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NANOstructured Transition Metal Sulfide Catalysts for Electrochemical Water Splitting

A Thesis in Chemistry
by
Alex M. Wiltrout

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The thesis of Alex M. Wiltzout was reviewed and approved* by the following:

Raymond E. Schaak
DuPont Professor of Materials Chemistry
Thesis Advisor

Christine D. Keating
Professor of Chemistry

Thomas E. Mallouk
Evan Pugh University Professor of Chemistry, Physics, Biochemistry, and Molecular Biology
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

With the world’s population steadily on the rise, there will continue to be an ever-increasing demand for energy. However, fossil fuels, which currently supply the world with an overwhelming portion of its energy needs, are quickly becoming depleted at a much faster rate than they are being generated. Most people use fossil fuels for their everyday energy needs, namely because compared to other alternative energy sources, it is cheaper and much more readily accessible. However, if one is looking to invest in a sustainable, long-term solution to the energy crisis that we currently face, these non-renewable energy sources are less than ideal. One possible solution to this problem is to begin using hydrogen as a fuel source instead. Hydrogen is an ideal alternative for a number of reasons, namely because it possesses the largest energy density by mass of any element, and that burning it produces no harmful byproducts, only water. The current industry standard for hydrogen production is primarily limited to production via steam-methane reformation and the water-gas shift reaction. However, these processes are not ideal for large-scale hydrogen production, and are detrimental to the environment because of the large amounts of CO and CO₂ that are produced. One potentially cleaner alternative is proposed through electrochemical water splitting, whereby water is decomposed in hydrogen and oxygen. However, materials that catalyze these reactions are often quite rare and expensive, examples being Pt and IrO₂. For this reason, the work hereafter aims to seek out new Earth-abundant materials, with a focus on transition metal sulfide systems, which can be used as catalysts to help catalyze the decomposition of water.

Our work begins by investigating the catalytic activity of CuCo₂S₄ nanoparticles for the oxygen evolution reaction. Much of the focus insofar has been primarily concerned with transition metal oxide-based materials, however, metal sulfide systems are slowly gaining momentum. Those that do exist and have been tested for the oxygen evolution reaction (OER),
often show moderate activity. By introducing additional elements into the system, we hope to further enhance the material’s OER activity. Highly crystalline and nonagglomerated colloidal CuCo$_2$S$_4$ nanoparticles, which were previously inaccessible in the literature, were synthesized using low-temperature, solution-based synthetic routes. The CuCo$_2$S$_4$ nanoparticles were found to be highly active for OER under strongly alkaline conditions. Surface studies of the material suggest that mixed-metal sulfides, such as CuCo$_2$S$_4$, may in fact serve as precursors to oxides and/or hydroxides, which are likely the catalytically active species in solution.

In addition to the work on the OER half reaction, a number of cobalt (Co$_3$S$_4$, CoS, Co$_9$S$_8$) and nickel sulfide (Ni$_3$S$_2$, α-NiS, Ni$_9$S$_8$, Ni$_3$S$_4$) nanoparticle systems were investigated for use as potential hydrogen evolution reaction (HER) electrocatalysts. These materials were the target of this study because of their relatively low cost and high abundance within the Earth’s crust, as well as because they are known hydrodesulfurization (HDS) catalysts. Both HER and HDS rely upon a process by which hydrogen reversibly binds to the surface of a material. The hope was that one could then selectively target active HER catalysts, by identifying what materials are also good HDS catalysts. However, upon testing the cobalt and nickel sulfide nanoparticles, a correlation between HER and HDS could not be discerned.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry/voltammogram</td>
</tr>
<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>DDT</td>
<td>1-Dodecanethiol</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
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<tr>
<td>HDS</td>
<td>Hydrodesulfurization</td>
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<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry/voltammogram</td>
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<tr>
<td>ODE</td>
<td>1-Octadecene</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>OLAC</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>OLAM</td>
<td>Oleylamine</td>
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<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>STEM-EDS</td>
<td>Scanning transmission electron microscopy - energy dispersive spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOP</td>
<td>Tri-n-octylphosphine</td>
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<tr>
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<tr>
<td>TOPO</td>
<td>Tri-$n$-octylphosphine oxide</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
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Chapter 1

Introduction

1.1 Electrochemical Water Splitting

With a current population of over seven billion as well as a continually growing energy sector, it’s only expected that the global energy demand will also be quite large. Everything from cell phones to hot water heaters to automobiles are dependent on some form of energy, whether it be electrical or chemical, in order to function. By the year 2035, the global energy demand is projected to rise a staggering 52.53% to nearly 769.8 quadrillion BTU, an increase of about 1.6% per year.¹ Much of this energy demand is currently being satisfied by non-renewable energy sources such as petroleum, coal, and natural gas. However, these fuels are not ideal for long-term energy needs due to scarcity, cost, and environmental friendliness.

The discovery of cost-efficient ways to produce hydrogen is important for the establishment of a hydrogen economy in an effort to satisfy the global energy demand. Hydrogen is an ideal molecule in which to store energy as it possesses the largest energy density by mass of any element (143 MJ/kg).² Additionally, when hydrogen is burned to release its chemical energy, it forms only pure water as a byproduct, instead of harmful greenhouse gases such as CO and CO₂. The current industry standard for hydrogen production is primarily limited to production via steam-methane reformation and the water-gas shift reaction (Equations 1 and 2, respectively).³⁶ However, these processes are not ideal for large-scale hydrogen production and are detrimental to the environment because of the large amounts of CO and CO₂ that are produced.

\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \]  
(Eq. 1)
One potentially clean alternative to the above mentioned reactions is proposed through electrochemical water splitting, whereby water is decomposed in hydrogen and oxygen.\(^3,6\) The hydrogen evolution reaction (HER) is the reductive half-reaction that participates in the production of hydrogen. This reaction can be performed under both acidic and alkaline environments, as illustrated in Equations 3 and 4, respectively.\(^6\)

\[
2H_2O^+ + 2e^- \leftrightarrow 2H_2O + H_2(g) \quad \text{(Eq. 3)}
\]

\[
2H_2O + 2e^- \leftrightarrow 2OH^- + H_2(g) \quad \text{(Eq. 4)}
\]

The HER is also paired with the oxygen evolution reaction (OER), the oxidative half-reaction whereby oxygen is produced. Like the HER, the OER can also be performed under both acidic and alkaline conditions (Equations 5 and 6, respectively).\(^6\)

\[
2H_2O \leftrightarrow 4H^+ + 4e^- + O_2(g) \quad \text{(Eq. 5)}
\]

\[
4OH^- \leftrightarrow 2H_2O + 4e^- + O_2(g) \quad \text{(Eq. 6)}
\]

The water splitting reaction used to produce both hydrogen and oxygen, however, is an energetically unfavorable process. The overall water splitting reaction (Equation 7) requires 237.2 kJ/mol\(_{H_2}\) to convert water into both hydrogen and oxygen.\(^2,6\)

\[
2H_2O \leftrightarrow 2H_2(g) + O_2(g) \quad \text{(Eq. 7)}
\]

For this reason, electrolysis cells require an external source of energy on the order of 1.23 V for the water decomposition to take place under standard conditions.

The energy necessary to drive these reactions to completion, though it could potentially come from a number of different energy sources, would ideally consist of energy provided from the Sun. Solar energy is an ideal candidate, since harvesting energy directly from sunlight provides a viable means of accessing an almost unlimited clean and abundant energy supply. Any device capable of catalyzing solar-driven electrochemical water splitting, however, must first
satisfy a number of criteria. A proposed such device is illustrated in Figure 1-1. First and foremost, the device must be able to effectively separate any hydrogen and oxygen gas that is produced from the reaction to avoid creating an explosive mixture of the two gases. This partitioning may be accomplished done by creating a membrane to separate the production of hydrogen and oxygen. Second, the device must have photoelectrodes with appropriate band gaps that provide the energy necessary to split water. The device pictured in Figure 1-1 makes use of this by means of a dual band gap semiconducting system, whereby the photoanode with a band gap of 1.7 eV and the photocathode with a band gap of 1.1 eV provide the necessary energy. The use of staggered band gaps in such a way allows the photocathode to absorb the lower-energy light, without having to worry about it being absorbed first by the photoanode. This multi-electrode system should increase efficiency as well as allow for separate generation of H₂ and O₂.
In addition to roles the photoelectrodes play in providing the energy necessary to split water, the device also needs a way to take that energy and effectively catalyze the decomposition of water. Some photoelectrodes exist that are able to themselves photocatalytically produce both hydrogen and oxygen, however, materials such as these are often suffer from relatively low catalytic efficiencies. For this reason, it is necessary to add catalysts to the surfaces of the photoelectrodes that can effectively catalyze both the HER and OER. The use of appropriate catalysts can dramatically increase the rate of the reaction, particularly if the catalyst is nanostructured, thereby creating a high surface area material. However, it is also important that these catalysts must demonstrate excellent oxidative/reductive stability in contact with aqueous electrolyte solutions in order to avoid material degradation.

