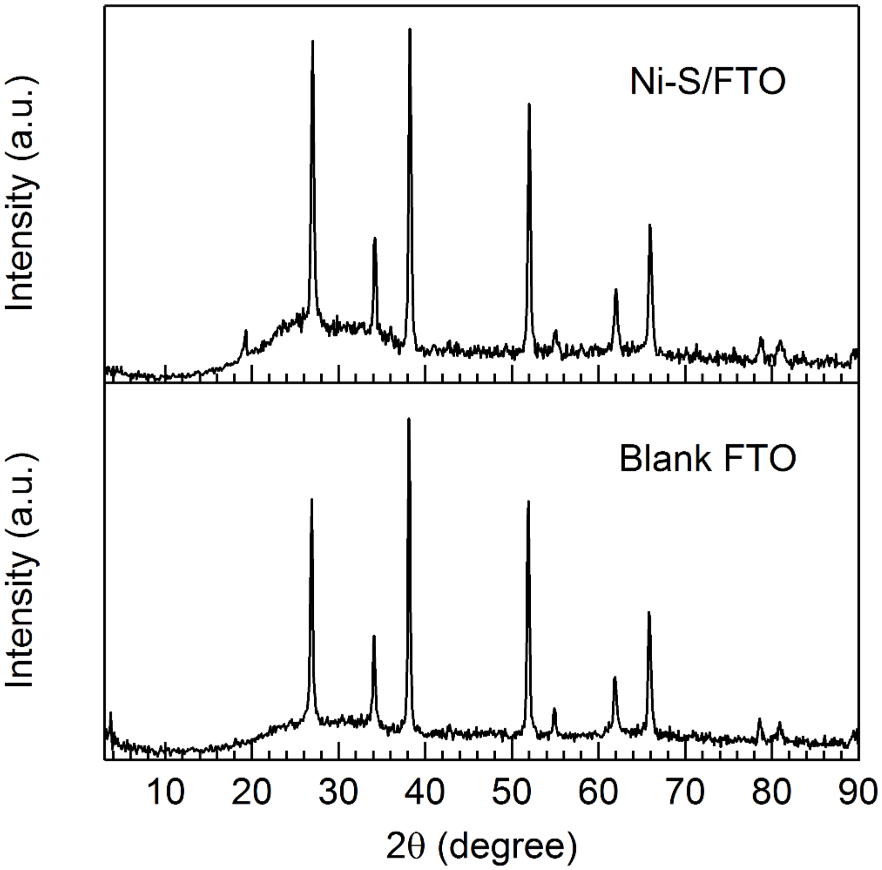

Figure 2-4. XRD of Ni-S/FTO and blank FTO.

sulphur in the deposited film were confirmed by energy dispersive X-ray spectroscopy (EDS), Figure 2-3. The signals of Sn, O, Si, and F are attributed to the FTO-coated glass substrate. The powder X-ray diffraction (XRD) pattern of Ni-S/ FTO is compared to that of a blank FTO as shown in Figure 2-4. All the XRD peaks are due to the presence of FTO, whereas no unique diffraction was noticed for the Ni-S film. Hence, it is concluded that the Ni-S film is amorphous in nature. Elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) for four Ni-S/FTO samples prepared with different surface areas indicates that the average mass loading of Ni is 81.50 µg/cm^2 and the Ni/S ratio is close to 1.55 (Table 2-1).

Table 2-1. ICP-OES data of four Ni-S/FTO samples.

Sample	**Area (cm^2)**	**Ni (µmol)**	**S (µmol)**	**[Ni] (µg/cm^2)**	**Ni/S**
1	0.385	0.5479	0.3845	83.61	1.4
2	0.735	1.0005	0.7884	79.89	1.25
3	0.750	1.0601	0.6443	82.96	1.65
4	0.750	1.0165	0.5443	79.55	1.85
Average				**81.50**	**1.55**

1-4. Catalytic activity of the Ni-S film

The HER catalysis of the Ni-S film was first evaluated in neutral water. Figure 2-5a shows the polarization curve of Ni-S/FTO in pH 7 phosphate buffer at a scan rate of 2 mV/s. The polarization curve of a blank FTO electrode is also included as a comparison. It is apparent that the blank FTO did not show any HER catalytic activity until –0.95 V *vs.* SHE, however a catalytic current was observed for Ni-S/FTO beyond –0.55 V *vs.* SHE (Figure 2-5b). Further scanning towards negative potential produced a dramatic

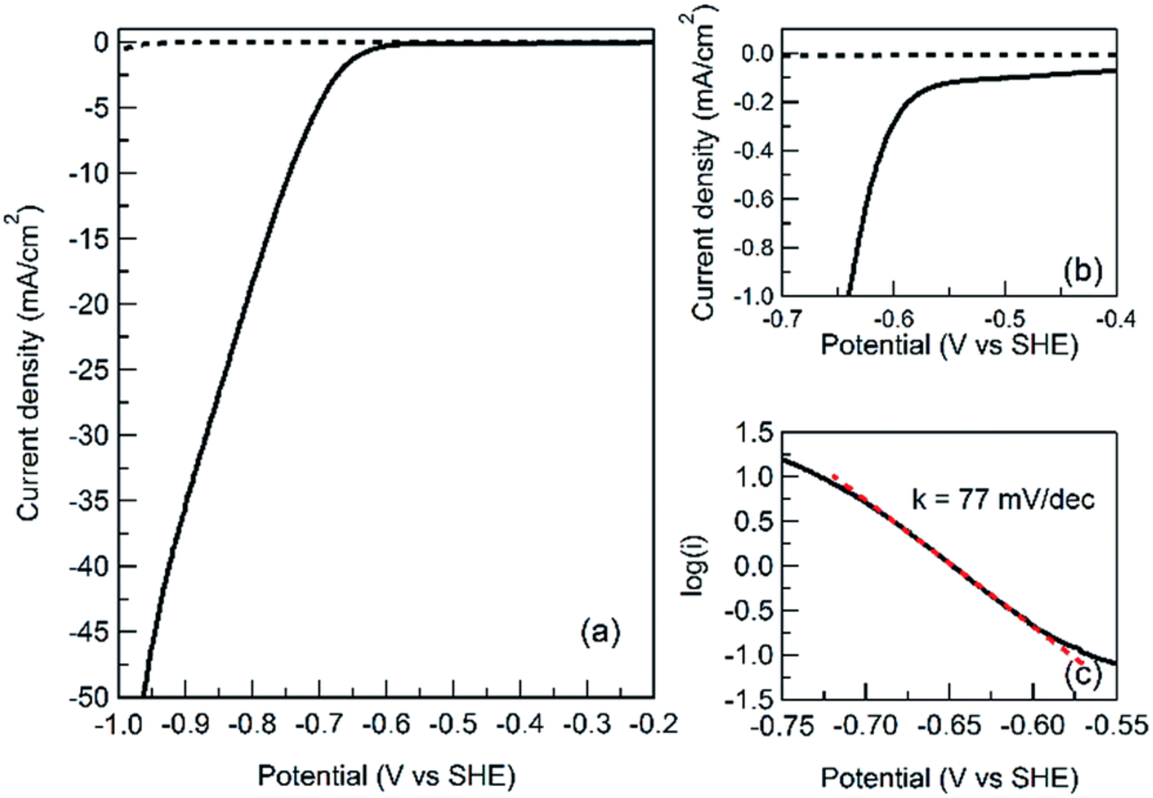

Figure 2-5. (a and b) Polarizations of Ni-S/FTO (solid) and blank FTO (dotted) in pH 7 phosphate buffer (scan rate: 2 mV/s), and (c) Tafel plot of Ni-S/FTO (black solid) with its linear fitting (red dotted) in the region of –0.55 to –0.65 V *vs.* SHE.

increase in current density, accompanied by vigorous growth and release of hydrogen bubbles from the electrode surface. To reach current densities of 1 and 10 mA/cm^2, the Ni-S/FTO electrode required overpotentials of –227 and –330 mV, respectively. These values compare favorably with other solid-state earth-abundant HER catalysts at pH 7.[6], [9] Notably, the linear fitting of the Tafel plot (Figure 2-5c) rendered a Tafel slope of 77 mV/dec, which is among the smallest Tafel slopes obtained for non-noble metal HER catalysts in neutral water.[6], [9] For instance, the MoS_2 film showed a Tafel slope of 86 mV/dec at pH 7, and the first-row transition metal doping in MoS_2 did not decrease the Tafel slope (87-96 mV/dec).[10] An electrodeposited nickel hydroxide/oxide film was reported to be active for hydrogen evolution catalysis, however it required an overpotential of −452 mV to reach 1.5 mA/cm^2 with a much larger Tafel slope (226 mV/dec) in a borate buffer (pH 9.2).[9] Although the Co-S film prepared in a similar manner exhibited a better onset overpotential than the Ni-S film, the former possessed a larger Tafel slope (93 mV/dec).[7]

It was reported that three principal steps are involved in the hydrogen evolution reaction: Volmer (discharge), Tafel (recombination), and Heyrovsky (desorption) steps.[11] Depending on which one is the limiting step, the Tafel slope could be 29, 38, or 116 mV/dec, respectively. The deviation of the 77 mV/dec slope of the Ni-S film from these three principal values indicates the complexity of the hydrogen evolution mechanism of this system.

We next investigated the Faradaic efficiency of the Ni-S film in HER catalysis through a chronopotentiometry experiment maintaining a catalytic current of 2 mA for 2.5 h. As shown in Figure 2-6, the increasing amount of generated hydrogen was measured by gas chromatography and compared with the theoretical amount assuming that all the passed charge was used to produce H_2. The close match of the measured and calculated hydrogen volume demonstrates a 100% Faradaic efficiency of Ni-S/FTO in HER electrocatalysis. Given the average loading mass of Ni (81.5 μg/cm^2), the mole of Ni (0.534 μmol) in the Ni-S film is only ~0.5% of the mole of hydrogen (0.1 mmol) produced during the 2.5 h electrolysis.

In order to assess the long-term stability of the Ni-S film for HER catalysis, an extended electrolysis was carried out. Figure 2-7a presents the accumulated charge of Ni-S/FTO in pH 7 phosphate buffer at −0.700 V *vs.* SHE for 100 h. A nearly linear charge accumulation over time clearly demonstrates the robust durability of the Ni-S film for

HER electrocatalysis, which is corroborated by the steady current over the entire course (Figure 2-7a, inset). It should be noted that a blank FTO electrode only generated negligible charge build-up under the same conditions. Calculations from the average loading mass of Ni (Table 2-1) and passed charge during the 100 h electrolysis resulted in

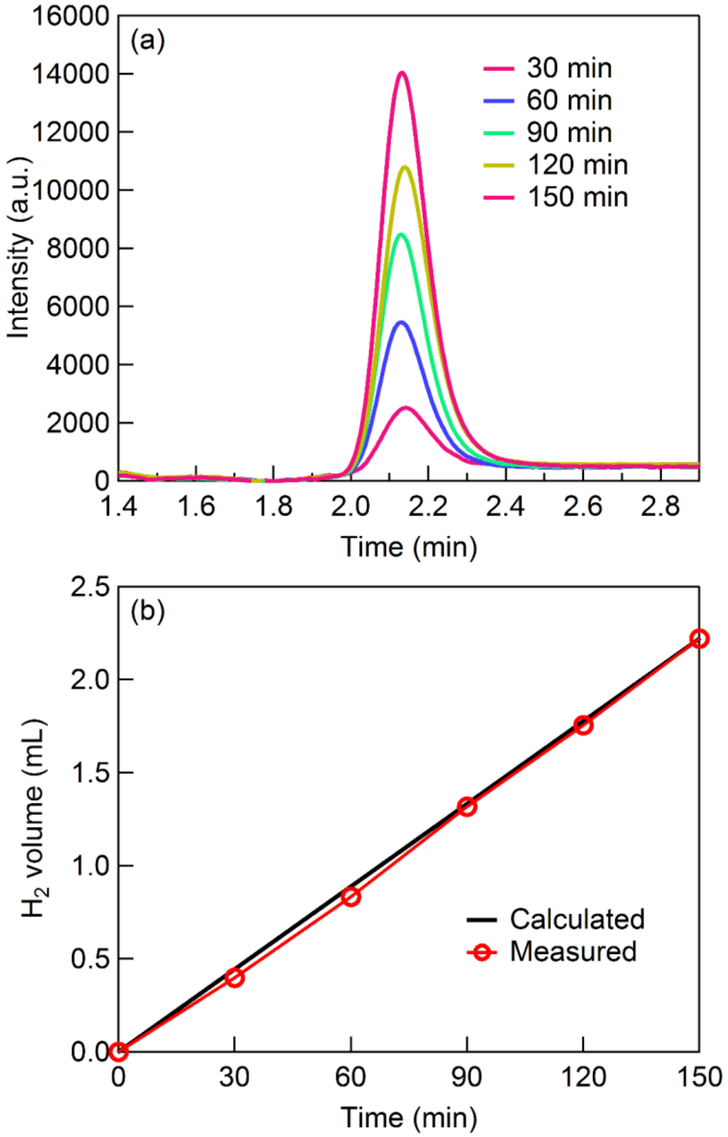

Figure 2-6. (a) Gas chromatograms of generated H_2 during a 2.5 h chronopotentiometry experiment of Ni-S/FTO at 2 mA in pH 7 phosphate buffer. (b) Overlay of the measured H_2 volume (red) from gas chromatography every 30 min and the calculated H_2 volume (black) based on the assumption that all the passed charge during the electrolysis was used to produce H_2.

a turnover number of 925 mole H_2 per mole Ni. It should be noted that this value only represents an underestimated activity of the Ni-S film, since catalysis is expected to occur at the active sites on the surface. From the very stable catalytic current over the entire electrolysis, it is highly anticipated that the Ni-S film will maintain its catalytic activity for a much longer duration than 100 h.

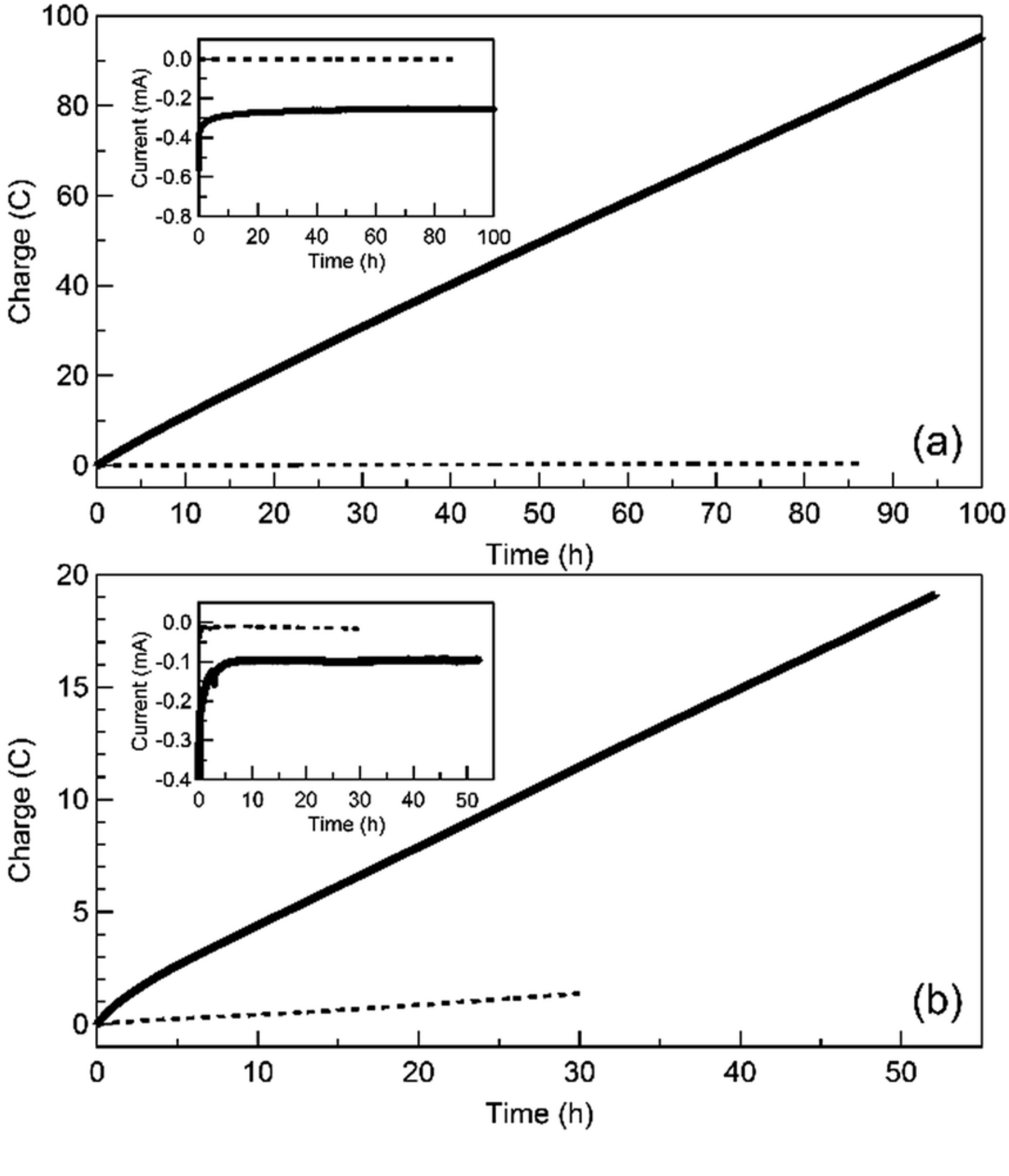

Figure 2-7. Long-term controlled potential electrolysis of Ni-S/FTO (solid line) in (a) 1.0 M phosphate buffer of pH 7 at –0.700 V *vs.* SHE and (b) filtered Great Salt Lake water at –0.959 V *vs.* SHE. The insets in (a) and (b) show the corresponding current over time.

Given the low cost and wide availability, natural water is an ideal substrate for water splitting. A natural water sample collected from the Great Salt Lake was filtered through a medium frit to remove insoluble particles and directly used as an electrolyte solution. As depicted in Figure 2-7b, a long-term electrolysis of the Ni-S film was conducted in the Great Salt Lake water at –0.959 V *vs.* SHE over 50 h. Despite an initial current decrease during the first few hours, the catalytic current stabilized and persisted for the rest of the period (Figure 2-7b, inset). Hydrogen formation was confirmed by gas chromatography. A 30 h electrolysis of a blank FTO electrode did not generate an appreciable amount of hydrogen under the same conditions, implying that the species in the Great Salt Lake water were not able to form *in situ* HER catalysts that can compete with the Ni-S film. Overall, these results demonstrate that the Ni-S film is a competent and robust HER catalyst even in natural water. Such a remarkable robustness of the Ni-S film prompted us to explore its catalytic performance under extreme conditions. Since the majority of solid-state HER catalysts reported recently were studied in strong acidic media, we first investigated the HER catalysis of Ni-S/FTO in 0.5 M H_2SO_4. As shown in Figure 2-8, Ni-S/FTO was able to reach catalytic current densities of 1, 10, and 20 mA/cm^2 at overpotentials of –150, –213, and –243 mV, respectively. A linear fitting of its Tafel plot resulted in a Tafel slope of 52 mV/dec (Figure 2-8, inset). An electrolysis of Ni-S/FTO at –0.168 V *vs.* SHE was conducted for 90 min (Figure 2-9). The catalytic current decreased during the first half hour, followed by stabilization during the following hours. The initial decrease was likely due to the dissolution and/or detachment of the catalyst film from the FTO electrode.

