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

Nan Jiang
Utah State University

Follow this and additional works at: https://digitalcommons.usu.edu/etd

Part of the Biochemistry Commons, and the Chemistry Commons

Recommended Citation
Jiang, Nan, "First-Row Transition Metal Sulfides and Phosphides as Competent Electrocatalysts for Water Splitting" (2017). All Graduate Theses and Dissertations. 6480.
https://digitalcommons.usu.edu/etd/6480

This Thesis is brought to you for free and open access by the Graduate Studies at DigitalCommons@USU. It has been accepted for inclusion in All Graduate Theses and Dissertations by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.
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.  Lisa M. Berreau, Ph.D.
Major Professor  Committee Member

Lance C. Seefeldt, Ph.D.  Mark R. McLellan, Ph.D.
Committee Member  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.
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 electrocatalysts 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.
ACKNOWLEDGMENTS

First of all, I would like to express my sincere gratitude to my supervisor, Dr. Yujie Sun, for all that I have learned from him throughout my academic program at Utah State University. He helped me greatly to develop my skills in the research of chemical reactions, to improve my understanding of the fields of electrochemistry and catalysis, and to gain a deep appreciation for the perseverance required to perform such research. The joy and enthusiasm he has for his research will be contagious and motivational for my entire life.

I would especially like to thank my committee members, Drs. Lisa M. Berreau, Lance C. Seefeldt, Cheng-Wei Tom Chang, and T. C. Shen for their support and assistance throughout the entire process. I appreciate their support, encouragement, and suggestions, which greatly help me for my professional growth.

I also like to thank FenAnn Shen at the Microscopy Core Facility of Utah State University. She helped me take lots of beautiful scanning electron microscopy images of my catalysts. To Marina Popova, Dr. Sheraz Gul, and Dr. Junko Yano, I thank them for conducting X-ray diffraction and X-ray absorption spectroscopy for some of my samples. With the help of them, I was able to successfully characterize my samples and finish my first paper at Utah State University.

I would also like to thank all of my labmates, Meili Sheng, Dr. Bo You, Dr. Xin Liu, and Xuan Liu for helping me through my three years here at Utah State University. I thank them for discussing research and solving many problems with me together. I am very glad that I also had the opportunity to work with many outstanding undergraduate
researchers in the Sun Lab, including Lia Bogoev, Jeffrey Chipman, Raquel Boonstra, and Irina Terrero Rodriguez.

I also want to thank all my friends here in Logan. Research plays a big part of my life here, but not all of it. We have shared many great moments like hiking and fishing together. I give special thanks to my family for their encouragement, moral support, and patience as I worked my way from the very beginning of my graduate years to this stage. I could not have done it without all of you.

Finally, I thank the Department of Chemistry and Biochemistry and Utah State University for offering me the opportunity to pursue my master degree. I also thank Logan city which is a beautiful place to live and a great place to conduct research.

Nan Jiang, 2017
CONTENTS

Page

ABSTRACT ........................................................................................................ iii
PUBLIC ABSTRACT ................................................................................. v
ACKNOWLEDGMENTS .............................................................................. vii
LIST OF TABLES ......................................................................................... x
LIST OF FIGURES ....................................................................................... xi

CHAPTER
I. INTRODUCTION ...................................................................................... 1
  1-1. Background ...................................................................................... 1
  1-2. References ....................................................................................... 8

II. NICKEL SULFIDES AS EFFICIENT ELECTROCATALYSTS FOR
    HYDROGEN EVOLUTION FROM WATER ............................................. 15
  1-1. Introduction ...................................................................................... 15
  1-2. Preparation of the Ni-S film ............................................................. 17
  1-3. Characterization of the Ni-S film ...................................................... 18
  1-4. Catalytic activity of the Ni-S film .................................................... 20
  1-5. Composition of the Ni-S film ............................................................ 31
  1-6. Conclusion ....................................................................................... 38
  1-7. References ....................................................................................... 38

III. COBALT PHOSPHIDES AS COMPETENT ELECTROCATALYSTS FOR
    OVERALL WATER SPLITTING .............................................................. 41
  1-1. Introduction ...................................................................................... 41
  1-2. Preparation of the Co-P film ............................................................ 43
  1-3. Characterization of the Co-P film ..................................................... 45
  1-4. Catalytic activity of the Co-P film .................................................... 46
  1-5. Conclusion ....................................................................................... 55
  1-6. References ....................................................................................... 55

IV. CONCLUSION ........................................................................................ 59
  1-1. Conclusion ....................................................................................... 59
  1-2. References ....................................................................................... 62

APPENDICES-COPYRIGHT ......................................................................... 64
CURRICULUM VITAE .................................................................................. 83
LIST OF TABLES