Figure 1-1: Schematic for a photoelectrolysis device proposed by Gray. The multi-component system is designed to be used under acidic electrolyte environments and is comprised of a photoanode, photocathode, OER catalyst, HER catalyst, and a H⁺ permeable membrane.
1.2 Known Electrocatalysts for Hydrogen Evolution and Water Oxidation

In an effort to first route out what materials might work best as HER or OER electrocatalysts, single-metal catalyst materials were first investigated. A correlation between M-H bond strength and the logarithm of the HER exchange current density under acidic conditions was first demonstrated by Trasatti, where he observed a volcano relation between the two (Figure 1-2a). What this correlation suggested is that the most active HER catalysts, such as platinum, have intermediate bond strengths (50-65 kcal mol$^{-1}$). Trasatti later went on to demonstrate another volcano plot relation for OER catalysts (Figure 1-2b), where he observed that the overpotential necessary for oxygen production directly correlated with enthalpy of the transition metal oxide in acidic and alkaline conditions.

The OER volcano plots that Trasatti presents indicate that some of the best catalysts in both acidic and alkaline environments are RuO$_2$ and IrO$_2$. Further studies have shown that these rare-earth metal oxides are in fact the best OER catalysts currently available, particularly in acid, where they are some of the only materials that display both excellent OER activity and stability. However, a major drawback of these highly-active materials is their rarity and cost.
In an effort to move away from precious metals, numerous studies have instead focused on testing more Earth-abundant materials that behave similarly to their rare-earth counterparts. In doing so, a number of highly active OER catalysts, particularly under alkaline conditions, have been discovered. Some of the most active include a number of nickel and/or iron layered double hydroxides\textsuperscript{17,18} and perovskite-based metal oxide materials\textsuperscript{19,20}.

Just as precious-metal oxides were some of the most active OER catalysts, noble metals, particularly those such as platinum, palladium, rhodium, iridium, and rhenium, are some of the most active HER catalysts in both acidic and alkaline environments. Like RuO\textsubscript{2} and IrO\textsubscript{2}, these catalysts also suffer from the same shortfalls in terms of cost and rarity. When looking for alternative materials using Trasatti’s volcano plot, nickel would be the next potential candidate to investigate, given its Earth-abundant nature and proximity to other active noble metal catalysts. Investigations indicate that nickel is indeed a highly active HER catalyst under alkaline conditions\textsuperscript{21,22}. Furthermore, alloying nickel with other Earth-abundant elements such as iron, cobalt, molybdenum, and tungsten has also been shown to increase the catalytic activity for HER\textsuperscript{22-25}. However, despite binary transition metal alloys of nickel being active and stable under alkaline environments, the same is not true when using acid. Under acidic conditions, these alloys actually begin to dissolve into solution. To circumvent this issue with dissolution, a number of metal phosphide nanoparticle systems were studied, and shown to be both catalytically active and stable under acidic conditions\textsuperscript{26-30}. Some of the most active systems included CoP and FeP nanoparticles, which displayed HER activities that could directly compete with those observed for platinum.
1.3 Transition Metal Sulfides

In addition to noble metal and transition metal phosphide catalysts, transition metal sulfides have also emerged as an interesting group of materials that show potential to be used as catalysts for electrochemical processes. Among this group of materials, molybdenum sulfide (MoS\textsubscript{2}) is one of the most studied Earth-abundant, acid stable HER catalysts.\textsuperscript{4} Up until 2005, MoS\textsubscript{2} was generally thought of as a relatively poor HER catalyst because in its bulk form, it showed little to no activity.\textsuperscript{31} However, since Nørskov and coworkers demonstrated that MoS\textsubscript{2} nanoparticles are active HER catalysts, this system has become one of the most heavily researched and attractive targets for HER catalysis.\textsuperscript{32} Through both computational and experimental work, the high HER activity seen in nanoparticulate MoS\textsubscript{2} was determined to be due to the exposure of certain edge sites. Density functional theory (DFT) calculations concluded that the edge sites, specifically the Mo-edges (10\overline{1}0) with 50\% sulfur adsorption, would be ideal for hydrogen evolution. This behavior was later shown experimentally by Chorkendorff and coworkers where single sheets of MoS\textsubscript{2} were grown on Au(111) producing truncated triangular nanoplatelets with exposed Mo- and S-edge sites.\textsuperscript{4,33} Recent work has focused on ways of improving the catalytic activity of MoS\textsubscript{2} for HER even more. Dai and coworkers have demonstrated improved performance from MoS\textsubscript{2} nanoparticles grown on reduced graphene oxide (RGO) sheets.\textsuperscript{34} The addition of small amounts of either cobalt or tungsten along the edges of MoS\textsubscript{2} nanoparticles have also shown a marked increase in HER activity.\textsuperscript{4,35} Cobalt/tungsten is used in order to promote hydrogen evolution along the active Mo-edge by binding to the relatively inactive S-edges, forming (Co/W)S\textsubscript{c} at the surface. The increase in HER activity is believed to be attributed to both the promotion of hydrogen adsorption sites along the Mo-edge, as well as the (Co/W)S\textsubscript{c}-edge as illustrated in Figure 1-3.
In addition to metal oxides and hydroxides, transition metal sulfides have also started to gain attention as promising catalysts for the OER. A number of metal sulfide systems have been investigated, with most systems containing cobalt and/or nickel as their main metal components. One such system is $\text{Co}_3\text{S}_4$, which is particularly interesting because of the structural similarities that can be drawn from known, OER-active $\text{Co}_3\text{O}_4$ catalysts. To further improve upon the OER activity, additional elements, such as nickel, are often added, or the catalyst is deposited on an electrically conductive support, such as graphene. Most recently, Chen and coworkers were able to synthesize NiS nanosheets grown on a stainless steel mesh support via a one-pot hydrothermal approach. At a current density of 10 mA cm$^{-2}$ and under alkaline conditions, the NiS nanosheets were able to directly compete with some of the best-known RuO$_2$ and IrO$_2$ catalysts, reaching a sub-300 mV overpotential.
1.4 Experimental Work

The following chapters discuss our attempts to selectively synthesize and characterize a number of nanoscale transition metal sulfide systems in an effort to identify materials that have the potential to be electrochemically active catalysts for either HER or OER. Chapter 2 identifies spinel-type copper cobalt sulfide, CuCo$_2$S$_4$, as a highly active catalyst for the OER. By substituting a copper atom for cobalt in a traditional Co$_3$S$_4$ system, we hoped to further enhance its catalytic behavior, just as was observed for the NiCo$_2$S$_4$ nanoparticles synthesized by Zhang and coworkers. Nonagglomerated, colloidal CuCo$_2$S$_4$ nanoparticles, which were previously inaccessible in the literature, were selectively synthesized in a standard solution-based method by which dissolved metal precursors are allowed to react with sulfur, injected into the system, at high temperatures. The resulting CuCo$_2$S$_4$ nanoparticles offer superior surface area enhancement relative to that of its bulk counterparts. We show that the CuCo$_2$S$_4$ nanoparticles achieve current densities of 10 mA cm$^{-2}$ under strongly alkaline conditions at OER overpotentials of approximately 395 mV. Surface studies of the nanoparticles show evidence of oxide formation, suggesting that the small decline in OER activity is a direct result oxidation at the surface of the nanoparticles.

In chapter 3, we focus our studies on a number of cobalt (Co$_3$S$_4$, CoS, Co$_9$S$_8$) and nickel sulfide (Ni$_3$S$_2$, α-NiS, Ni$_9$S$_8$, Ni$_3$S$_4$) systems, with the aim of selectively synthesizing each phase, and then testing it for HER activity. The materials selected for testing were chosen for two reasons: 1) their relatively low cost yet high abundance within the Earth’s crust, and 2) the fact that a number of cobalt and nickel sulfides are known hydrodesulfurization (HDS) catalysts. MoS$_2$, in addition to being an Earth-abundant, acid stable HER catalyst, is also a well-known HDS catalyst. Given that both processes rely upon a material’s ability to reversibly bind hydrogen to its surface, effort was made to establish a correlation between the two. However,
upon testing the cobalt and nickel sulfide nanoparticles, a correlation between HER and HDS
could not be discerned. Although identifying HDS catalysts in order to target HER catalysts
showed some success, the observed HER activity appears to be much more directly affected by
other factors, such as crystal structure, morphology, and size.

1.5 References

(1) Energy Information Association; U.S. Department of Energy: Washington DC;


(6) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.;


(8) McDonald, M. B.; Bruce, J. P.; McEleney, K.; Freund, M. S. ChemSusChem 2015, 8, 2645-
2654.

410.

2013, 15, 9315-9325.

(11) Li, L.; Duan, L.; Xu, Y.; Gorlov, M.; Hagfeldt, A.; Sun, L. Chem. Commun. 2010, 46, 7307-
7309.