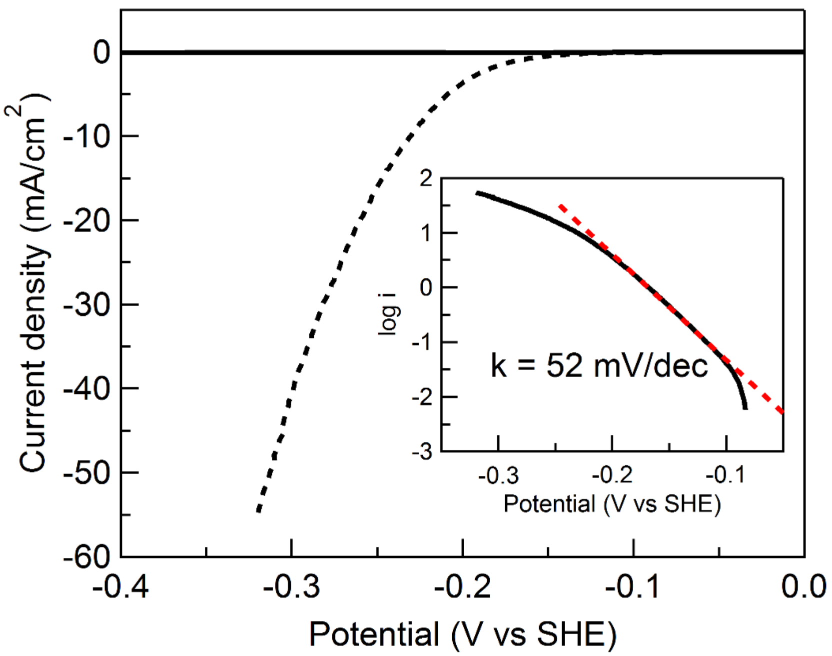

Figure 2-8. Polarizations of Ni-S/FTO (dotted) and blank FTO (solid) in 0.5 M H2SO4 at a scan rate of 2 mV/s. Inset shows the corresponding Tafel plot and slope of Ni-S/FTO.

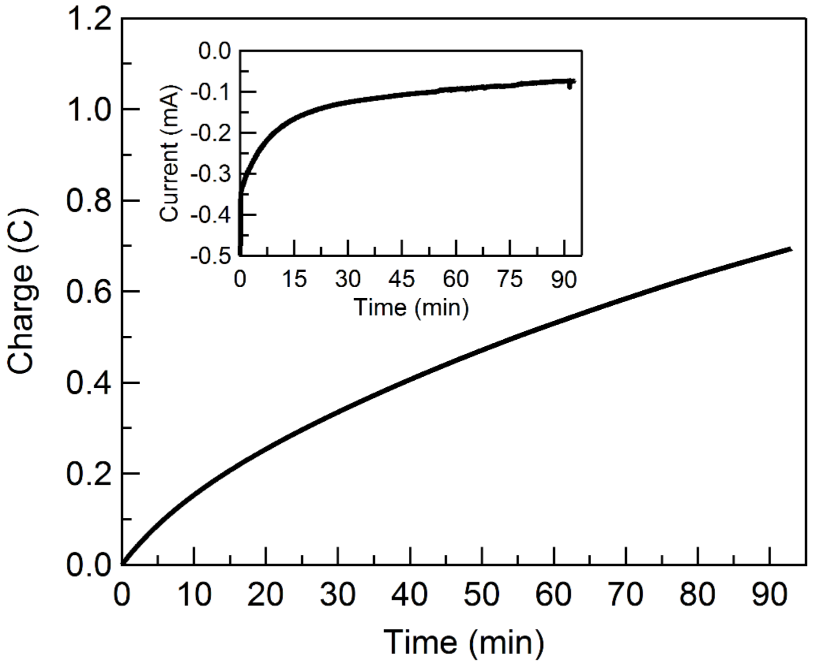

Figure 2-9. Controlled potential electrolysis shows the accumulated charge *vs.* time for Ni-S/FTO in 0.5 M H_2SO_4 with an applied potential of –0.168 V *vs.* SHE. Inset shows current *vs.* time during the electrolysis.

We next assessed the HER catalytic performance of the Ni-S film in 1.0 M KOH. A catalytic current density of 20 mA/cm^2 was achieved at −1.05 V *vs.* SHE with a Tafel slope of 88 mV/dec (Figure 2-10). A 7 h electrolysis of Ni-S/FTO at −1.05 V *vs.* SHE afforded an essentially linear charge build-up with no current decrease during the entire period (Figure 2-11). It demonstrates the great stability of Ni-S/FTO in strong basic media. Based on the aforementioned experimental results, the Ni-S/FTO can act as an excellent HER catalyst under neutral, acidic, and alkaline conditions with remarkable robustness.

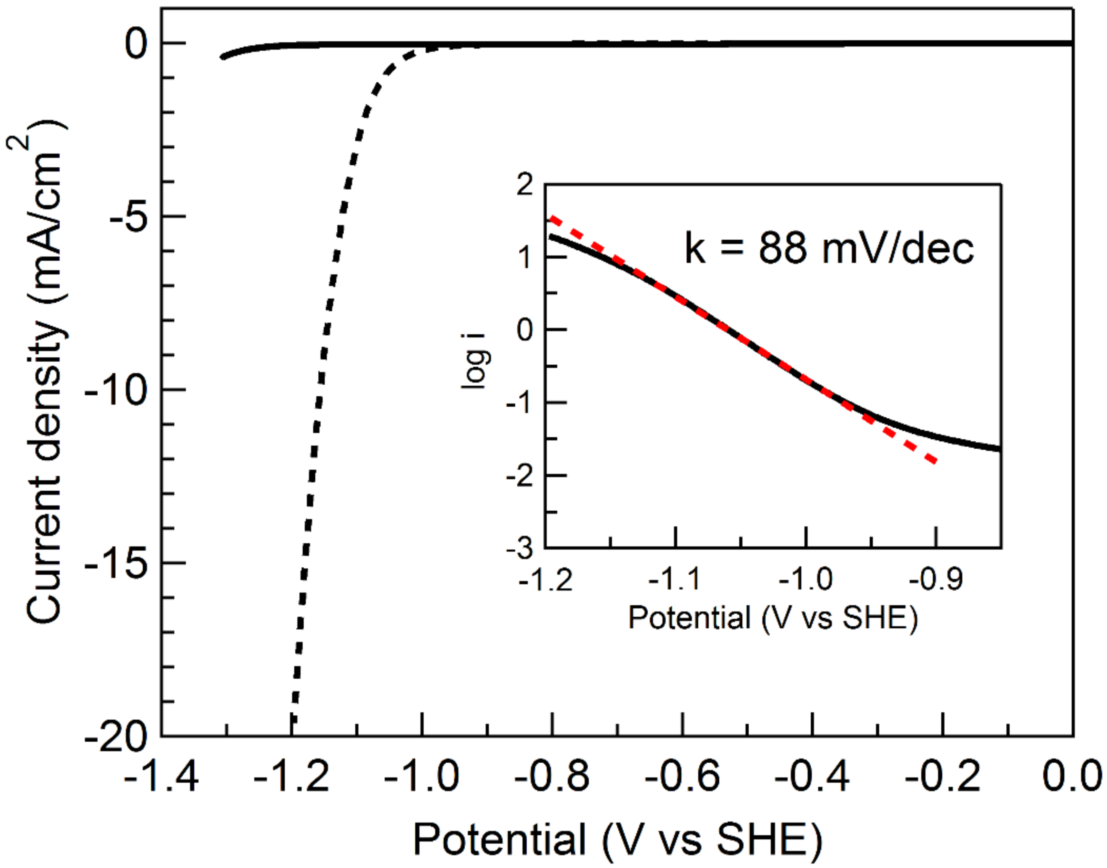

Figure 2-10. Polarizations of Ni-S/FTO (dotted) and blank FTO (solid) in 1.0 M KOH at a scan rate of 2 mV/s. Inset shows the corresponding Tafel plot and slope of Ni-S/FTO.

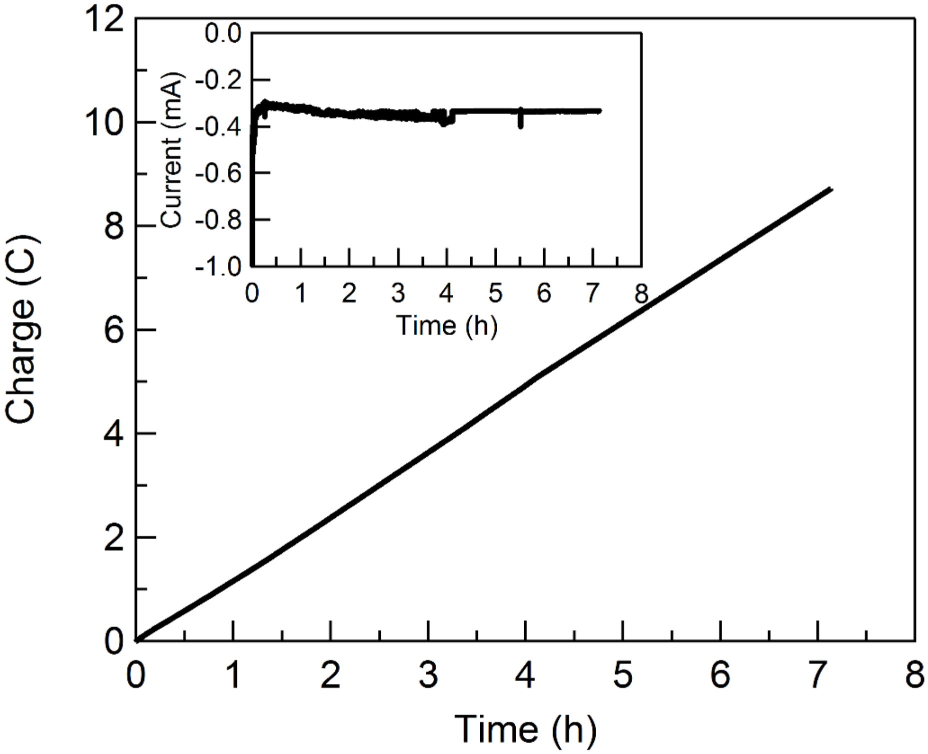

Figure 2-11. Controlled potential electrolysis shows the accumulated charge *vs.* time for Ni-S/FTO in 1.0 M KOH at an applied potential of –1.05 V *vs.* SHE. Inset shows current *vs.* time during the electrolysis.

During the electrocatalytic studies of the Ni-S film, an activation process was observed. As shown in Figure 2-12, consecutive cathodic scans led to an increase in catalytic current and a stabilized current density was achieved after roughly 9 to 10 scans. To investigate the catalyst properties before and after electrochemical experiments, a controlled potential electrolysis of a freshly prepared Ni-S/FTO electrode was conducted at –0.689 V *vs.* SHE for 1 h. Electric impedance spectra (EIS) of the Ni-S film before and after the 1 h electrolysis are compared in Figure 2-13. The Nyquist plots indicate that there was no substantial resistance change of the catalyst film, showing a slight increase from 100 to 110 Ω. Therefore, resistance change can be ruled out as a cause of the enhanced activity.

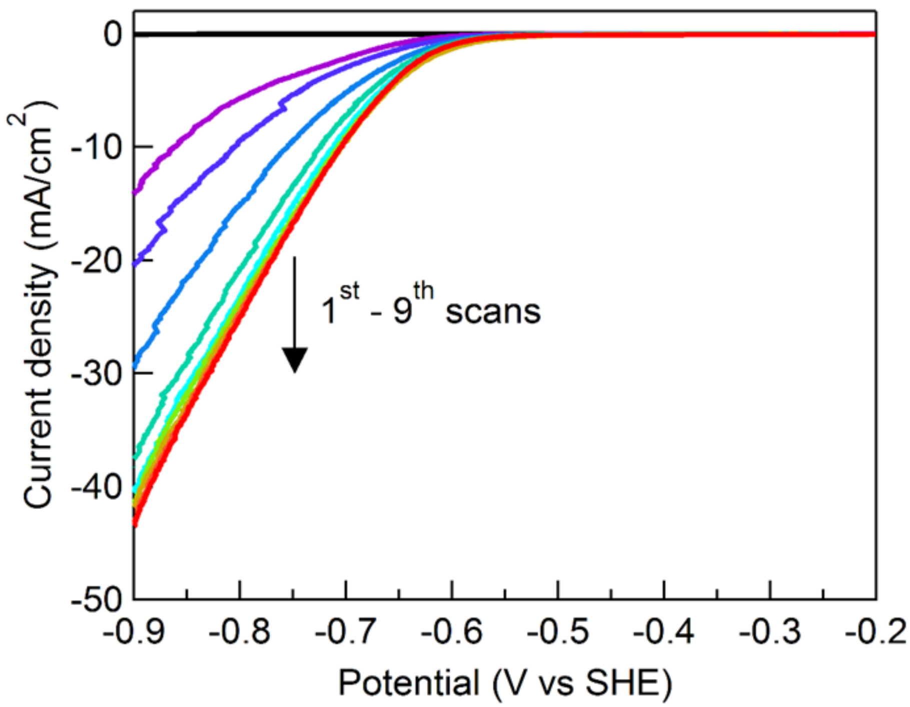

Figure 2-12. Consecutive nine polarizations of Ni-S/FTO in 1.0 M phosphate buffer at pH 7 (scan rate: 2 mV/s). The black curve is for a blank FTO electrode under the same condition.

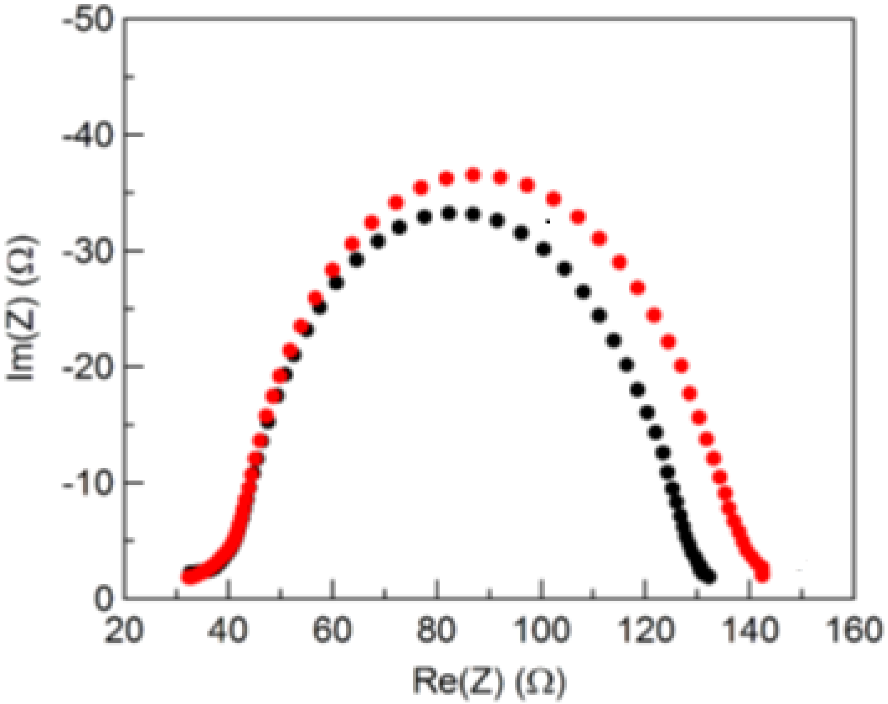

Figure 2-13. Nyquist plots of Ni-S/FTO before (black) and after (red) the 1 h electrolysis.

It has been reported that cyclic voltammetry at non-Faradaic potentials is able to probe the electrochemical double layer as a means for estimating the effective electrode surface area.[12] By plotting the difference in current density between the anodic and cathodic scans ($\Delta j = j_a - j_c$) at a certain overpotential against the scan rate, a linear relationship could be obtained. Fitting these data to a straight line enables the extraction of the geometric double layer capacitance (C_{dl}), which is known to be proportional to the effective electrode surface area. The extracted slopes of these fitting lines allow a comparison of the relative surface areas of electrodes with different morphologies, especially when these electrodes consist of the same material. Figure 2-14a and b present the cyclic voltammograms of a Ni-S/FTO electrode before and after the 1 h electrolysis in the non-Faradaic region of –0.26 to –0.16 V *vs.* SHE. As increased accordingly. Depicted

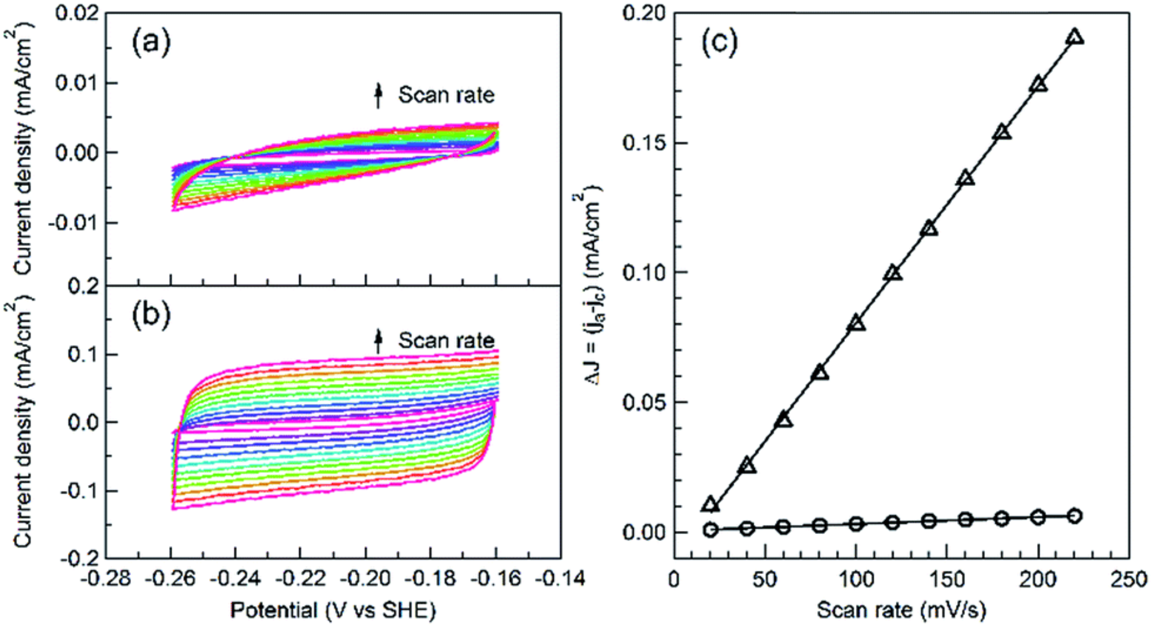

Figure 2-14. Cyclic voltammograms of Ni-S/FTO in the non-Faradaic region before (a) and after (b) a 1 h electrolysis at –0.689 V vs. SHE in pH 7 phosphate buffer, and (c) scan rate dependence of the current densities of the pre- (circle) and post- (triangle) electrolysis Ni-S films at –0.21 V vs. SHE.

in Figure 2-14c are the plots of Δj *vs.* scan rate. The calculated capacitance of the post-electrolysis Ni-S film is 455.7 µF, nearly 34 times that before electrolysis (13.5 µF), which indicates that the effective surface area of the post-electrolysis film is nearly 34 times that of the pre-electrolysis sample. This result is consistent with the rougher and more porous surface of the Ni-S film after electrolysis (Figure 2-2b) compared to a fresh Ni-S film (Figure 2-2a). A larger surface area is able to provide more active sites for the hydrogen evolution reaction, leading to increased catalytic current density. Therefore, the observed activation process is probably due to the enhanced specific surface area resulting from surface reorganization under electrochemical conditions.

