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COLLOIDAL NANOCHEMISTRY

APPLIED TO THE DISCOVERY AND CHARACTERIZATION OF EARTH-ABUNDANT NANOPARTICLES AS CATALYSTS FOR THE HYDROGEN EVOLUTION REACTION AND CO₂ PHOTOREDUCTION

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Chemistry

by

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Abstract

Colloidal nanosynthesis has become a powerful fundamental and practical science with increasing methodologies available for the formation of highly controllable, high surface area nanoparticles. By expanding these methodologies to targeted nanomaterials, we have been able to synthesize and characterize new catalytic nanoparticle systems, primarily for the catalysis of the hydrogen evolution reaction (HER) but also for CO₂ photoreduction to carbonaceous fuels. Both of these reactions offer exciting potential routes toward a clean energy future if they can be produced and perform with enough cost efficiency.

We begin with a discussion of the capabilities of colloidal nanosynthesis, followed by the intricacies of the HER and CO₂ photoreduction. For the HER, replacing highly active noble metals with Earth-abundant, active, and stable materials is a major goal. The majority of this dissertation will focus on the discovery, characterization, and evaluation of new materials to satisfy this goal. For this, we will start by reporting on the synthesis and evaluation of new amorphous molybdenum phosphide and amorphous tungsten phosphide nanoparticles as HER catalysts. Each of the full HER evaluations will include linear scan voltammetry for testing the activity of each material, comparison versus a platinum standard electrode and a bare Ti foil substrate as controls, then sustained cyclic voltammetry as well as a galvanostatic hold for stability testing. We will then discuss the discovery of hollow nanospheres of FeP as an exceptionally active HER catalyst. This will be followed by the establishment of a synthetic route to colloidal transition metal silicide nanoparticles. Ni₂Si, Pd₂Si, and Cu₃Si nanoparticles were all

synthesized preliminarily tested for their ability to catalyze the HER. Next, we discuss phase control of cobalt sulfide nanomaterials and establish parameters in a non-polar synthesis to make each of three crystalline phases, and begin to compare them for the HER. After this, we will show specific colloidally controlled manipulations of TiO₂ truncated bipyramidal nanoparticles, including size control of Ag domains grown on TiO_2 and multilayered assemblies of TiO_2 nanoparticles. Finally, we delve into the challenges and opportunities of CO₂ photoreduction before concluding. Briefly, for CO₂ reduction, activity has typically been low compared to the HER, product selectivity remains a major hurdle, and there is a lack of standardization in testing methods, though the infrastructures of first world countries are already built for carbon based fuels, and CO_2 itself provides an excellent feedstock from a growing pollutant. We highlight colloidally synthesized SnO nanosheets with primarily exposed (001) facets as selective for ethanol production from CO₂ and water, then directly compare CuPt alloy nanospheres against Pt nanospheres on a TiO₂ substrate for CO₂ photoreduction to methane. Each of the chapters included will illustrate the powerful capabilities of colloidal nanosynthesis, as they can be applied to learn about and discover solutions to real world problems such as the development clean energy technologies.

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Chapter 1

Introduction

Colloidal Nanoparticle Synthesis for Heterogeneous Catalysis

Over the past two decades, colloidal nanoparticle synthesis has matured from a fundamental science into a powerful tool for producing materials that span a variety of applications including optics, electronics, magnetism, and catalysis.¹ Colloidal methods can allow for exceptional control over particle size, shape, composition, crystal structure, size distribution and monodispersity, which can have a significant impact on the chemical and physical properties of the material.^{1,2} For example, morphology and size of semiconductor nanoparticles can be tailored via colloidal methods, which allows scientists to tune their optical properties.^{2,3} Precise modulation of absorption and photoluminescence properties in these materials has led to an array of applications including fluorescent labels for biomedical technologies, light-harvesting materials in solar cells, and light-emitting diode components for brightly colored display monitors.³⁻⁶ As another example, iron oxide nanocrystals exhibit size-dependent magnetic properties that can be tuned using colloidal methods, and are being used as contrast agents in biomedical applications.⁷ Another advantage of using colloidal nanoparticles for materials applications is their high dispersibility, which makes them amenable to solution-based casting, spincoating, printing, and roll to roll processing, which are highly scalable processes.⁸⁻¹⁰ As colloidal methods continue to mature, growing capabilities are leading to new nanoscale materials, which are finding use in a variety of applications, including heterogeneous catalysis.

There are many advantages to using colloidal nanoparticles for heterogeneous catalysis applications. Increasing the surface area of catalyst materials offers an inherent advantage over bulk materials, by increasing the number of active sites where catalysis can occur. Colloidal nanoparticle synthesis can be considered a bottom-up method that can provide access to new nanomaterials that traditional top-down techniques are not readily able to. Some uniform (composition and size) amorphous nanomaterials, for example, are accessible via colloidal techniques, as are some non-equilibrium phase materials.¹¹⁻¹³ Top-down, high temperature, solid state techniques often rely on reaching thermodynamically stable states and crystal structures in order to achieve compositional uniformity, while size uniformity of nanoparticles from top-down methods such as ballmilling is typically poor. Conversely, colloidal techniques are also capable of producing nanoparticles of uniform composition but with size uniformity as good as within a few nanometers of inter-particle variation. Knowledge of material composition, size, and exposed surfaces are all important to the intrinsic study of a material as a catalyst. Therefore, even with readily made, thermodynamically stable, crystalline catalysts, the ability to synthesize highly uniform nanoparticles via colloidal nanosynthesis can be useful beyond an inherently high surface area for catalysis studies. Also, for a given catalytic material, there are often specific crystal facets which are more selective or active for a specific catalytic reaction than others. For example, it has been shown on single crystals of Pt that benzene hydrogenation on the (100) surface will yield only cyclohexane whereas the (111) surface will yield both cyclohexane and cyclohexene.¹⁴ Colloidal nanosynthesis methods have been used to form Pt nanocubes with only (100) surfaces exposed, providing a high surface area catalyst with product selectivity for the hydrogenation of benzene to cyclohexane.¹⁴ For ionic material catalysts, crystal structure, composition, and shape/facet control are significant factors in determining catalytic activity. For example, cobalt phosphide nanospheres as phase pure CoP and Co₂P have been directly compared as electrocatalysts for the hydrogen evolution reaction. Results show that CoP nanospheres, with identical loading and nearly identical size distribution and surface area, are statistically more active than Co₂P nanospheres.¹⁵ In this same system, highly branched CoP nanostructures were synthesized via colloidal methods with primarily exposed (111) surfaces, were significantly less active than the CoP nanospheres with similar surface areas and multiple facets exposed on the surface.¹⁶ Colloidal methods such as this for controlling shape or even directing the formation of 2-D inorganic or singularly faceted nanostructures allows for studies on the effect of facet control on catalytic activity and then for primarily exposing the catalytically desirable facets. For these reasons it is imperative to be able to controllably synthesize potential catalysts of a variety of materials on the nanoscale to effectively improve the catalysis of many specific and unique reactions. However, fundamental synthetic challenges remain as only a limited number of nanomaterials are readily available to be synthesized and manipulated via colloidal methods. The majority of this dissertation will focus on expanding colloidal nano-synthesis methods to new, earth abundant and catalytically relevant materials.

Catalyzing Water Electrolysis: The HER in Photoelectrochemical Cells

The ability to effectively facilitate water electrolysis with cost effective materials and methods is a highly sought, "Holy Grail" of heterogeneous catalysis and materials chemistry. When coupled with a renewable energy source such as solar or wind power, this technology has the potential to provide clean hydrogen fuel on a global scale, while simultaneously offsetting the use of carbon based fuels and their negative environmental impact.¹⁷ Water electrolysis can be divided into two half reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). In this work, we focus on materials for catalysis of the HER, though both reactions are necessary for water splitting to occur. The HER can be readily catalyzed by platinum, however platinum is a noble metal of high cost and low abundance, which translates poorly to global scalability.^{18,19} Therefore, discovering earth-abundant alternatives which can effectively facilitate the reaction is of great interest.

The research in the HER relevant chapters of this dissertation (Chapters 2-6), is part of a greater effort by the National Science Foundation's Center for Chemical Innovation in Solar Fuels. The primary goal of this center is to develop the scientific basis for a solar-driven water-splitting device with earth-abundant materials. Research from this center and others working in this field has led to a proposed design for a photoelectrochemical cell which is outlined in Figure 1-1.²⁰ The cell consists of photoanode and photocathode rods, which are oriented to efficiently capture sunlight by allowing specific wavelengths of light to be absorbed by the photoanode while others pass through to the photocathode. The photoanode and photocathode rods will be decorated with surface-bound OER and HER catalysts, respectively, to utilize the generated photocurrent for splitting water into H_2 and O_2 gas. Between the photocathode and photoanode half-cells is an H^+ permeable membrane, which keeps hydrogen and oxygen products separated, thus preventing the formation of an explosive mixture of the two. Although it is likely that this design will change and mature with new research advances and limitations, it provides a motivating model for solar-driven water electrolysis and specifically, motivation for the discovery of dispersible nanoparticles as HER catalysts.



Figure 1-1: The "Powering the Planet" photoelectrochemical cell design for solar water splitting. Reproduced with permission from reference 20.

The HER is a well-studied electrochemical reaction that is generally understood to proceed by one of two mechanisms on metal surfaces, with the primary steps outlined in the chemical equations shown below. In both cases, the discharge step occurs. This is predominantly followed by either step a or b to form molecular hydrogen determined by interactions of reactant and intermediate species on the metal surface.²¹

Discharge step:
$$HA + e^{-*} \rightarrow H^{**} + A^{-*}$$

a) $HA + H^{**} + e^{-*} \rightarrow H_2 + A^{-*}$
b) $2H^{**} \rightarrow H_2$

In the equations, the asterisk (*) is representative of surface-bound species on the electrode and A⁻ refers to the conjugate base of the acidic proton (ie. H₂O under acidic conditions and OH⁻ in alkaline media). The HER is capable of proceeding under acidic, basic, or neutral conditions; however, Lewis and co-workers have shown with modeling and simulation that a voltage penalty of several hundred millivolts at low current densities is assocoiated with operation at near-neutral pH buffered electrolyte solutions due to the formation of a pH gradient and mass transport limitations at electrode surfaces.²² This simulated voltage loss was larger than the combined voltage loss from highly active Pt and Co-Pi, HER and OER catalyst overpotentials, thus limiting the capability of solar-driven water electrolysis under near-neutral conditions. Additionally, there are currently no viable options for a stable OH⁻ exchange membrane (which is highly desirable in a functional device) with high ionic conductivity for prolonged operation under strongly basic conditions.²³ Lower efficiencies have been observed due to decreased ion conductivity versus proton exchange membranes, and significant

efficiency losses occur as anion exchange membrane degradation occurs in alkaline media. As a membrane based system is preferable for a safe separation of H_2 and O_2 products as well as to prevent product recombination within the cell, this limits the ability of solar-driven water electrolysis under basic conditions. For these reasons, the focus of our research has been on developing acid-stable nanoparticle catalysts for the HER.

Over the past few decades, there has been a growing effort in science, engineering, and materials-focused communities to synthesize and test new materials for the HER. When pure metals were initially evaluated as hydrogen evolution catalysts, trends began to develop showing that a moderate metal-hydrogen bond strength was required to achieve the greatest hydrogen evolution activity.²¹ This is shown as a volcano-style plot in Figure 1-2.²⁴ Presumably, if hydrogen is bound too strongly to the metal, discharge of H₂ would be energetically unfavorable, and if bound too weakly, prolonged adhesion would be unfavorable. Some noble metals, such as Pt, Ir, Rh, and Re, possess a nearly ideal metal-hydrogen bond strength which results in exemplary HER activities. It was later discovered, however, that by alloying certain HER-active metals that weakly bind hydrogen with those that strongly bind hydrogen, highly active materials can be produced.²⁵ NiMo alloys in particular, are highly active presumably due to their ability to effectively facilitate both adsorption and desorption of the hydrogen species, though this remains to be proven.²⁶ While these materials are still of interest for basic and neutral operating conditions, they are not very stable under acidic operating conditions. Ionic materials such as MoS_2 began to fill the void for acid stable HER catalysts. Although MoS₂ is not very active as a bulk material, MoS₂ nanomaterials can be highly active for the HER due to an increase in the number of HER-active edge sites

in the nanomaterial versus the bulk.²⁷ MoS_2 also affords reasonable stability under acidic conditions.²⁸ The activity, however was still significantly below that of Pt, which inspired further research.