Chapter 2

Solution Synthesis of Thiospinel CuCo$_2$S$_4$ Nanoparticles

2.1 Introduction

Transition metal sulfides that adopt the spinel crystal structure are commonly referred to as thiospinels. Thiospinels have an ideal formula of AB$_2$S$_4$, where A and B are typically divalent and trivalent metal cations, respectively, although other oxidation states and off-stoichiometry formulas sometimes can be accommodated. Among the most common thiospinels are single-metal systems (A = B), such as Fe$_3$S$_4$, Ni$_3$S$_4$, and Co$_3$S$_4$, and these materials are widely studied for their magnetic, electronic, and catalytic properties. Solid solutions, which bridge the A$_3$S$_4$ and AB$_2$S$_4$ end members, are also known. The Co$_3$S$_4$–CuCo$_2$S$_4$ system is particularly interesting in that regard. Substitution of some of the cobalt in Co$_3$S$_4$ with copper generates a solid solution, ultimately forming the end member CuCo$_2$S$_4$. CuCo$_2$S$_4$, which is the mineral carrollite, is a normal spinel, with copper occupying the tetrahedral sites and cobalt occupying octahedral sites (Figure 2-1). CuCo$_2$S$_4$, which is paramagnetic and metallic, displays several interesting electronic and magnetic properties. For example, CuCo$_2$S$_4$ was found to be weakly antiferromagnetic at low temperatures and is also an $s$-wave superconductor. In addition, CuCo$_2$S$_4$ was reported to be catalytically active for the oxygen reduction reaction (ORR).

CuCo$_2$S$_4$ is typically synthesized as bulk powders and crystals from its corresponding elemental powders in evacuated silica tubes at temperatures in excess of 500 °C.$^{13,14}$ With the desire to access higher surface area materials for applications in catalysis, CuCo$_2$S$_4$ was synthesized at lower temperatures under a reducing atmosphere (H$_2$S/H$_2$, 300 °C), although the particles were quite large and agglomerated, and decomposed into copper and cobalt sulfides upon continued heating in H$_2$S/H$_2$ at 300 °C.$^{15}$ Colloidal nanoparticles of CuCo$_2$S$_4$, with the high surface areas that are desirable for catalytic studies, have not been reported, to our knowledge. Accordingly, we report here a low-temperature, solution-based synthetic route that produces colloidal nanoparticles of highly crystalline CuCo$_2$S$_4$ at temperatures as low as 200 °C, which helps to facilitate the formation of smaller and more dispersed particles. We confirm the colocalization of Cu and Co in the nanoparticles and also study the process by which they form, providing insights that we anticipate will be useful in the colloidal synthesis of other mixed-metal thiospinel nanoparticles. CuCo$_2$S$_4$ has been shown to be active for electrocatalytic oxygen reduction,$^{12}$ and other thiospinels have also been studied as catalysts for the oxygen evolution.
reaction (OER). Given their small size and high dispersibility, we therefore studied the electrocatalytic properties of the colloidally synthesized CuCo$_2$S$_4$ nanoparticles for the OER in alkaline aqueous solutions.

2.2 Experimental

2.2.1 Materials

All chemicals were used as received. Cobalt(III) acetylacetonate [99.99%, trace metals basis], copper(II) acetylacetonate [≥99.99%, trace metals basis], Nafion [perfluorinated ion-exchange resin, 5 wt %], and tri-$n$-octylphosphine oxide [TOPO, 99%] were purchased from Sigma-Aldrich. Sulfur powder (~325 mesh, 99.5%) and oleic acid [OLAC, tech. 90%] were purchased from Alfa Aesar. Oleylamine [OLAM, > 50%] was purchased from TCI America. Solvents, including hexanes and isopropanol (IPA), were all of analytical grade. All syntheses were carried out under argon, using standard Schlenk line techniques.

2.2.2 Synthesis of Cu$_2$CoS$_4$ Nanoparticles

In a typical synthesis, 10 mL OLAM and 1.0 mL OLAC were mixed with copper(II) acetylacetonate (39.3 mg, 0.15 mmol), cobalt(III) acetylacetonate (178 mg, 0.5 mmol), and 0.15 g of TOPO in a 50-mL three-neck flask. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water. The mixture was then heated to 200 °C under argon over 10 min. At this point, sulfur (32 mg, 1 mmol) dissolved in 3 mL of OLAM was injected into the solution. Once the temperature returned to 200 °C, the solution was allowed to react for 1 h. After the reaction was complete, the heating mantle was removed, and the resulting black solution was allowed to cool to room temperature. The solution was removed and cleaned using a 5:1 IPA/hexanes mixture. The product was collected by centrifugation (12 000 rpm, 5 min). This cleaning process was repeated twice more.
2.2.3 Electrochemical Measurements

All electrochemical measurements were obtained using a Gamry Instruments Reference 600 potentiostat. The working electrodes consisted of 5 mm glassy carbon disks, with a surface area of 0.196 cm$^2$. The glassy carbon electrodes were polished with alumina before each use. Samples were prepared for analysis by first dispersing 2.5 mg of catalyst in 0.15 mL of Nafion solution and 0.85 mL of H$_2$O/IPA (4:1 ratio), and then sonicating for at least 30 min. Approximately 8 µL of the catalyst ink was deposited onto the glassy carbon substrates (≈0.1 mg cm$^{-2}$). The working electrodes were mounted onto a Pine Instrument Company rotating disk electrode (RDE), which utilized a Compact Pine Rotator. All measurements were performed in 1.0 M KOH, using a single-compartment three-electrode cell that contained a mercury/mercury oxide (Hg/HgO) reference electrode and a nickel mesh counter electrode. Before analysis, the electrolyte solution was purged with O$_2$ for at least 30 min. A constant stream of bubbling O$_2$ was maintained for all further electrochemical experiments. All measurements were performed at room temperature, 1200 rpm, and were $iR$-compensated. Polarization data were acquired using a sweep rate of 10 mV s$^{-1}$. Short-term electrochemical stability was measured by holding the current density galvanostatically at 10 mA cm$^{-2}$ for 15 h. Long-term electrochemical stability was assessed using cyclic voltammetric cycling between 0.2 and 0.8 V vs Hg/HgO at 50 mV s$^{-1}$.

2.2.4 Characterization

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker-AXS D8 Advance diffractometer with Cu Kα radiation and a LynxEye 1-D detector. The CrystalMaker/CrystalDiffract software package was used to simulate XRD patterns for CuCo$_2$S$_4$ and Co$_3$S$_4$. Microscopy samples were prepared by drop-casting a dilute solution of CuCo$_2$S$_4$ in hexanes onto a 400 mesh Formvar and carbon-coated Ni grid (Electron Microscopy Sciences). Transmission electron microscopy (TEM) images were obtained using a JEOL 1200 microscope at an accelerating voltage of 80 kV. High-resolution TEM (HRTEM) images, energy-dispersive
X-ray spectroscopy (EDS) data, and scanning transmission electron microscopy images coupled with EDS analysis (STEM-EDS) were performed using a FEI Titan³ G2 microscope equipped with a spherical aberration corrector on the probe-forming lens at an accelerating voltage of 200 kV. EDS maps were acquired in the Titan using ChemiSTEM quad detectors at a current of 0.6 nA. Standardless Cliff-Lorimer quantification was performed on the deconvoluted EDS line intensity data using the Bruker Esprit software. ES Vision software (Emispec) was used for EDS data processing. Selected-area electron diffraction (SAED) was performed on a JEOL-2010 LaB₆ TEM microscope operating at an accelerating voltage of 80 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra XPS system utilizing a monochromatic Al Kα source (1486.6 eV). High-resolution spectra were obtained at a pass energy of 23.5 eV, a step size of 0.1 eV, and a dwell time of either 600 or 1200 ms per step. All spectra were referenced to the C 1s peak (284.8 eV).

2.3 Results & Discussion

2.3.1 Synthesis of Cu₂CoS₄ Nanoparticles

For synthesis of the CuCo₂S₄ nanoparticles, copper(II) acetylacetonate and cobalt(III) acetylacetonate were heated to 200 °C in a mixture of oleylamine and oleic acid. At 200 °C, a solution of sulfur dissolved in oleylamine was injected into the reaction mixture and then allowed to continue heating for 1 h. A representative TEM image, shown in Figure 2-2a, indicates that the CuCo₂S₄ product consists of highly dispersed, quasispherical particles with an average diameter (across the largest part of each particle) of 10 ± 4 nm. The SAED pattern, shown in the inset to Figure 2-2a, is consistent with the formation of spinel-type CuCo₂S₄. A representative HRTEM image of a CuCo₂S₄ particle reveals that they are largely single-crystalline (Figure 2-
The lattice fringes observed by HRTEM were 3.3 Å, which correspond well to the (220) plane of spinel-type CuCo$_2$S$_4$, which has a spacing of 3.346 Å.

![Figure 2-2: (a) TEM image with corresponding SAED pattern (inset) for CuCo$_2$S$_4$ nanoparticles. (b) HRTEM image of a representative CuCo$_2$S$_4$ nanoparticle, highlighting the 3.3 Å lattice fringes that correspond to the (220) planes.](image)

The powder XRD pattern for the CuCo$_2$S$_4$ nanoparticles, shown in Figure 2-3, matches well with that which is expected for a thiospinel compound. The diffraction pattern can be indexed to a cubic unit cell with $a = 9.48(2)$ Å, which compares favorably with the lattice constant previously reported in the literature for bulk CuCo$_2$S$_4$ ($a = 9.478$ Å). The XRD pattern matches well with the SAED pattern shown previously in Figure 2-2a. The broad XRD peaks are also consistent with the nanocrystalline nature of the particles. Scherrer analysis of the XRD peak widths indicates an average grain size of approximately 9 nm, which is consistent with the particle diameters observed by TEM. The XRD pattern observed for the CuCo$_2$S$_4$ nanoparticles
also is close to that of Co$_2$S$_4$, which has the same crystal structure and similarly sized cations. The lattice constant associated with the CuCo$_2$S$_4$ nanoparticles is, however, measurably larger: $a = 9.48(2)$ Å for the CuCo$_2$S$_4$ nanoparticles vs $a = 9.478$ Å for bulk CuCo$_2$S$_4$ vs $a = 9.406$ Å for bulk Co$_2$S$_4$. Because of the small lattice constant difference between CuCo$_2$S$_4$ and Co$_2$S$_4$, several EDS analyses were used to confirm the incorporation of Cu, and therefore the formation of CuCo$_2$S$_4$.