Table                                                                                                      Page
2-1. ICP-OES data of four Ni-S/FTO samples .................................................................................. 20
2-2. Ni EXAFS curve fitting parameters of the post-electrolysis film ............................................. 37
3-1. ICP-OES data of the as-prepared, after 2 h HER electrolysis, and after 2 h OER electrolysis Co-P/Cu films ........................................................................................................................................ 46
3-2. Comparison of selected non-precious HER electrocatalysts in alkaline media ........................................... 48
3-3. Comparison of selected non-precious OER electrocatalysts in alkaline media .................................................. 52
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1.</td>
<td>A typical potentiodynamic deposition for the preparation of Ni-S films on FTO</td>
<td>17</td>
</tr>
<tr>
<td>2-2.</td>
<td>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-electrolysis one</td>
<td>18</td>
</tr>
<tr>
<td>2-3.</td>
<td>EDS of a Ni-S film deposited on FTO</td>
<td>19</td>
</tr>
<tr>
<td>2-4.</td>
<td>XRD of Ni-S/FTO and blank FTO</td>
<td>19</td>
</tr>
<tr>
<td>2-5.</td>
<td>(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</td>
<td>21</td>
</tr>
<tr>
<td>2-6.</td>
<td>(a) Gas chromatograms of generated H₂ during a 2.5 h chronopotentiometry experiment of Ni-S/FTO at 2 mA in pH 7 phosphate buffer. (b) Overlay of the measured H₂ volume (red) from gas chromatography every 30 min and the calculated H₂ volume (black) based on the assumption that all the passed charge during the electrolysis was used to produce H₂</td>
<td>23</td>
</tr>
<tr>
<td>2-7.</td>
<td>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</td>
<td>24</td>
</tr>
<tr>
<td>2-8.</td>
<td>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</td>
<td>26</td>
</tr>
<tr>
<td>2-9.</td>
<td>Controlled potential electrolysis shows the accumulated charge vs. time for Ni-S/FTO in 0.5 M H₂SO₄ with an applied potential of −0.168 V vs. SHE. Inset shows current vs. time during the electrolysis</td>
<td>26</td>
</tr>
<tr>
<td>2-10.</td>
<td>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</td>
<td>27</td>
</tr>
</tbody>
</table>
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................................. 28

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.................................................. 29

2-13. Nyquist plots of Ni-S/FTO before (black) and after (red) the 1 h electrolysis.......................................................................................................................................... 29

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........................................................................................................... 30

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 .............................................................. 32

2-16. XPS spectra and fittings of Ni 2p of Ni-S/FTO before (a) and after (b) the 1 h electrolysis................................................................................................................................ 33

2-17. XPS spectra and fittings of S 2p of Ni-S/FTO before (a) and after (b) the 1 h electrolysis................................................................................................................................ 34

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........................................................................................................... 35

2-19. (a) Crystal structure of Ni₃S₂ viewed through the body diagonal direction; (b) selected region of the Ni₃S₂ structure highlighting its trigonal bipyramidal core (green: nickel; yellow: sulfur) ............................................ 37

3-1. A typical potentiodynamic deposition for the preparation of Co-P films on copper foil (scan rate: 5 mV/s)................................................................................. 44

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................................. 45

3-3. XPS survey of the as-prepared Co-P film ............................................................................. 46
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 H₂ evolution electrolysis at η = −107 mV .......................................................... 47

3-5. XPS spectra of (a) Co 2p and (b) P 2p regions of Co-P films after HER (top) or OER (bottom) electrolysis ............................................................................................................. 49

3-6. XPS survey of the post-HER Co-P film ......................................................................................... 50

3-7. (a) Polarization curves of Co-P (red), IrO₂ (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 IrO₂; (b) corresponding Tafel plots of Co-P (red) and IrO₂ (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 ........................................................................................................ 51

3-8. XPS survey of the post-OER Co-P film .......................................................................................... 53

3-9. (a) Polarization curves of Co-P/Co-P (red), IrO₂/Pt-C (blue), Pt-C/Pt-C (yellow), and IrO₂/IrO₂ (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), IrO₂/Pt-C (blue), Pt-C/Pt-C (yellow), and IrO₂/IrO₂ (black) and their associated linear fittings (dotted lines); (c) long-term controlled potential electrolysis of Co-P/Co-P (red) and IrO₂/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 IrO₂/Pt-C (blue)); (d) generated H₂ and O₂ 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. .......................................................................................... 54
CHAPTER I
INTRODUCTION

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

---

pathways. 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).

\[
\begin{align*}
2H^+_{(aq)} + 2e^- & \rightarrow H_2(g) \quad \text{(acidic)} \\
2H_2O_{(aq)} + 2e^- & \rightarrow H_2(g) + 2OH^{-}_{(aq)} \quad \text{(alkaline)} \\
H^+_{(aq)} + M + e^- & \rightarrow M{\cdot}H^* \quad \text{(acidic)} \\
H_2O + M + e^- & \rightarrow M{\cdot}H^* + OH^{-}_{(aq)} \quad \text{(alkaline)} \\
M{\cdot}H^* + H^+_{(aq)} + e^- & \rightarrow M + H_2(g) \quad \text{(acidic)} \\
M{\cdot}H^* + H_2O + e^- & \rightarrow M + OH^{-}_{(aq)} + H_2(g) \quad \text{(alkaline)} \\
2M{\cdot}H^* & \leftrightarrow 2M + H_2(g) \quad \text{(both acidic and alkaline)}
\end{align*}
\]

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 \( \eta \) (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)\[^3\]:
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.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[10]} Recent years have witnessed the emergence of several promising solid-state HER catalysts composed of earth-abundant elements. For example, metal alloys,\textsuperscript{[11]} metal oxides/hydroxides,\textsuperscript{[12]} chalcogenides,\textsuperscript{[13]} carbides,\textsuperscript{[14]} phosphides,\textsuperscript{[15]} and even metal-free nanomaterials\textsuperscript{[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.\cite{17}