1-5. Composition of the Ni-S film

To further probe the surface composition of the Ni-S film, X-ray photoelectron spectroscopy (XPS) was conducted (Figure 2-15). Figure 2-15a includes the XPS survey spectra of the Ni-S films before and after the same 1 h electrolysis. Before electrolysis, all the observed peaks can be assigned to anticipated elements, including Ni and S, in Ni-S/FTO. The Sn 3d and 3p peaks are attributed to the FTO substrate. It is worth noting that no Pt and/or Ag peaks were detected, indicating that Ni-S/FTO is free of noble metal impurities. The high-resolution region of Ni 2p spectra (Figure 2-15b) shows peaks at 853.1 and 870.3 eV, corresponding to Ni $2p_{3/2}$ and $2p_{1/2}$, respectively.[13] The shoulder around 855-860 eV implies the presence of $Ni(OH)_2$ and $NiSO_4$.[13] XPS fitting of the Ni $2p_{3/2}$ peak of the pre- and post-electrolysis samples resulted in similar binding energies (Figure 2-16). For instance, the fitted peak at 853.04 eV of the post-electrolysis sample is similar to those reported for Ni_3S_2,[14] NiS,[15] and NiS_2.[16] The similarity in the binding energy of the Ni $2p_{3/2}$ peak of different nickel sulfides is known.[13] The process giving rise to the Ni $2p_{3/2}$ peak is mainly of metal (Ni) character, with little contribution from the surrounding ligands. This also explains why it is close to that of Ni metal (852.5 ± 0.2 eV).[13] Therefore, we cannot solely rely on the binding energy of the Ni $2p_{3/2}$ peak to determine the identity of nickel sulfide in the Ni-S film. Whereas, the simulated peaks at 854.73 and 857.00 eV can be assigned to $Ni(OH)_2$ and $NiSO_4$, respectively.[13] Spectral fitting of the high resolution region of the S 2p signal (Figure 2-17) resulted in a doublet of 162.31 and 163.51 eV (161.82 and 163.00 eV for the pre-electrolysis sample), corresponding to S $2p_{1/2}$ and $2p_{3/2}$, respectively.

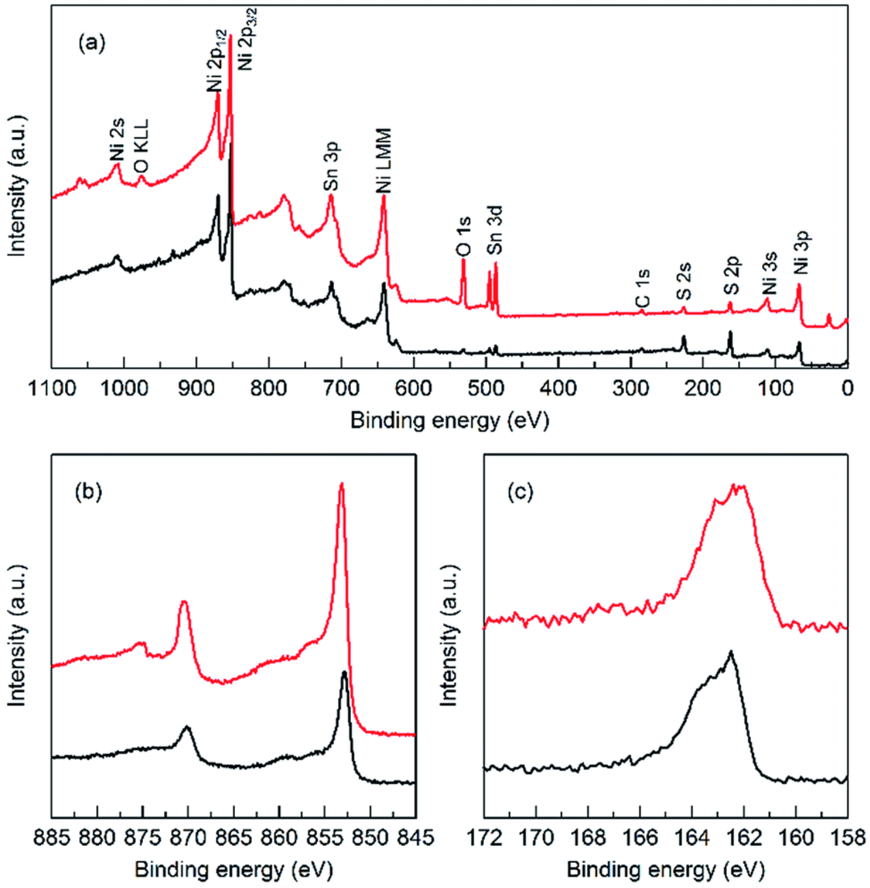

Figure 2-15. XPS spectra of the Ni-S films before (black) and after (red) a 1 h electrolysis at −0.689 V *vs.* SHE in pH 7 phosphate buffer: (a) survey, (b) Ni 2p region, and (c) S 2p region.

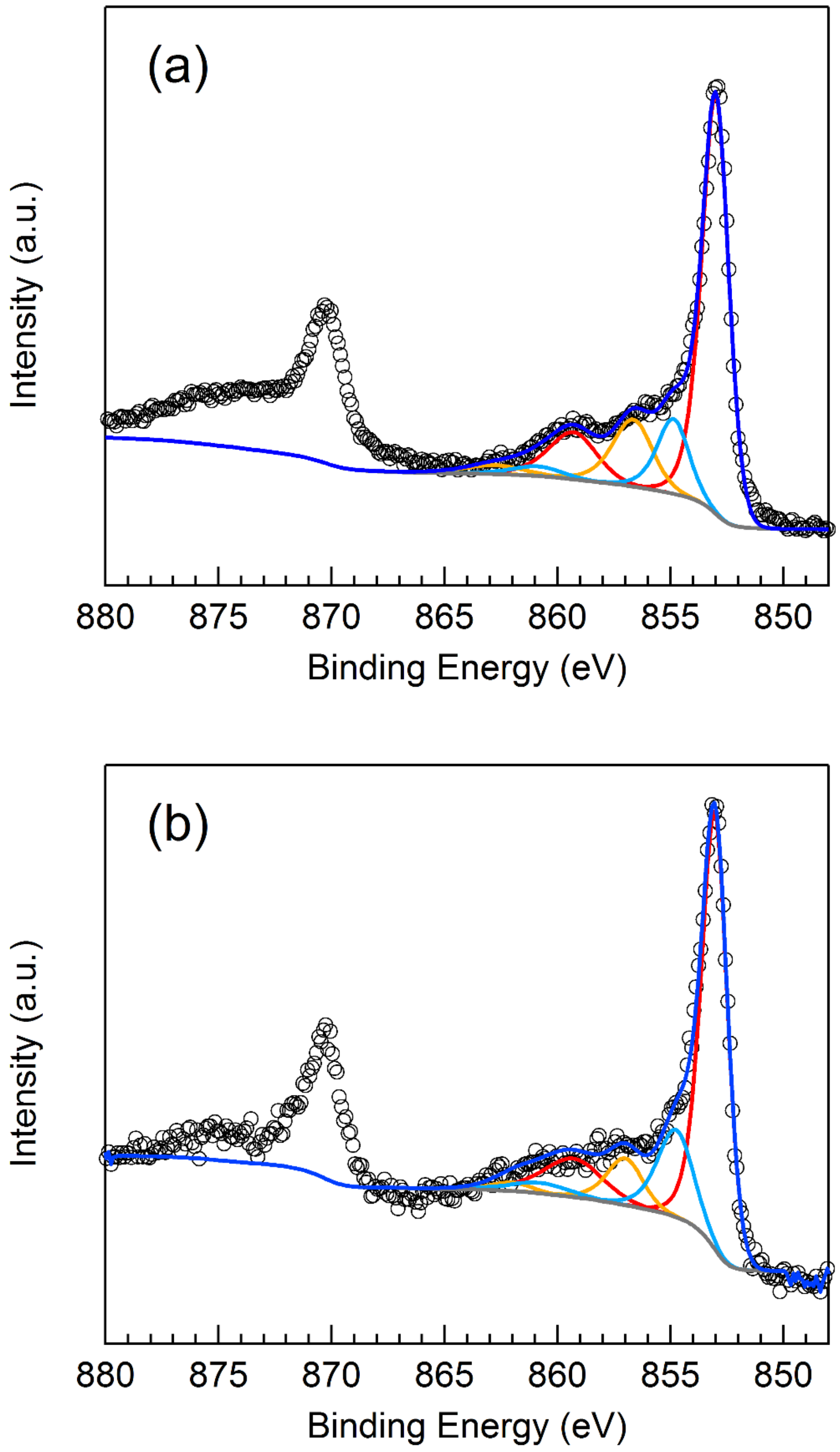

Figure 2-16. XPS spectra and fittings of Ni 2p of Ni-S/FTO before (a) and after (b) the 1 h electrolysis.

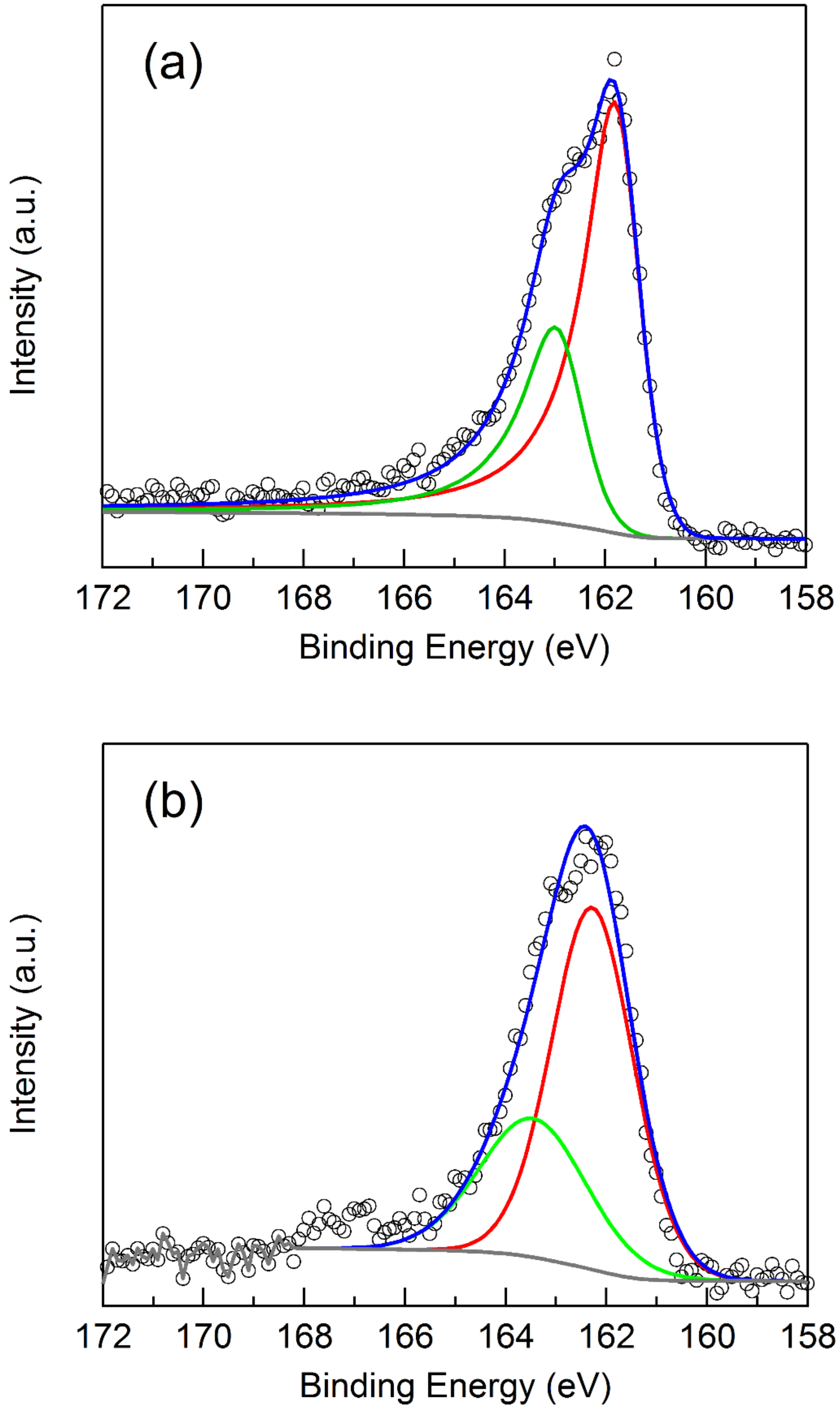

Figure 2-17. XPS spectra and fittings of S 2p of Ni-S/FTO before (a) and after (b) the 1 h electrolysis.

In order to gain more insights into the atomic structure of the bulk Ni-S film, X-ray absorption spectroscopy (XAS) was carried out. The Ni K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of a Ni-S film before and after the 1 h electrolysis are shown in Figure 2-18a and c, respectively. The XANES spectrum of the post-electrolysis sample is almost identical to that of the pre-electrolysis counterpart. The Ni K-edge XANES spectrum of $Ni(OH)_2$ is also included in Figure 2-18a (blue trace) as a comparison. The drastic difference in the

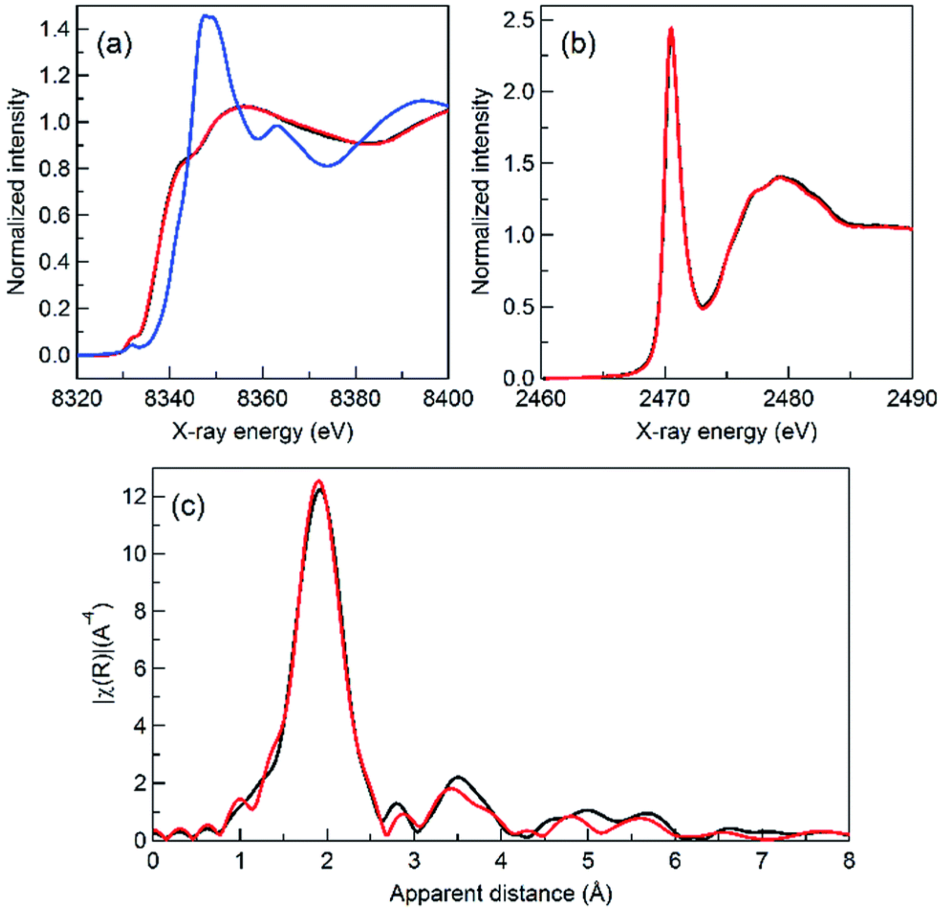

Figure 2-18. Ni K-edge (a) and S K-edge (b) XANES spectra and Ni EXAFS spectra (c) of the Ni-S films before (black) and after (red) a 1 h electrolysis at –0.689 V *vs.* SHE in pH 7 phosphate buffer. The blue curve in (a) is the Ni K-edge XANES spectrum of $Ni(OH)_2$ as a comparison.

spectral shape and energy of the Ni-S film and $Ni(OH)_2$ unambiguously rules out the latter as a major component of the film. In addition, compared with the reported XANES spectra of Ni,[17] NiO,[17] NiS,[18] and NiS_2,[19] the appreciable involvement of these species in the Ni-S film can also be excluded. In fact, the Ni K-edge XANES spectrum of the Ni-S film resembles that of Ni_3S_2 very well, which is further supported by the Ni EXAFS spectra (Figure 2-18c).[17],[19] Ni_3S_2 (heazlewoodite) is one of the stable forms of nickel sulphides.[20] Each nickel atom in crystalline Ni_3S_2 occupies a pseudotetrahedral site in an approximately body-centered cubic sulfur lattice.[21] The N_3S_2 units are interconnected through short Ni-S and Ni-Ni distances, 2.2914(5) and 2.5319(9) Å, respectively, within the Ni_3S_2 unit. However, the Ni-S and Ni-Ni distances are even shorter between Ni_3S_2 units, being 2.2534(5) and 2.4966(4) Å, respectively. Figure 2-19 displays the crystal structure of Ni_3S_2 and highlights its trigonal bipyramidal core. Ni EXAFS linear combination fitting of the post-electrolysis Ni-S film (Table 2-2) suggests that its major component is Ni_3S_2 with a small contribution of $Ni(OH)_2$ (8%). The bond distances of Ni-S (2.27(0.04) Å) and Ni-Ni (2.51(0.04) Å) resulting from the EXAFS fitting well match those in the crystal structure of Ni_3S_2. The short Ni-Ni distances in Ni_3S_2 have been proposed to be indicative of metal-metal bonding.[20] Indeed, the fitted Ni-Ni distance in the Ni-S film (2.51 Å) is very close to that in metallic nickel (2.49 Å). This result is also consistent with the close binding energy of the Ni $2p_{3/2}$ peak of the Ni-S film (Figure 2-18b) and Ni metal.[13] Overall, the combination of the XPS and XAS results, together with the ICP-OES data, unambiguously demonstrates that Ni_3S_2 is the major composition of the Ni-S film.