![Experimental powder XRD pattern for the CuCo$_2$S$_4$ nanoparticles (top), with the simulated pattern of CuCo$_2$S$_4$ shown for comparison (bottom). Indexing corresponds to spinel-type CuCo$_2$S$_4$.](image)

EDS data for an ensemble of CuCo$_2$S$_4$ nanoparticles, shown in Figure 2-4, confirm the average elemental composition of the CuCo$_2$S$_4$ nanoparticles, indicating an atomic ratio for Cu to Co of approximately 1:2. These results also are consistent with the STEM-EDS elemental mapping data, shown in the inset to Figure 2-4. The combined STEM-EDS element maps indicate that the particles contain evenly distributed Cu (red), Co (green), and S (blue). The Cu appears to incorporate into each CuCo$_2$S$_4$ particle, and no cobalt sulfide impurities were observed by STEM-EDS. However, STEM-EDS element mapping did indicate the presence of a small
population of particles corresponding to an amorphous copper sulfide impurity, which did not appear by XRD or SAED (Figure 2-5). In total, this amorphous impurity was determined to account for approximately 5–10% of the overall sample when analyzed using STEM-EDS elemental mapping.

Figure 2-4: EDS spectrum and STEM-EDS elemental map (inset) of CuCo$_2$S$_4$ nanoparticles.
2.3.2 Phase Selectivity

As mentioned previously, nanoparticulate CuCo$_2$S$_4$ synthesized by heating to 300 °C in H$_2$S/H$_2$ decomposes to binary copper and cobalt sulfides under those same conditions. Accordingly, we were interested in studying the temperature dependence of CuCo$_2$S$_4$ nanoparticle formation and stability under the solution-based reaction conditions used here, which ultimately produces CuCo$_2$S$_4$ nanoparticles at a lower temperature (200 °C) than the H$_2$S/H$_2$ method (300 °C). We found that phase-pure CuCo$_2$S$_4$ nanoparticles could only be synthesized at temperatures at or below 200 °C. As the XRD patterns shown in Figure 2-6a illustrate, higher reaction temperatures led to the disappearance of CuCo$_2$S$_4$, with evidence of decomposition to the binary metal sulfides pentlandite (Co$_9$S$_8$) and roxbyite (Cu$_7$S$_4$). By 280 °C, CuCo$_2$S$_4$ was completely replaced by the binary sulfides. At temperatures below 200 °C, the XRD data indicates that pure-phase CuCo$_2$S$_4$ still forms, but TEM images reveal that the nanoparticles are morphologically different, with more anisotropic and irregular shapes (Figure 2-7).

Figure 2-5: STEM-EDS elemental map of CuCo$_2$S$_4$ nanoparticles containing small amounts of an amorphous copper sulfide impurity.
Figure 2-6: Experimental powder XRD patterns demonstrating the effect that varying (a) reaction temperatures and (b) initial metal precursor ratios has on the product that is produced. The reflections marked for Cu$_7$S$_4$, Co$_9$S$_8$, and Cu$_{1.8}$S do not correspond to every peak for each phase, but rather the unique, characteristic, and diagnostic reflections for each.
Similar behavior is observed in reactions at 200 °C when the Cu to Co precursor ratios are varied (Figure 2-6b). As more Cu is added to the system, instead of forming a Cu-rich $\text{Cu}_{1+x}\text{Co}_{2-x}\text{S}_4$ solid solution, the CuCo$_2$S$_4$ reflections are gradually replaced by those of Cu$_7$S$_4$. This copper sulfide impurity can be identified by the emergence of reflections at 47° and 49° 2θ for both the 1:1 and 2:1 Cu to Co ratios. When the Co in the reaction is completely replaced by Cu, the product is found to consist primarily of a mixture of Cu$_7$S$_4$ and digenite (Cu$_{1.8}$S). However, when no Cu is added to the synthesis, the product does not form Co$_3$S$_4$, but rather NiAs-type CoS.

**2.3.3 Electrocatalysis Using Cu$_2$CoS$_4$ Nanoparticles**

Having access to highly dispersible and small-diameter nanoparticles of CuCo$_2$S$_4$, we sought to evaluate their performance as electrocatalysts for the OER in alkaline aqueous solutions, given prior reports of CuCo$_2$S$_4$ as an electrocatalyst and also the reported OER activity of related binary thiospinels such as Co$_3$S$_4$. Linear sweep voltammetry (LSV) measurements were conducted using a glassy carbon electrode in an O$_2$-saturated electrolyte solution, sweeping from 0.0 to 0.9 V vs Hg/HgO. Overpotentials were calculated by first measuring the open-circuit
potential of a Pt mesh electrode in order to determine the RHE potential. This then allowed the \( \text{H}_2\text{O}/\text{O}_2 \) redox couple for the electrolyte solution to be calculated. The \( \text{CuCo}_2\text{S}_4 \) nanoparticles, at a low mass loading of 0.1 mg cm\(^{-2}\) on a glassy carbon electrode, produced an operationally relevant current density of 10 mA cm\(^{-2}\) at a relatively small OER overpotential of 395 mV (Figure 2-8). Compared to both a clean glassy carbon electrode and a comparable platinum electrode, the \( \text{CuCo}_2\text{S}_4 \) nanoparticles were much more active for the OER. The corresponding Tafel plot, shown in the inset to Figure 2-8, indicates a Tafel slope of 115 mV/decade. The observed overpotentials and Tafel slopes are higher than the best-performing OER catalysts in alkaline media, but still comparable. For example, at similar current densities (10 mA cm\(^{-2}\)), \( \text{Co}_3\text{O}_4 \) on N-doped reduced mildly oxidized graphene oxide has an overpotential of 310 mV and a Tafel slope of 67 mV/decade,\(^{18}\) \( \alpha\)-Ni(OH)\(_2\) has an overpotential of 331 mV and a Tafel slope of 42 mV/decade,\(^{19}\) and \((\text{Pr}_{0.5}\text{Ba}_{0.5})\text{CoO}_4\) has an overpotential of 300 mV and a Tafel slope of \( \sim90 \) mV/decade.\(^{20}\)

Figure 2-8: Polarization data in 1.0 M KOH for a \( \text{CuCo}_2\text{S}_4 \) nanoparticle electrode (green), along with Pt (orange) and glassy carbon (blue) electrodes for comparison. Inset shows corresponding Tafel plot for a \( \text{CuCo}_2\text{S}_4 \) electrode.
Given the close relationship between CuCo$_2$S$_4$ and Co$_3$S$_4$, as well as the known OER activity of Co$_3$S$_4$, Co$_3$S$_4$ nanoparticles were synthesized and evaluated for comparison. At similar mass loadings and current densities, the Co$_3$S$_4$ nanoparticles also had an OER overpotential of 395 mV, which is consistent with what is observed in the literature for this material. Despite small differences in surface areas due to slightly different particle sizes, the incorporation of copper into Co$_3$S$_4$ to form CuCo$_2$S$_4$ did not change the initial OER activity. Nanoparticles of the copper sulfide phase that was observed upon decomposition, Cu$_7$S$_4$, were also synthesized and evaluated, and were found to be much less active than either CuCo$_2$S$_4$ or Co$_3$S$_4$, with an OER overpotential at 10 mA cm$^{-2}$ of 559 mV. Despite the observation that the OER activity of CuCo$_2$S$_4$ is not significantly different from Co$_3$S$_4$, its electrocatalytic activity is still comparable to some of the most active, Earth-abundant catalysts in alkaline aqueous media to date, which have OER overpotentials that typically fall between 300 mV and 500 mV.