It is known that all the cofactors in hydrogenases ubiquitously involve metal-sulfur interactions.\cite{6} Inspired by the blueprints of hydrogenase active sites, increasing efforts have been devoted to exploring 1\textsuperscript{st}-row transition metal chalcogenides, such as CoS\textsubscript{x},\cite{18} CoSe\textsubscript{2},\cite{19} FeS,\cite{20} FeSe\textsubscript{2},\cite{21} and NiS\textsubscript{x},\cite{22} as potential HER catalysts. The success of 1\textsuperscript{st}-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.\cite{23} Due to its terrestrial abundance and involvement in [Ni-Fe] hydrogenases,\cite{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\textsubscript{2} production recently. Typical examples include nickel alloys,\cite{24} sulfides,\cite{25} selenides,\cite{26} oxides/hydroxides,\cite{27} and phosphides,\cite{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\textsubscript{2} evolution under acidic, neutral, or alkaline conditions. For instance, metal–organic framework-derived NiS nanostructures have been demonstrated as HER catalysts in 1.0 M KOH.\cite{25} Similarly, NiS\textsubscript{2} of various nanostructures was reported to exhibit remarkable HER catalytic performance in strongly acidic electrolytes.\cite{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.\cite{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 Ni₃S₂. This was the first time that Ni₃S₂ 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 Ni₂P (001) as the dilution effect of phosphorous would make Ni₂P (001) behave more like hydrogenases rather than pure metal. 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, 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 H₂ generation, a roughly equal amount of efforts have been devoted to exploring cobalt phosphides and molybdenum phosphides as potential HER catalysts.

As a four-electron/four-proton process, O₂ 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 CO₂ 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 O₂ evolution center of photosystem II, where water oxidation to O₂ takes
place. Recently, the crystal structure of the O₂ evolution center, which contains a Mn₄CaO₅ cluster, was obtained with a 1.9 Å resolution. The cubane-type Mn₄CaO₅ cluster has been an inspiration source for many scientists aiming at developing competent O₂ evolution catalysts. Inspired, but not constrained, by nature, a large library of molecular catalysts has been reported, 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.

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. For example, H₂–CoCat, metallic cobalt coated with a cobalt-oxo/hydroxo-phosphate layer can be prepared via electrodeposition in a phosphate buffer containing cobalt salts. It is able to mediate H₂ evolution in aqueous solution. Remarkably, it can be converted via anodic equilibration into the amorphous cobalt oxide film (O₂–CoCat or CoPi) catalysing O₂ 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, H₂–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).\(^\text{[32\%]}\) 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 H₂ 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 \textit{in situ} electrocatalytic conditions.

1-2. References


2014, 26, 4826-4831; (d) X. Chen, D. Wang, Z. Wang, P. Zhou, Z. Wu, F. Jiang, 


CHAPTER II

NICKEL SULFIDES AS EFFICIENT ELECTROCATALYSTS FOR HYDROGEN EVOLUTION FROM WATERb

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 MoS2.[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 MoS2 materials possessed promising HER activity via density functional theory (DFT) calculation.[4] Later, Chorkendoff et al. experimentally confirmed that the electrocatalytic HER performance of MoS2 was indeed correlated with

the number of its edge sites.\cite{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.\cite{6} Inspired by the blueprints of hydrogenase active sites and encouraged by the success of 2$^{\text{nd}}$-row transition metal chalcogenides in HER electrocatalysis, increasing efforts have been devoted to exploring 1$^{\text{st}}$-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.\cite{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.\cite{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$_3$S$_2$.

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](image-url). 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-electrolysis.
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/cm² 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area (cm²)</th>
<th>Ni (µmol)</th>
<th>S (µmol)</th>
<th>[Ni] (µg/cm²)</th>
<th>Ni/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.385</td>
<td>0.5479</td>
<td>0.3845</td>
<td>83.61</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
<td>0.735</td>
<td>1.0005</td>
<td>0.7884</td>
<td>79.89</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>0.750</td>
<td>1.0601</td>
<td>0.6443</td>
<td>82.96</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>0.750</td>
<td>1.0165</td>
<td>0.5443</td>
<td>79.55</td>
<td>1.85</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>81.50</strong></td>
<td><strong>1.55</strong></td>
</tr>
</tbody>
</table>

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/cm², 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 MoS₂ film showed a Tafel slope of 86 mV/dec at pH 7, and the first-row transition metal doping in MoS₂ 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 $-452 \text{ mV}$ to reach $1.5 \text{ mA/cm}^2$ with a much larger Tafel slope ($226 \text{ mV/dec}$) in a borate buffer (pH 9.2).\cite{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 ($93 \text{ mV/dec}$).\cite{7}