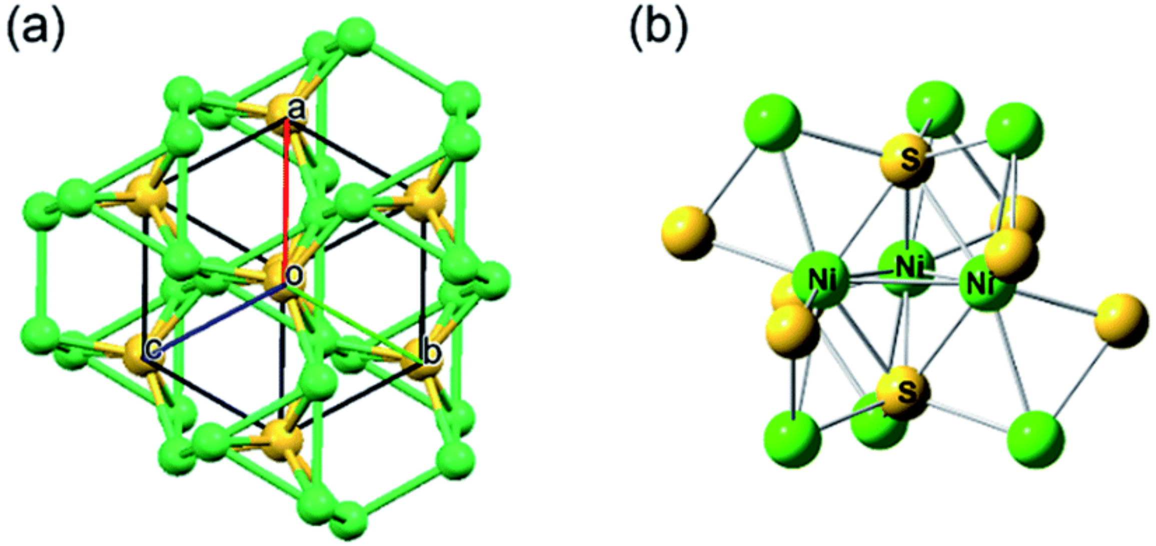

Figure 2-19. (a) Crystal structure of Ni_3S_2 viewed through the body diagonal direction; (b) selected region of the Ni_3S_2 structure highlighting its trigonal bipyramidal core (green: nickel; yellow: sulfur).

Table 2-2. Ni EXAFS curve fitting parameters of the post-electrolysis film (S_0 was fixed to 0.83. N is the coordination number and σ^2 is the Debye-Waller factor. ΔE is the EXAFS threshold energy. R factor (%) indicates the goodness of the fit. Bold letters are the fixed parameters. Values in parentheses indicate uncertainties.).

Fit	**NiO_x:NiS_x**		**Path**	**R (Å)**	**N**	**σ^2 (Å^2)**	**R (%)**
1	$Ni(OH)_2$	0.08 (0.10)	NiO	2.03 (0.03)	**6**	0.015 (0.005)	7.5 ΔE = –4.1
			NiNi	3.08 (0.05)	**6**	0.003 (0.005)	
	Ni_3S_2	0.92 (0.10)	NiS	2.27 (0.04)	**4**	0.007 (0.002)	
			NiNi	2.51 (0.04)	**4**	0.009 (0.002)	
			NiNi	3.76 (0.11)	**8**	0.023 (0.018)	
			NiNi	4.04 (0.06)	**6**	0.011 (0.004)	
2	Ni_3S_2	1	NiS	2.24 (0.04)	**4**	0.009 (0.002)	8.7 ΔE = –9.9
			NiNi	2.48 (0.03)	**4**	0.008 (0.001)	
			NiNi	3.78 (0.12)	**8**	0.025 (0.016)	
			NiNi	4.00 (0.05)	**6**	0.011 (0.003)	
3	$Ni(OH)_2$	0.11 (0.12)	NiO	2.03 (0.02)	**6**	0.002 (0.001)	13.4 ΔE = 5.0
			NiNi	3.14 (0.04)	**6**	0.003 (0.005)	
	NiS_2	0.89 (0.12)	NiS	2.32 (0.01)	**6**	0.006 (0.001)	
			NiS	3.53 (0.08)	**6**	0.014 (0.012)	
			NiNi	4.12 (0.05)	**12**	0.017 (0.006)	
4	NiS_2	1	NiS	2.32 (0.01)	**6**	0.007 (0.001)	12.7 ΔE = 5.0
			NiS	3.37 (0.31)	**6**	0.039 (0.058)	
			NiNi	4.13 (0.04)	**12**	0.018 (0.006)	

1-6. Conclusion

In summary, we have demonstrated that amorphous Ni-S films prepared by facile potentiodynamic deposition were efficient, robust, and inexpensive HER catalysts in a variety of aqueous media, ranging from strong acidic, neutral, strong basic, to natural water. The catalyst possesses a Tafel slope of 77 mV/dec, a Faradaic efficiency of 100%, and superior stability for at least 100 h at pH 7. An initial activation process was observed, which was likely due to the increased surface area of the Ni-S film resulting from surface reorganization under electrocatalytic conditions. Finally, surface and structural characterizations via SEM, EDS, ICP-OES, XRD, XPS, and XAS concluded the amorphous nature of the Ni-S film with a major composition of Ni_3S_2, which was preserved during the electrochemical experiments.

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CHAPTER III

COBALT PHOSPHIDES AS COMPETENT ELECTROCATALYSTS FOR OVERALL WATER SPLITTING[c]

1-1. Introduction

Electrocatalytic water splitting, which consists of H_2 and O_2 evolution reactions (HER and OER), has attracted increasing interest in the last few years because of its critical importance in the context of renewable energy research.[1] Most efforts in this field are devoted to developing HER catalysts under strongly acidic conditions for proton-exchange membrane electrolyzers whereas OER catalysts under strongly basic conditions for alkaline electrolyzers.

Besides aforementioned transition-metal sulfides, transition-metal phosphides, have shown catalytic performance for HER in strongly acidic electrolytes. In 2013, Schaak *et al.* reported the exciting HER activity of Ni_2P nanoparticles under acidic conditions.[2] When loaded on titanium foil, these Ni_2P nanoparticles showed excellent HER performance in 0.5 M H_2SO_4 with an overpotential of only –130 mV to reach a catalytic current density of 20 mA/cm^2 plus robust stability. It has been revealed that the Volmer step was the rate-determining step based on X-ray absorption fine structure spectroscopy (XAFS) and density functional theory (DFT) calculations for hydrogen adsorption over the (001) and (002) facets of Ni_2P nanoparticles.[3] A similar thermolysis method was also applied to prepare hollow CoP nanoparticles.[4] The resulting CoP

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nanoparticles exhibited even better performance than that of Ni_2P, only requiring an overpotential of −85 mV to afford a current density of 20 mA/cm^2. Taking advantage of the high conductivity and large surface area of carbon cloth, CoP nanowires anchored on carbon cloth (CoP/CC) have been investigated for HER electrocatalysis.[5] Such a hybrid CoP/CC cathode displayed a small onset overpotential of −38 mV and a decent Tafel slope of 51 mV/dec. Similar synergistic HER activity of CoP nanoparticles decorated on carbon nanotubes was reported by the same group.[6] Recently, iron and copper phosphides, such as FeP, Fe_2P, and Cu_3P, have also been explored for HER due to their more abundance and hence lower cost.[7]

On the other hand, many innovative noble-metal-free OER catalysts based on the oxides/hydroxides of cobalt,[8] nickel,[9] manganese,[10] iron,[11] and copper[12] have been reported with mediocre to excellent OER catalytic activities under basic conditions. Despite these advances, challenges for large-scale water splitting catalysis still exist. For instance, to accomplish overall water splitting, it is necessary to integrate both HER and OER catalysts in the same electrolyte. Unfortunately, the current prevailing approaches often lead to inferior overall performance because of the incompatibility of the two types of catalysts functioning under the same condition. Therefore, it is highly desirable to develop bifunctional and low-cost electrocatalysts that are simultaneously active for both HER and OER in the same electrolyte. As ionic conductivity is usually higher at extreme pH values than under neutral conditions and the overpotential loss of OER is much larger than that of HER, plus most earth-abundant OER catalysts are vulnerable in strongly acidic media, we are particularly interested in developing competent bifunctional water splitting catalysts under strongly alkaline conditions.

To increase the portfolio of bifunctional electrocatalysts for overall water splitting, both transition metal chalcogenides and phosphides have been reported with bifunctionality for overall water splitting very recently.[13] For example, Hu's group demonstrated that Ni_2P, an excellent HER catalyst aforementioned, was also highly active for OER.[13a] The Ni_2P nanoparticles can serve as both cathode and anode catalysts to generate 10 mA/cm^2 at 1.63 V for an alkaline water electrolyzer. The high activity is attributed to the core-shell (Ni_2P/NiO_x) structure of the transformed catalyst under anodic conditions. Recently, Shalom *et al.* synthesized Ni_5P_4 film by direct phosphidation of a commercial Ni foam and demonstrated its outstanding HER and OER activity under basic conditions.[14] For overall water splitting, the cell voltage to afford 10 mA/cm^2 was 1.70 V for Ni_5P_4 films. Sun *et al.* employed a similar method to obtain NiSe nanowire film on a Ni foam (NiSe/NF) by a hydrothermal treatment of Ni foam with NaHSe as the Se source.[13b] Herein, we describe an electrodeposited cobalt-phosphorous (Co-P) film which could be directly utilized as electrocatalysts for both HER and OER under strongly alkaline conditions (1.0 M KOH).

1-2. Preparation of the Co-P film

Prior to electrodeposition, copper foils were rinsed with water and ethanol thoroughly to remove residual organic species. For linear sweep voltammetry experiments, a circular copper foil with a 3 mm diameter was prepared and pasted on the rotating disk glassy carbon electrode, then the assembled electrode was exposed to the deposition solution (50 mM $CoSO_4$, 0.5 M NaH_2PO_2, and 0.1 M NaOAc in water). A platinum wire was used as the counter electrode and a Ag/AgCl (sat.) electrode as the reference electrode. Nitrogen was bubbled through the electrolyte solution for at least 20 min prior to deposition and maintained during the entire deposition process. The potential of consecutive linear scans was cycled 15 times between −0.3 and −1.0 V *vs.* Ag/AgCl at a scan rate of 5 mV/s under stirring and a rotation rate of 500 rpm. After deposition, the assembled electrode was removed from the deposition bath and rinsed with copious water gently. The prepared Co-P film can be directly used to collect its polarization curves or stored under vacuum at room temperature for future use. For samples prepared for controlled potential electrolysis, a copper foil was directly used as the working electrode with a geometric area of 0.3 cm^2 exposed to the electrolyte. The deposition potential window and cycle number are the same as aforementioned. A typical potentiodynamic deposition of Co-P films is shown in Figure 3-1.

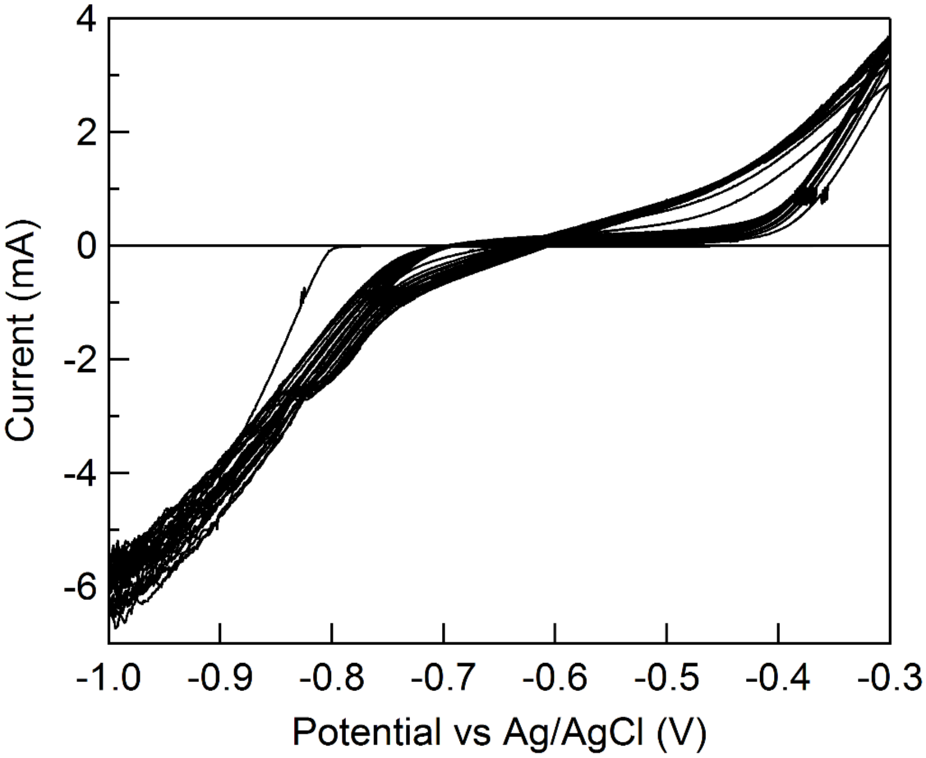

Figure 3-1. A typical potentiodynamic deposition for the preparation of Co-P films on copper foil (scan rate: 5 mV/s).

1-3. Characterization of the Co-P film

The SEM images of the as-prepared Co-P film showed nearly complete coverage of the rough film on copper foil (Figure 3-2a). No crystalline particles or aggregates were observed. The cross section SEM image revealed the thickness of the film in 1-3 μm (Figure 3-2a inset). The Co 2p XPS spectrum (Figure 3-2b) displays two peaks at 778.3 and 793.4 eV, corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$ binding energies, respectively.[15] These values are extremely close to those of metallic cobalt.[15] The P 2p XPS spectrum (Figure 3-2c) exhibits a dominant peak at 129.5 eV, which can be attributed to the phosphide signal.[15] A broad feature at approximately 133.6 eV is assigned to phosphate.[15] The XPS survey of the as-prepared film (Figure 3-3) showed all the anticipated elements. In addition, elemental analysis of the as-prepared Co-P film gave the amount of Co and P as 2.52 and 0.19 mg/cm^2, respectively, with a molar ratio of 6.98 (Table 3-1).

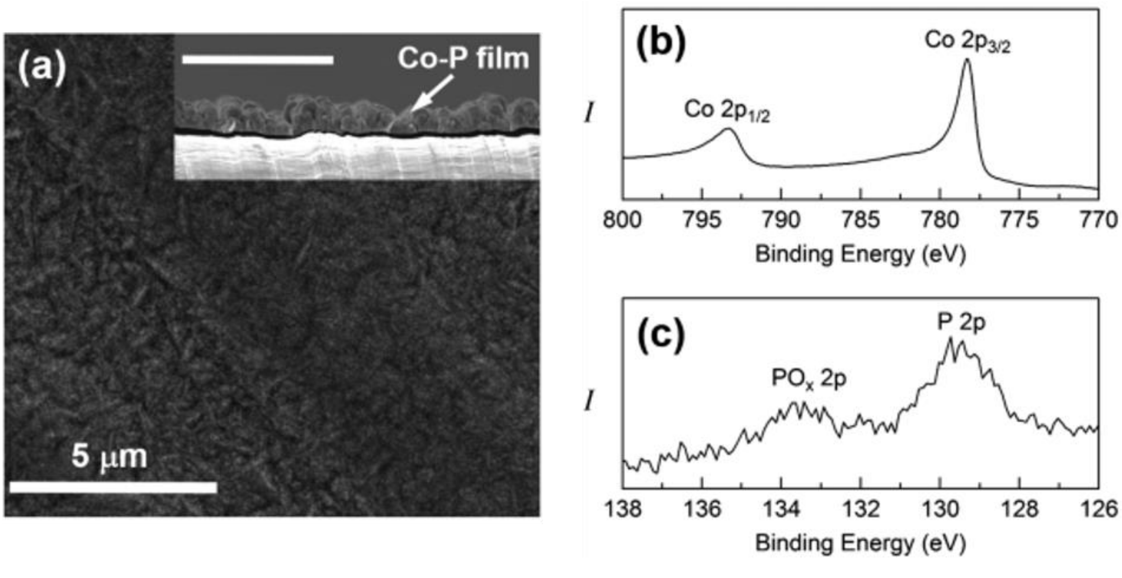

Figure 3-2. (a) SEM image of an as-prepared Co-P film. Inset: the cross section of the Co-P film. Scale bars are both 5 μm. (b and c) XPS spectra of an as-prepared Co-P film: (b) Co 2p region and (c) P 2p region.

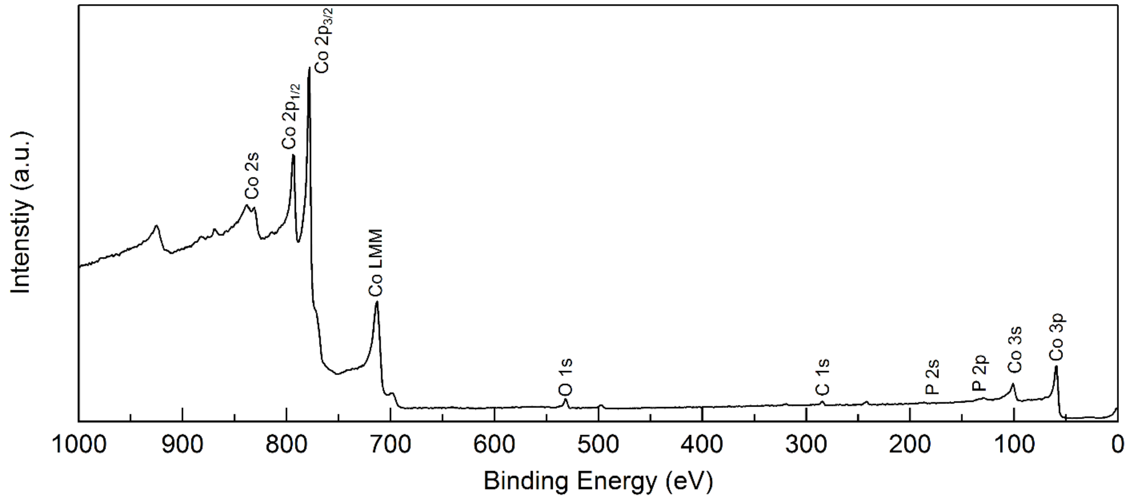

Figure 3-3. XPS survey of the as-prepared Co-P film.