Figure 1-2: Volcano plot relation for HER activity in acidic solution showing exchange current densities of pure metals versus their metal-hydrogen bond strength. Adapted with permission from reference 24. Copyright 1972 Elsevier.

In targeting other possible acid stable catalysts, we noted that several catalysts which had been identified in literature as active for the HER were also known to be active for the hydrodesulfurization (HDS) reaction. Both reactions share the commonality of a need to reversibly bind hydrogen to the material surface, which may lead to similar catalyst requirements despite significantly different reaction conditions. This led to the discovery of Ni₂P and then CoP as highly active catalysts with notable acid stability for the HER.^{29,30} As we continued to target new materials for the HER with HDS literature as a guide, we also developed colloidal nanosynthetic methods to provide access to nanomaterials of known HDS active catalysts. This is the foundation for the HER

relevant chapters in this thesis (Chapters 2-6), leading to the synthesis and electrochemical testing of relevant phosphide, silicide, and sulfide nanomaterials.

Fuels from the Photoreduction of Carbon Dioxide with Water

The reduction of carbon dioxide to produce useful carbon based fuels has the potential to mitigate both the growing energy crisis and problems associated with anthropogenic CO₂ emissions simultaneously. Carbon dioxide is a waste product of combustion reactions and has been produced in vast, growing amounts since the industrial revolution. Correspondingly, The Carbon Dioxide Information Analysis Center reports global CO₂ pollution emissions now exceed 30 billion metric tons per year, up from 5 billion metric tons in 1950.³¹ Also, according to the intergovernmental panel on climate change, CO₂ is the primary greenhouse gas responsible for a surface warming of 0.6° C over the past century.³² Continued pollution and climate change may lead to significant environmental problems. As such, CO₂ would be an excellent feedstock material if it could economically and responsibly be reduced back to useful fuels.

Although CO₂ reduction has similar features to the HER, there are some key differences. When water is used as the reducing agent, both require a form of water splitting to produce a fuel as the reduction product and O₂ as the oxidation product. The minimum potential requirements are therefore very similar (greater than ~1.23 eV), though actual required potential can change for CO₂ reduction as many different final products are possible.³³ During CO₂ reduction, a combination of adsorbed CO₂ species and H₂O species on a surface are radicalized and reformed into various products, which

are determined by the amounts of each reactant, the applied electrochemical potential, and the surface interactions.³⁴ As a result, many molecules from carbon monoxide, to methane, to long chain hydrocarbons, to hydrogen are all possible reduction products. Therefore, it is a major goal in CO₂ reduction to achieve product selectivity leading to the formation of specific desired fuels, as opposed to the HER where product formation is not an issue and catalyst activity is the primary metric for evaluating materials. With control over composition, size, and exposed surfaces amongst other features, colloidal synthesis of nanomaterials provides an opportunity to design specific catalysts to promote product selectivity and activity.

The reduction of CO₂ with sunlight would provide an ideal reaction pathway were the renewable energy of the sun can be captured as carbonaceous fuel products. However, this requires a photoconductive material, which adds a new level of complexity to an already challenging problem. Theoretically, a material that absorbs sunlight with a bandgap of approximately 1.23 eV or greater has the potential to photo-reduce CO₂ with H₂O. However, many materials with larger band gaps than this will primarily absorb UV light, which is only a small part of the solar spectrum. Photoconductive materials each possess unique charge transport capabilities; therefore, even if the light absorption of a material matches well with the solar spectrum, the material may not efficiently transport electrons and holes to the surface, and instead allow charge carriers to recombine without promoting the catalytic reaction. Adding to the complexity, many photo-absorbing materials are not very catalytically active for this particular reaction. Therefore, there are two proposed routes to approach a solution to this problem, and discover new materials for this reaction. One route is to synthesize and test new photocatalytic, single domain, nanomaterials with control over the exposed surface for directing product formation. The other route is to evaluate new catalytically active materials, regardless of their intrinsic photo-absorbing properties, by attaching them to a known photoconductive material with appropriate photo-absorbing properties (i.e. band gap and charge mobility). We outline a framework to address each of these and provide further details in Chapter 8.

Experimental Reports

In the following chapters, we demonstrate that colloidal nanoparticle synthesis is a powerful tool, allowing access to nanoparticle systems with potential as heterogeneous catalysts, focusing on the catalysis of the HER and CO₂ photoreduction. Synthetic challenges are surmounted in each of these chapters, allowing specific, targeted materials to be synthesized and evaluated for catalytic reactions. Chapters 2-6 focus on the synthesis of targeted metal phosphide, silicide, and sulfide nanomaterials and their evaluation, primarily as electrochemical HER catalysts in aqueous acidic media. Chapter 2 highlights a highly active amorphous molybdenum phosphide nanoparticle catalyst, which is followed by Chapter 3, covering the evaluation of an amorphous tungsten phosphide nanoparticle catalyst made with an analogous synthesis. Chapter 4 focuses on uniform, crystalline FeP hollow nanospheres, which show exceptional activity for the HER, and are also demonstrated to be useful as co-catalyst materials on TiO₂ for the photoreduction of water. In Chapter 5, a novel route to the solution synthesis of transition metal silicide nanoparticles is established, and each of Pd₂Si, Ni₂Si, and Cu₃Si are evaluated showing a range of activities for the electrochemical HER. Chapter 6 then addresses the conditions required for obtaining CoS, Co₉S₈, and CoS₂ nanocrystals via non-polar colloidal routes, followed by a preliminary evaluation of these materials for the HER. Each of the above systems in Chapters 2-6 was specifically targeted for the HER based on the materials previously being established for the hydrodesulfurization reaction well hydrogen manipulation reactions (hydrogenation, as as for other hydrodenitrogenation, etc). In Chapter 7, titanium dioxide is synthesized as uniform, colloidally stable, truncated bipyramids which are uniquely manipulated to form linked chains and multilayered assemblies, in addition to being used as seed particles to form Ag-Ti O_2 hybrid nanocrystals with controllably sized Ag domains. Finally, Chapter 8 outlines a framework for evaluating materials as CO₂ reduction photocatalysts and cocatalayts, highlighting nanosheets of SnO as a potential photocatalyst and CuPt alloy nanospheres as a co-catalyst on a photoconductive substrate.

1.1 References

- (1) Y. Yin, A. P. Alivisatos, *Nature* **2005**, *437*, 664.
- (2) X. Peng, L Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P Alivisatos, *Nature* 2000, 404, 59.
- (3) P. V. Kamat, J. Phys. Chem. C, 2008, 112, 18737.
- (4) E. H. Sargent, *Nature Photon.* **2012**, *6*, 133.
- (5) I. L. Medintz, H. T. Uyeda, E. R. Goldman, H Mattoussi, *Nature Mater.* 2005, 4, 435.
- (6) Q. Sun, Y. A. Wang, L. S. Li, D. Wang, T. Zhu, J. Xu, C. Yang, Y. Li, *Nature Photon.* **2007**, *1*, 717.
- Y. Jun, Y. Hun, J. Choi, J. Lee, H. Song, S. Kim, S. Yoon, K. Kim, J. Shin, J. Suh, J. Cheon, J. Am. Chem. Soc. 2005, 127, 5733.
- (8) F. C. Krebs, Sol. Energ. Mat. Sol. Cells, 2009, 93, 394.

- (9) E. Tekin, P. J. Smith, U. S. Schubert, *Soft Matter*, **2007**, *4*, 703.
- (10) S. Jeong, L. Hu, H. R. Lee, E. Garnett, J. W. Choi, Y. Cui, *Nano Lett.* **2010**, *10*, 2989.
- (11) I. T. Sines, R. Misra, P. Schiffer, R. E. Schaak, Angew. Chem. Int. Ed. 2010, 49, 4638.
- J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis, R. E. Schaak. *Chem. Mater.* 2014, 26, 4826.
- (13) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak. *Chem. Commun.* 2014, 50, 11026.
- (14) A. R. Tao, S. Habas, P. Yang, *small*, **2008**, *3*, 310.
- (15) J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney, R. E. Schaak, *Chem. Mater.* Just Accepted Manuscript. DOI: 10.1021/acs.chemmater.5b01284. 2015.
- E. J. Popczun, C. W. Roske, C. G. Read, J. C. Crompton, J. M. McEnaney, J. F. Callejas, N. S. Lewis, R. E. Schaak. J. Mater. Chem. A, 2015, 3, 5420.
- (17) N. S. Lewis, D. G. Nocera, Proc. Natl. Acad. Sci. U.S.A 2006, 103, 15729.
- (18) H. B. Gray, *Nature Chem.* **2009**, *1*, 7.
- (19) D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, J. G. Chen, *Angew. Chem. Int. Ed.* 2010, *49*, 9859.
- (20) H. B. Gray, Engineering & Science, 2008, 2, 26.
- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N.
 S. Lewis, *Chem. Rev.* 2010, *110*, 6446.
- J. Jin, K. Walczak, M. R. Singh, C. Karp, N. S. Lewis, C. Xiang, *Energy Environ. Sci.* **2014**, 7, 3371.

- (23) Y. Leng, G. Chen, A. J. Mendoza, T. B. Tighe, M. A. Hickner, C. Wang J. Am. Chem. Soc. 2012, 134, 9054.
- (24) S. Trasatti, J. Electroanal. Chem. 1972, 39, 163.
- (25) D. E. Brown, M. N. Mahmood, M. C. M. Man, A. K. Turner, *Electrochim. Acta*, 1984, 29, 1551.
- (26) J. R. McKone, B. F. Sadtler, C. A. Werlang, N. S. Lewis, H. B. Gray, ACS Catal.
 2013, 3, 166.
- (27) T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science*, 2007, 317, 100.
- (28) Z. Wu, B. Fang, Z. Wang, C. Wang, Z. Liu, F. Liu, W. Wang, A. Alfantazi, D. Wang,D. P. Wilkinson, *ACS Catal.* 2013, *3*, 2101.
- (29) E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, J. Am. Chem. Soc. 2013, 135, 9267.
- (30) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, Angew. Chem., Int. Ed. 2014, 53, 5427.
- (31) T. A. Boden, G. Marland, R. J. Andres, Global, Regional, and National Fossil-Fuel CO₂ Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A doi 10.3334/CDIAC/00001_V2010
- (32) Intergovernmental Panel on Climate Change 2001. Climate Change 2001: The Scientific Basis. Cambridge University Press: Cambridge, U.K., 2001.
- (33) Izumi, Y. Coord. Chem. Rev. 2012, 257, 171.
- (34) D. Uner, M. Oymak, *Catalysis Today*. **2012**, *181*, 82.