It was reported that three principal steps are involved in the hydrogen evolution reaction: Volmer (discharge), Tafel (recombination), and Heyrovsky (desorption) steps.\cite{11} Depending on which one is the limiting step, the Tafel slope could be 29, 38, or $116 \text{ mV/dec}$, respectively. The deviation of the $77 \text{ mV/dec}$ 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 $2 \text{ mA}$ for $2.5 \text{ h}$. 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 $\text{H}_2$. 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 ($81.5 \mu\text{g/cm}^2$), the mole of Ni ($0.534 \mu\text{mol}$) in the Ni-S film is only $-0.5\%$ of the mole of hydrogen ($0.1 \text{ mmol}$) produced during the $2.5 \text{ h}$ 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 $-0.700 \text{ V vs. SHE}$ for $100 \text{ h}$. 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 H₂ during a 2.5 h chronopotentiometry experiment of Ni-S/FTO at 2 mA in pH 7 phosphate buffer. (b) Overlay of the measured H₂ volume (red) from gas chromatography every 30 min and the calculated H₂ volume (black) based on the assumption that all the passed charge during the electrolysis was used to produce H₂.
a turnover number of 925 mole H₂ 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 H₂SO₄. As shown in Figure 2-8, Ni-S/FTO was able to reach catalytic current densities of 1, 10, and 20 mA/cm² 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 H2SO4 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.

![Polarization curves 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.](image)

*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.*
Controlled potential electrolysis shows the accumulated charge vs. time for Ni-S/FTO in 1.0 M KOH at an applied potential of $-1.05 \text{ V vs. SHE}$. 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 $-0.689 \text{ V vs. SHE}$ 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 $\Omega$. 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.\textsuperscript{[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

\textbf{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 2p3/2 and 2p1/2, respectively.\textsuperscript{[13]} The shoulder around 855-860 eV implies the presence of Ni(OH)\textsubscript{2} and NiSO\textsubscript{4}.\textsuperscript{[13]} XPS fitting of the Ni 2p3/2 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\textsubscript{3}S\textsubscript{2},\textsuperscript{[14]} NiS,\textsuperscript{[15]} and NiS\textsubscript{2}.\textsuperscript{[16]} The similarity in the binding energy of the Ni 2p3/2 peak of different nickel sulfides is known.\textsuperscript{[13]} The process giving
rise to the Ni 2p\textsubscript{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).\textsuperscript{[13]} Therefore, we cannot solely rely on the binding energy of the Ni 2p\textsubscript{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)\textsubscript{2} and NiSO\textsubscript{4}, respectively.\textsuperscript{[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\textsubscript{1/2} and 2p\textsubscript{3/2}, respectively.

\textit{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](image)

*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 Ni₁₇, NiO₁₇, NiS₁₈ and NiS₂₁₉ 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 Ni₃S₂ very well, which is further supported by the Ni EXAFS spectra (Figure 2-18c₁₇,₁₉) Ni₃S₂ (heazlewoodite) is one of the stable forms of nickel sulphides.¹²⁰ Each nickel atom in crystalline Ni₃S₂ occupies a pseudotetrahedral site in an approximately body-centered cubic sulfur lattice.¹²¹ The Ni₃S₂ units are interconnected through short Ni-S and Ni-Ni distances, 2.2914(5) and 2.5319(9) Å, respectively, within the Ni₃S₂ unit. However, the Ni-S and Ni-Ni distances are even shorter between Ni₃S₂ units, being 2.2534(5) and 2.4966(4) Å, respectively. Figure 2-19 displays the crystal structure of Ni₃S₂ 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 Ni₃S₂ 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 Ni₃S₂. The short Ni-Ni distances in Ni₃S₂ have been proposed to be indicative of metal-metal bonding.¹²⁰ 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 2p₃/₂ 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 Ni₃S₂ is the major composition of the Ni-S film.
Figure 2.19. (a) Crystal structure of Ni₃S₂ viewed through the body diagonal direction; (b) selected region of the Ni₃S₂ structure highlighting its trigonal bipyramidal core (green: nickel; yellow: sulfur).

Table 2-2. Ni EXAFS curve fitting parameters of the post-electrolysis film (S₀ was fixed to 0.83. N is the coordination number and σ² is the Debye-Waller factor. ∆E is the EXAFS threshold energy. R factor (%) indicates the goodness of the fit. Bold letters are the fixed parameters. Values in parentheses indicate uncertainties.).

<table>
<thead>
<tr>
<th>Fit</th>
<th>NiOₓ:NiSₓ</th>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>σ² (Å²)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(OH)₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.015 (0.005)</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.015 (0.005)</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ni(OH)₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni₃S₂</td>
<td>NiO</td>
<td>2.03 (0.03)</td>
<td>6</td>
<td>0.003 (0.005)</td>
<td></td>
</tr>
</tbody>
</table>
**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$_3$S$_2$, which was preserved during the electrochemical experiments.