Table 3-1. ICP-OES data of the as-prepared, after 2 h HER electrolysis, and after 2 h OER electrolysis Co-P/Cu films.

Sample	**Area (cm^2)**	**[Co] (mg/cm^2)**	**[P] (mg/cm^2)**	**Co/P mole ratio**
Fresh prepared	0.3	2.52	0.19	6.89
After 2 h HER	0.3	2.48	0.12	10.5
After 2 h OER	0.3	2.47	0.12	9.74

1-4. Catalytic activity of the Co-P film

We first evaluated the HER activity of the Co-P film in strong alkaline solution (Figure 3-4). It is evident that the blank copper foil did not show any HER catalytic activity before –0.3V *vs.* RHE. In contrast, a rapid cathodic current rise was observed for Co-P beyond –50 mV *vs.* RHE (Figure 3-4a inset). Further scanning towards negative potential produced a dramatic increase in current density along with vigorous evolution of H_2 bubbles from the electrode surface. The Co-P film required an overpotential of only –94 mV to reach a current density of 10 mA/cm^2. Such a low overpotential requirement compares favorably to other reported HER catalysts at pH 14 (Table 3-2). Remarkably,

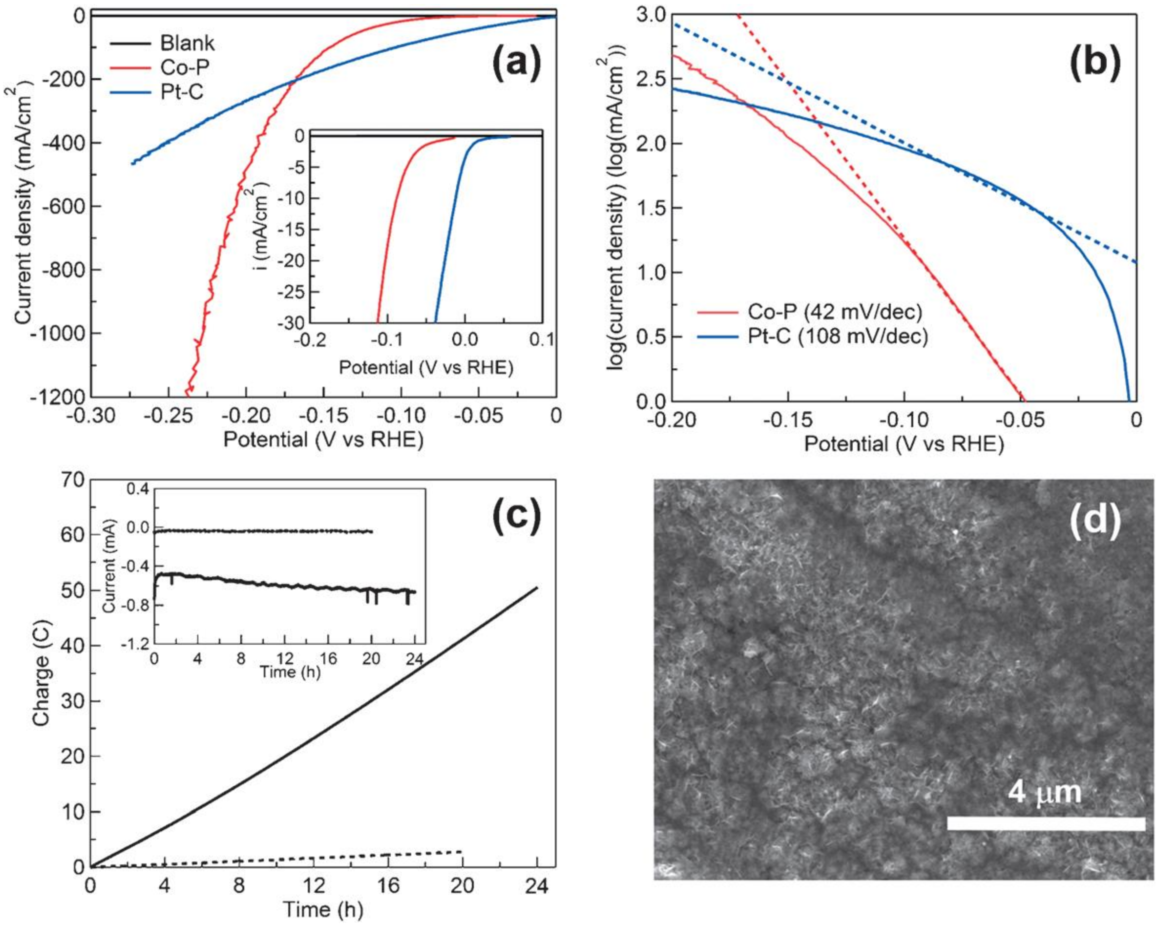

Figure 3-4. (a) Polarization curves of Co-P (red), Pt/C (blue), and blank Cu foil (black) in 1 M KOH at a scan rate of 2 mV/s and a rotating rate of 2000 rpm (Inset: expanded region around the onsets of the polarization curves); (b) corresponding Tafel plots of Co-P film (red) and Pt/C (blue) with their associated linear fittings (dotted lines); (c) long-term controlled potential electrolysis of Co-P (solid) and blank Cu foil (dotted) in 1 M KOH at an overpotential of –107 mV (Inset: the corresponding current change over time of Co-P (bottom trace) and blank Cu foil (top trace) during the electrolysis); (d) SEM image of Co-P after 2 h H_2 evolution electrolysis at $\eta = -107$ mV.

the Co-P film was able to produce a catalytic current density of 1000 mA/cm^2 within an overpotential of –227 mV. The linear fitting of its Tafel plot (Figure 3-4b) gave a Tafel slope of 42 mV/dec, which is among the smallest Tafel slopes of reported HER catalysts in alkaline media (Table 3-2). Although Pt-C (loading amount: 1 mg/cm^2) exhibited a very small catalytic onset potential, its Tafel slope (108 mV/dec) was significantly larger

Table 3-2. Comparison of selected non-precious HER electrocatalysts in alkaline media.

Catalysts	**Electrolyte**	**j (mA/cm^2)**	**η (mV)**	**Tafel slop (mV/dec)**	**Reference**
Co-P film	**1 M KOH**	**10** **20** **100**	**94** **115** **158**	**42**	**This work**
CoP/CC	1 M KOH	10 100	209 >500	129	*J. Am. Chem. Soc.* **2014**, *136*, 7587.
Co-S/FTO	1 M KOH	1	480	N/A	*J. Am. Chem. Soc.* **2013**, *135*, 17699.
Co-NRCNTs	1 M KOH	10 20	370 >450	N/A	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372.
Ni_2P	1 M KOH	20	205	N/A	*J. Am. Chem. Soc.* **2013**, *135*, 9267.
$Ni/Ni(OH)_2$	0.1 M KOH	10	>300	128	*Angew. Chem. Int. Ed.* **2012**, *51*, 12495.
MoB	0.1 M KOH	10	225	59	*Angew. Chem. Int. Ed.* **2012**, *51*, 12703.
MoS_{2+x}/FTO	1 M KOH	10	310	N/A	*Angew. Chem. Int. Ed.* **2015**, *54*, 667.
Amorphous MoS_x	0.1 M KOH	10	540	N/A	*Chem. Sci.* **2011**, *2*, 1262.
FeP NAs/CC	1 M KOH	10	218	146	*ACS Catal.* **2014**, *4*, 4065.

than that of the Co-P film. Therefore, beyond –167 mV *vs.* RHE, the catalytic current density of Co-P surpassed that of Pt-C. Additionally, the Co-P film also exhibited superior long-term stability. A 24 h controlled potential electrolysis at $\eta = -107$ mV showed a nearly linear charge accumulation and steady current over the entire course of electrolysis (Figure 3-4c). The blank copper foil generated negligible charge build-up under the same conditions.

To probe the morphology and composition of the Co-P film after HER electrocatalysis, the SEM and XPS results of a post-HER Co-P film were collected. As shown in Figure 3-4d, the film still maintained a uniform coverage on the copper foil and no apparent clusters or aggregates were observed. Its Co 2p XPS spectrum showed two peaks at 793.2 and 778.2 eV (Figure 3-5a), corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$ states, respectively. The similarity of the Co 2p peaks of the post-HER Co-P film compared to those of the as-prepared one (Figure 3-2b) implied the major composition of the film preserved as metallic cobalt during HER. Furthermore, a peak at 129.3 eV was observed from the P 2p XPS spectrum of the post-HER sample (Figure 3-5b); while the phosphate peak at 133.6 eV originally observed for the as-prepared Co-P film (Figure 3-2c) was absent. Its absence is likely due to the dissolution of cobalt phosphate under cathodic condition. As shown in Figure 3-6, the XPS survey of as-prepared (Figure 3-3) and post-HER Co-P films exhibited similar, implying their similar composition. Elemental analysis of the post-HER film gave Co and P amounts of 2.48 and 0.12 mg/cm^2 with a Co/P ratio of 10.5 (Table 3-1).

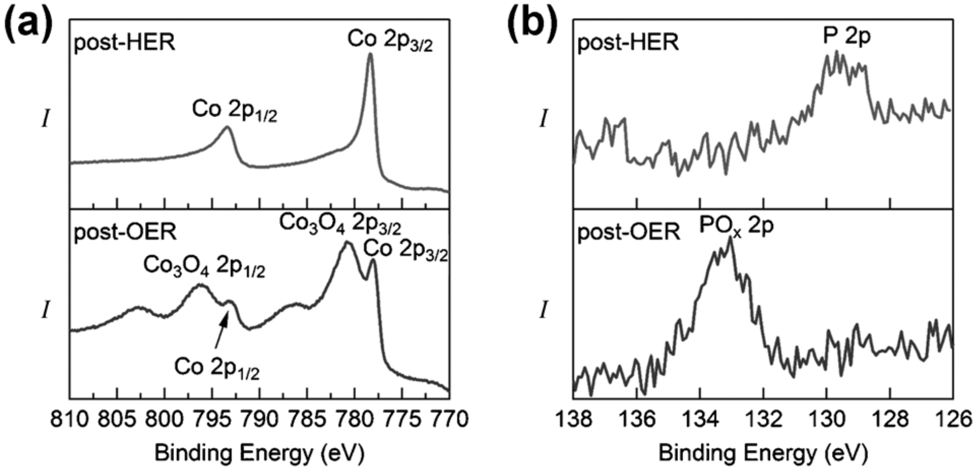

Figure 3-5. XPS spectra of (a) Co 2p and (b) P 2p regions of Co-P films after HER (top) or OER (bottom) electrolysis.

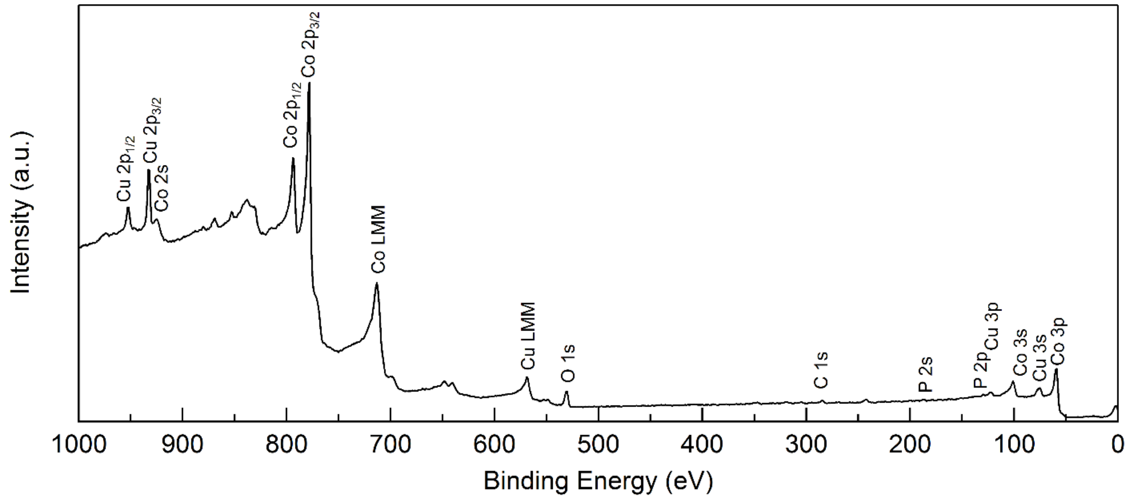

Figure 3-6. XPS survey of the post-HER Co-P film.

We next assessed the catalytic activity of the Co-P film for OER in the same electrolyte (Figure 3-7). As expected, a blank copper did not show appreciable anodic current before 1.7 V *vs.* RHE. The OER catalytic current density of the Co-P film increased dramatically beyond 1.53V *vs.* RHE (Figure 3-7a inset). It could reach current densities of 10, 100, and 500 mA/cm^2 at η = 345, 413, and 463 mV, respectively, lower than those of IrO_2 and many other reported OER catalysts (Table 3-3). Linear fitting of its Tafel plot resulted in a Tafel slope of 47 mV/dec (Figure 3-7b). As one of the state-of-the-art OER catalysts, IrO_2 (loading amount: 1 mg/cm^2) was able to catalyze OER at a lower onset of approximately 1.50 V *vs.* RHE, however its performance was quickly exceeded by that of the Co-P film beyond 1.58 V *vs.* RHE. In fact, the Tafel slope of Co-P (47 mV/dec) is even lower than that of IrO_2 (55 mV/dec), demonstrating more favorable OER kinetics of the Co-P. Besides high OER activity, the Co-P film also features excellent stability, as revealed by a 24 h controlled potential electrolysis at η = 343 mV (Figure 3-7c).

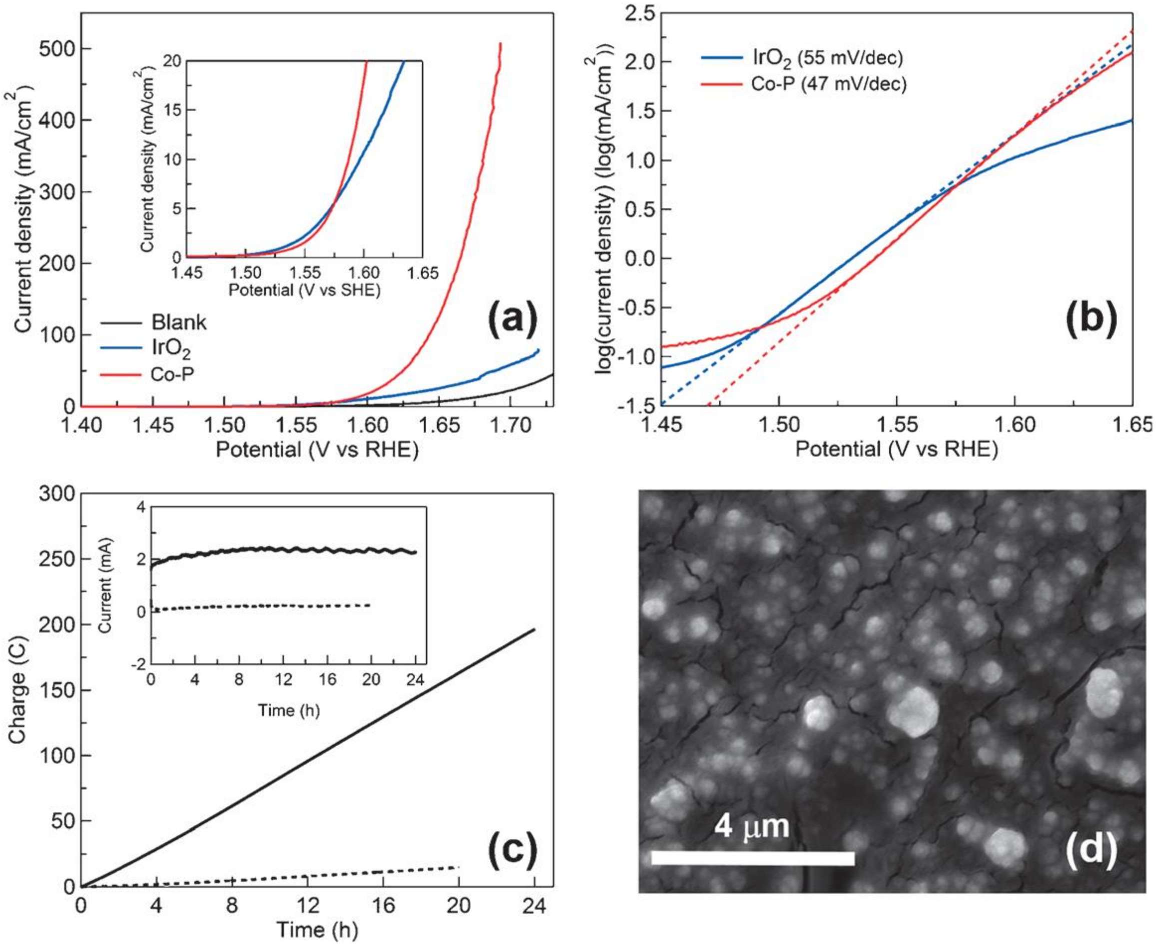

Figure 3-7. (a) Polarization curves of Co-P (red), IrO$_2$ (blue), and blank Cu foil (black) in 1 M KOH at a scan rate of 2 mV/s and a rotating rate of 2000 rpm (Inset: the expanded region around the onsets of the polarization curves of Co-P and IrO$_2$; (b) corresponding Tafel plots of Co-P (red) and IrO$_2$ (blue) with their associated linear fittings (dotted lines); (c) long-term controlled potential electrolysis of Co-P (solid) and blank Cu foil (dotted) in 1 M KOH at an overpotential of 343 mV (Inset: the corresponding current change over time of Co-P (solid) and blank Cu foil (dotted) during the electrolysis); (d) SEM image of Co-P after a 2 h OER electrolysis at η = 343 mV.

The SEM image (Figure 3-7d) of the post-OER Co-P film indicates it contains large nanoparticle aggregates, in sharp contrast to the rough and porous morphology of the as-prepared and post-HER samples (Figure 3-2a and Figure 3-4d). An intense O 1s peak was observed in the XPS survey spectrum of the post-OER film (Figure 3-8), which demonstrated a large concentration of O. The Co 2p spectrum displayed two peaks at

Table 3-3. Comparison of selected non-precious OER electrocatalysts in alkaline media.