Chapter 2

Amorphous Molybdenum Phosphide Nanoparticles for Electrocatalytic Hydrogen Evolution

2.1 Introduction

Water electrolysis to generate hydrogen via the hydrogen-evolution reaction (HER), which in acidic solutions involves the electrocatalytic reduction of protons to molecular hydrogen, underpins several emerging clean-energy technologies.^{1,2} The HER is most effectively catalyzed by Pt, but the expense and scarcity of Pt motivates the search for non-noble-metal alternative electrocatalysts.^{3,4} Molybdenum-based materials that comprise a diverse range of compositions, structures, activities, and stabilities are among the most widely studied non-Pt heterogeneous HER electrocatalysts. For example, nanostructured MoS₂ is a benchmark HER electrocatalyst that is active and stable in acidic media.^{5,6} The HER activity of MoS₂, including the nature of the catalytically active sites and the impact of nanostructuring on achieving maximum activity, has been investigated in detail.^{7,8} Molecular mimics of the MoS₂ active site,⁹ as well as amorphous MoS_x materials,^{10,11} have also been studied as HER catalysts. Additionally, MoB and Mo₂C have been identified as active HER catalysts that are stable in both acidic and alkaline aqueous solutions.¹² MoN has also been shown to catalyze the HER in acidic solutions.¹³ Ni-Mo^{14,15} and other molybdenum alloys^{16,17} are highly active HER catalysts in alkaline solutions, but are generally unstable in acidic media when exposed to anodic conditions. Nitrogen incorporation, for example to generate Ni-Mo-N nanocomposites, has been shown to improve the acid stability of such systems.¹³ Several

ternary molybdenum compounds are also known to be active and acid-stable HER catalysts, including $Co_{0.6}Mo_{1.4}N_2^{-18}$ and Cu_2MoS_4 .¹⁹

Transition metal phosphides, including Ni₂P,^{20,21} CoP,²² and FeP,²³ have recently been identified as promising HER electrocatalysts. These materials also catalyze the high-temperature hydrodesulfurization (HDS) reaction,²⁴ as does MoS₂ and many of the other known Mo-based HER catalysts.^{25,26} Although HDS and the HER are distinct catalytic processes with different mechanisms, some commonalities, including the reversible binding and dissociation of H₂, exist between both reactions.^{1,27,28} Hence known HDS catalysts may, by analogy, also prove to be viable HER catalysts. Molybdenum phosphide, MoP, is an active HDS catalyst,^{29,30} and has been predicted theoretically to be more active and stable for HDS than Mo, MoC, and MoN.³¹ MoP is reactions. also known to catalyze other classes including several of hydrodenitrogenation,^{32,33} hydrazine decomposition,³⁴ and hydrogenation.³⁵

We report herein the solution-phase synthesis of discrete, uniform, and amorphous MoP nanoparticles with diameters of approximately 4 nm and show that they are thermally stable – remaining as discrete, uniform, and amorphous 4-nm particles – upon annealing in 5% H₂/Ar beyond 450 °C. We also demonstrate that the amorphous MoP nanoparticles are active and acid-stable electrocatalysts for the HER. Overpotentials as low as -90 and -105 mV (-110 and -140 mV without iR correction) were required to produce operationally relevant current densities of -10 and -20 mA cm⁻², respectively, at MoP mass loadings of ~1 mg cm⁻². Hence, the nanoparticulate MoP electrocatalyst is superior to bulk MoB and Mo₂C, which have been reported to exhibit overpotentials of approximately -210 to -240 mV at a current density of -20 mA cm⁻².¹² MoP also is

comparable in HER activity to some of the most active MoS_2 and MoS_x electrocatalysts,^{5,6} as well as to nanostructured Mo_2C supported on carbon nanotubes.³⁶ Amorphous MoP nanoparticles therefore represent an important addition to the growing family of active and acid-stable Mo-based HER electrocatalysts.

2.2 Results and Discussion

phosphide Molybdenum were nanoparticles synthesized by heating molybdenum(0) hexacarbonyl and trioctylphosphine (TOP) in squalane to 320 °C for 2 h. After allowing the solution to cool to room temperature, the particles were washed with ethanol and hexanes, and were isolated by centrifugation. Transmission electron microscopy (TEM) images (Figures 2-1a, 2-1b, and 2-2) indicated that the particles were guasi-spherical and uniform in size, with an average diameter of 4.2 ± 0.5 nm. The 4-nm diameter particles represent those that form most readily in this system, and no attempt was made to modify or vary their size. High-resolution TEM (HRTEM) images (Figure 2-1c) showed no evidence of crystallinity, suggesting that the particles were amorphous. Consistently, the selected-area electron diffraction (SAED) pattern (Figure 21d) showed only diffuse rings. The corresponding powder X-ray diffraction (XRD) pattern (Figure 2-3) also indicated that the as-synthesized MoP nanoparticles were amorphous. Upon heating to temperatures above 600 °C, the particles began to crystallize and grew in size, revealing the formation of crystalline WC-type MoP in high yield (Figure 2-3). In addition to demonstrating the thermal stability of the amorphous MoP nanoparticles, this behavior upon annealing suggests that the as-synthesized amorphous particles had an average composition close to that of MoP, because no off-stoichiometry phases were observed upon heating.



Figure 2-1: (a,b) TEM images, (c) HRTEM image, and (d) SAED pattern of the assynthesized amorphous MoP nanoparticles.



Figure 2-2: Wide area TEM image of as-synthesized amorphous MoP nanoparticles.



Figure 2-3: Powder XRD patterns for MoP nanoparticles as-synthesized, after annealing under $H_2(5\%)/Ar(95\%)$ to 450 °C, and after annealing under Ar to 600 – 800 °C. For comparison, a simulated pattern for crystalline WC-type MoP is shown at the top.

Energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) provided further insight into the composition of the amorphous MoP nanoparticles. An EDS spot scan on a single as-synthesized MoP nanoparticle (Figure 2-4a) indicated that Mo and P were both present in the particle and that the Mo:P ratio was ~ 1:1. EDS analysis of an ensemble of MoP nanoparticles, which were thoroughly washed with chloroform to remove any excess TOP, yielded a Mo:P ratio of 39:61 (Figure 2-4b). Consistently, ICP-AES data of the entire sample indicated a Mo:P ratio of 38:62. After removing the surface-bound ligands by heating at 450 °C in

H₂/Ar for 2 h, the Mo:P ratios were determined to be 44:56 by EDS and 41:59 by ICP-AES. On the basis of the EDS and ICP-AES data, the amorphous MoP nanoparticles are therefore slightly phosphorus-rich, although further studies are needed to elucidate more fully any particle-to-particle compositional variation. Given their composition and crystallization behavior upon annealing, the nanoparticles could be considered as MoP_x precursors to the MoP catalyst, but are labeled as "MoP" throughout because of the overall ~1:1 stoichiometry of the as-tested material.



Figure 2-4: (a) Spot and (b) ensemble EDS spectra for amorphous MoP nanoparticles. Background scans are shown for comparison.

The electrocatalytic HER activity was evaluated in 0.50 M H_2SO_4 using a standard electrochemical setup. The amorphous MoP nanoparticles were deposited onto a 0.20 cm² Ti foil substrate (chosen for its negligible HER activity and its ability to

facilitate adhesion of the nanoparticles) at a mass loading of ~ 1 mg cm⁻², and the organic ligands were removed by heating the as-prepared MoP/Ti electrode in flowing H₂(5%)/Ar(95%) at 450 °C for 2 h – conditions under which the particles remain amorphous and do not grow in size (Figures 2-3 and 2-5). Diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) data indicated that the peaks between 3200 cm⁻¹ and 2700 cm⁻¹, which are characteristic C-H vibrational modes of the organic surface ligands, disappeared upon annealing (Figure 2-6). During the annealing process, the MoP particles remained amorphous, as determined by both powder XRD (Figure 2-3) and SAED (Figure 2-5) data.



Figure 2-5: TEM image of amorphous MoP nanoparticles heated to 450 °C in $H_2(5\%)/Ar(95\%)$ and corresponding SAED pattern, indicating that the particles remained amorphous.


Figure 2-6: DRIFT spectra of as-synthesized amorphous MoP nanoparticles (top) and of the amorphous MoP nanoparticles after heating to 450 °C in $H_2(5\%)/Ar(95\%)$.

Figure 2-7 shows plots of the current density *vs.* potential for a representative MoP/Ti electrode, along with Pt and Ti control electrodes. Current density *vs.* potential data for additional electrodes are presented in Figure 2-8. As expected, the bare Ti substrate was not an active HER catalyst, while Pt was highly active. The best amorphous MoP nanoparticle electrodes, tested immediately after annealing (as were all of the electrodes shown in Figures 2-7 and 2-8), produced current densities (*j*) of -10 and -20 mA cm⁻² at overpotentials (η) of -90 and -105 mV (-110 mV and -140 mV without iR correction), respectively. These values compare favorably with, and in some cases are superior to, those of other molybdenum-based HER electrocatalysts with similar mass loadings in acidic media,^{5,6,12,36} including two very recent reports of crystalline MoP

nanostructures having much larger morphological features ($\eta = -125$ to -150 mV at j = -10 mA cm⁻²).³⁷ Note that when the samples and electrodes were not freshly prepared and annealed immediately prior to testing, the overpotentials were higher, ranging from $\eta = -90$ to -125 (-110 to -145 without iR correction) and -105 to -140 mV (-140 to -175 mV without iR correction) at j = -10 and -20 mA cm⁻², respectively. This variability was attributed to sample instability, after annealing, under ambient conditions, likely due to oxidation.



Figure 2-7: Polarization data in 0.50 M H_2SO_4 for a representative MoP/Ti electrode at a mass loading of ~1 mg cm⁻², along with crystalline bulk MoP, Pt, and Ti for comparison. The dashed lines correspond to the data after application of an iR correction.



Figure 2-8: Polarization data in 0.50 M H_2SO_4 for three distinct MoP/Ti electrodes (red, green, and blue), each at a mass loading of ~1 mg cm⁻², as well as Ti and Pt electrode controls. Dashed lines correspond to iR corrected data.

Tafel analysis (Figure 2-9) was carried out for Pt and MoP/Ti electrodes, using iR corrected data. Pt exhibited an exchange current density of 4.6 x 10^{-3} A cm⁻² and a slope of 30 mV/decade, which is consistent with the expected behavior. ^{20,22} The amorphous MoP nanoparticles exhibited an exchange current density of 1.2 x 10^{-4} A cm⁻² and a Tafel slope of 45 mV/decade. This behavior indicates that the mechanism of hydrogen evolution is different from that of Pt.³⁸ The Tafel slope for the MoP/Ti electrodes does not match any of the standard HER Tafel slopes of 29, 38, or 116 mV/decade,³⁸ but is comparable to Tafel slopes reported for other non-noble metal nanostructured catalysts such as Ni₂P (46 mV/decade),²⁰ CoP (50 mV/decade)²² and MoS₂ (50 mV/decade).⁷



Figure 2-9: Tafel plot for a MoP/Ti electrode and a Pt control using iR corrected data.

The acid stability of a representative amorphous MoP/Ti electrode was evaluated by holding the current density constant at -10 mA cm⁻² for 18 h in 0.50 M H₂SO₄,. Over this time period, the overpotential increased only slightly, from an initial value of -113 mV (-125 mV without iR correction) for this particular MoP/Ti electrode to -118 mV (-130 mV without iR correction) (Figure 2-10a), indicating excellent stability under operating conditions. Accelerated degradation studies using 500 cyclic voltammetry (CV) sweeps between -0.3 V and 0.2 V *vs*. the potential of the reversible hydrogen electrode, RHE, were used to simulate some aspects of the long-term operational stability (Figure 2-10b). Over 500 cycles, the overpotential at *j* = -10 mA cm⁻² increased slightly, from -91 mV to -98 mV (-110 mV to -117 mV without iR correction), which is consistent with the galvanostatic behavior described above. Some of the amorphous MoP nanoparticle sample flaked off of the electrode during these long tests, so the slight increase in overpotential during the galvanostatic and accelerated degradation tests may be attributable to a decrease in mass loading over time.



Figure 2-10: (a) Plot of overpotential (iR corrected) vs. time for a MoP/Ti electrode (j = -20 mA cm^{-2}). (b) Polarization data for a MoP/Ti electrode initially and after 500 cyclic voltammetric sweeps between -0.3 to 0.2 V vs. RHE. The dashed lines are iR corrected data. The data in both (a) and (b) were acquired in 0.50 M H₂SO₄ for MoP/Ti electrodes having a mass loading of ~ 1 mg cm⁻².

The faradaic H_2 yield was also evaluated for electrodes coated with either amorphous MoP nanoparticles or with Pt nanoparticles. In this experiment, 30 C of charge was passed at -10 mA for 50 min for 0.2 cm² Ti foil electrodes that each were coated with electrocatalyst at a mass loading of 1 mg cm⁻². The MoP/Ti and Pt/Ti electrodes produced nominally identical quantities of H_2 under these conditions, and the amount of H_2 evolved agreed closely with the theoretical value based on Faraday's law, implying a quantitative faradaic yield.

The HER activity of bulk, crystalline, commercial MoP was also evaluated for comparison to the HER behavior of the amorphous MoP nanoparticles. For bulk MoP, overpotentials of approximately -295 and -325 mV (-320 and -370 mV without iR correction) were required to produce current densities of -10 and -20 mA cm⁻², respectively (Figure 2-7). To generate comparable cathodic current densities, bulk MoP therefore exhibits higher overpotentials than bulk MoB and Mo₂C.¹² Nanocrystalline, carbon-supported Mo₂C (η = -154 mV at j = -10 mA cm⁻²)³⁶ is significantly more active than bulk Mo₂C (η = -254 mV at j = -10 mA cm⁻²).¹² For MoS₂, the bulk, crystalline material is not a highly active HER electrocatalyst, but amorphous and nanocrystalline MoS₂ samples are active for the HER. This difference is due, in part, to the increased number of exposed active sites, which occur at the edges rather than on the basal planes that are preferentially exposed in MoS₂ crystallites.^{5,6} For MoP, elucidation of the reasons for the increased activity of the amorphous nanoparticles relative to the bulk, crystalline powder requires further studies to disentangle the relative contributions of specific structural motifs, nanostructuring, and crystallinity on the HER activity.