The alkaline stability of the CuCo$_2$S$_4$ nanoparticles was first evaluated galvanostatically by holding at a current density of 10 mA cm$^{-2}$ for 15 h (Figure 2-9a). During the 15-h test, the OER overpotential increased by approximately 45 mV to a final overpotential of 440 mV. Accelerated degradation studies were also performed using cyclic voltammetry (CV), as shown in Figure 2-9b. Here, the electrocatalyst was cycled between 0.2 and 0.8 V vs Hg/HgO. After 500 cycles, the overpotential of the CuCo$_2$S$_4$ nanoparticles increased from 395 to approximately 450 mV. We attribute the loss in activity during cycling and galvanostatic testing to particle desorption off of the glassy carbon substrate and oxidation of the particles, as discussed below.
To better understand the catalytic performance of the CuCo$_2$S$_4$ nanoparticles, XPS was used to characterize the surface. XPS revealed that the surface of the as-synthesized CuCo$_2$S$_4$ nanoparticles consisted primarily of carbon and oxygen, which is expected due to the use of oleic acid as an organic surface-stabilizing agent. Cu, Co, and S were also present. However, the low intensity of the carbon peaks resulting from C–O bonds at 286.5–289.0 eV in the C 1s spectrum (Figure 2-10a), despite the strong O 1s signal (Figure 2-10b), indicates that the observed oxygen is not due to just surface ligands, but also to surface oxidation. It is well-known that surface oxidation readily occurs in bulk CuCo$_2$S$_4$ upon exposure to air. This is readily apparent in the CuCo$_2$S$_4$ nanoparticles upon examination of the Cu 2p, Co 2p, and S 2p regions of the XPS spectra (Figure 2-10c–e). The spin-orbit doublet corresponding to Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ is readily observed in the Cu 2p region at 952.2 and 932.3 eV ($\Delta E = 19.9$ eV), respectively. However, the emergence of a weak, higher binding energy peak observed at 934 eV in the Cu 2p region (Figure 2-10c) is typical of Cu$^{2+}$ hydroxyl and/or sulfoxy species caused by oxidation. The Co 2p$_{3/2}$ region also shows similar behavior, as evidenced by a broad peak at 781 eV (Figure 2-10d),
which can also be attributed to Co$^{2+}$ hydroxyl and/or sulfoxyl species.$^{30}$ Signs of oxidation were further prevalent in the S 2p region, where in addition to the overlapping spin-orbit doublets (S 2p$_{1/2}$ and S 2p$_{3/2}$) present at 162.4 and 161.3 eV ($\Delta E = 1.1$ eV), respectively, a peak attributed to sulfate was also observed at 169 eV (Figure 2-10e).$^{30,31}$ The O 1s region was broad, containing overlapping peaks that originated from oxide and hydroxyl groups (Figure 2-10b).

Figure 2-10: XPS high-resolution spectra of the (a) C 1s, (b) O 1s, (c) Cu 2p, (d) Co 2p$_{3/2}$, and (e) S 2p regions for the CuCo$_2$S$_4$ nanoparticles.

Characterization of the oxidation occurring at the CuCo$_2$S$_4$ surface helps to rationalize the observed OER activity and corresponding degradation upon prolonged testing. Cycling at such high oxidative potentials likely serves to fully oxidize the already partially oxidized CuCo$_2$S$_4$ surface. Indeed, the OER activity after cycling correlates well with that of other CuCo$_2$O$_4$ catalysts, which display OER overpotentials at 10 mA cm$^{-2}$ ranging from 420 to 450 mV.$^{32-34}$ It
is also well-known, on the basis of Pourbaix diagrams, that oxides of Cu and Co become hydroxides in strongly alkaline aqueous solutions under highly positive potentials. This suggests that the 3d transition metal sulfide nanoparticles, including CuCo$_2$S$_4$, and possibly other related materials as well, may be best classified as precursors to 3d transition metal oxides and hydroxides that are already well-known OER catalysts in alkaline media, rather than as catalysts themselves.

2.4 Conclusions

In summary, the thiospinel CuCo$_2$S$_4$ has been synthesized as nanoparticles using a low-temperature, solution-based chemical route. The CuCo$_2$S$_4$ nanoparticles were found to be active electrocatalysts for the OER, with initial OER overpotentials of approximately 395 mV required to produce operationally relevant current densities of 10 mA cm$^{-2}$. However, the CuCo$_2$S$_4$ nanoparticles readily oxidize upon exposure to air, which is believed to lead to a decrease in activity during accelerated degradation studies.

2.5 References


Chapter 3

Investigation of Transition Metal Sulfide Nanoparticles as Electrocatalysts for the Hydrogen Evolution Reaction

3.1 Introduction

When designing new systems or picking a group of materials to target, it is often beneficial to start from what we in the scientific community already know. Therefore, when considering new transition metal sulfide materials to target that may hold potential to be active hydrogen evolution reaction (HER) catalysts, the most obvious place to start is with MoS$_2$. Molybdenum sulfides, particularly MoS$_2$, are some of the most studied Earth-abundant, acid stable HER catalysts. Though originally shown to be relatively inactive towards HER, it was later determined that the material’s morphology played a crucial role in determining whether or not it was catalytically active.$^{1-3}$ Theoretical and experimental data concluded that the edge sites, specifically the Mo-edges (10$ar{1}$0) with 50% sulfur adsorption, would be ideal for hydrogen evolution. To further enhance the material’s HER activity, small amounts of cobalt or tungsten were observed to increase exposure of the (10$ar{1}$0) Mo-edges by selectively binding to the relatively inactive S-edges.$^4$

Not only is MoS$_2$ a very active HER catalyst, but it is also a highly active catalyst for hydrodesulfurization (HDS).$^{2,5}$ HDS catalysts are commonly used to remove sulfur impurities from natural gas and other refined petroleum products.$^6$ Regardless of its use, both HER and HDS rely upon a material’s ability to reversibly bind hydrogen to its surface. For HDS, H$_2$ dissociates to produce H$_2$S, thereby eliminating sulfur, while adsorbed hydrogen atoms on the surface of a HER catalyst can react to form H$_2$.$^{7,8}$ In the case of MoS$_2$, the active sites for both
HDS and the HER are believed to be the under-coordinated Mo-edges as opposed to the high surface area basal planes.\textsuperscript{1,2,8,9} Furthermore, one of the best known catalysts for HDS, a cobalt-molybdenum material with some sulfur incorporation, is very similar to that of the highly active cobalt-promoted MoS\textsubscript{2} catalyst used for HER. A correlation between HDS and the HER is also seen in a number of other catalyst systems, including NiMo,\textsuperscript{10,11} Mo\textsubscript{2}C,\textsuperscript{12,13} and Ni\textsubscript{2}P.\textsuperscript{14} Given these similarities, we hypothesize that materials that are commonly used for HDS, may have the potential to be active electrocatalysts for the HER as well.

In addition to MoS\textsubscript{2} and its related systems, there are also a large number of additional transition metal sulfides that are active catalysts for HDS. In an article published by Pecoraro and Chianelli, the authors systematically discuss a number of notable metal sulfide HDS catalysts, specifically addressing how they compare to one another.\textsuperscript{8} Just as is the case for HER, some of the most active HDS catalysts consist of noble metal sulfides, providing further support for a potential correlation between HDS and HER catalysts. However, these noble metal sulfides may not be the best targets due to their limited availability and cost. For this reason, we have focused on the more Earth-abundant first-row transition metal sulfides. A number of more Earth-abundant first-row transition metal sulfides appear to be active for HDS, though not as much so as the 4d and 5d transition metal sulfide catalysts. Of particular interest are the metal sulfides corresponding to that of cobalt (Co\textsubscript{9}S\textsubscript{8}) and nickel (Ni\textsubscript{3}S\textsubscript{2}), which appear to be some of the most active first-row HDS catalysts. Cobalt sulfide itself is already of interest, as it was used to help promote hydrogen absorption site along the Mo-edge in MoS\textsubscript{2}.\textsuperscript{4} Therefore, given their Earth-abundant nature, as well as their longstanding use as HDS catalysts, cobalt and nickel sulfides are interesting targets for potential HER catalysts. Herein we report a phase-selective synthesis of a number of cobalt (Co\textsubscript{3}S\textsubscript{4}, CoS, Co\textsubscript{9}S\textsubscript{8}) and nickel sulfide (Ni\textsubscript{3}S\textsubscript{2}, α-NiS, Ni\textsubscript{9}S\textsubscript{8}, Ni\textsubscript{3}S\textsubscript{4}) nanoparticle systems, which we then analyze for catalytic activity with respect to the HER.
3.2 Experimental

3.2.1 Materials

All chemicals were used as received. Nickel(II) acetylacetonate [95%], tri-\textit{n}-octylphosphine oxide [TOPO, 99%], 1-octadecene [ODE, 90%], 1-dodecanethiol [DDT, $\geq$98%], cobalt(II) chloride [CoCl$_2$], benzyl ether [98%], carbon disulfide [CS$_2$, anhydrous, $\geq$99%], and titanium foil [99.7%, 0.25 mm thickness] were purchased from Sigma-Aldrich. Sulfur powder [$\sim$325 mesh, 99.5%], octacarbonyl dicobalt [stabilized with 1-5% hexane], 1,2-dichlorobenzene [DCB, 99%], and oleic acid [OLAC, tech. 90%] were purchased from Alfa Aesar. Oleylamine [OLAM, $>50\%$], tri-\textit{n}-octylphosphine [TOP, $>85.0\%$], and 1,2-hexadecanediol [$>98\%$] were purchased from TCI America. Chloroform [CHCl$_3$] was purchased from EMD Millipore Corp. Solvents, including hexanes, acetone, ethanol, and isopropanol (IPA), were all of analytical grade. All syntheses were carried out under argon, using standard Schlenk line techniques. Silver paint was purchased from SPI supplies and the two-part epoxy adhesive [HYSOL 9460] was purchased from McMaster-Carr.