Catalysts	**Electrolyte**	**η (mV) at 10 mA/cm^2**	**Tafel slop (mV/dec)**	**Reference**
Co-P film	**1.0 M KOH**	**345**	**47**	**This work**
NiCo LDH	1.0 M KOH	367	40	*Nano Lett*. **2015**, *15*, 1421.
Cu-N-C/graphene	0.1 M KOH	>770	N/A	*Nat*. *Commun*. **2014**, *5*, 5285.
CoCo LDH	1.0 M KOH	393	59	*Nat*. *Commun*. **2014**, *5*, 4477.
Co$_3$O$_4$/rm-GO	1.0 M KOH	310	67	*Nat*. *Mater*. **2011**, *10*, 780.
MnO$_x$/Au	0.1 M KOH	>480	N/A	*J. Am. Chem. Soc.* **2014**, *136*, 4920.
Ca$_2$Mn$_2$O$_5$/C	0.1 M KOH	>470	149	*J*. *Am*. *Chem*. *Soc*. **2014**, *136*, 14646.
Co$_x$O$_y$/NC	0.1 M KOH	430	N/A	*Angew. Chem. Int. Ed*. **2014**, *53*, 8508.
De-LiCoO$_2$	0.1 M KOH	>400	50	*Nat*. *Commun*. **2014**, *5*, 4345.
CoMn LDH	1.0 M KOH	324	43	*J*. *Am*. *Chem*. *Soc*. **2014**, *136*, 16481.
NiFeO$_x$ film	1.0 M NaOH	>350	N/A	*J*. *Am*. *Chem*. *Soc*. **2013**, *135*, 16977.
CoO/NG	1.0 M KOH	340	71	*Energy Environ. Sci*. **2014**, *7*, 609.
CoO$_x$ film	1.0 M KOH	403	42	*J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 17253.
α-MnO$_2$-SF	0.1 M KOH	490	77.5	*J*. *Am*. *Chem*. *Soc*. **2014**, *136*, 11452.
MnO$_x$ film	1.0 M KOH	563	49	*J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 17253.
NiFeO$_x$ film	1.0 M NaOH	>350	N/A	*J*. *Am*. *Chem*. *Soc*. **2013**, *135*, 16977.
Fe-Ni oxides	1.0 M KOH	>375	51	*ACS Catal*. **2012**, *2*, 1793.
Zn$_x$Co$_{3-x}$O$_4$	1.0 M KOH	330	51	*Chem*. *Mater*. **2014**, *26*, 1889.
Ni$_x$Co$_{3-x}$O$_4$	1.0 M KOH	~370	59-64	*Adv*. *Mater*. **2010**, *22*, 1926.

780.7 and 796.3 eV (Figure 3-5a), which can be assigned to oxidized cobalt, Co_3O_4, plus its satellite peaks at 786.3 and 802.7 eV.[16] However, the metallic cobalt 2p peaks at 778.0 and 793.0 eV could still be well resolved. The P 2p spectrum showed a phosphate peak at 133.2 eV (Figure 3-5b), whereas the original phosphide feature at 129.5 eV disappeared completely. Taken together, it indicated that the original cobalt in the Co-P film was partially oxidized to Co_3O_4 and cobalt phosphate during OER. An OER electrocatalyst with a metallic cobalt core and cobalt oxide/hydroxide shell was reported.[17] Elemental analysis of the post-OER film resulted in the remaining amount of Co and P as 2.47 and 0.13 mg/cm^2 with a Co/P ratio of 9.74 (Table 3-1), still similar to those of the post- HER film.

Based on the results aforementioned, we anticipated that the Co-P film could act as a bifunctional electrocatalyst for overall water splitting. Hence, a two-electrode configuration was employed (Figure 3-9a). When the as-prepared Co-P films were used as electrocatalysts for both anode and cathode (Co-P/Co-P couple), a catalytic current was observed when the applied potential was larger than 1.56 V with a Tafel

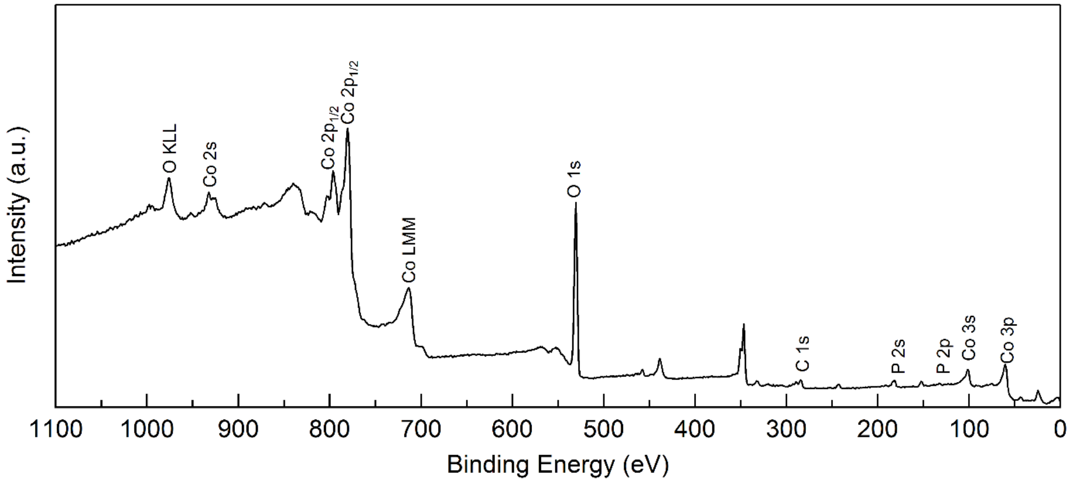

Figure 3-8. XPS survey of the post-OER Co-P film.

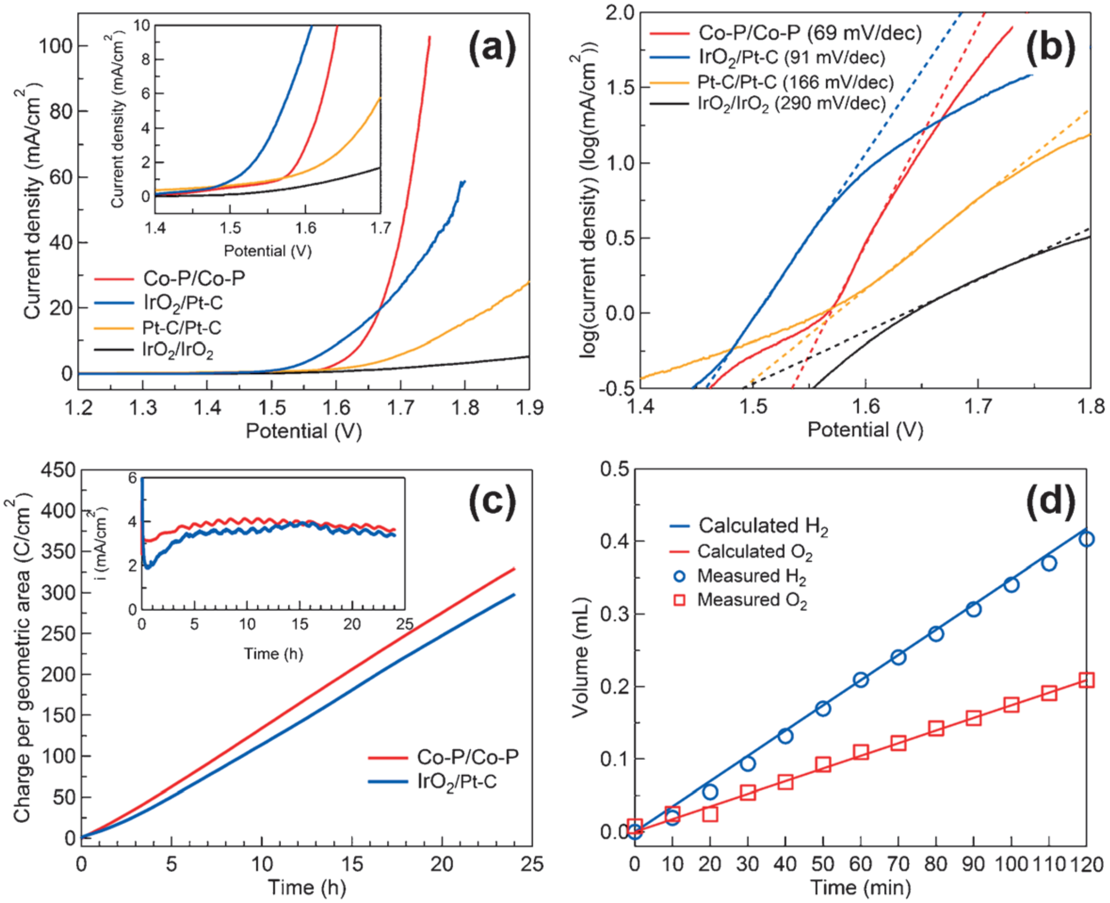

Figure 3-9. (a) Polarization curves of Co-P/Co-P (red), IrO$_2$/Pt-C (blue), Pt-C/Pt-C (yellow), and IrO$_2$/IrO$_2$ (black) for overall water splitting in 1 M KOH at a scan rate of 2 mV/s (Inset: the expanded region around the onsets of those polarization curves); (b) corresponding Tafel plots of Co-P/Co-P (red), IrO$_2$/Pt-C (blue), Pt-C/Pt-C (yellow), and IrO$_2$/IrO$_2$ (black) and their associated linear fittings (dotted lines); (c) long-term controlled potential electrolysis of Co-P/Co-P (red) and IrO$_2$/Pt-C (blue) in 1 M KOH at an overpotential of 400 mV (Inset: the corresponding current change over time of Co-P/Co-P (red) and IrO$_2$/Pt-C (blue)); (d) generated H$_2$ and O$_2$ volumes over time *vs.* theoretical quantities assuming a 100% Faradaic efficiency for the overall water splitting of Co-P/Co-P in 1 M KOH at η = 400 mV.

slope of 69 mV/dec. The rapid catalytic current density exceeded 100 mA/cm^2 at 1.744 V. When Pt-C or IrO$_2$ (loading amount: 1 mg/cm^2 for both Pt-C and IrO$_2$) was used for both electrodes (Pt-C/Pt-C or IrO$_2$/IrO$_2$ couple), much diminished catalytic current densities were obtained with large Tafel slopes of 166 and 290 mV/dec, respectively. Since Pt is well-established for HER and IrO$_2$ for OER, the integration of Pt-C on cathode and IrO_2 on anode was expected to produce the excellent catalytic system. Indeed, the IrO_2/Pt-C couple was able to catalyze water splitting with an onset around 1.47 V (Figure 3-9a inset). However, the Tafel slope of IrO_2/Pt-C is 91 mV/dec, larger than that of Co-P/Co-P (69 mV/dec). Therefore, when the applied potential was higher than 1.67 V, Co-P/Co-P was able to surpass IrO_2/Pt-C in catalyzing overall water splitting. In addition, the Co-P/Co-P couple maintained excellent stability as manifested by the steady current change and nearly linear charge accumulation for a 24 h electrolysis (Figure 3-9c). In fact, the integrated activity of IrO_2/Pt-C was slightly inferior to that of the Co-P/Co-P couple under the same conditions. Figure 3-9d indicates the produced H_2 and O_2 quantified by gas chromatography match the calculated amount based on passed charge well and the volume ratio of H_2 and O_2 is close to 2, leading to a Faradaic efficiency of 100%.

1-5. Conclusion

In conclusion, we have demonstrated that electrodeposited Co-P films could act as bifunctional electrocatalysts for overall water splitting. The catalytic activity of the Co-P films can rival the state-of-the-art catalysts, requiring $\eta = -94$ mV for HER and $\eta = 345$ mV for OER to reach 10 mA/cm^2 with Tafel slopes of 45 and 47 mV/dec, respectively. It could also be directly utilized as electrocatalysts for both anode and cathode with superior efficiency, strong robustness, and 100% Faradaic yield. The understanding of real-time composition and structural evolution of the films during electrolysis requires future *in situ* spectroscopic study.

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CHAPTER IV

CONCLUSION

1-1. Conclusion

This thesis starts with an introduction on the fundamental concepts and the current status of electrocatalysts for overall water splitting. Water splitting with renewable energy input to produce H_2 and O_2 has been widely considered as a promising approach to alleviate our reliance on fossil fuels, match growing energy demands, and simultaneously satisfy increasingly stringent environmental regulations because of the clean nature of H_2 as a fuel.[1] Recent years have witnessed the increasing popularity of transition metal-based catalysts as competent H_2 and O_2 evolution catalysts, whose activities rapidly approach those of platinum group benchmarks. Even within a relatively short period of time, tremendous progress has been made in this field.[2] Not only catalysts need to be composed of inexpensive elements, they are also desirable to be prepared at low energy cost. Besides the cost and activity of catalysts, the coupling of HER and OER catalysts in the same electrolyte is mandatory to accomplish overall water splitting. The current prevailing approaches often result in incompatible integration of the two catalysts and lead to inferior overall performance. It remains a grand challenge to develop bifunctional electrocatalysts active for both HER and OER.

In Chapter II, I summarized our work on Ni-S films which were prepared by facile potentiodynamic deposition. The Ni-S films could act as active HER catalysts in aqueous media. Notably, the Ni-S films showed catalytic activity in water with a wide range of pH values (0 to 14), as well as in natural water collected from the Great Salt Lake. In pH 7 phosphate buffer, a current density of 60 mA/cm^2 could be achieved with a

Tafel slope of 77 mV/dec and a Faradaic efficiency of 100%. A long-term bulk electrolysis of the Ni-S film exhibited steady current over 100 h with no deactivation, demonstrating its superior stability in neutral water. Moreover, an initial activation process was observed, which is likely due to the increase in the effective surface area of the Ni-S film under electrocatalytic conditions. A suite of characterization techniques, including X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS), were conducted to probe the composition and structure of the Ni-S film, revealing that its major component was Ni_3S_2 which was preserved under electrocatalytic conditions.[3]

To increase the portfolio of bifunctional electrocatalysts for overall water splitting, we developed electrodeposited Co-P films which could be directly utilized as electrocatalysts for both HER and OER under strongly alkaline conditions (1.0 M KOH). The Co-P film is unique because of the following reasons: (i) it is prepared by facile electrodeposition with low-cost regents under ambient conditions and it can be directly employed as an electrocatalyst for both HER and OER without any post treatment; (ii) the catalytic activity of the Co-P film can rival the state-of-the-art catalysts (Pt and IrO_2), requiring $\eta = -94$ mV for HER and $\eta = 345$ mV for OER to reach 10 mA/cm^2 with Tafel slopes of 45 and 47 mV/dec, respectively; (iii) it can be utilized as a catalyst for both the anode and cathode of overall water splitting catalysis under strongly alkaline conditions with superior efficiency and strong robustness. Various characterization and analytical techniques were applied to study the morphology and composition of the Co-P film prior to and post electrocatalysis. It was concluded that the major components of the Co-P film are metallic cobalt and cobalt phosphide for the as-prepared and post-HER samples, whereas it was partially oxidized to cobalt oxides/hydroxides/phosphates on the surface during OER. Different from many reported hybrid systems, no conductive supports of high surface area, such as graphenes, carbon nanotubes, and nickel foams, were involved in the current system.[4]

Along these encouraging developments, there still exist many challenges and opportunities in this exciting field. Since most inexpensive HER electrocatalysts only function well under strongly acidic electrolytes where most OER catalysts are not stable, this incompatibility of HER and OER catalysts functioning in the same electrolyte poses a sever hindrance in developing practical devices for overall water splitting. Therefore, more efforts should shift toward exploring and developing competent HER electrocatalysts under alkaline (or neutral) conditions, which can be seamlessly integrated with most OER electrocatalysts. Our progress in the development of bifunctional electrocatalysts for overall water splitting in strongly basic electrolytes represent a promising direction. Secondly, the HER catalytic activities of those non-precious electrocatalysts in terms of mass activity, overpotential, and stability need to be further improved for practical applications. Currently, high catalytic current always accompanies large catalyst loading, which would complicate device fabrication and increase entire cost. Structure engineering and hybrid composition can be powerful tools in improving the specific activity and long-term stability.[5] In addition, it is of paramount importance to introduce greener methods for catalyst synthesis, such as electrodeposition. The involvement of expensive precursors, toxic or corrosive reagents, hazardous byproducts, and high temperature/pressure/vacuum conditions should be minimized.

As a heterogeneous reaction, electrocatalytic water splitting deals with interfaces between liquid, solid, and gas phases under electric potentials. It is well known that many electrocatalysts will transform from resting states to catalytic active states under operating conditions. Therefore, electrocatalytic *in situ* spectroscopic studies should be systematically carried out to elucidate the detailed mechanistic steps and provide insights in the composition-activity relationship of different HER catalysts. Theoretical computation, particularly DFT calculation, should contribute significantly to these studies.[6] Despite the success of DFT calculation in rationalizing the observed trend of many metals as electrocatalysts, it often over simplify the real electrocatalytic conditions. The influence of electric field, double layer formation, catalyst defects, solvation, substrate transportation, and concentration gradient, should all be well considered in describing the actual electrocatalytic condition, which warrants further studies of many years ahead.

Considering the cost and working environment for practical applications, the development of first-row transition metal chalcogenides and phosphides as electrocatalysts via facile electrodeposition method is highly desirable. We have reported Ni-S film as an active HER electrocatalyst and Co-P film as a bifunctional electrocatalyst for overall water splitting, respectively. Our work about developing first-row transition metal sulfides and phosphides as competent electrocatalytsts for water splitting is beneficial for design other promising catalysts in the future.