Given the known HER activity of Mo₂C, X-ray photoelectron spectroscopy (XPS) was used to analyze the C 1s region (282-292 eV) of the as-tested, annealed amorphous MoP nanoparticles and to compare the behavior with that of pure, bulk powders of Mo, Mo₂C, and MoP (Figure 2-11). Analysis of the XPS data for the C 1s region of bulk Mo₂C (Figure 2-11a) revealed that adventitious carbon, which was present for all samples at a binding energy of 285 eV, was the predominant species. The XPS spectrum for bulk Mo₂C also showed a carbon peak that was consistent with a metal carbide (283-284 eV), matching well with that expected for Mo₂C.^{39,40} Carbon signals attributable to two

distinct carbon-oxygen environments were also present at 286.2 and 289.5 eV, and these binding energies are consistent with those expected for C-O and carbonate species, respectively.⁴¹ For comparison, bulk Mo exhibited the same adventitious carbon and carbon-oxygen peaks, but exhibited no detectable signal from a metal carbide. (Figure 2-11d) Samples of bulk MoP produced similar XPS signals to those observed from MoP nanoparticles (Figure 2-11c). The MoP nanoparticles also exhibited predominantly adventitious carbon, with contributions from carbon-oxygen species comparable to what was observed for bulk Mo, MoP, and Mo₂C (Figure 2-11b). No measurable carbide peak was observed in the MoP nanoparticle sample. While very low levels of molybdenum carbide species may be present at the surface, the XPS data suggest that the observed HER activity of the amorphous MoP nanoparticles is not largely attributable to Mo₂C impurities. *In-situ* studies are in progress to determine the actual chemical composition of the surface of this and related catalyst systems.



Figure 2-11: XPS spectra of the C 1s region for (a) bulk Mo₂C, (b) amorphous MoP nanoparticles, (c) bulk MoP, and (d) bulk Mo. Peak assignments (indicated by dashed numbered lines): #1 corresponds to metal carbide, #2 corresponds to adventitious carbon, #3 corresponds to C-O, and #4 corresponds to carbonate. Notably, the Mo₂C C 1s spectrum contained a significant contribution from metal carbide type carbon (283-284 eV), whereas no significant intensity was observed in that region for amorphous MoP nanoparticle samples or other standards shown in the figure.

2.3 Conclusions

In conclusion, discrete, uniform, and amorphous MoP nanoparticles have been synthesized, shown to be thermally stable upon annealing in 5% H_2/Ar to temperatures above 450 °C, and demonstrated to be highly active HER electrocatalysts. With overpotentials as low as -90 and -105 mV (-110 and -140 mV without iR correction) at

current densities of -10 and -20 mA cm⁻², respectively, for freshly annealed MoP/Ti electrodes with mass loadings of ~1 mg cm⁻², these amorphous MoP nanoparticles compete favorably with the reported performances of the best nanostructured MoS₂, MoS_x, and Mo₂C HER electrocatalysts, and are superior to the HER activity reported for bulk Mo-containing HER electrocatalysts including bulk MoB, Mo₂C, and MoP. The amorphous MoP nanoparticles also showed excellent stability during sustained operation in acidic aqueous solutions. Two complementary reports that appeared very recently also describe similar HER activity in crystalline MoP with different nanostructured morphologies.⁴¹ The observation that MoP, a known HDS catalyst, is also a highly active HER catalyst further strengthens the growing correlation between these two catalytic reactions and provides new ground to further expand the search for new HER electrocatalysts that do not contain expensive noble metals.

2.4 Experimental Details

Chemicals and Materials. Molybdenum hexacarbonyl [98%, Mo(CO)₆ Lot #MKAA0692] (Sigma-Aldrich), squalane [98%, C₃₀H₆₂ Lot #10169326] (Alfa-Aesar), trioctylphosphine [tech. 90%, P(C8H16)₃, Lot #SHBC8966V] (Sigma-Aldrich), titanium foil [99.7%, 0.25 mm thickness], and sulfuric acid [99.999%] (Sigma-Aldrich) were used as received. High-quality colloidal Ag paint was purchased from SPI Supplies, two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr, and bulk molybdenum phosphide [99.5%, MoP Lot #K02U029] was purchased from Alfa Aesar.

Synthesis of Amorphous Molybdenum Phosphide Nanoparticles. [Caution: This reaction has the potential to liberate pyrophoric phosphorus and therefore should be

considered to be highly flammable and corrosive. Only appropriately trained personnel should carry out this reaction and do so under rigorously air-free conditions.] Squalane (7 mL, 13.41 mmol) and trioctylphosphine (3 mL, 6.73 mmol) were added to a 50-mL three-necked, round-bottom flask equipped with a reflux condenser, a thermometer adapter, a thermometer, a rubber septum, and a borosilicate-coated stir bar. To remove water, the mixture was moderately stirred and heated to 120 °C under vacuum. The solution was placed under an Ar atmosphere, and $Mo(CO)_6$ (264 mg, 1 mmol) was added. The reaction mixture was then heated to 320 °C for 2 h. The solution began to darken at ~ 260 °C and turned black at 320 °C. After 2 h at 320 °C, the reaction was slowly cooled by turning off the heating mantle until the reaction solution temperature reached 200 °C, at which point the heating mantle was removed, to produce more rapid cooling. The contents of the reaction mixture were transferred into two centrifuge tubes. To collect the nanoparticles, 5 mL of hexanes and 15 mL of ethanol were added to each tube, followed by centrifugation at 12,000 rpm for 3 min. The particles were then resuspended in 5 mL of hexanes, and the collection process was repeated two additional times. The final product was redispersed in hexanes and was placed in a 20-mL scintillation vial for immediate subsequent use.

Preparation of Working Electrodes. Electrochemical preparation and characterization were performed with slight modifications to previous procedures utilized to determine the properties of Ni₂P nanoparticles as HER catalysts.²⁰ A stock solution of amorphous MoP nanoparticles (10 mg/mL) was prepared in hexanes, with 4- μ L increments of the solution (20 μ L total) used to deposit the nanoparticles onto 0.2 cm² pieces of Ti foil. Once dry, the amorphous MoP-decorated Ti foils were annealed at 450

 $^{\circ}$ C under 5% H₂/Ar to remove surfactants and to aid in adhering the particles to the Ti surface. After annealing, the foils were attached to a polyvinyl chloride-coated Cu wire. A two-part epoxy was then used to insulate all of the conductive surfaces from the electrode solution except the amorphous MoP-decorated side of the Ti electrode.

Electrochemical Measurements. Electrochemical measurements were performed using a Princeton Applied Research Versastat 3 potentiostat. All measurements were performed in 0.50 M H₂SO₄, using a two-compartment, three-electrode cell. To inhibit contamination of the working electrode by the contents of the counter electrode solution, the two compartments were separated by a Nafion® membrane. Measurements were performed using a mercury/mercurous sulfate (Hg/Hg₂SO₄) reference electrode and a Pt mesh counter electrode. The raw electrochemical data were collected without any corrections for uncompensated resistance.

Polarization data were obtained at a sweep rate of 1 mV s⁻¹, whereas the solution was rapidly stirred with a magnetic stir bar. For all sweeps, a constant value for the RHE potential was maintained by continually bubbling the solution with ~1 atm of researchgrade H₂(g). After electrochemical characterization of the molybdenum phosphide nanoparticles, the RHE potential was determined by measurement of the open-circuit potential of a clean Pt electrode in the electrolyte solution. The short-term electrochemical stability was measured galvanostatically over a duration of 18 h. Longterm electrochemical stability measurements were performed by use of cyclic voltammetric sweeps at 100 mV s⁻¹ between +0.2 V and -0.3 V vs RHE. For iR correction, prior to the electrochemical testing of the electrode the uncompensated Ohmic resistance value for each electrode in the electrolyte solution was measured using the high frequency pulse iR determination function of the Versastat 3 potentiostat. The uncompensated resistance was ~ 20 Ω for bulk MoP and ~ 7.7 Ω for amorphous MoP nanoparticles in 0.50 M H₂SO₄.

Quantitative Hydrogen Yield Measurements. Quantitative H_2 yield measurements were performed in 0.50 M H_2SO_4 using a two-electrode, single compartment cell that contained graphitic carbon as a counter electrode. A cathodic current of 10 mA was passed continuously through the 0.2 cm² working electrode over a duration of 50 min (3000 s), resulting in 30 C of total charge passed. An inverted graduated cylinder that contained the electrolyte solution was positioned to capture the H_2 bubbles that evolved from the working electrode. The volume of gas collected from amorphous MoP nanoparticle electrodes matched the volume collected from Pt nanoparticle electrodes, with each producing measured gas yields of 3.98 ± 0.03 mL, as compared to the theoretical H_2 yield of 3.74 mL calculated for 30 C of charge at 1 atm and 20 °C ambient conditions using Faraday's law of electrolysis and the ideal gas law. Pt electrodes were evaluated after the yield measurements for the amorphous MoP electrodes.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced via the CrystalMaker / CrystalDiffract software package. Transmission electron microscopy (TEM) images were collected using a Philips 420 microscope that was operated at an accelerating voltage of 80 kV. High-resolution TEM (HRTEM) images were acquired using a JEOL 2010 microscope with a LaB₆ electron source at an accelerating voltage of 200 kV. Scanning

transmission-electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS) was performed using a JEOL 2010F field emission microscope, which was outfitted with an EDAX solid-sate X-ray detector. ES Vision software (Emispec) was used for EDS data processing, with the Mo and P L-shell transitions, which do not appreciably overlap, chosen for quantitative EDS analysis. All microscopy samples were prepared by casting 0.7 μ L of dispersed MoP in hexanes onto a 400 mesh Formvar and carbon-coated copper grid (Electron Microscopy Sciences). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were acquired using a Bruker IFS 66/s spectrometer (Bruker Optics, Billerica, MA). Nanoparticle samples were diluted in KBr for analysis and DRIFT spectra were processed with OPUS 6.0 (Bruker Optics, Billerica, MA). X-ray photoelectron spectroscopy (XPS) analysis was performed on a monochromatic Al K α source Kratos Axis Ultra operating at 14 kV and 20 mA for an X-ray power of 280 W. Spectra were collected with a photoelectron takeoff angle of 90° from the sample surface plane and were referenced to the C 1s peak with a binding energy of 285 eV.

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F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis, R. E. Schaak. *Chem. Mater.* 2014, 26, 4826. Copyright 2014 American Chemical Society.

2.5 References

- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446.
- (2) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A* **2006**, *103*, 15729.
- (3) H. B. Gray, *Nat. Chem.* **2009**, *1*, 7.
- (4) D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless,
 R. W. Birkmire, J. G. Chen, *Angew. Chem., Int. Ed.* 2010, 49, 9859.
- B. Hinneman, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, L.
 B. Chorkendorff, J. K. Nørskov, J. Am. Chem. Soc. 2005, 127, 5308.
- (6) Y Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, J. Am. Chem. Soc. 2011, 133, 7296.
- (7) J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.* **2012**, *11*, 963.
- R. R. Chianelli, M H. Siadati, M. P. De la Rosa, G. Berhault, J. P. Wilcoxon, R. Bearden Jr., B. L. Abrams, *Catal. Rev.* 2006, 48, 1.
- (9) H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science* 2012, 335, 698.
- (10) J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman, T. F. Jaramillo, *ACS Catal.* **2012**, *2*, 1916.
- (11) H. Vrubel, D. Merki, X. Hu, *Energy Environ. Sci.* **2012**, *5*, 6136.
- (12) H. Vrubel, X. Hu, Angew. Chem., Int. Ed. 2012, 51, 12703.
- W. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu, R. R. Adzic, *Angew. Chem.*, *Int. Ed.* 2012, *51*, 6131.