**1-7. References**


CHAPTER III

COBALT PHOSPHIDES AS COMPETENT ELECTROCATALYSTS FOR OVERALL WATER SPLITTING

1-1. Introduction

Electrocatalytic water splitting, which consists of H₂ and O₂ 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. 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 Ni₂P nanoparticles under acidic conditions. When loaded on titanium foil, these Ni₂P nanoparticles showed excellent HER performance in 0.5 M H₂SO₄ with an overpotential of only −130 mV to reach a catalytic current density of 20 mA/cm² 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 Ni₂P nanoparticles. A similar thermolysis method was also applied to prepare hollow CoP nanoparticles. The resulting CoP

---

nanoparticles exhibited even better performance than that of Ni$_2$P, 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$_2$P, and Cu$_3$P, 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\(_2\)P, an excellent HER catalyst aforementioned, was also highly active for OER.\(^{[13a]}\) The Ni\(_2\)P 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\(_2\)P/NiO\(_x\)) structure of the transformed catalyst under anodic conditions. Recently, Shalom et al. synthesized Ni\(_5\)P\(_4\) 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\(_5\)P\(_4\) 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\(_2\)PO\(_2\), 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 cm² 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](image.png)

*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. 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.](image-url)
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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area (cm²)</th>
<th>[Co] (mg/cm²)</th>
<th>[P] (mg/cm²)</th>
<th>Co/P mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh prepared</td>
<td>0.3</td>
<td>2.52</td>
<td>0.19</td>
<td>6.89</td>
</tr>
<tr>
<td>After 2 h HER</td>
<td>0.3</td>
<td>2.48</td>
<td>0.12</td>
<td>10.5</td>
</tr>
<tr>
<td>After 2 h OER</td>
<td>0.3</td>
<td>2.47</td>
<td>0.12</td>
<td>9.74</td>
</tr>
</tbody>
</table>

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 −0.3 V 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 H₂ bubbles from the electrode surface. The Co-P film required an overpotential of only −94 mV to reach a current density of 10 mA/cm². 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.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>( j ) (mA/cm(^2))</th>
<th>( \eta ) (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-P film</td>
<td>1 M KOH</td>
<td>10 20 100</td>
<td>94 115 158</td>
<td>42</td>
<td>This work</td>
</tr>
<tr>
<td>Amorphous MoS(_x)</td>
<td>0.1 M KOH</td>
<td>10</td>
<td>540</td>
<td>N/A</td>
<td><em>Chem. Sci.</em> 2011, 2, 1262.</td>
</tr>
</tbody>
</table>

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](image_url). XPS spectra of (a) Co 2p and (b) P 2p regions of Co-P films after HER (top) or OER (bottom) electrolysis.
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 1.53 V vs. RHE (Figure 3-7a inset). It could reach current densities of 10, 100, and 500 mA/cm$^2$ at $\eta = 345$, 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 $\eta = 343$ 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 $\eta = 343$ 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.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>$\eta$ (mV) at 10 mA/cm$^2$</th>
<th>Tafel slop (mV/dec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-P film</td>
<td>1.0 M KOH</td>
<td>345</td>
<td>47</td>
<td>This work</td>
</tr>
<tr>
<td>NiCo LDH</td>
<td>1.0 M KOH</td>
<td>367</td>
<td>40</td>
<td><em>Nano Lett.</em> 2015, 15, 1421.</td>
</tr>
<tr>
<td>Cu-N-C/graphene</td>
<td>0.1 M KOH</td>
<td>&gt;770</td>
<td>N/A</td>
<td><em>Nat. Commun.</em> 2014, 5, 5285.</td>
</tr>
<tr>
<td>De-LiCoO$_2$</td>
<td>0.1 M KOH</td>
<td>&gt;400</td>
<td>50</td>
<td><em>Nat. Commun.</em> 2014, 5, 4345.</td>
</tr>
<tr>
<td>$\alpha$-MnO$_2$/SF</td>
<td>0.1 M KOH</td>
<td>490</td>
<td>77.5</td>
<td><em>J. Am. Chem. Soc.</em> 2014, 136, 11452.</td>
</tr>
<tr>
<td>Zn$<em>x$Co$</em>{3-x}$O$_4$</td>
<td>1.0 M KOH</td>
<td>330</td>
<td>51</td>
<td><em>Chem. Mater.</em> 2014, 26, 1889.</td>
</tr>
<tr>
<td>Ni$<em>x$Co$</em>{3-x}$O$_4$</td>
<td>1.0 M KOH</td>
<td>~370</td>
<td>59-64</td>
<td><em>Adv. Mater.</em> 2010, 22, 1926.</td>
</tr>
</tbody>
</table>
780.7 and 796.3 eV (Figure 3-5a), which can be assigned to oxidized cobalt, Co$_3$O$_4$, plus its satellite peaks at 786.3 and 802.7 eV.\textsuperscript{[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$_3$O$_4$ and cobalt phosphate during OER. An OER electrocatalyst with a metallic cobalt core and cobalt oxide/hydroxide shell was reported.\textsuperscript{[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

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-8.png}
\caption{XPS survey of the post-OER Co-P film.}
\end{figure}
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 $\eta = 400$ mV.

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.

1-6. References

[1] (a) S. Chu, A. Majumdar, Nature 2012, 484, 294-303; (b) T. R. Cook, D. K.


2078.


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 H₂ and O₂ 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 H₂ as a fuel.¹ Recent years have witnessed the increasing popularity of transition metal-based catalysts as competent H₂ and O₂ 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/cm² 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$_3$S$_2$ 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.\cite{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 severe 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.\cite{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. 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 electrocatalyststs for water splitting is beneficial for design other promising catalysts in the future.

1-2. References


When you publish in a Royal Society of Chemistry journal, you keep the copyright of the manuscript. On this page you can learn more about our Licence to Publish and the rights you retain as an author. We also explain where you can deposit and share your article, and how to request permission to re-use other people’s work.