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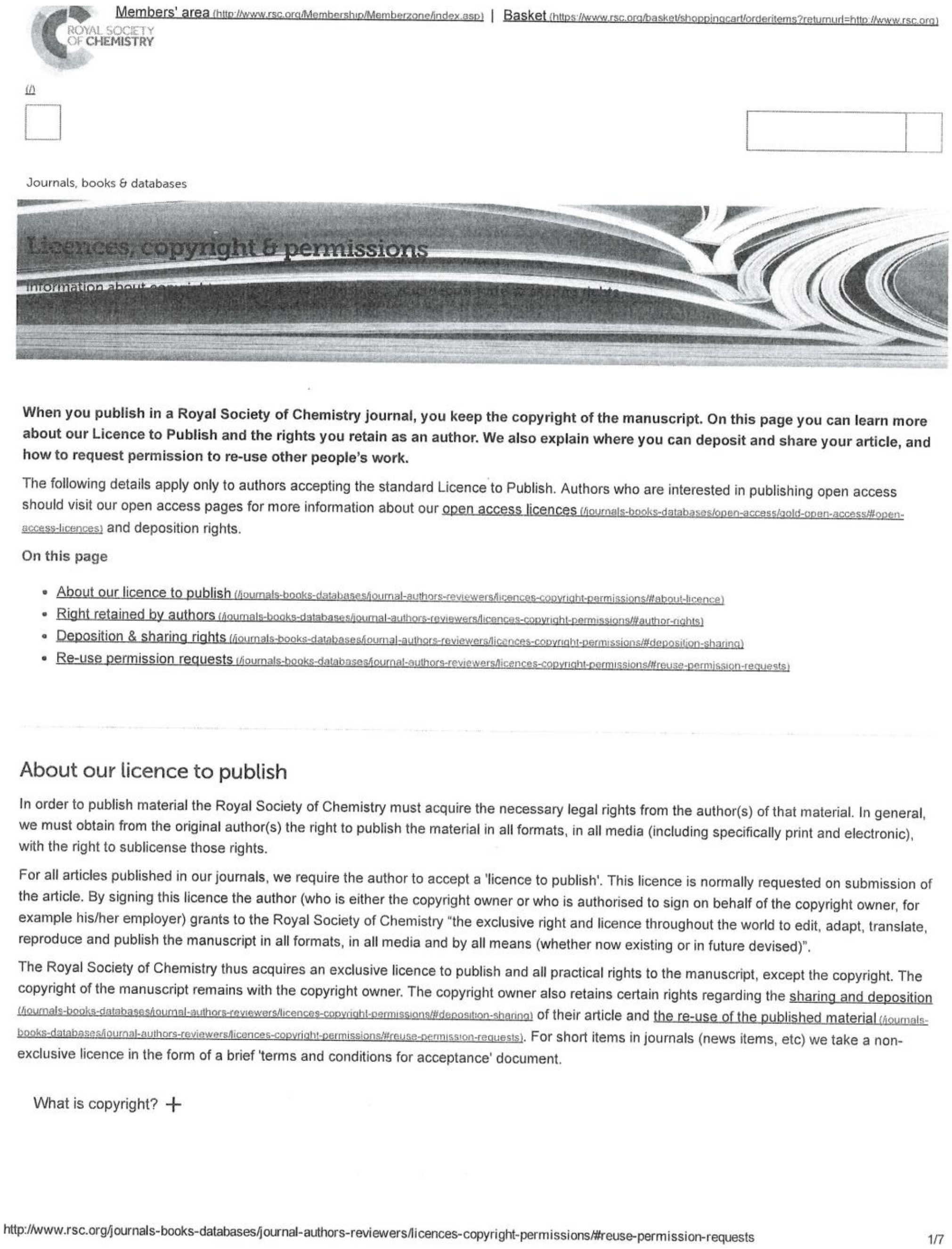

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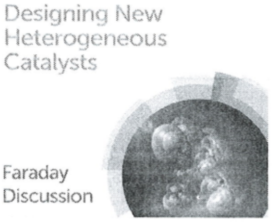

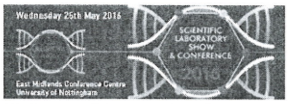

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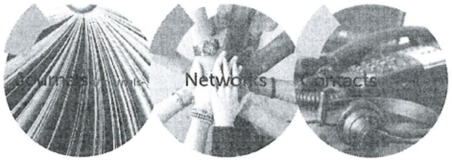

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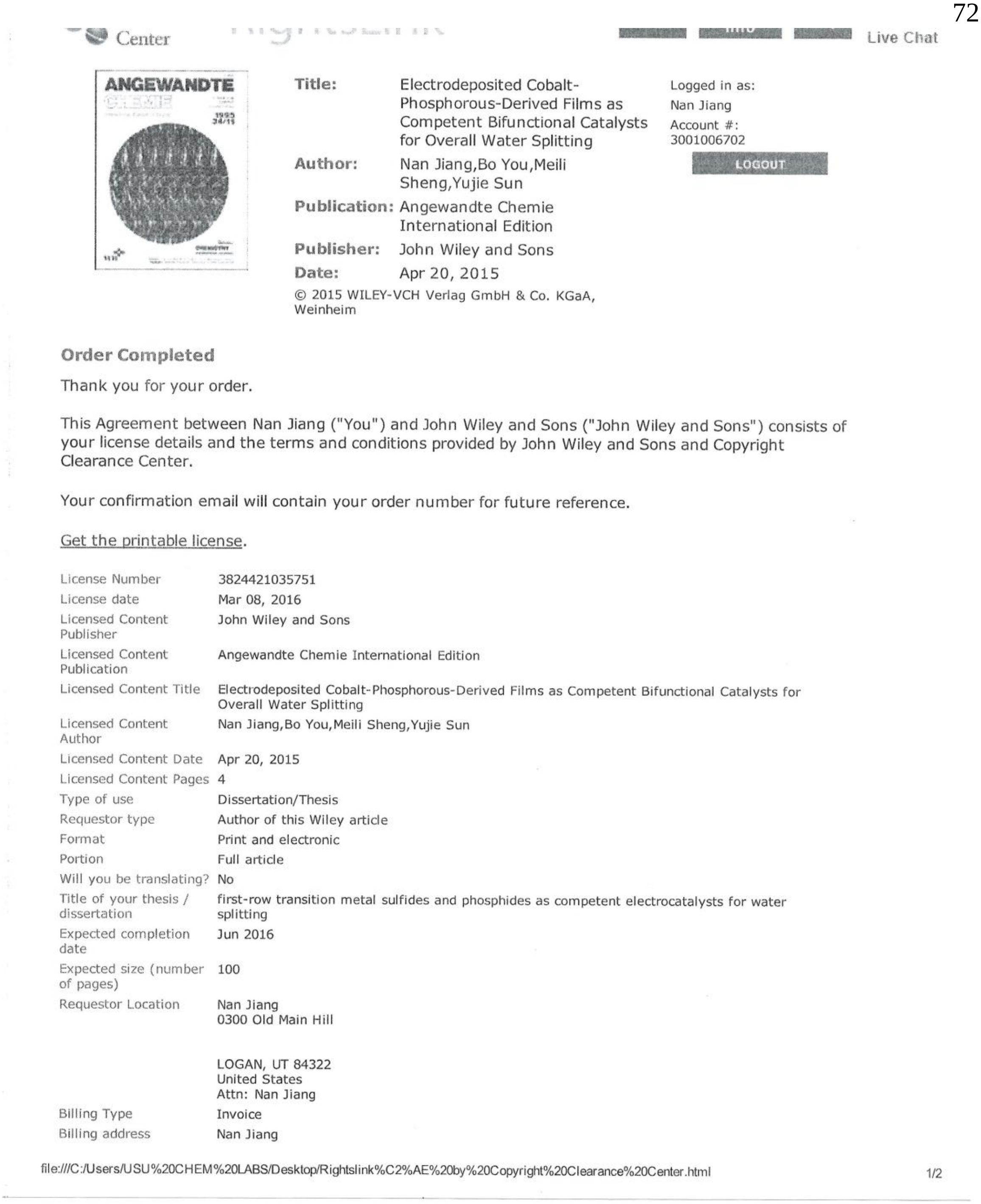

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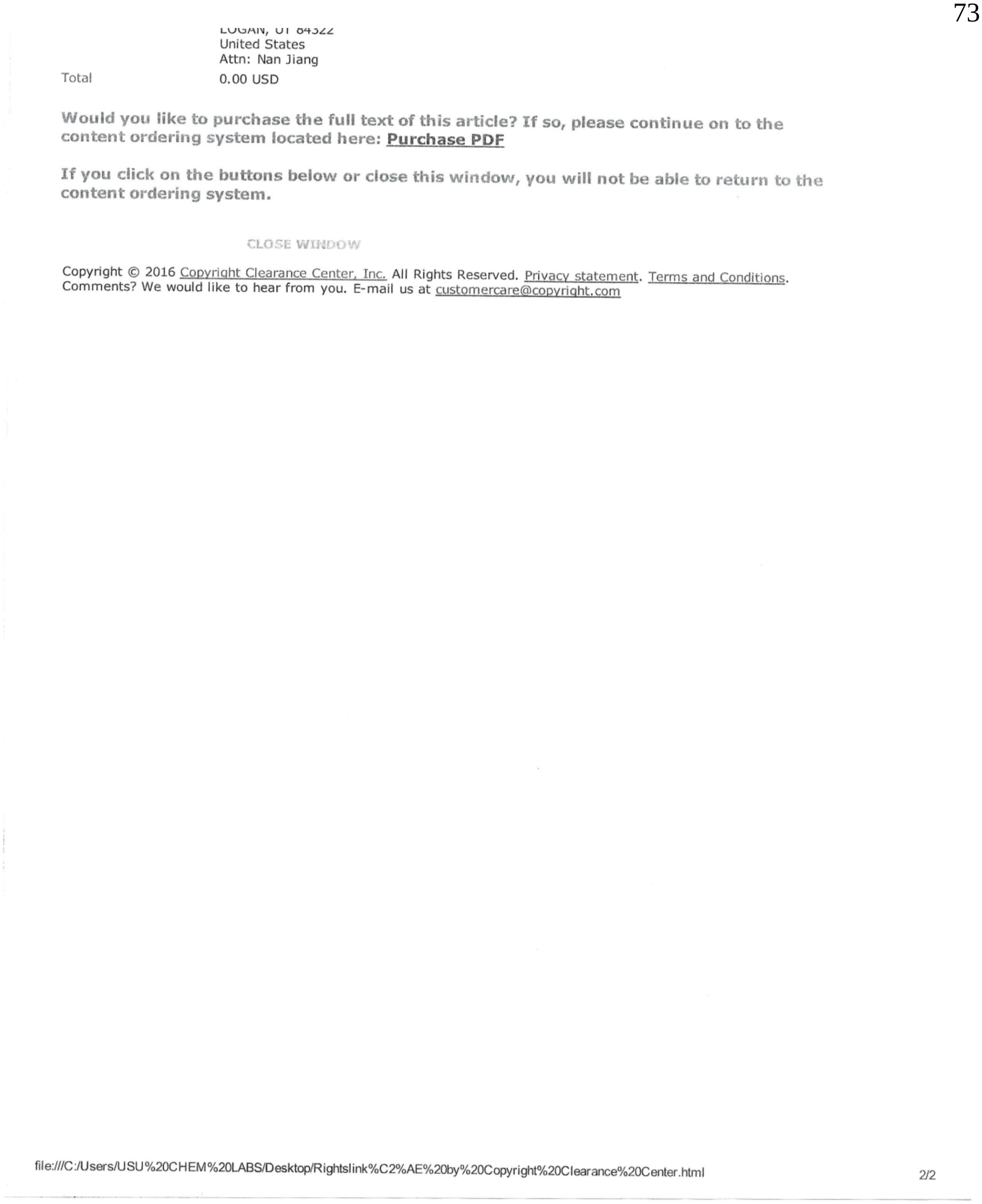

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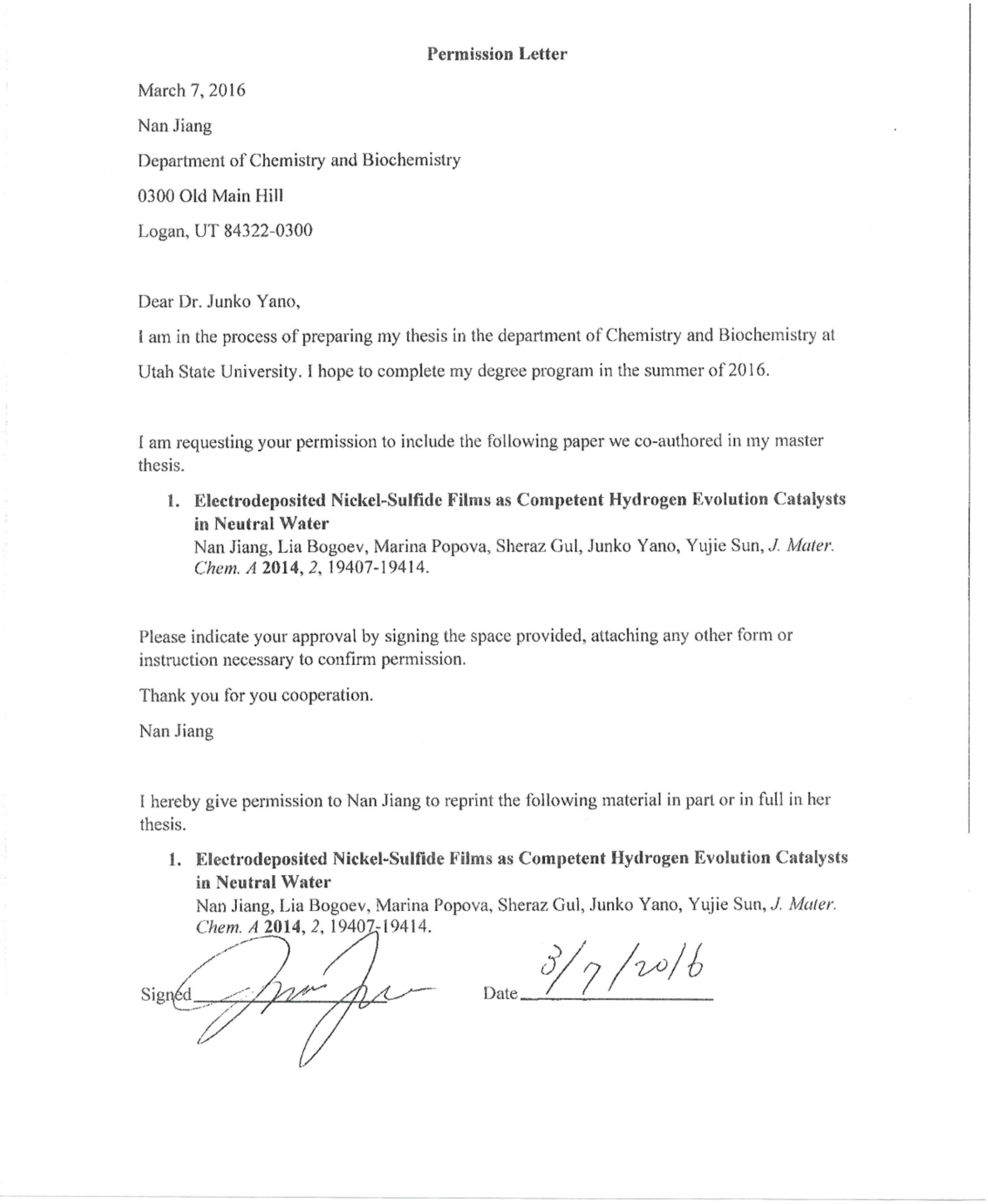

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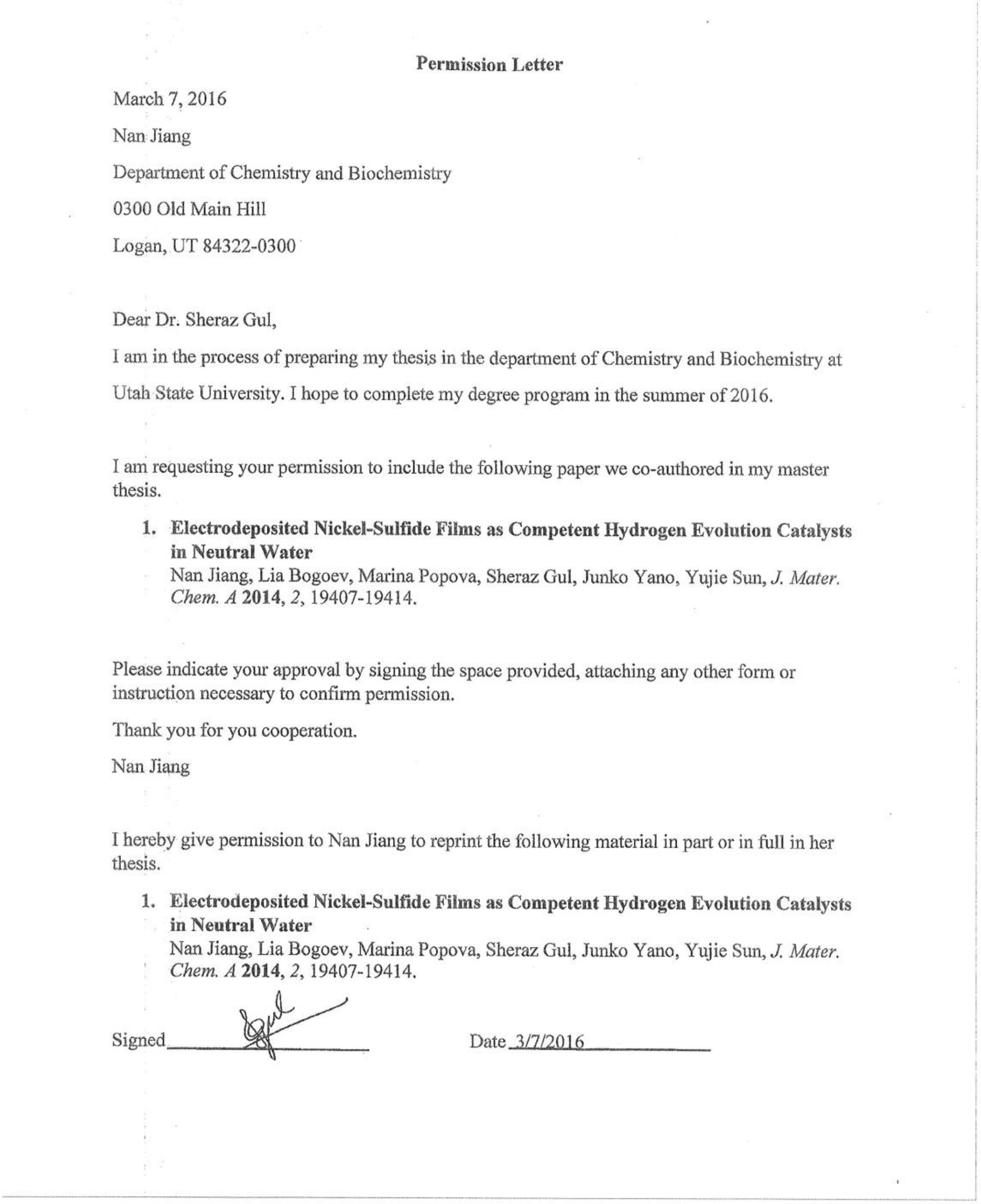

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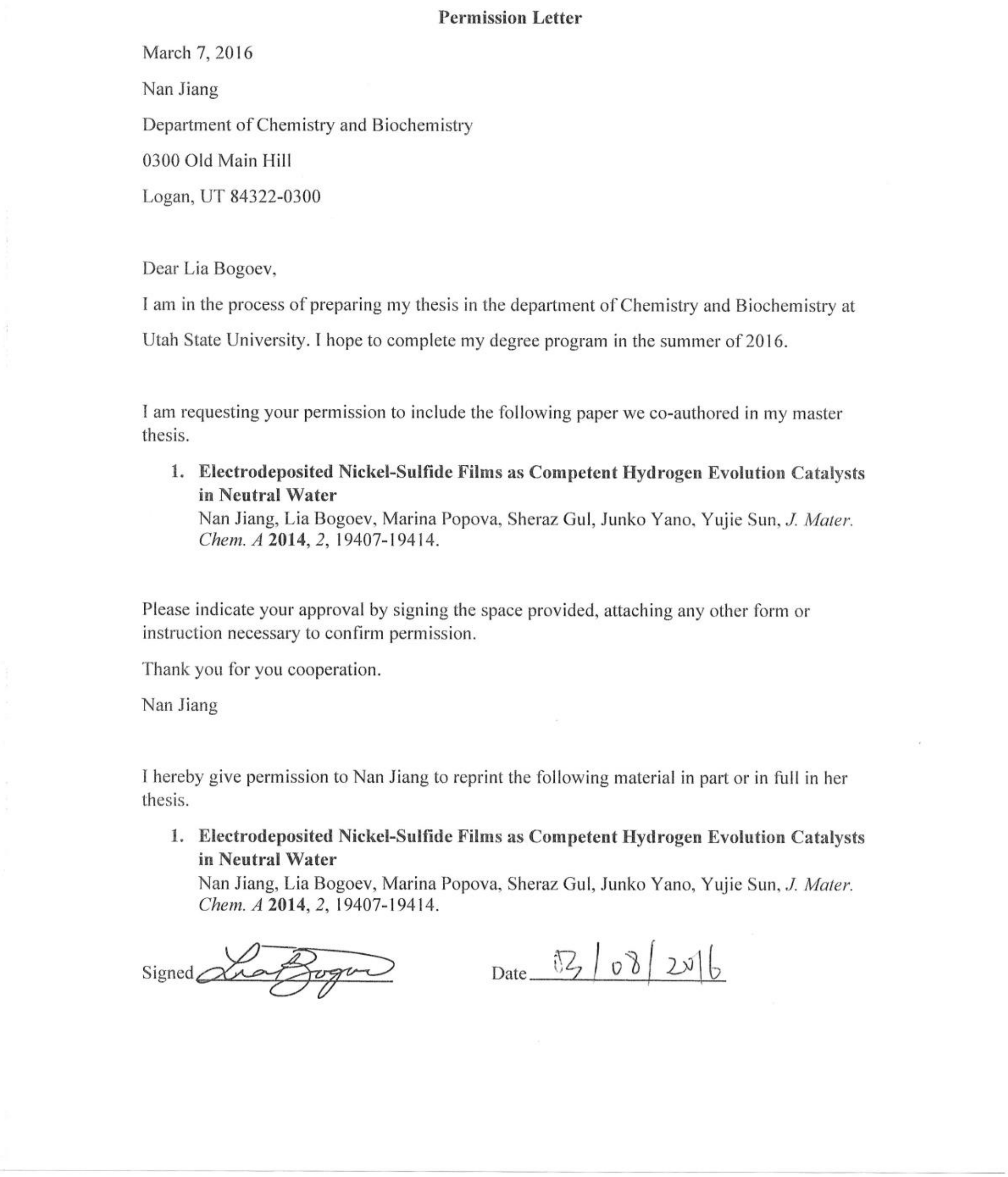

Permission Letter

March 7, 2016

Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Lia Bogoev,

I am in the process of preparing my thesis in the department of Chemistry and Biochemistry at Utah State University. I hope to complete my degree program in the summer of 2016.