- (14) D. E. Brown, M. N. Mahmood, A. K. Turner, S. M. Hall, P. O. Fogarty, *Int. J. Hydrogen Energy* 1982, 7, 405.
- (15) I. A. Raj, K. I. Vasu, J. Appl. Electrochem. 1990, 20, 32.
- (16) C. Fan, D. L. Piron, A. Sleb, P. J. Paradis, J. Electrochem. Soc. 1994, 141, 382.
- (17) A. Subramaniaa, A. R. Sathiya Priya, V. S. Muralidharan, Int. J. Hydrogen Energy 2007, 32, 2843.
- B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic, P. G. Khalifah, J. Am. Chem.
 Soc. 2013, 135, 19186.
- P. D. Tran, M. Nguyen, S. S. Pramana, A. Bhattacharjee, S. Y. Chiam, J. Fize, M. J. Field, V. Artero, L. H. Wong, J. Loob, J. Barber, *Energy Environ. Sci.* 2012, *5*, 8912.
- (20) E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis, R. E. Schaak, J. Am. Chem. Soc. 2013, 135, 9267.
- (21) L. Feng, H. Vrubel, M. Bensimon, X. Hu, Phys. Chem. Chem. Phys. 2014, 16, 5917.
- (22) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak, Angew. Chem., Int. Ed. 2014, 53, 5427.
- (23) Y. Xu, R. Wu, J. Zhang, Y. Shi, B. Zhang, Chem. Commun. 2013, 49, 6656.
- (24) S. T. Oyama, J. Catal. 2003, 216, 343.
- (25) R. Prins, V. H. J. De Beer, G. A. Somorjai, *Catal. Rev.* **1989**, 31, 1.
- (26) J. R. Grechowiak, I. Wereszczako-Zielinska, K. Mrozinska, Catal. Today 2007, 119, 23.
- (27) P. Liu, J. A. Rodriguez J. Am. Chem. Soc. 2005, 127, 14871.

- (28) P. Liu, J. A. Rodriguez, J. T. Muckerman. J. Phys. Chem. B 2004, 108, 18796.
- (29) D. C. Phillips, S. J. Sawhill, R. Self, M. E. Bussell, J. Catal. 2002, 207, 266.
- (30) S. T. Oyama, P. Clark, V. L. S. Teixeira da Silva, E. J. Lede, F. G. Requejo, J. Phys. Chem. B 2001, 105, 4961.
- (31) P. Liu, J. A. Rodriguez, *Catal. Lett.* **2003**, *91*, 247.
- (32) W. Li, B. Dhandapani, S. T. Oyama, *Chem. Lett.* **1998**, *27*, 207.
- (33) C. Stinner, R. Prins, T. Weber, J. Catal. 2000, 191, 438.
- (34) R. Cheng, Y. Shu, M. Zheng, L. Li, J. Sun, X. Wang, T. Zhang, J. Catal. 2007, 249, 397.
- (35) P. Yang, Z. Jiang, P. Ying, C. Li, J. Catal. 2008, 253, 66.
- W. Chen, C. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu,
 R. R. Adzic, *Energy Environ. Sci.* 2013, *6*, 943.
- (37) (a) P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J-Y. Wang, K. H. Lim, X. Wang, *Energy Environ. Sci.* 2014, 7, 2624. (b) Z. Xing, Q. Liu, A. M. Asiri, X. Sun, *Adv. Mater.* 2014, 26, 5702.
- (38) J. O. M. Bockris, E. C. Potter, J. Electrochem. Soc. 1952, 99, 169.
- (39) J. M. Manoli, P. Da Costa, M. Brun, M. Vrinat, F. Maugé, C. Potvin, J. Catal.
 2004, 221, 365.
- (40) B. Dai, L. Fu, Z. Zou, M. Wang, H. Xu, S, Wang, Z. Liu, *Nat. Commun.* 2011, 2:522, 1.
- S. Z. Mortazavi, P. Parvin, A. Reyhani, S. Mirershadi, R. Sadighi-Bonabi, J. Phys. D: Appl. Phys. 2013, 46, 165303.

Chapter 3

Electrocatalytic Hydrogen Evolution Using Amorphous Tungsten Phosphide Nanoparticles

3.1 Introduction

Despite its scarcity and high cost, platinum is one of the most widely used catalysts for chemical reactions that underpin many clean energy technologies, including fuel cells and solar fuel generators.^{1.2} For example, water electrolysis relies on the hydrogen-evolution reaction (HER), which in acidic solutions involves the electrocatalytic reduction of protons to molecular hydrogen.³ Pt is an exceptional HER electrocatalyst, producing large cathodic current densities at low overpotentials.^{3,4} Recently, several new acid-stable HER electrocatalysts have been identified as less expensive and more Earth-abundant alternatives to Pt, including MoS₂,^{5,6} CoSe₂,⁷ Co_{0.6}Mo_{1.4}N₂,⁸ Ni₂P,^{9,10} CoP,^{11,12} and MoP.¹³ Each of these systems represents an important development in the search for non-noble-metal HER electrocatalysts, which is important for global scalability where cost and performance must both be considered. Each unique catalyst offers a distinct combination of structure, composition, and properties that collectively can provide useful insights for predicting new catalytic materials and for beginning to interrogate the mechanisms by which they function.

We report herein the colloidal synthesis of uniform amorphous tungsten phosphide (WP) nanoparticles with average diameters of 3 nm that are thermally stable upon heating beyond 450 °C. The amorphous tungsten phosphide nanoparticles are also active and acid-stable HER electrocatalysts, representing a new addition to the growing library of non-noble-metal materials that catalyze the HER. These WP nanoparticles add to an important family of known tungsten-based HER catalysts as well, including WS_2 ,¹⁴ WC,¹⁵ and W_2N .¹⁶ Interestingly, WP is also a known hydrodesulfurization (HDS) catalyst.¹⁷ While HDS and HER are distinct catalytic processes, the reversible binding and dissociation of H₂ represents a possible mechanistic commonality.^{3,18,19} The discovery that WP catalyzes the HER further strengthens the hypothesis that known HDS catalysts offer viable targets for active HER catalysts.

3.2 Results and Discussion

To synthesize the amorphous WP nanoparticles, W(CO)₆ and trioctylphosphine (TOP) were heated to 320 °C for 2 h in squalane. Figures 3-1a and 3-2 show a transmission-electron microscopy (TEM) image of the isolated product, which formed quasi-spherical particles with an average diameter of 3.1 ± 0.4 nm. The corresponding selected-area diffraction (SAED) pattern (Figure 3-1b), showed no evidence of crystallinity, with only diffuse rings present. Likewise, a high-resolution TEM (HRTEM) image of a representative nanoparticle showed no lattice fringes (Figure 3-1c). Energy-dispersive X-ray spectroscopy (EDS) data (Figure 3-3), taken from an ensemble of particles, indicated the presence of W and P with a molar ratio of approx. 43:57 before annealing and 47:53 after annealing in H₂(5%)/Ar(95%) at 450 °C, which were the conditions used to pre-treat the WP nanoparticle working electrodes. The data therefore suggest that the isolated nanoparticles were amorphous tungsten phosphide with a composition close to WP.



Figure 3-1: (a) TEM image and (b) SAED pattern of as-synthesized, amorphous WP nanoparticles. (c) HRTEM image of single amorphous WP nanoparticles.



Figure 3-2: TEM image (wide area) of the as-synthesized amorphous WP nanoparticles.



Figure 3-3: EDS spectra of the amorphous WP nanoparticles as-synthesized (red), as well as after annealing under $H_2(5\%)/Ar(95\%)$ at 450 °C (blue).

The powder XRD pattern of the bulk, as-synthesized product (Figure 3-4) was consistent with the SAED and HRTEM data, showing no sharp diffraction peaks. The nanoparticles remained amorphous upon heating to 450 °C in H₂(5%)/Ar(95%), as evidenced by both XRD (Figure 3-4) and SAED (Figure 3-4, inset). Crystallization began to occur when the nanoparticles were heated above 600 °C. At 800 °C, powder XRD data indicated the formation of crystalline MnP-type WP in high yield, which is consistent with the composition of the as-synthesized sample.



Figure 3-4: Powder XRD patterns for WP nanoparticle samples (from bottom to top) as-synthesized, after annealing in $H_2(5\%)/Ar(95\%)$ to 450 °C, and after annealing under Ar to 800 °C. A simulated powder XRD pattern for crystalline WC-type WP is shown at the top.

Working electrodes for evaluating HER activity were prepared by depositing the as-synthesized amorphous WP nanoparticles onto 0.20 cm² Ti foil substrates (which are catalytically inert but promote nanoparticle adhesion) at mass loadings of approx. 1 mg cm⁻². To remove the ligands bound to the nanoparticle surfaces, the WP/Ti electrodes were then heated to 450 °C in flowing H₂(5%)/Ar(95%) for 2 h. The amorphous nature of the WP nanoparticles was maintained under these conditions, as shown in Figure 3-4. The C-H vibrational modes present in the as-synthesized sample (attributed to the surface-bound ligands) could not be detected after annealing, as monitored by diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) (Figure 3-5).



Figure 3-5: DRIFT spectra of the amorphous WP nanoparticles as-synthesized (top) and after heating to 450 °C in $H_2(5\%)/Ar(95\%)$.

Figure 3-6 shows plots of current density *vs* potential for several WP/Ti electrodes, along with Ti foil and Pt mesh as controls. Ti is not an active HER catalyst, while Pt is a highly active, benchmark catalyst, and the polarization data in Figure 3-6 are consistent with these known catalytic properties. The WP/Ti electrodes required overpotentials as low as -120 mV and -140 mV to produce current densities of -10 mA cm⁻² and -20 mA cm⁻², respectively. While it can be difficult to directly benchmark catalytic performance against literature reports, these overpotentials compare favorably with those of other tungsten-based HER electrocatalysts at similar mass loadings in acidic media. For example, current densities of -10 mA cm⁻² have been produced by exfoliated

WS₂ nanosheets,¹⁴ WC nanoparticles,²⁰ and W₂N nanorods¹⁶ with overpotentials of approx. 220 mV, 125 mV, and 500 mV, respectively. Faradaic H₂ yield measurements were carried out for both the WP/Ti and Pt electrodes. For each system, 30 C of charge was passed at -10 mA over a duration of 50 min. The quantity of H₂ produced by the WP/Ti and Pt electrodes were essentially identical under these conditions, and the amount of H₂ evolved agreed closely with the theoretical value based on Faraday's law. This implies a quantitative faradaic yield.



Figure 3-6: Plots of current density vs. potential in 0.50 M $H_2SO_4(aq)$ for representative samples of WP nanoparticles and bulk WP, deposited onto a Ti foil substrate at a mass loading of ~1 mg cm⁻². Pt and the bare Ti foil substrate are shown as controls. Raw data are shown as solid lines and the iR-corrected data are shown as dashed lines.



Figure 3-7: Tafel analysis [plots of overpotential vs. log[|(current density)|] for Pt and three distinct WP/Ti electrodes, using iR corrected data. For Pt, the extrapolated exchange current density was 4.6 x 10-3 A cm⁻² and the slope of the linear region of the Tafel plot was 30 mV decade⁻¹. Both of these values are consistent with the behavior expected for Pt.^{9,20} For the amorphous WP nanoparticles, the extrapolated exchange current density was 4.5 x 10-5 A cm⁻² and the slope of the linear region of the Tafel plot was 54 mV decade⁻¹. This suggests that the HER mechanism on WP is different from that on Pt. While the slopes of the Tafel plots for the WP/Ti electrodes do not match any of those expected for standard HER mechanisms (29, 38, or 116 mV decade⁻¹), they are comparable to Tafel slopes reported for other nanostructured catalysts in non-noble metal systems, including Ni₂P (46 mV decade⁻¹),⁹ CoP (50 mV decade⁻¹),¹¹ and WS₂ (55 mV decade⁻¹).

The acid stability of the WP/Ti electrodes was evaluated using galvanostatic measurements and current density vs potential (*J-E*) scans in 0.50 M H₂SO₄(aq). At a constant current density of -10 mA cm⁻², the overpotential of the tested electrode increased only slightly over 18 h, from an initial value of -124 mV to -131 mV, indicating

excellent stability (Figure 3-8a). Also, polarization data were collected before and after 500 *J-E* scans between -0.3 V and 0.2 V (*vs* the potential of the reversible hydrogen electrode, RHE). This particular WP/Ti electrode produced an overpotential of -121 mV at a current density of -10 mA cm⁻², and the overpotential increased slightly to -130 mV after the 500 *J-E* cycles had been completed (Figure 3-8b). This slight increase in overpotential is consistent with loss of material from the electrode, which was observed visually, as opposed to significant particle degradation.