The following details apply only to authors accepting the standard Licence to Publish. Authors who are interested in publishing open access should visit our open access pages for more information about our open access licence (http://www.rsc.org/publications/open-access/open-access-licences) and deposition rights.

On this page

- About our licence to publish (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights)
- Right retained by authors (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/rights-retained-by-authors)
- Deposition & sharing rights (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/deposition-sharing-rights)
- Re-use permission requests (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/re-use-permission-requests)

About our licence to publish

In order to publish material the Royal Society of Chemistry must acquire the necessary legal rights from the author(s) of that material. In general, we must obtain from the original author(s) the right to publish the material in all formats, in all media (including specifically print and electronic), with the right to sublicense those rights.

For all articles published in our journals, we require the author to accept a 'licence to publish'. This licence is normally requested on submission of the article. By signing this licence the author (who is either the copyright owner or who is authorised to sign on behalf of the copyright owner, for example her/his employer) grants to the Royal Society of Chemistry "the exclusive right and licence throughout the world to edit, adapt, translate, reproduce and publish the manuscript in all formats, in all media and by all means (whether now existing or in future devised)."

The Royal Society of Chemistry thus acquires an exclusive licence to publish and all practical rights to the manuscript, except the copyright. The copyright of the manuscript remains with the copyright owner. The copyright owner also retains certain rights regarding the sharing and deposition (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/sharing-deposition) of their article and the re-use of the published material (http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/re-use-permission-requests). For short items in journals (news items, etc) we take a non-exclusive licence in the form of a brief ‘terms and conditions for acceptance’ document.

What is copyright? +

http://www.rsc.org/publications/our-rights/how-we-use-copyright-share-our-rights/re-use-permission-requests
In the licence to publish, the author provides the assurances that we need to publish the material, including assurances that the work is original to the author; that the work has not been published already and that permissions have been obtained if previously published material has been included.

If the manuscript includes material that belongs to someone else (for example, a figure or diagram), we require the author to obtain all permissions that may be needed from third parties. If you wish to reuse material that was not published originally by the Royal Society of Chemistry please see Reuse permission requests.

Download the Royal Society of Chemistry licence to publish.

Rights retained by authors

When the author accepts the exclusive licence to publish for a journal article, he/she retains certain rights that may be exercised without reference to the Royal Society of Chemistry.

Reproduce/republish portions of the article (including the abstract).

Photocopy the article and distribute such photocopies and distribute copies of the PDF of the article for personal or professional use only (the Royal Society of Chemistry makes this PDF available to the corresponding author of the article upon publication. Any such copies should not be offered for sale. Persons who receive or access the PDF mentioned above must be notified that this may not be made available further or distributed.).

Adapt the article and reproduce adaptations of the article for any purpose other than the commercial exploitation of a work similar to the original.

Reproduce, perform, transmit and otherwise communicate the article to the public in spoken presentations (including those that are accompanied by visual material such as slides, overheads and computer projections).

The author(s) must submit a written request to the Royal Society of Chemistry for any use other than those specified above.

All cases of republication/reproduction must be accompanied by an acknowledgement in the form: 'Published in [Journal Name], [Year], [Volume], [Issue], [Page Numbers].'

Deposition and sharing rights

The following details apply only to authors accepting the standard licence to publish. Authors who have accepted one of the open access licences to publish, or are thinking of doing so, should refer to the details for open access deposition rights.

Deposition by the Royal Society of Chemistry

The Royal Society of Chemistry shall deposit the accepted version of the submitted article in non-commercial repository(ies) as deemed appropriate, including but not limited to the funding agency repository(ies) of the author(s). There shall be an embargo to making the above deposited material available to the public that will be 12 months from the date of acceptance.

Deposition by the author(s)

When the author accepts the licence to publish for a journal article, he/she retains certain rights concerning the deposition of the whole article.

Deposit the accepted version of the submitted article in their institutional repository(ies). There shall be an embargo of 12 months from the date of acceptance, after which the article will be made available to the public. There shall be a link from this article to the PDF of the version of record on the Royal Society of Chemistry’s website, once this final version is available.

Make available the accepted version of the submitted article via the personal website(s) of the author(s) or via the intranet(s) of the organisation(s) where the author(s) work(s): no embargo period applies.

http://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/royal-society-of-chemistry-license-to-publish
Re-use permission requests

Material published by the Royal Society of Chemistry and other publishers is subject to all applicable copyright, database protection, and other rights. Therefore, for any publication, whether printed or electronic, permission must be obtained to use material for which the author(s) does not already own the copyright. This material may be, for example, a figure, diagram, table, photo or some other image.

Author reusing their own work published by the Royal Society of Chemistry

You do not need to request permission to reuse your own figures, diagrams, etc. that were originally published in a Royal Society of Chemistry publication. However, permission should be requested for use of the whole article or chapter except if reusing it in a thesis. If you are including an article or book chapter published by us in your thesis please ensure that your co-authors are aware of this.

Reuse of material that was published originally by the Royal Society of Chemistry must be accompanied by the appropriate acknowledgement of the publication. The form of the acknowledgement is dependent on the journal in which it was published originally, as detailed in "Acknowledgements".