I am requesting your permission to include the following paper we co-authored in my master thesis.

1. **Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water**
   Nan Jiang, Lia Bogoev, Marina Popova, Sheraz Gul, Junko Yano, Yujie Sun, *J. Mater. Chem. A* **2014**, *2*, 19407-19414.

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Thank you for you cooperation.

Nan Jiang

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Signed Lia Bogoev Date 03/08/2016

Permission Letter

March 7, 2016

Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Bo You,

I am in the process of preparing my thesis in the department of Chemistry and Biochemistry at Utah State University. I hope to complete my degree program in the summer of 2016.

I am requesting your permission to include the following paper we co-authored in my master thesis.

1. **Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting**
   Nan Jiang, Bo You, Meili Sheng, Yujie Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 6251-6254.

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Signed Bo You Date 03/08/2016

Permission Letter

March 7, 2016

Nan Jiang

Department of Chemistry and Biochemistry

0300 Old Main Hill

Logan, UT 84322-0300

Dear Yujie Sun,

I am in the process of preparing my thesis in the department of Chemistry and Biochemistry at Utah State University. I hope to complete my degree program in the summer of 2016.

I am requesting your permission to include the following papers we co-authored in my master thesis.

1. **Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation, Chapter 6 Hybrid Molecular-Nanomaterial Assemblies for Water Splitting Catalysis**
   Nan Jiang, Meili Sheng, Yujie Sun, ISBN: 978-1-84973-959-7.
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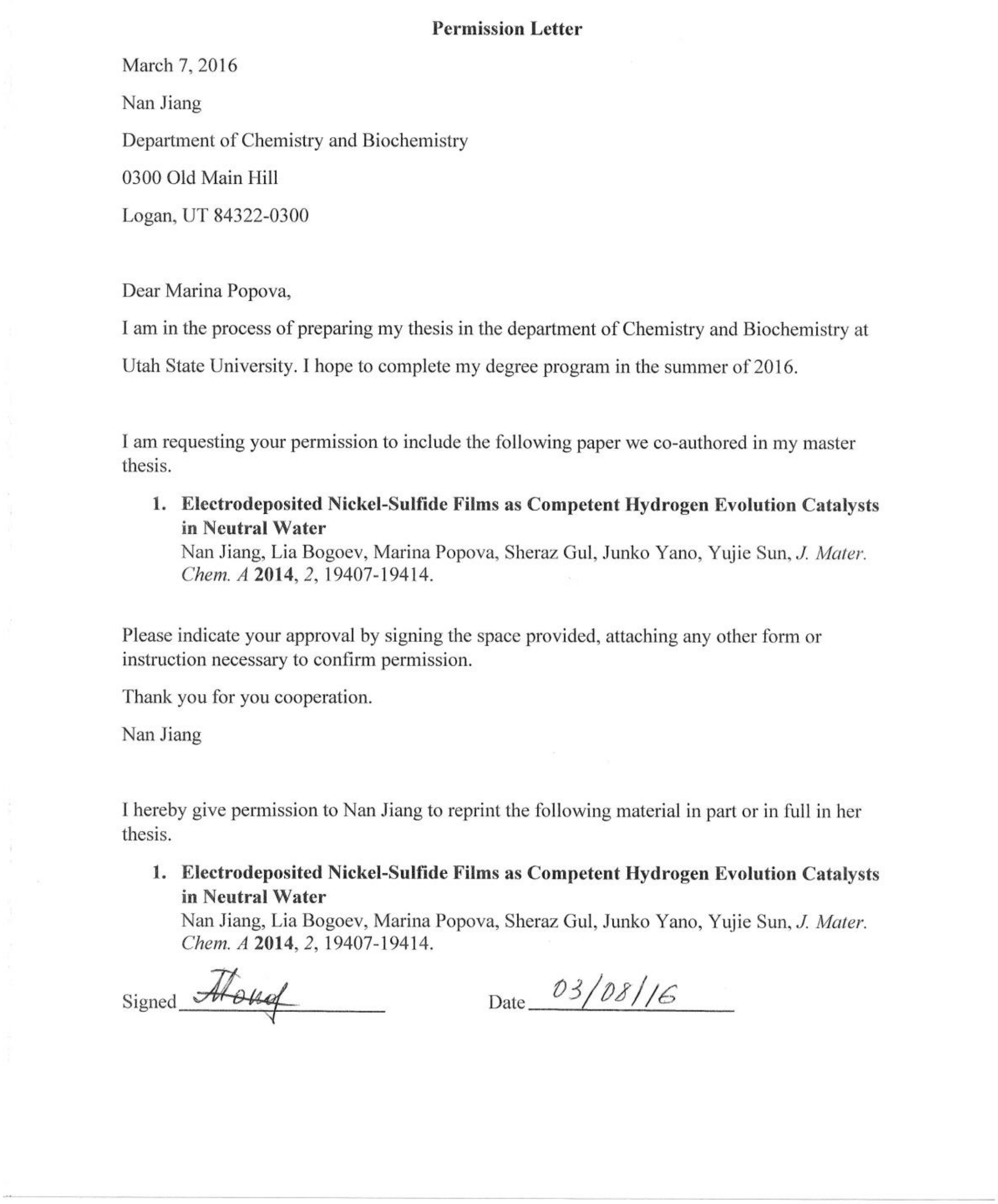
Signed________________ Date 3/8/2016



Permission Letter

March 7, 2016

Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Marina Popova,

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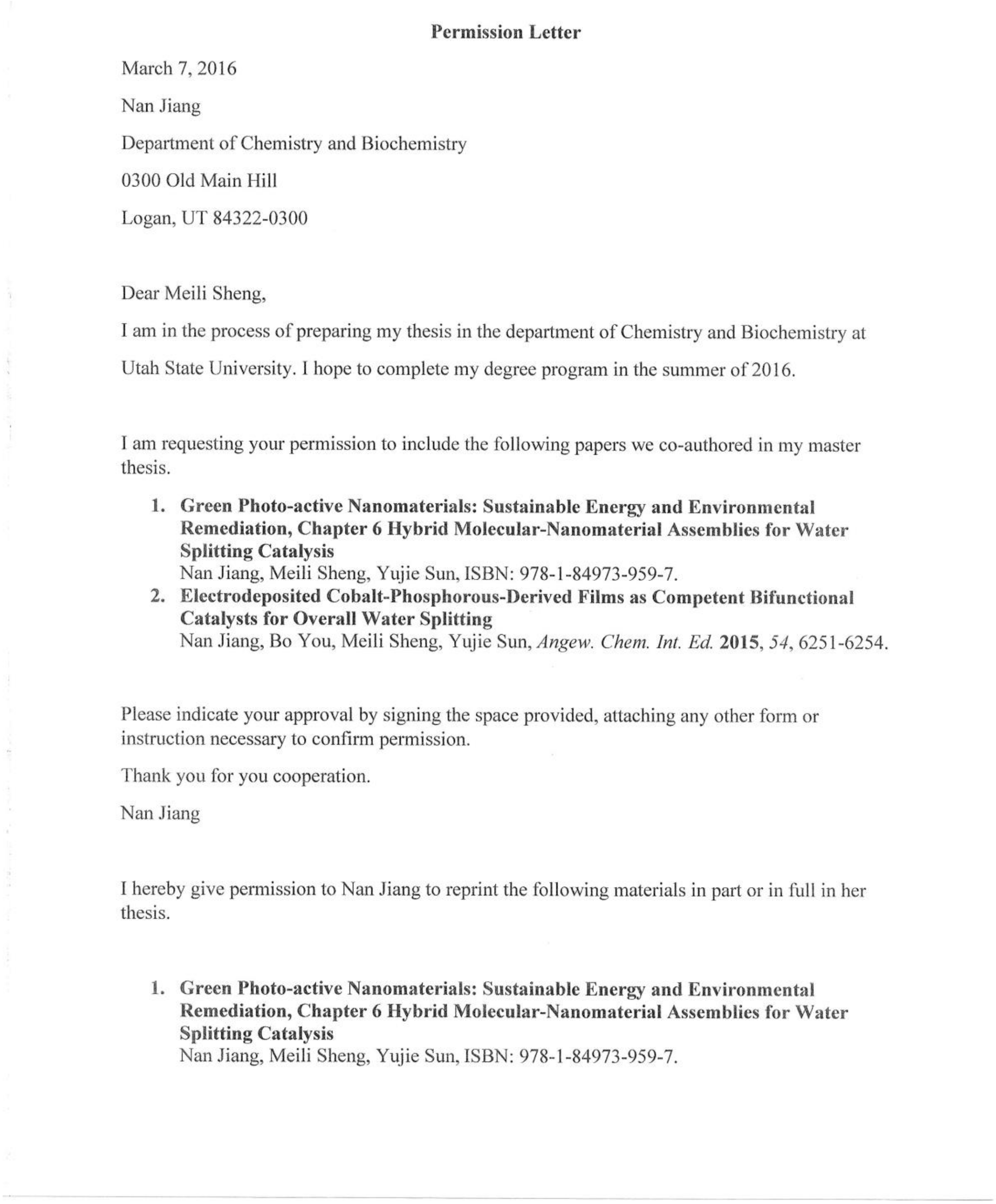
Signed________________ Date 03/08/16



Permission Letter

March 7, 2016

Nan Jiang

Department of Chemistry and Biochemistry

0300 Old Main Hill

Logan, UT 84322-0300

Dear Meili Sheng,

I am in the process of preparing my thesis in the department of Chemistry and Biochemistry at Utah State University. I hope to complete my degree program in the summer of 2016.

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1. **Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation, Chapter 6 Hybrid Molecular-Nanomaterial Assemblies for Water Splitting Catalysis**
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   Nan Jiang, Bo You, Meili Sheng, Yujie Sun, *Angew. Chem. Int. Ed.* **2015**, *54*, 6251-6254.

Signed Meili Sh Date 03/08/2016

CURRICULUM VITAE

Widtsoe Lab 306
Department of Chemistry and Biochemistry
Utah State University
Logan, UT 84322-0300

Email:jiangnansaibei@gmail.com
Phone: (435) 797-1419
Fax: (435) 797-3390

EDUCATION

Graduate student (Inorganic Chemistry)	Utah State University	09/2013 to present
Supervisor: Prof. Yujie Sun	GPA: 3.75	
M.S. (Inorganic Chemistry)	Jilin University, China	06/2013
Supervisor: Prof. Xiaoyang Liu	GPA: 3.81	
B.S. (Chemistry and Biotechnology)	Jilin University, China	06/2010
	GPA: 3.63	

RESEARCH EXPERIENCES

(1) 09/2013-present Research Assistant/Teaching Assistant, Utah State University

“Developing Inexpensive Catalysts for Renewable Energy Catalysis”

(2) 06/2010-06/2013 Research Assistant, Jilin University

“Direct Microwave-Assisted Amino Acid Synthesis by the Reaction of Succinic Acid and Ammonia in the Presence of Magnetite”

(3) 08/2009-06/2010 Research Assistant, Jilin University

“A Facile Microwave-assisted Synthesis of Natural Amino Acids from Carboxylic Acid and Ammonia”

(4) 10/2007-08/2008 Research Assistant, Jilin University

“Extraction, Separation and Purification of Sucrose from Beer Yeast”

PUBLICATIONS

At Utah State University

(1) You, B.; **Jiang, N.**; Sheng, M.; Bhushan, M. W.; Sun, Y.* "Hierarchically Porous Urchin-like Ni_2P Superstructures Supported on Nickel Foam as Efficient Bifunctional Electrocatalysts for Overall Water Splitting" ***ACS Catal.***, 2016, *6*, 714-721.

(2) **Jiang, N.**; You, B.; Sheng, M.; Sun, Y.* "Bifunctionality and Mechanism of Electrodeposited Nickel-phosphorous Films for Efficient Overall Water Splitting" ***ChemCatChem***, 2016, *8*, 106-112.

Note: highlighted on the ***Back Cover***.

(3) You, B.; **Jiang, N.**; Sun, Y.* "Morphology-activity Correlation in Hydrogen Evolution Catalyzed by Cobalt Sulfides" ***Inorg. Chem. Front.***, 2016, *3*, 279-285.

(4) **Jiang, N.**; Tang, Q.; Sheng, M.; You, B.; Jiang, D.; Sun, Y.* “Nickel Sulfides for Electrocatalytic Hydrogen Evolution under Alkaline Conditions: A Case Study of Crystalline NiS, NiS_2, and Ni_3S_2 Nanoparticles” ***Catal. Sci. Technol.***, 2016, *6*, 1077-

1084.

(5) You, B.; **Jiang, N.**; Sheng, M.; Gul, S.; Yano, J.; Sun, Y.* "High-Performance Overall Water Splitting Electrocatalysts Derived from Cobalt-Based Metal-organic Frameworks" ***Chem. Mater.***, 2015, *27*, 7636-7642.

(6) You, B.; **Jiang, N.**; Sheng, M.; Drisdell, D. S.; Yano, J.; Sun, Y.* "Bimetal-organic Framework Self-adjusted Synthesis of Support Free Non-precious Electrocatalysts for Efficient Oxygen Reduction" ***ACS Catal.***, 2015, *5*, 7068-7076.

(7) Sheng, M.; **Jiang, N.**; Gustafson, S.; You, B.; Ess, D.H.;* Sun, Y.* "A Nickel Complex with A Biscarbene Pincer-type Ligand Shows High Electrocatalytic Reduction of CO_2 Over H_2O" ***Dalton Trans.***, 2015, *44*, 16247-16250.

(8) **Jiang, N.**; Sheng, M.; Sun, Y.* "Chapter VI: Hybrid Molecular-nanomaterials Assemblies for Water Splitting Catalysis", *Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation*, 2015, 108-141, Royal Society of Chemistry.

(9) **Jiang, N.**;# You, B.;# Sheng, M.; Sun, Y.* "Electrodeposited Co-P-derived Films as Competent Bifunctional Catalysts for Overall Water Splitting" ***Angew. Chem. Int. Ed.***, 2015, *54,* 6251-6254. (#equally contributed)

*Note: highlighted on the **Back Cover**.*

(10) You, B.; #**Jiang, N.**;# Sheng, M.; Sun, Y.* "Microwave *vs.* Solvothermal Synthesis of Hollow Cobalt Sulfide Nanoprisms for Electrocatalytic Hydrogen Evolution and Supercapacitor" ***Chem. Commun.***, 2015, *51*, 4252-4255. (#equally contributed)

(11) **Jiang, N.**; Bogoev, L.; Popova, M.; Gul, S.; Yano, J.; Sun, Y.* "Electrodeposited Nickel-sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water" ***J. Mater. Chem. A***, 2014, *2*, 19407-19414.

At Jilin University

(12) **Jiang, N.**; Liu, D.; Shi, W.; Hua, Y.; Wang, C.; Liu, X.* "Direct Microwave-assisted Amino Acid Synthesis by the Reaction of Succinic Acid and Ammonia in the Presence of Magnetite" ***Int. J. Astrobiol.,*** 2013, *12*, 331-336.

RESEARCH PRESENTATIONS

(1) 249th National Meeting of the American Chemical Society, Denver, Colorado, 2015

Jiang, N.; Sun, Y. *"Metal Sulfides and Phosphides as Competent Hydrogen Evolution Catalysts in Water"*

(2) NanoUtah 2014, Nanotechnology Conference & Exhibition, Salt Lake City, Utah, 2014

Jiang, N.; Sun, Y. "*Nickel Sulfides as Competent Hydrogen Evolution Catalysts in Neutral Water*"

(3) 3rd Governor's Annual Energy Development Summit, Salt Lake City, Utah, 2014

Jiang, N.; Bogoev, L.; Sun, Y. *"Electrodeposited Nickel-sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water"*

(4) Graduate Research Symposium, Utah State University, Logan, Utah, 2014

Jiang, N.; Sun, Y. "*Hydrogen Evolution from Neutral Water Catalyzed by Cobalt*

Sulfide Nanoparticles”

AWARDS

(1) Governor's Energy Leadership Scholars, State of Utah	2016
(2) Award for Early Research Progress in Chemistry	2015
(3) Governor's Energy Leadership Scholars, State of Utah	2014
(4) Outstanding Graduate Student Scholarship, Jilin University	2010/2011/2012
(5) Entrance Scholarship for Outstanding New Graduate Student, Jilin University	2010
(6) Undergraduate Scholarship, Jilin University	2008/2009/2010