Figure 3-8: (a) Plot of overpotential vs. time for a WP/Ti electrode held for 18 h at a constant current density of -20 mA cm⁻². (b) Plot of current density vs. potential for a WP/Ti electrode, as well as an analogous plot of the same electrode after 500 J-E scans (-0.3 to 0.2 V, vs. RHE). The data in (a) are iR corrected; the dashed lines correspond to iR corrected data in (b). All data were acquired for WP/Ti electrodes in 0.50 M H₂SO₄ with a mass loading of ~1 mg cm⁻².

X-ray photoelectron spectroscopy (XPS) indicated no detectable Pt contamination on the WP/Ti electrodes. XPS was also used to analyze the C 1s region of H₂/Ar treated WP nanoparticles (Figure 3-9), because tungsten carbide (WC) is also a known HER electrocatalyst.^{15,20} The major contributor to the C 1s region of the WP nanoparticles, as well as to WP and WC bulk control samples, was adventitious C-C type carbon that was detected on all of the samples. Additionally, two small carbon-oxygen peaks that appeared in each sample aligned with the binding energies expected for C-O (286.2 eV) and carbonate (289.5 eV), which are both classified as adventitious species.²¹ Importantly, the peak in the WC control sample that is attributed to tungsten carbide species (282.7 eV)^{22,23} was not detected in either the WP bulk control or the WP nanoparticles. Indeed, the WP sample did not exhibit a measurable peak in the metal carbide region, suggesting that the observed HER activity of the WP/Ti electrode is inherent to WP and not likely to be attributable to WC impurities.



Figure 3-9: XPS spectra showing the C 1s region for the amorphous WP nanoparticles, along with bulk WC and bulk WP (the sample annealed at 800 °C) for comparison. The dashed numbered lines correspond to the following peak assignments: metal carbide (#1), adventitious carbon (#2), C-O (#3), and carbonate (#4). The WP C 1s spectra contained no significant contribution from tungsten carbide type carbon (282.7 eV).

3.3 Conclusions

In summary, amorphous WP nanoparticles have been synthesized and demonstrated to be highly active HER electrocatalysts that require overpotentials as low as -120 mV and -140 mV at current densities of -10 mA cm⁻² and -20 mA cm⁻², respectively. These values compare favorably with highly active nanostructured tungsten-based HER electrocatalysts that have been reported previously, including WS₂, W₂N, and WC. The WP/Ti electrodes also exhibit excellent stability under operating conditions in strongly acidic aqueous solutions. Hence WP represents an important addition to the growing family of non-noble-metal, tungsten-based HER electrocatalysts.

3.4 Experimental Details

Chemicals and Materials. Tungsten hexacarbonyl [99%, W(CO)₆, Strem Chemicals, Lot #21669500], squalane [98%, $C_{30}H_{62}$, Alfa-Aesar, Lot #10169326], trioctylphosphine [tech. 90%, P(C8H16)₃, Sigma-Aldrich, Lot #SHBC8966V], titanium foil [99.7%, 0.25 mm thickness], and sulfuric acid [99.999%, Sigma-Aldrich] were used as received. High-quality colloidal Ag paint was purchased from SPI Supplies and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr.

Synthesis of Amorphous Tungsten Phosphide Nanoparticles. Squalane (7.0 mL, 13 mmol) and trioctylphosphine (3.0 mL, 6.7 mmol) were added to a 50-mL threenecked, round-bottom flask equipped with a reflux condenser, a thermometer adapter, a thermometer, a rubber septum, and a borosilicate-coated stir bar. The mixture was moderately stirred and heated to 120 °C under vacuum, to remove any water that was present. After placing the solution under an Ar atmosphere, 352 mg (1 mmol) of $W(CO)_6$ was added. The reaction mixture was then heated to 320 °C for 2 h. At ~ 270 °C the solution began to darken, and turned black at 320 °C. After remaining for 2 h at 320 °C, the heating mantle was turned off to allow the reaction to slowly cool until the temperature reached 200 °C. At this point, the heating mantle was removed, to allow the sample to cool to room temperature more rapidly. After transferring the reaction solution to a centrifuge tube, the nanoparticles were collected by adding hexanes (5 mL) and ethanol (15 mL) to the tube, followed by centrifugation (12,000 rpm, 3 min). The particles were then resuspended in hexanes (5 mL), and this process was repeated two additional times. After isolating the final product, the particles were redispersed in hexanes and placed in a vial (20 mL) for use.

Preparation of Working Electrodes. Protocols for preparing electrodes were modified slightly from previous reports.^{9,13b} First, a stock solution of the WP nanoparticles, at a concentration of 10 mg mL⁻¹, was prepared in hexanes. Next, WP nanoparticles were deposited onto 0.2 cm^2 pieces of Ti foil using 5-µL increments of the solution, up to a total of 20 µL. The WP-decorated Ti foils were allowed to dry, heated at 450 °C in 5% H₂/Ar, then attached to a polyvinylchloride-coated Cu wire. The conductive surfaces, with the exception of the WP-decorated side, were insulated from the solution using a two-part epoxy.

Electrochemical Measurements. All electrochemical measurements were performed in 0.50 M H₂SO₄ using a two-compartment, three-electrode cell and a

Princeton Applied Research Versastat 3 potentiostat. The two compartments were separated by a Nafion® membrane to prevent contamination of the working electrode by the contents of the counter electrode solution. A mercury/mercurous sulfate (Hg/Hg₂SO₄) electrode and a Pt mesh electrode were used as the reference and counter Raw electrochemical data were collected without any electrodes, respectively. corrections for uncompensated resistance. To apply an iR correction, the uncompensated Ohmic resistance value for each electrode in the electrolyte solution was measured prior to the electrochemical testing of the electrode using the high frequency pulse iR determination function of the Versastat 3 potentiostat. The uncompensated resistance was ~ 31 Ω for bulk WP and ~ 11 Ω for amorphous WP nanoparticles in 0.50 M H₂SO₄. A sweep rate of 2 mV s⁻¹, with rapid stirring using a magnetic stir bar, was used to acquire the polarization data. Research-grade $H_2(g)$ was continuously bubbled through the solution at ~1 atm to maintain a constant value for the RHE potential. The RHE potential was determined after electrochemical characterization of the tungsten phosphide nanoparticles by measurement of the open-circuit potential of a clean Pt mesh electrode in the electrolyte solution. For galvanostatic stability measurements, the current density was held at 10 mA cm⁻² for 18 h. Cyclic voltammetric sweeps, to further evaluate the acid stability, were carried out between +0.2 V and -0.3 V (vs. RHE) at 100 mV s⁻¹.

Quantitative Hydrogen Yield Measurements. To quantify the H_2 yield in 0.50 M $H_2SO_4(aq)$ (two-electrode, single compartment cell with a graphitic carbon counter electrode), a cathodic current of 10 mA was passed continuously through a 0.2 cm² WP/Ti working electrode over a duration of 50 min (3000 s). This resulted in the passage

of 30 C of total charge. The $H_2(g)$ that was evolved was collected in an inverted graduated cylinder, placed above the working electrode, that contained the electrolyte solution. The WP/Ti electrodes produced a volume of $H_2(g)$ that was equivalent to the volume collected above comparable Pt nanoparticle electrodes. Each produced 3.97 \pm 0.03 mL of gas. This volume of gas is comparable to the theoretical faradaic H_2 yield of 3.74 mL calculated for 30 C of charge at 1 atm and 20 °C. To avoid any possible Pt contamination, the Pt electrodes were evaluated after completion of the WP/Ti yield measurements.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using CrystalMaker / CrystalDiffract. All samples for microscopic analysis were prepared by drop-casting 0.7 μ L of dilute, dispersed WP in hexanes onto a Cu grid (400 mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmission-electron microscopy (TEM) images were collected using a Philips 420 microscope (80 kV). High-resolution TEM (HRTEM) images were obtained using a JEOL 2010 microscope (LaB₆, 200 kV). Scanning transmission-electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS) was performed using a JEOL 2010F field emission microscope, which was equipped with an EDAX solid-sate X-ray detector. STEM-EDS data were processed using ES Vision software (Emispec). The W L-shell and P K-shell transitions were used for quantitative EDS analysis, since these transitions do not overlap appreciably. X-ray photoelectron spectroscopic (XPS) measurements were collected on a

Kratos Axis Ultra (monochromatic Al K α source, 14 kV, 20 mA, 280 W X-ray power) with a photoelectron take-off angle of 90° from the sample surface plane. All spectra were referenced to the C_{1s} peak (285 eV). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were collected using a Bruker IFS 66/s spectrometer. Nanoparticle samples were diluted in KBr for analysis and DRIFT spectra were processed with Bruker OPUS 6.0 software.

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3.5 References

- (35) H. B. Gray, *Nature Chem.* **2009**, *1*, 7.
- (36) D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless, R.
 W. Birkmire and J. G. Chen, *Angew. Chem., Int. Ed.* 2010, 49, 9859.
- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and
 N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446.
- (38) B. C. H. Steele and A. Heinzel, *Nature* **2001**, *414*, 345.
- B. Hinneman, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, L. B. Chorkendorff and J. K. Nørskov, J. Am. Chem. Soc. 2005, 127, 5308.
- (40) Y Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, J. Am. Chem. Soc. 2011, 133, 7296.

- (41) D. Kong, H. Wang, Z. Lu and Y. Cui, J. Am. Chem. Soc. 2014, 136, 4897
- (42) B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic and P. G. Khalifah, J. Am. Chem. Soc. 2013, 135, 19186.
- (43) E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, J. Am. Chem. Soc. 2013, 135, 9267.
- (44) L. Feng, H. Vrubel, M. Bensimon and X. Hu, *Phys. Chem. Chem. Phys.* 2014, *16*, 5917.
- (45) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, Angew. Chem., Int. Ed. 2014, 53, 5427.
- (46) J. Tian, Q. Liu, A. M. Asiri and X. Sun, J. Am. Chem. Soc. 2014, 136, 7587.
- (47) (a) P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J-Y. Wang, K. H. Lim, X. Wang, *Energy Environ. Sci.* 2014, 7, 2624. (b) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis and R. E. Schaak, 2014, 26, 4826.
- (48) D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, T. Fujita, M. Chen, T. Asefa,
 V. B. Shenoy, G. Eda and M. Chhowalla, *Nature Mater.* 2013, *12*, 850.
- (49) W. Chen, J. T. Muckerman and E. Fujita, *Chem. Commun.* **2013**, *49*, 8896.
- (50) V. Chakrapani, J. Thangala and M. K. Sunkara, *Int. J. Hydrogen Energy*, 2009, 34, 9050.
- (51) S. T. Oyama, J. Catal. 2003, 216, 343.
- (52) P. Liu and J. A. Rodriguez, J. Am. Chem. Soc. 2005, 127, 14871.
- (53) P. Liu, J. A. Rodriguez and J. T. Muckerman, J. Phys. Chem. B 2004, 108, 18796.
- (54) A. T. Garcia-Esparza, D. Cha, Y. Ou, J. Kubota, K. Domen and K. Takanabe, *ChemSusChem* **2013**, *6*, 168.

- (55) S. Z. Mortazavi, P. Parvin, A. Reyhani, S. Mirershadi and R. Sadighi-Bonabi, J. Phys. D: Appl. Phys. 2013, 46, 165303.
- (56) A. Katrib, F. Hemming, P. Wehrer, L. Hilaire and G. Maire, *Topics Catal.* **1994**, *1*, 75.
- (57) Z. Xue, K. G. Caulton and M. H. Chisholm, *Chem. Mater.* **1991**, *3*, 384.