3.2.2 Synthesis of Hollow Co$_3$S$_4$ Nanoparticles

Co$_3$S$_4$ nanoparticles were prepared via a previously reported method by Alivisatos and coworkers.$^{15}$ In a 100-mL three-neck flask, 0.1 g TOPO was degassed under a blanket of argon at 60 °C for 20 minutes. To this solution, 0.1 mL OLAC and 15 mL DCB were added and heated to reflux ($\sim$180 °C). Cobalt nanoparticles were first synthesized by injecting into the reaction solution octacarbonyl dicobalt (360 mg, 1.07 mmol) that had been dissolved in 3 mL DCB. After 1 minute, a solution containing sulfur (130 mg, 4.0 mmol) dissolved in 5 mL DCB was also injected into the solution and allowed to react for 3 additional minutes. The resulting black-colored solution was then immediately removed from the hot flask and transferred to an air-free,
argon-filled vial, and then cooled to room temperature. The solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.

3.2.3 Synthesis of \( \text{Co}_3\text{S}_4 \) Nanoparticles

This synthesis of \( \text{Co}_3\text{S}_4 \) nanoparticles was adapted from a previously reported procedure by Jasieniak and coworkers.\(^{16} \) In a 50-mL three-neck flask, 9 mL of OLAM and 3 mL DDT were added under a blanket of argon. To this solution, 0.2 mL \( \text{CS}_2 \) was slowly added drop-wise while stirring to ensure the solution did not exceed the boiling point of \( \text{CS}_2 \) (46 °C). The reaction solution was stirred under argon for 10 minutes, at which point \( \text{CoCl}_2 \) (195 mg, 1.50 mmol) was added to the flask. The new mixture was heated under vacuum for 30 minutes at 110 °C to degas and remove any residual water. While heating, a color change from green to deep purple, almost black, was observed between 70 and 80 °C. Once degassed, the reaction solution was further heated under an atmosphere of argon to 250 °C, and maintained at that temperature for an additional 30 minutes. After cooling to roughly 60 °C, approximately 2 mL of chloroform, and 3 mL of acetone was added to the reaction flask. The resulting solution was centrifuged in glass centrifuge tubes (7000 rpm) to precipitate the synthesized nanoparticles. After centrifugation, the supernatant was discarded, and the product was redispersed in a 10:1 ethanol/hexanes solution, which was centrifuged again. This process was repeated twice.

3.2.4 Synthesis of \( \text{CoS} \) Nanoparticles

In a typical synthesis, 9 mL OLAM and 1.0 mL OLAC were mixed with \( \text{CoCl}_2 \) (130 mg, 1 mmol) and sulfur (32 mg, 1 mmol) in a 50-mL three-neck flask. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water. The mixture was then heated to 220 °C under argon over 15 min. Once at the desired 220 °C, the solution was allowed to react for 1 h. After the reaction was complete, the heating mantle was removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.
3.2.5 Synthesis of Co$_9$S$_8$ Nanoparticles

This synthesis of Co$_9$S$_8$ nanoparticles was adapted from a previously reported procedure by Schaak and coworkers.\textsuperscript{17} The Co$_3$S$_4$ nanoparticles starting material used in this procedure are taken from the hollow Co$_3$S$_4$ nanoparticles synthesized above. In a 50-mL three-neck flask, 10 mg of the previously synthesized Co$_3$S$_4$ nanoparticles are mixed with a 5 mL excess of TOP. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water. The mixture was then heated to 250 °C under argon over 20 min. Once at the desired 250 °C, the solution was allowed to react for 1 h. After the reaction was complete, the heating mantle was removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.

3.2.6 Synthesis of Ni$_3$S$_2$ Nanoparticles

In a typical synthesis, 8.5 mL ODE, 1.5 mL OLAM, and 0.5 mL OLAC were mixed with nickel(II) acetylacetonate (405 mg, 1.58 mmol) and sulfur (24.0 mg, 0.750 mmol) in a 50-mL three-neck flask. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water. The mixture was then heated to 180 °C under argon over 10 min. Once at the desired 180 °C, the solution was allowed to react for 30 min. Care must be taken to not let the reaction go over 200 °C, as crystalline nickel nanoparticles will begin to form above this temperature. After the reaction was complete, the heating mantle was removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.

3.2.7 Synthesis of α-NiS Nanoparticles

In order to synthesize α-NiS nanoparticles, nickel nanoparticles were first synthesized and used as precursor particles. Nickel(II) acetylacetonate (257 mg, 1 mmol) was mixed with 8.5 mL benzyl ether, 1 mL OLAM, and 0.5 mL TOP in a 50 mL three-neck flask. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual
water. The mixture was then heated to 230 °C under argon over 10 min. Once the temperature reached 230 °C, the solution was allowed to react for 45 min. A color change to dark brown eventually became apparent, indicative of the reduction of the nickel(II) acetylacetonate, forming nickel nanoparticles. After the reaction was complete, the heating mantle was removed, and the resulting brown solution was allowed to cool to room temperature. The resulting solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.

The as-made nickel nanoparticles were then sulfidated in order to make α-NiS nanoparticles. The nickel nanoparticles dispersed in 200 μL hexanes were added to another 50 mL three-neck flask along with 7.5 mL OLAM and 0.5 mL OLAC. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water and hexanes. The mixture was then heated to 230 °C under argon over 15 min. Once the temperature reached 230 °C, a solution of sulfur (52 mg, 1.6 mmol) dissolved in 2 mL OLAM was injected into the reaction mixture. After the temperature returned to 230 °C, the solution was allowed to react for 1 h. After the reaction was complete, the heating mantle was removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to those used to clean the nickel nanoparticles.

3.2.8 Synthesis of Ni₉S₈ Nanorods

To synthesize Ni₉S₈ nanorods, nickel nanoparticles were first needed. The nickel nanoparticles were synthesized in the same manner that they were for the α-NiS nanoparticles. The as-made nickel nanoparticles were then sulfidated in order to make Ni₉S₈ nanorods. The nickel nanoparticles dispersed in 200 μL hexanes were added to another 50 mL three-neck flask along with 10 mL OLAM and 2 mL DDT. The mixture was heated to 110 °C under vacuum, and held at this temperature for 30 min to drive off any residual water and hexanes. The mixture was then heated to 240 °C under argon over 15 min. Once the temperature reached 240 °C, the solution was allowed to react for 3.5 h. After the reaction was complete, the heating mantle was
removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to those used to clean the nickel nanoparticles.

3.2.9 Synthesis of Ni₃S₄ Nanopyramids

Ni₃S₄ nanopyramids were prepared via a previously reported method by Batteas and coworkers. In a 50-mL three-neck flask, 5 mL of ODE, 0.6 mL OLAM, and 0.2 mL OLAC with mixed with nickel(II) acetylacetonate (405 mg, 1.6 mmol) and 1,2-hexadecanediol (105 mg, 0.4 mmol) and heated to 90 °C under a blanket of argon. After reaching 90 °C, 0.45 mL DDT was injected into the reaction mixture. The reaction temperature was then raised to 120 °C and maintained for 40 min, before being heated to 225 °C where it remained for 2 additional minutes. After the reaction was complete, the heating mantle was removed, and the resulting solution was allowed to cool to room temperature. The solution was centrifuged and cleaned in a manner similar to that described in Chapter 2.

3.2.10 Preparation of Working Electrodes

To make working electrodes for use in electrochemical experiments, a stock solution of the catalyst material (with a known concentration) was prepared. In 5-10 μL increments, the catalyst stock solution was deposited onto 0.2 cm² samples of Ti foil to achieve a mass loading of approximately 1.0 mg cm⁻², and allowed to dry. The foils were then affixed with silver paint to a polyvinylchloride-coated copper wire that had been threaded through a 6 mm diameter glass capillary. To-part epoxy adhesive was then used to cover all surfaces except for the catalyst-coated side of the foil.

3.2.11 Electrochemical Measurements

All electrochemical measurements were obtained using a Gamry Instruments Reference 600 potentiostat. The working electrodes were prepared using Ti foil as described previously. Measurements under alkaline conditions were performed in 1.0 M KOH, using a single-compartment three-electrode cell that contained a mercury/mercury oxide (Hg/HgO) reference
electrode and a nickel mesh counter electrode. Measurements under acidic conditions were performed in 0.5 M H₂SO₄, using a two-compartment, three-electrode cell that contained either a saturated calomel electrode (SCE) or a mercury/mercurous sulfate (Hg/Hg₂SO₄) reference electrode, and a graphite rod counter electrode. Before analysis, the electrolyte solution was purged with H₂ for at least 30 min. A constant stream of bubbling H₂ was maintained for all further electrochemical experiments. Polarization data were acquired using a sweep rate of 10 mV s⁻¹. Short-term electrochemical stability was measured by holding the current density galvanostatically at 10 mA cm⁻² over varied periods of time. Long-term electrochemical stability was assessed using cyclic voltammetric cycling between 0.1 and -0.4 V vs RHE at 50 mV s⁻¹.

3.2.12 Characterization

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker-AXS D8 Advance diffractometer with Cu Kα radiation and a LynxEye 1-D detector. The CrystalMaker/CrystalDiffract software package was used to simulate XRD patterns for comparison. Microscopy samples were prepared by drop-casting a dilute solution of the sample material in hexanes onto a 400 mesh Formvar and carbon-coated Cu grid (Electron Microscopy Sciences). Transmission electron microscopy (TEM) images were obtained using a JEOL 1200 microscope at an accelerating voltage of 80 kV.