Material published by the Royal Society of Chemistry to be used in another of our publications

Authors contributing to our publications (journal articles, book or book chapters) do not need to formally request permission to reproduce material contained in another Royal Society of Chemistry publication. However, permission should be requested for use of a whole article or chapter. For all cases of reproduction the correct acknowledgement of the reproduced material should be given. The form of the acknowledgement is dependent on the journal in which it was published originally, as detailed in the "Acknowledgements" section.

Acknowledgements

The Royal Society of Chemistry publishes some journals in partnership with, or on behalf of, other organisations; these journals require a specific wording of the acknowledgement when work is reproduced from them. The text for the acknowledgement for these journals, and the standard wording to be used by all other journals are given below.

Standard acknowledgement

Reproduced from Ref. XX with permission from the Royal Society of Chemistry.

Non-standard acknowledgements

Reproduction of material from NJC (New Journal of Chemistry)
Reproduced from Ref. XX with permission from the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry.

Reproduction of material from Photochemical & Photobiological Sciences (PPS)
Reproduced from Ref. XX with permission from the European Society for Photobiology, the European Photochemistry Association, and the Royal Society of Chemistry.

Reproduction of material from PCCP (Physical Chemistry Chemical Physics)
Reproduced from Ref. XX with permission from the PCCP Owner Societies.

Reproduction of material from Inorganic Chemistry Frontiers
Reproduced from Ref. XX with permission from the Chinese Chemical Society (CCS), Peking University (PKU), and the Royal Society of Chemistry.

Reproduction of material from Organic Chemistry Frontiers
Reproduced from Ref. XX with permission from the Chinese Chemical Society (CCS), Shanghai Institute of Organic Chemistry (SIOC), and the Royal Society of Chemistry.

http://www.rsc.org/journals-licensing/journal-authors-reviewers/licences-copyright-permissions/#rsc-press-reprint-permission-requests
We must ensure that the material we publish does not infringe the copyright of others. We require the author(s) to obtain, at the earliest opportunity, the relevant permissions that might be needed from third parties to include material that belongs to someone else.

Please contact the publisher/copyright owner of the third party material to check how they wish to receive permission requests. Please plan to submit your request well ahead of publication of your material.

The most common procedures for permission requests are outlined below.

- A number of publishers have opted out of receiving express permissions as long as they fall under the rules of the STM Permission Guidelines (http://www.isce.org/index.php?option=com_docman&task=cat_view&gid=29&Itemid=86).
- If they do not fall into the category above, the majority of publishers now use RightsLink from the Copyright Clearance Center (CCC) to process their requests.
- Other publishers have their own permission request forms and/or specify what information they need to process any permission request.
- If the publisher/copyright owner does not have a specific procedure please complete and submit the permission request form for non-RSC material (http://www.rsc.org/RightsLink/permissionrequestforms/permissionrequestform-drncatitativeplannedtags.pdf).
- Send the form to the permission administrator or editor of the relevant publication.
- If the copyright owner has opted to publish under a Creative Commons licence, licensees are required to obtain permission to do any of the things with a work that the law reserves exclusively to a licensor and that the licence does not expressly allow. Licensees must credit the licensor, keep copyright notices intact on all copies of the work, and link to the license from copies of the work.

In all cases the following rights need to be obtained:

Permission is required to include the specified material in the work described and in all subsequent editions of the work to be published by the Royal Society of Chemistry for distribution throughout the world, in all media including electronic and microfilm and to use the material in conjunction with computer-based electronic and information retrieval systems, to grant permissions for photocopying, reproductions and reprints, to translate the material and to publish the translation, and to authorise document delivery and abstracting and indexing services.

Please note that the Royal Society of Chemistry is also a signatory to the STM Permission Guidelines.

Using material published by the Royal Society of Chemistry in material for another publisher

If you require permission to use material from one of our publications or website in a publication not owned by us, and you are not the author of our publication, the following procedures should be followed.

Before sending in any request you should check that the material you wish to reproduce is not credited to a source other than the Royal Society of Chemistry. The credit for an image will be given in the caption of the image or sometimes in the list of references. Please plan to submit your request well ahead of publication of your material. Please note that we are unable to supply artwork for the material you may wish to reproduce.

Reproducing material from a Royal Society of Chemistry journal

To request permission to reproduce material from a Royal Society of Chemistry journal please use RightsLink.

Using RightsLink +

Reproducing material from other Royal Society of Chemistry publications

If you are reproducing material from a Royal Society of Chemistry book, education or science policy publication or a Royal Society of Chemistry website you must complete and submit the online permission request form (http://www.rsc.org/RightsLink/permissionrequestforms/permissionrequestform-drncatitativeplannedtags.pdf) (or the RSC version of the permission request form for Royal Society of Chemistry material (http://www.rsc.org/RightsLink/permissionrequestforms/permissionrequestform-drncatitativeplannedtags.pdf)).

Requests are usually for use of a figure or diagram, but they may also be for use of the entire article or chapter. Requests to use individual figures or diagrams are invariably granted. Permission for another publisher to print an entire Royal Society of Chemistry article or chapter may be granted in special circumstances.

http://www.rsc.org/journals-books-databases/journal-authors-reviews/licences-copyright-permissions/request-permission-requests
Education in Chemistry, and other non-journal publications of the Royal Society of Chemistry. For these requests please complete and send the form to our publishing services team.

Advertisement

Carbon emission savings are running in circles.
And that's a good thing.