Chapter 4

Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles

4.1 Introduction

Platinum is the most widely used material for the electrocatalytic and photocatalytic production of molecular hydrogen (H₂) from water through the hydrogenevolution reaction (HER). Although Pt is highly active and stable under the often harsh operational conditions used in electrolyzers and photoelectrochemical cells,¹ Pt is expensive and scarce.² Hence, several new Earth-abundant HER catalysts have emerged, including MoS₂,^{3,4} Ni-Mo,⁵ CoSe₂,⁶ CoS₂,⁷ Ni₂P,^{8,9} CoP,^{10,11} MoP,^{12,13} and WP,¹⁴ as well as other related materials.¹⁵⁻¹⁹ Iron-based alternatives are especially attractive because Fe is the most abundant transition metal, comprising $\sim 5\%$ of the Earth's crust.²⁰ Accordingly, the price of iron is typically at least two orders of magnitude less than that of other highly abundant and catalytically relevant metals for the HER, including Ni and Co.²⁰ Iron-based clusters also have been found to be the catalytically active sites in [FeFe] and [Fe]-only hydrogenases, which are highly active and efficient biological HER catalysts.²¹ A few moderately active iron-based heterogeneous HER catalysts have been reported, including porous FeP nanosheets,²² pyrrhotite-type FeS nanoparticles,²³ and polycrystalline films of pyrite-type FeS₂.¹⁶ Despite these reports, however, highly active HER catalysts composed of high-quality iron-based nanoparticulate materials – which are among the most desired because of their cost, abundance, and processability - have not yet been identified.

We report herein that iron phosphide (FeP) nanoparticles are exceptionally active as both electrocatalysts and photocatalysts for sustained hydrogen production in either acidic or neutral-pH aqueous solutions. With overpotentials of -50 mV in 0.50 M H₂SO₄ and -102 mV in 1.0 M phosphate buffered saline (PBS), respectively, both at an operationally relevant current density of -10 mA cm⁻², FeP outperforms comparable, previously reported non-noble metal nanoparticle HER electrocatalysts in both acidic and neutral-pH aqueous solutions. In addition, when immobilized on TiO₂, the FeP nanoparticles effect the photocatalytic generation of hydrogen under UV irradiation in acidic and neutral-pH aqueous solutions, making FeP/TiO₂ a fully Earth-abundant system for sustained photocatalytic hydrogen production. This high electrocatalytic and photocatalytic activity, coupled with the high terrestrial abundance and low cost of its constituent elements, makes FeP an important addition to the growing family of transition metal phosphide nanostructures that have been identified as active HER catalysts.

4.2 Results and Discussion

To synthesize the FeP nanoparticles, Fe nanoparticles were prepared by decomposing Fe(CO)₅ in a mixture of oleylamine and 1-octadecene at 190 °C, followed by reaction with trioctylphosphine (TOP) at 340 °C for 1 h. This procedure is modified from a previous report.²⁴ Transmission-electron microscopy (TEM) images (Figure 4-1) indicated the formation of spherical, hollow particles with an average diameter of 13 ± 2 nm. The corresponding high-resolution TEM (HRTEM) image (Figure 4-1b) revealed that the hollow particles were single crystalline and faceted, and are therefore morphologically similar to other transition-metal phosphide nanoparticles formed by chemically transforming metal seed particles into phosphides using TOP.^{8,10,20} The

lattice fringes observed by HRTEM were 2.9 Å and 2.6 Å, which corresponded well to the (002) and (200) planes of MnP-type FeP, respectively.



Figure 4-1: (a) TEM and (b) HRTEM image of the FeP nanoparticles.

The powder X-ray diffraction (XRD) pattern for the product corresponded well with that expected for nanocrystalline MnP-type FeP (Figure 4-2a). Scherrer analysis of the peak widths indicated an average grain size of 11 nm, which is consistent with the average particle size observed by TEM and suggests that the nanocrystalline particles observed by TEM comprise the bulk of the sample. A selected-area electron diffraction (SAED) pattern acquired from an ensemble of particles (Figure 4-2b) exhibited rings that were fully indexed to MnP-type FeP, consistent with the bulk XRD data. The energy-dispersive X-ray spectroscopy (EDS) data (Figure 4-3) indicated a Fe:P ratio of 44:56, which is consistent with the expected FeP stoichiometry, along with a slight excess of P that is likely due to surface-bound TOP.


Figure 4-2: (a) Powder XRD data and (b) SAED pattern for the FeP nanoparticles. Both simulated and experimental XRD and SAED data are shown for comparison.



Figure 4-3: EDS spectrum of the as-synthesized FeP nanoparticles.

Working electrodes with FeP nanoparticle mass loadings of 1 mg cm⁻² on Ti substrates were heated for 2 h at 450 °C in H₂(5%)/Ar(95%), to remove the surface ligands (Figure 4-4). The electrocatalytic HER activity was then evaluated in acidic [0.50 M H₂SO₄,] and neutral-pH [1.0 M PBS] aqueous solutions. No Pt contamination was detectable by X-ray photoelectron spectroscopy (XPS).



Figure 4-4: DRIFT spectra of FeP nanoparticles as-synthesized (top) and after heating under $H_2(5\%)/Ar(95\%)$ to 450 °C (bottom). The region corresponding to the C-H stretching frequencies (present because of the surface ligands in the as-synthesized sample and absent after annealing) is highlighted.

Figure 4-5 shows polarization (current density vs potential) data for three individual FeP/Ti electrodes, along with data for Ti, which is not an active HER catalyst, as well as data for Pt, which is a benchmark HER catalyst. In acidic solutions, the FeP/Ti electrodes produced current densities of -10 mA cm⁻² and -20 mA cm⁻² at overpotentials of -50 mV and -61 mV respectively (i.e. $\eta_{-10\text{mA/cm}}^2 = -50$ mV and $\eta_{-20\text{mA/cm}}^2 = -61$ mV). These overpotentials approached those of the Pt electrode $(\eta_{-10\text{mA/cm}}^2 = -18 \text{ mV} \text{ and } \eta_{-10\text{mA/cm}}^2)$ $_{20\text{mA/cm}}^2$ = -26 mV), and are lower than those of other relevant and comparable systems in acidic solutions tested under identical conditions, including Ni₂P $(\eta_{-20mA/cm}^2 = -130 \text{ mV})^8$ and CoP $(\eta_{-20mA/cm}^2 = -85 \text{ mV})$.¹⁰ Previously reported overpotentials at comparable current densities and mass loadings suggest that the electrocatalytic HER activity of the FeP/Ti electrodes also compares favorably to that of other relevant systems, including $CoSe_2 (\eta_{-20mA/cm}^2 = -150 \text{ mV}),^6 CoS_2 (\eta_{-20mA/cm}^2 = -162 \text{ mV}),^7 MoS_2/RGO (\eta_{-20mA/cm}^2 = -162 \text{ mV}),^7 MoS_2/RO (\eta_{-20mA/cm}^2 = -162$ 185 mV),⁴ polycrystalline films of pyrite-type FeS₂ ($\eta_{-10mA/cm}^2 = -265$ mV),¹⁶ and porous FeP nanosheets $(\eta_{-20mA/cm}^2 = -325 \text{ mV})$.²² The enhanced activity of our FeP nanoparticles relative to the HER activity of porous FeP nanosheets previously reported may be due in part to the increased accessible surface area produced by the small particle sizes, in conjunction with ligand removal via thermal annealing, as well as to other intrinsic factors that include crystallinity and phase purity.



Figure 4-5: Polarization data for three distinct FeP/Ti electrodes, along with Pt and Ti, in (a) $0.50 \text{ M H}_2\text{SO}_4$ and (b) 1.0 M PBS.

The FeP/Ti electrodes also functioned as highly active HER electrocatalysts in neutral-pH aqueous solutions, with $\eta_{-10\text{mA/cm}}^2 = -102 \text{ mV}$ and $\eta_{-20\text{mA/cm}}^2 = -136 \text{ mV}$. For comparison, Pt exhibited a high HER activity, as expected ($\eta_{-10\text{mA/cm}}^2 = -45 \text{ mV}$ and $\eta_{-20\text{mA/cm}}^2 = -65 \text{ mV}$), while the bare Ti foil exhibited large overpotentials. While less active than in acidic solutions, these overpotential values in neutral-pH solutions are comparable to those of CoP nanowire arrays ($\eta_{-10\text{mA/cm}}^2 = -106 \text{ mA}$)¹¹ and compare favorably to other related systems, including Mo₂C ($\eta_{-1\text{mA/cm}}^2 = -200 \text{ mV}$),¹⁷ MoB ($\eta_{-1\text{mA/cm}}^2 = -250 \text{ mV}$),¹⁷ pyrrhotite-type FeS nanoparticles ($\eta_{-0.7\text{mA/cm}}^2 = -450 \text{ mV}$),²³ and Coembedded nitrogen-doped carbon nanotubes ($\eta_{-10\text{mA/cm}}^2 = -540 \text{ mV}$).²⁵

For the Pt electrode in 0.50 M H₂SO₄, the slope of the Tafel plot [overpotential *vs* log(current density)] was ~30 mV/decade, with an exchange current density of 2.49×10^{-3} A cm⁻² (Figure 4-6). Both values are consistent with the known behavior of Pt for the HER.^{8,10} For the FeP/Ti electrodes in 0.50 M H₂SO₄, Tafel analysis yielded a slope of ~37 mV/decade.



Figure 4-6: Tafel plots of overpotential vs. log(current density) of several FeP/Ti electrodes and of a Pt electrode. The slopes were obtained by applying a linear fit between -30 mV to -80 mV for the FeP samples and -20 mV to -50 mV for the Pt electrode.

The FeP Tafel slope is comparable to Tafel slopes for related systems such as MoS_2 on reduced graphene oxide (41 mV/decade),⁴ CoSe₂ (42 mV/decade),⁶ and Co-embedded nitrogen-doped carbon nanotubes (42 mV/decade)²⁵ and is significantly lower than the Tafel slopes for Ni₂P (46 mV/decade)⁸ and CoP (50 mV/decade).¹⁰ The exchange current density for FeP/Ti in acidic solutions was 4.3×10^{-4} A cm⁻², consistent with the high activity of FeP and intermediate between that of the Pt control (2.49 × 10⁻³ A cm⁻²) and

Ni₂P $(3.3 \times 10^{-5} \text{ A cm}^{-2})$.⁸ The turnover frequency (TOF) in 0.50 M H₂SO₄ at $\eta = 100$ mV was estimated to be 0.277 s⁻¹, which is comparable to prior reports for related systems.⁸⁻¹¹ The faradaic efficiencies of both an FeP/Ti electrode and the Pt control were determined by maintaining a current of -10 mA for 50 min, thus passing 30 C of charge. The amount of H₂ collected was consistent with that expected based on the amount of charge passed through the system, suggesting a quantitative faradaic yield.

The stabilities of the FeP/Ti electrodes in acidic and neutral solutions were first evaluated under galvanostatic conditions at a current density of -10 mA cm⁻² for 16 h. Over this time period, the overpotentials increased by approximately 52 mV in acidic solutions, but by only by ~35 mV in neutral-pH solutions (Figure 4-7a). Accelerated degradation studies were also performed using cyclic voltammetry (CV), in which the FeP/Ti electrodes were cycled between +0.1 V and -0.15 V vs RHE (reversible hydrogen electrode). After 500 and 1000 cycles, the overpotential in acidic solutions increased by approx. 19 and 25 mV, respectively (Figure 4-7b). Several factors could lead to such overpotential increases during CV cycling and galvanostatic testing in 0.50 M H₂SO₄, including sample degradation and the formation of surface oxides. XRD data for the FeP/Ti electrodes after 500 and 1000 cycles in 0.50 M H₂SO₄ confirmed that the nanocrystalline MnP-type FeP phase persisted. Notably, the analogous CV cycling experiments and galvanostatic testing in 1.0 M PBS showed no measurable increase in overpotential (Figure 4-7c), indicating that the FeP particles were very stable under neutral-pH conditions.



Figure 4-7: Plots for FeP/Ti electrodes in $0.50 \text{ M H}_2\text{SO}_4$ and 1.0 M PBS, respectively, of (a) overpotential vs. time, and (b,c) current density vs. potential, initially and after 500 and 1000 CV sweeps between +0.1 and -0.15 V vs RHE.

In addition to serving as an efficient HER electrocatalyst, FeP nanoparticles immobilized on TiO₂ photocatalytically generated hydrogen under UV illumination in acidic and neutral-pH aqueous solutions. For this purpose, the FeP nanoparticles were adsorbed onto Degussa P25 TiO₂ using a literature protocol.²⁶ A TEM image of the FeP/TiO₂ sample (Figure 4-8a), along with a corresponding HRTEM image (Figure 4-8b) and STEM-EDS element map (Figure 4-8c), confirmed that the FeP nanoparticles remain unchanged in morphology, uniformity, composition, or phase after deposition onto the TiO₂.



Figure 4-8: (a) TEM image, (b) HRTEM image, and (c) STEM-EDS element maps of the FeP/TiO2 nanocomposite.