3.3 Cobalt Sulfide Electrocatalysts

3.3.1 Linnaeite (Co₃S₄) Nanoparticles

Cobalt sulfide nanoparticles, Co₃S₄, were synthesized via two distinctly separate preparations. The first method was taken from a previously reported method by Alivisatos and coworkers.¹⁵ Co₃S₄ nanoparticles were synthesized by sulfidating cobalt nanoparticles in a hot solution of TOPO, OLAC, and DCB at 180 °C. Powder XRD data, shown in Figure 3-1a,
confirmed the presence of spinel-type Co$_3$S$_4$. No trace of cobalt was present in the sample, suggesting that the initial cobalt nanoparticles had been completely converted to the sulfide. A representative TEM image, shown in Figure 3-1b, indicates that the Co$_3$S$_4$ product consists of hollow, highly-dispersed, spherical particles, with an average diameter of 16 ± 4 nm. Hollow nanoparticles of Co$_3$S$_4$ form in solution from the reaction of cobalt nanoparticles with sulfur, via a nanoscale Kirkendall pathway.$^{19-22}$

Co$_3$S$_4$ nanoparticles were also synthesized via a second method that was adapted from a previously reported procedure by Jasieniak and coworkers.$^{16}$ In this synthetic procedure, Co$_3$S$_4$
nanoparticles were produced through the generation and decomposition of cobalt oleyldithiocarbamates and dodecyltrithiocarbonates in solution at 250 °C. Upon completion of the decomposition of the initial metal precursors, the solution yielded a black precipitate that was readily isolatable. Powder XRD of the sample confirmed the presence of spinel-type \( \text{Co}_3\text{S}_4 \), with a diffraction pattern matching that of the hollow \( \text{Co}_3\text{S}_4 \) nanoparticles shown above in Figure 3-1a. However, unlike that previous \( \text{Co}_3\text{S}_4 \) sample, these nanoparticles were not hollow. Instead, TEM images indicated that the nanoparticles were composed of an agglomerated mixture of nanoparticles with a wide range of particle morphologies, with lengths on the order of 35-50 nm (Figure 3-1c). Though several attempts were made to isolate one specific morphology, the \( \text{Co}_3\text{S}_4 \) nanoparticles could not be separated from one another.

Both sets of \( \text{Co}_3\text{S}_4 \) nanoparticles were deposited onto titanium substrates and studied electrochemically in both 1 M KOH and 0.5 M \( \text{H}_2\text{SO}_4 \). The representative polarization curves are shown in Figure 3-2. Under alkaline conditions (Figure 3-2a), the \( \text{Co}_3\text{S}_4 \) nanoparticles appear to be moderately active with respect to the HER. At loading densities of approximately 1.0 mg cm\(^{-2}\), the hollow \( \text{Co}_3\text{S}_4 \) nanoparticles achieved a current density of -10 mA cm\(^{-2}\) at an overpotential of -300 mV vs RHE. The agglomerated \( \text{Co}_3\text{S}_4 \) nanoparticle mixture behaved very similarly, where at similar loadings, the nanoparticles achieved a current density of -10 mA cm\(^{-2}\) at an overpotential of -285 mV vs RHE. In terms of stability in alkaline media, the \( \text{Co}_3\text{S}_4 \) nanoparticles, which were evaluated galvanostatically by holding at a current density of -10 mA cm\(^{-2}\), were determined to be only moderately stable, showing a 50 mV increase in overpotential just over 3 h into the run.

Both sets of \( \text{Co}_3\text{S}_4 \) nanoparticles were also tested under acidic conditions, however, the material was relatively unstable, and fell off the Ti substrate within 30 minutes. This behavior is most likely due to the fact that most sulfides tend to dissolve in solution when exposed to strongly acidic environments. The effects of the acid on the \( \text{Co}_3\text{S}_4 \) nanoparticles are further demonstrated
when some of the powdered sample is allowed to set in 0.5 M H₂SO₄. After 12 hours, trace amounts of CoSO₄ become visible in the XRD pattern. The fact that the CoSO₄ impurity is visible on the XRD pattern suggests that the bulk of the material is being affected by the acid, rather than what is only on the surface. Despite the materials’ instability in acid, the Co₃S₄ nanoparticles did show promising initial HER activity, especially the agglomerated Co₃S₄ nanoparticles with mixed morphologies (Figure 3-2b). At loading densities of approximately 1.0 mg cm⁻², the agglomerated Co₃S₄ nanoparticles achieved a current density of -10 mA cm⁻² at an overpotential of -165 mV vs RHE. In an attempt to preserve this observed HER activity, the particles were both annealed, with the aim of creating better contact with the Ti substrate, and deposited onto the substrate using Nafion. When annealed, even at relatively low temperatures (200 °C), the material began to convert to a more sulfur-deficient cobalt sulfide phase, Co₉S₈. In an attempt to inhibit the effect of the acid, Nafion, which was used to allow for better continuous contact with the electrode, but still allow for transference of protons, was also unsuccessful in stabilizing the Co₃S₄ nanoparticles in acid.
3.3.2 NiAs-Type Cobalt Sulfide (CoS) Nanoparticles

Cobalt sulfide nanoparticles with a 1:1 stoichiometry, CoS, were synthesized using a one-pot heat-up method. To synthesize the CoS nanoparticles, cobalt(II) chloride and sulfur were added to a reaction flask and heated to 220 °C in a solution of OLAM and OLAC for a period of 1 h. Powder XRD data, shown in Figure 3-3a, confirmed the presence of NiAs-type CoS. The diffraction pattern contained no additional impurities. A TEM image representative of the CoS product is shown in Figure 3-3b. The nanoparticles represented in the image consist of a large agglomeration of different sized particles. Some of the smaller particles (5-20 nm) appear to be almost quasi-spherical in nature, while the larger particles (20-45 nm) appear almost faceted. This wide-ranging size distribution is indicative of the synthetic method employed to synthesize the particles, where all of the precursors are heated together in solution from the start.
Polarization data for the CoS nanoparticles in 1 M KOH is shown in Figure 3-3c. Under alkaline conditions, the CoS nanoparticles appear to be moderately active with respect to the HER, although less active than the Co$_3$S$_4$ nanoparticles looked at previously. At loading densities of approximately 1.0 mg cm$^{-2}$, the CoS nanoparticles achieved a current density of -10 mA cm$^{-2}$ at an overpotential of -360 mV vs RHE. When tested under highly acidic conditions, the CoS
particles were unstable. Given the differences in structure, size, and morphology, the HER activity of the CoS nanoparticles is expected to be somewhat different from Co₃S₄. However, in order to better understand the role that these factors play with respect to HER activity, particles with a much narrower size distribution and more similar morphology are needed.

3.3.3 Cobalt Pentlandite (Co₉S₈) Nanoparticles

Cobalt sulfide nanoparticles of the phase Co₉S₈ were synthesized from a method that was adapted from a previously reported procedure by Schaak and coworkers.¹⁷ This method utilizes conversion chemistry by means of a TOP extraction in order to convert the hollow Co₃S₄ nanoparticles into the sulfur-deficient Co₉S₈ nanoparticles. TOP, a common ligand used to stabilize the surfaces of nanoparticles, readily reacts with chalcogens to form TOP-X (X = S, Se, Te) complexes. Therefore, given its affinity for sulfur, as well as relatively large formation constant for TOP-S, the ligand will readily extract sulfur from a metal sulfide such as Co₃S₄, transforming it into its most stable metal-rich phase.¹⁷ Powder XRD, shown in Figure 3-4a, confirms the success of the TOP extraction. The diffraction pattern contained no visible impurities. A representative TEM image, shown in Figure 3-4b, indicates that in addition to obtaining phase selectivity, morphology retention was also observed. The product contained hollow Co₉S₈ nanoparticles, similar to the starting sulfur-rich Co₃S₄, with an average diameter of 15 ± 5 nm.
Electrochemical data for the Co$_9$S$_8$ nanoparticles deposited on Ti foil substrates is shown in Figure 3-4c. Under alkaline conditions, the Co$_9$S$_8$ nanoparticles appear to be moderately active with respect to the HER and comparable to what was already observed for Co$_3$S$_4$ nanoparticles. At loading densities of approximately 1.0 mg cm$^{-2}$, the Co$_9$S$_8$ nanoparticles achieved a current density of $-10$ mA cm$^{-2}$ at an overpotential of $-300$ mV vs RHE. Despite their different crystal
structures, both Co$_8$S$_8$ and Co$_3$S$_4$ have very similar HER activities. It is possible that these similarities may be attributed to the retention of both the size and morphology of the particles. Like the Co$_3$S$_4$ nanoparticles, the Co$_8$S$_8$ nanoparticles were only somewhat stable under alkaline conditions, decreasing by 50 mV only after 1 h when holding the current density constant at -10 mA cm$^{-2}$. When tested under highly acidic conditions, the Co$_9$S$_8$ particles were unstable.