It's Smart, Sustainable, Surprising.

Contact our Contracts & Copyright Executive
Email: Send an email

Contact our Publishing customer services team
Email: Send an email

Share

Advertisement

Advan
DIRECT MS66 ANALYSIS OF TLC WITHOUT SCRAPPING SPOTS.

http://www.rsc.org/journals/books-databases/journal-authors-reviewers/permissions

Spotlight

http://www.rsc.org/journals/books-databases/journal-authors-reviewers/permissions/permissions-requests
Order Completed

Thank you for your order.

This Agreement between Nan Jiang ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

Your confirmation email will contain your order number for future reference.

**Get the printable license.**

<table>
<thead>
<tr>
<th>License Number</th>
<th>3824421035751</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Mar 06, 2016</td>
</tr>
<tr>
<td>Licensed Content</td>
<td>John Wiley and Sons</td>
</tr>
<tr>
<td>Publisher</td>
<td>Angewandte Chemie International Edition</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting</td>
</tr>
<tr>
<td>Author</td>
<td>Nan Jiang, Bo You, Meili Sheng, Yujie Sun</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Apr 20, 2015</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>4</td>
</tr>
<tr>
<td>Type of use</td>
<td>Dissertation/Thesis</td>
</tr>
<tr>
<td>Requestor type</td>
<td>Author of this Wiley article</td>
</tr>
<tr>
<td>Format</td>
<td>Print and electronic</td>
</tr>
<tr>
<td>Portion</td>
<td>Full article</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title of your thesis / dissertation</td>
<td>first-row transition metal sulfides and phosphides as competent electrocatalysts for water splitting</td>
</tr>
<tr>
<td>Expected completion date</td>
<td>Jun 2016</td>
</tr>
<tr>
<td>Expected size (number of pages)</td>
<td>100</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Nan Jiang</td>
</tr>
<tr>
<td></td>
<td>0380 Old Main Hill</td>
</tr>
<tr>
<td></td>
<td>LOGAN, UT 84322</td>
</tr>
<tr>
<td></td>
<td>United States</td>
</tr>
<tr>
<td></td>
<td>Attn: Nan Jiang</td>
</tr>
<tr>
<td>Billing Type</td>
<td>Invoice</td>
</tr>
<tr>
<td>Billing address</td>
<td>Nan Jiang</td>
</tr>
</tbody>
</table>

...
Would you like to purchase the full text of this article? If so, please continue on to the content ordering system located here: Purchase PDF

If you click on the buttons below or close this window, you will not be able to return to the content ordering system.

CLOSE WINDOW

Copyright © 2016 Copyright Clearance Center, Inc. All Rights Reserved. Privacy statement, Terms and Conditions, Comments? We would like to hear from you. E-mail us at customercare@copyright.com
Permission Letter

March 7, 2016
Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Dr. Junko Yano,
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

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.

1. Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water

Signed [Signature] Date 3/7/2016
Permission Letter

March 7, 2016
Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Dr. Sheraz Gul,

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

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.

1. Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water

Signed ___________________ Date: 3/7/2016
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

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.

1. Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water

Signed [Signature] 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

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.

1. Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting

Signed Bo You Date 5/3/16
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

2. **Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water**

3. **Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting**

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.
1. **Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation, Chapter 6 Hybrid Molecular-Nanomaterial Assemblies for Water Splitting Catalysis**

2. **Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water**

3. **Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting**

Signed

Date **3/18/2016**
March 7, 2016
Nan Jiang
Department of Chemistry and Biochemistry
0300 Old Main Hill
Logan, UT 84322-0300

Dear Marina Popova,

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**

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following material in part or in full in her thesis.

1. **Electrodeposited Nickel-Sulfide Films as Competent Hydrogen Evolution Catalysts in Neutral Water**

Signed  

Date  03/08/16
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.

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 Catalyst**

2. **Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting**

Please indicate your approval by signing the space provided, attaching any other form or instruction necessary to confirm permission.

Thank you for your cooperation.

Nan Jiang

I hereby give permission to Nan Jiang to reprint the following materials in part or in full in her thesis.

1. **Green Photo-active Nanomaterials: Sustainable Energy and Environmental Remediation, Chapter 6 Hybrid Molecular-Nanomaterial Assemblies for Water Splitting Catalyst**
2. Electrodeposited Cobalt-Phosphorous-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting

Signed [Signature]
Date 03/08/2016
CURRICULUM VITAE

Widtsoe Lab 306                      Email: jiangansaibei@gmail.com
Department of Chemistry and Biochemistry Phone: (435) 797-1419
Utah State University Fax: (435) 797-3390
Logan, UT 84322-0300

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 Ni₂P Superstructures Supported on Nickel Foam as Efficient Bifunctional

(2) Jiang, N.; You, B.; Sheng, M.; Sun, Y.* "Bifunctionality and Mechanism of
    Electrodeposited Nickel-phosphorous Films for Efficient Overall Water
    Note: highlighted on the Back Cover.

(3) You, B.; Jiang, N.; Sun, Y.* "Morphology-activity Correlation in Hydrogen Evolution

(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, NiS₂, and Ni₃S₂ Nanoparticles” Catal. Sci. Technol., 2016, 6, 1077-


Note: highlighted on the Back Cover.


At Jilin University


**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
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