3.4 Nickel Sulfide Electrocatalysts

3.4.1 Heazlewoodite (Ni$_3$S$_2$) Nanoparticles

Like the previously synthesized cobalt sulfide nanoparticle phases, nickel sulfide nanoparticles were synthesized in a similar fashion. Ni$_3$S$_2$ nanoparticles were synthesized using a one-pot heat-up method. To synthesize the Ni$_3$S$_2$ nanoparticles, nickel(II) acetylacetonate and sulfur were added to a reaction flask and heated to 180 °C in a solution of ODE, OLAM, and OLAC for a period of 30 min. Powder XRD data, shown in Figure 3-5a, confirmed the presence of heazlewoodite-type Ni$_3$S$_2$. The diffraction pattern contained no additional impurities. However, if the reaction temperature was allowed to go above 200 °C, nickel particles would begin to crystallize. For this reason, maintaining a relatively low temperature of 180 °C was necessary to prevent nickel contamination. Representative TEM images (Figure 3-5b) show slightly agglomerated particles with a quasi-spherical morphology and an average diameter of 7 ± 3 nm.
Polarization data for the Ni$_3$S$_2$ nanoparticles in 1 M KOH is shown in Figure 3-5c. Under alkaline conditions, the Ni$_3$S$_2$ nanoparticles appear to be moderately active with respect to the HER, with activities on par with some of the most active cobalt sulfides studied in this work. At loading densities of approximately 1.0 mg cm$^{-2}$, the Ni$_3$S$_2$ nanoparticles achieved a current density of -10 mA cm$^{-2}$ at an overpotential of -300 mV vs RHE. However, unlike the cobalt
sulfide materials already examined, Ni$_3$S$_2$ is quite stable under alkaline conditions for extended periods of time. The alkaline stability of the Ni$_3$S$_2$ nanoparticles was first evaluated galvanostatically by holding at a current density of -10 mA cm$^{-2}$ for 18 h (Figure 3-6a). During the 18-h test, the HER overpotential decreased by approximately 50 mV to a final overpotential of roughly -250 mV vs RHE. Not only does Ni$_3$S$_2$ appear to be stable under alkaline conditions, but it also appears as though it gets better. Accelerated degradation studies were also performed to corroborate this data using cyclic voltammetry (CV), as shown in Figure 3-6b. Here, the electrocatalyst was cycled between 0.1 and -0.4 V vs RHE. After 1000 cycles, the overpotential of the Ni$_3$S$_2$ nanoparticles decreased from -300 to approximately -250 mV vs RHE. Despite its success in alkaline environment, when tested under highly acidic conditions, the Ni$_3$S$_2$ nanoparticles were still unstable.

Figure 3-6: (a) Plot of potential vs time for a Ni$_3$S$_2$ electrode held for 18 h at a constant current density of 10 mA cm$^{-2}$. (b) Plot of current density vs potential for a Ni$_3$S$_2$ electrode initially (purple), and also after 1000 CV sweeps (green) between 0.1 and -0.4 V vs RHE. Measurements performed in 1 M KOH.
3.4.2 High-Temperature Nickel Sulfide ($\alpha$-NiS) Nanoparticles

Nickel sulfide nanoparticles of the phase $\alpha$-NiS were synthesized in a two-step process. The first step involved the synthesis of nickel nanoparticles by means of reducing the initial nickel(II) acetylacetonate precursor. Once obtained, these nickel nanoparticles are sulfidated by means of a hot injection of sulfur dissolved in OLAM at 230 °C. Powder XRD data, shown in Figure 3-7a, confirmed the presence of the $\alpha$-NiS polymorph. No trace of nickel impurities were observed to be present in the sample via XRD, suggesting that the initial nickel nanoparticles had been completely converted to the sulfide. The nanoparticles themselves, as shown in the TEM image in Figure 3-7b, were perfectly monodisperse and mostly spherical, with an average diameter of 7 ± 2 nm.
Polarization data for the α-NiS polymorph under alkaline conditions is shown in Figure 3-7c. Under these conditions, the α-NiS nanoparticles appear to be only slightly to moderately active with respect to the HER. At loading densities of approximately 1.0 mg cm⁻², the α-NiS nanoparticles achieved a current density of -10 mA cm⁻² at an overpotential of -350 mV vs RHE. Furthermore, preliminary galvanostatic testing revealed an initial 50 mV increase in overpotential
while holding at a current density of -10 mA cm$^{-2}$ for 3 h. In comparison to the Ni$_3$S$_2$ nanoparticles, which have a similar size and morphology, the α-NiS nanoparticles are much less active. When tested for HER activity under highly acidic conditions, the α-NiS nanoparticles were observed to be relatively inactive.

3.4.3 Nickel Pentlandite (Ni$_9$S$_8$) Nanorods

Nickel pentlandite, Ni$_9$S$_8$, nanorods were prepared in a manner very similar to that of the α-NiS nanoparticles. Both synthetic procedures involved the synthesis of nickel nanoparticles by means of reducing an initial nickel(II) acetylacetonate precursor as the first step. This in turn is followed by selective sulfidation of the nickel nanoparticles to produce the desired product. However, instead of using sulfur powder as the sulfur source, DDT is used and heated at 240 °C until it decomposes, forming the desired Ni$_9$S$_8$ particles. Powder XRD analysis, shown in Figure 3-8a, confirms the presence and purity of the sample, ruling out any potential nickel contamination. The representative TEM image of the particles is shown in Figure 3-8b. The nanoparticles represented in the image consist of a large agglomeration of what appear to be nanorods. The observed nanorods are quite large, with an average length of 68 ± 6 nm, and a width of 14 ± 4 nm.
Electrochemical data pertaining to the synthesized Ni$_9$S$_8$ nanorods is shown in Figure 3-8c. Under alkaline conditions, the Ni$_9$S$_8$ nanoparticles appear to be only slightly to moderately active with respect to the HER. At loading densities of approximately 1.0 mg cm$^{-2}$, the Ni$_9$S$_8$ nanoparticles achieved a current density of -10 mA cm$^{-2}$ at an overpotential of -370 mV vs RHE. In addition to the Ni$_9$S$_8$ nanoparticles displaying relatively poor activity, they were also not very
stable in the electrolyte solution. After only minutes, holding the current density steady at \(-10\) mA cm\(^{-2}\), the catalyst readily desorbed from the Ti substrate. The same issue arose when testing the material under highly acid conditions as well. Oftentimes, desorption such as this can be prevented by annealing the sample directly on the Ti substrate. However, when the Ni\(_8\)S\(_8\) nanorods were annealed, they readily converted to the even more sulfur-deficient phase of Ni\(_3\)S\(_2\).

### 3.4.4 Polydymite (Ni\(_3\)S\(_4\)) Nanopyramids

The last phase of nickel sulfide that we were able to selectively synthesize, Ni\(_3\)S\(_4\), was prepared using a recently reported method devised by Batteas and coworkers.\(^{18}\) The reaction was somewhat similar to the prep used for the synthesis of Ni\(_8\)S\(_8\) nanorods, where the nickel precursor was converted to a metal sulfide by means of the decomposition of DDT. Structure analysis by means of powder XRD, shown in Figure 3-9a, confirmed that spinel-type Ni\(_3\)S\(_4\) was indeed the phase that was produced. In addition, TEM imaging also confirmed that the product consisted of agglomerated Ni\(_3\)S\(_4\) nanopyramids (Figure 3-9b). The Ni\(_3\)S\(_4\) nanopyramids were all very similar in size, with the distance from one vertex to another having a length of \(12 \pm 3\) nm.
Like the previously investigated nickel sulfide phases, the \( \text{Ni}_3\text{S}_4 \) nanopyramids were also tested for HER activity. The polarization data displayed in Figure 3-9c indicated that under alkaline conditions, the \( \text{Ni}_3\text{S}_4 \) nanoparticles appear to be only slightly to moderately active with respect to the HER. At loading densities of approximately 1.0 mg cm\(^{-2}\), the \( \text{Ni}_3\text{S}_4 \) nanopyramids achieved a current density of -10 mA cm\(^{-2}\) at an overpotential of -365 mV vs RHE. The \( \text{Ni}_3\text{S}_4 \)
nanopyramids also suffered from the same shortfalls as Ni₃S₈ nanorods in terms of stability. In both alkaline and acidic environments, the particles readily desorbed from the substrate after only a few minutes in solution.

3.5 Conclusions

In summary, a number of previously untested and inaccessible cobalt and nickel sulfide systems were selectively synthesized and tested for potential use as viable, Earth-abundant HER electrocatalysts. While all of the metal sulfides tested were relatively unstable under highly acidic environments, most of the materials tested under alkaline conditions showed moderate HER activity. Most notably, the HER activity of the synthesized Ni₃S₂ particles increased over time to -250 mV vs RHE, while maintaining a constant current density of 10 mA cm⁻². Furthermore, in spite of the fact that all of the tested materials were active towards the HER, not enough information was collected to say definitively that there is in fact a correlation between HDS and HER catalysts. Within the systems that were studied, a number of issues arose that would complicate making any such claim at this time. These include, but are not limited to being unable to consistently make particles with exactly the same size and morphology as well as having transition metal sulfides with a multitude of different possible phases. Even something as trivial as not having sufficient contact between the catalyst and the substrate may skew results. Only after these issues of standardization are addressed, can one effectively begin to draw any conclusions as to whether or not a correlation does indeed exist.
3.6 References