Photocatalysis was performed under UV illumination provided by a 200 W Hg(Xe) arc lamp that was fitted with a water filter to cut off the infrared radiation (Figure 4-9).



Figure 4-9: Spectrum of the 200 W Hg(Xe) arc lamp used for the photocatalysis experiments.

Methanol (MeOH) was used as a sacrificial electron donor and the gaseous reaction products were monitored at 10 min intervals by an on-line gas chromatograph (GC) with a thermal-conductivity detector (TCD). Figures 4-10a, 4-11, and 4-10b show the rates of H_2 production as well as the total amounts of H_2 produced as a function of time under acidic [50:50 MeOH:HCl(1M)] and neutral-pH [50:50 MeOH:H₂O] conditions for FeP/TiO₂, as well as for Pt/TiO₂ and TiO₂. All co-catalyst mass loadings were 1.5 wt %, as confirmed by atomic absorption spectroscopy. The TiO₂-supported FeP nanoparticles exhibited sustained photocatalytic H_2 production over 16 h with minimal decrease in activity under both acidic and neutral-pH conditions. After testing, the FeP/TiO₂ composite remained largely intact (Figure 4-12). Bare TiO₂ is a relatively inactive photocatalyst for hydrogen production, and indeed, TiO₂ alone showed a negligible rate of H₂ production. Consistently, the Pt/TiO₂ control was highly active for H₂ production, yielding average rates of 4.7 and 3.5 μ mol H₂ mg⁻¹ h⁻¹ in acidic and neutral-pH solutions, respectively. The average rates of H₂ production for FeP/TiO₂ were comparable, having values of 1.2 and 1.9 µmol H₂ mg⁻¹ h⁻¹ in acidic and neutral-pH solutions, respectively. The apparent quantum yields were 0.056 and 0.087 in acidic and neutral solutions, respectively, and were comparable to the quantum yields observed for related non-noble metal HER catalyst systems.²⁷ Notably, and in contrast to the Pt/TiO₂ control, FeP/TiO₂ was slightly more active under neutral-pH conditions than under acidic conditions.



Figure 4-10: Plots of (a) H_2 production rate vs. time and (b) amount of H_2 produced vs. time in acidic and neutral solutions using the FeP/TiO₂ nanocomposite and UV illumination, as described in the text.



Figure 4-11: Plot showing the rate of photocatalytic H_2 production vs. time for Pt/TiO₂ and FeP/TiO₂ samples, each in acidic and neutral-pH solutions, as well as a TiO₂ control. The FeP data are also included in Figure 4b of the main text.



Figure 4-12: HRTEM image of the FeP/TiO₂ sample after 16 h of photocatalytic testing in acidic solution, showing that the size, morphology, and crystallinity of the FeP nanoparticle persisted, as did its interface with the TiO_2 support.

4.3 Conclusions

In summary, FeP nanoparticles, as a highly Earth-abundant system, exhibit exceptionally high activity for electrocatalytic and photocatalytic H_2 production in both acidic and neutral-pH aqueous solutions. The observed overpotentials of -50 mV and -102 mV to produce current densities of -10 mA cm⁻² in 0.50 M H₂SO₄ and 1.0 M PBS, respectively, place FeP amongst the most active non-noble metal HER electrocatalysts reported to date. The FeP nanoparticles are substantially more active than previously reported iron-based materials, and are highly desirable non-Pt systems for global scalability because of the exceptionally high Earth abundance and low cost of Fe. Accordingly, FeP/TiO₂ was shown to comprise a fully Earth-abundant system for the sustained photocatalytic production of $H_2(g)$ from both acidic and neutral-pH aqueous solutions.

4.4 Experimental Details

Chemicals and Materials. Octadecene [90%, $C_{18}H_{36}$, Sigma-Aldrich], oleylamine [70%, C₁₈H₃₇N, Sigma-Aldrich], oleic acid [technical grade, 90%, Sigma-Aldrich], pentacarbonyliron [99.5%, Fe(CO)₅, Alfa-Aesar], squalane [98%, C₃₀H₆₂, Alfa-Aesar], tri-n-octylphosphine [>85%, P(C₈H₁₆)₃, TCI America], platinum(II) 2,4pentanedionate [Pt 48.0% min, Alfa-Aesar], titanium foil [99.7%, 0.25 mm thickness], potassium phosphate dibasic [>98%, K₂HPO₄, Sigma-Aldrich], sodium phosphate monobasic [>98%, NaH₂PO₄, Sigma-Aldrich], hydrochloric acid [37%, Sigma-Aldrich], sulfuric acid [99.999%, Sigma-Aldrich] and methanol [technical grade] were used as received. High-quality colloidal Ag paint was purchased from SPI Supplies and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr. Degussa P25 TiO₂ [Aeroxide® P25 titanium(IV) oxide nanopowder, 21 nm particle size (TEM), \geq 99.5% trace metals basis] was purchased from Sigma Aldrich, and 1.0 M PBS solution, with a measured pH of 6.5, was made by dissolving 69 g of NaH₂PO₄·H₂O (0.5 mol) and 71 g of Na₂HPO₄ (0.5 mol) in 1 L of water obtained from a Barnsted Nanopure column.

Synthesis of Hollow Iron Phosphide Nanoparticles. [Caution: This reaction should be considered to be highly corrosive and flammable because the high-temperature decomposition of a phosphine can liberate phosphorus, which is pyrophoric. Therefore, this reaction should only be carried out using rigorously air-free conditions by appropriately trained personnel.] Hollow iron phosphide nanoparticles were synthesized from colloidal iron nanoparticles by modifying a prior report.²⁴ 1-Octadecene (ODE, 10.0 mL, 31.3 mmol) and oleylamine (0.2 mL, 0.61 mmol) were added to a 50-mL, threenecked round bottom flask that was equipped with a reflux condenser, a thermometer adapter, a thermometer, a rubber septum, and a borosilicate-coated stir bar. The contents of flask were stirred and heated to 120 °C under vacuum for 30 min to remove any adventitious water, then placed under an Ar atmosphere. This ODE/oleylamine solution was then heated to 190 °C, at which point 0.35 mL of pentacarbonyliron was injected. The suspension was then maintained at 190 °C for 20 min. Five milliliters of the hot ODE/oleylamine mixture, which at this point now contained colloidal Fe nanoparticles, was then rapidly injected (using a glass syringe) into an second Ar-filled 50-mL threenecked flask containing squalane (7.0 mL, 13 mmol) and tri-n-octylphosphine (3.0 mL, 6.7 mmol) that had been heated to 340 °C for 1 h. The temperature dropped as a result of the injection and was brought back up to 320 °C and held at that temperature for 1 h. After the reaction was completed, the heating mantle was turned off and the solution was allowed to cool to 200 °C. The heating mantle was then removed to allow the sample to cool more rapidly to room temperature. The reaction solution was divided into two centrifuge tubes for collection and cleaning. The nanoparticles were collected by adding hexanes (5 mL) and ethanol (15 mL) to each tube, followed by centrifugation (12,000

rpm, 3 min). The particles were then resuspended in hexanes (5 mL), and this process was repeated twice more. Nanoparticles were redispersed in hexanes after isolation and placed in a vial (20 mL) for use.

Preparation of Working Electrodes. Electrode fabrication was analogous to that described in previous reports.^{8,10,12,14} FeP nanoparticles were deposited onto 0.2 cm² pieces of Ti foil using 5- μ L increments of a 10 mg mL⁻¹ solution, up to a total of 20 μ L. After drying, the FeP/Ti foils were heated at 450 °C in H₂(5%)/Ar(95%), and were then attached to a polyvinyl chloride-coated Cu wire. A two-part epoxy was used to insulate the conductive surfaces, with the exception of the FeP-decorated side of the Ti foil.

Electrochemical Measurements. Electrochemical measurements were acquired using a Gamry Instruments Reference 600 potentiostat and were performed in 1.0 M phosphate buffered saline (PBS) when testing in neutral-pH conditions or in 0.50 M H_2SO_4 when testing in acidic conditions. Current Interrupt (built into the potentiostat) was used to account for uncompensated solution resistance in all measurements. A three-electrode cell with two compartments was used, and the compartments were separated by a Nafion® membrane (Fuelcellstore.com) to inhibit contamination of the working electrode by the contents of the counter electrode solution. A mercury/mercurous sulfate (Hg/Hg₂SO₄) electrode was used as the reference electrode, and a Pt mesh electrode was used as the counter electrode at a sweep rate of 1 mV s⁻¹ while research-grade $H_2(g)$ was continuously bubbled through the solution, which was rapidly stirred with a magnetic stir bar.

clean Pt mesh electrode in the electrolyte solution allowed for the determination of the RHE potential after the electrochemical characterization of iron phosphide. An initial measure of electrochemical stability was obtained by holding the current density galvanostatically at 10 mA cm⁻² for 16 h. Long-term electrochemical stability was simulated using cyclic voltammetric sweeps between +0.1 V and -0.15 V *vs* RHE at 100 mV s⁻¹. Turnover frequencies were estimated as reported previously.^{8,10}

Quantitative Hydrogen Yield Measurements. Hydrogen yield measurements were performed in both the acidic and neutral solutions using a two-electrode, singlecompartment cell. Graphitic carbon was used as the counter electrode with either FeP/Ti or Pt as the working electrode. The evolved $H_2(g)$ was captured *via* an inverted graduated cylinder, positioned above the working electrode, which contained the electrolyte solution. In each experiment, a cathodic current of 10 mA was passed continuously through the 0.2 cm² working electrode over a 50 min (3000 s) duration, resulting in 30 C of total charge passed. For both acidic and neutral conditions, the FeP/Ti electrodes produced a volume of $H_2(g)$ that was equivalent to the volume collected above Pt nanoparticle electrodes. All experiments yielded 3.96 ± 0.03 mL of hydrogen. This is comparable to the faradaic theoretical H_2 yield of 3.74 mL calculated at 1 atm and 20 °C (ambient conditions) for 30 C of charge.

Synthesis of Pt Nanoparticles. The Pt nanoparticles were synthesized using an adaptation of a previously reported procedure.²⁸ In the synthesis, 100 mg of $Pt(acac)_2$, 10 mL of ODE, 1 mL of OLAC, and 1 mL of OLAM were added to a 50-mL, three-necked,

round-bottomed flask fitted with a condenser, magnetic stir bar, thermometer adapter, thermometer, and rubber septum at room temperature. The mixture was stirred under vacuum at ~120 °C for 20 min to remove any adventitious oxygen and water. The reaction was then placed under Ar and heated to 185 °C, and 0.1 mL of a previously prepared $Fe(CO)_5$ solution (0.75 M in ODE) was then quickly injected. The reaction proceeded at a temperature of 200 °C for 20 min. The product was then cooled to room temperature by removing the flask from the heating mantle and subsequently transferring the suspension to centrifuge tubes. Ethanol was added to the tubes (1:1 by volume), and the product was centrifuged at 10 000 rpm for 5 min. The black precipitate was redispersed in hexanes and ethanol (1:1 by volume) and centrifuged at 10 000 rpm. The product was then redispersed in hexanes and stored.



Figure 4-13: TEM image of Pt nanoparticles used as a control in the photocatalysis experiments.

Preparation of Pt/TiO₂ and FeP/TiO₂. The Pt and FeP nanoparticles were anchored onto Degussa P25 TiO₂ using an adaptation of a previously reported procedure.²⁶ A toluene solution of Pt or FeP nanoparticles of the appropriate concentration was added to a dispersion of TiO₂ in toluene. After stirring for 1 h, the solid was separated by centrifugation and washed with acetone, along with the use of mild sonication. The obtained slurry was then vacuum dried and heated for 2.5 h at 450 °C under a H₂(5%)/Ar(95%) atmosphere to remove the surface ligands and to ensure the formation of a robust solid-solid interface between the nanoparticles and the TiO₂support. The Pt/TiO₂ sample was annealed for 3 h in air at 350 °C.

Photocatalytic Testing. Approximately 50 mg of Pt/TiO₂ or FeP/TiO₂ was suspended with sonication in 50 mL of a 1:1 MeOH:H₂O solution (pH-neutral solution) or 1 M HCl (acidic solution). Prior to the tests the reactor was purged with Ar for ~25 min to ensure the removal of air. An Ar flow of 10 mL min⁻¹ was maintained during testing. UV illumination was provided by a 200 W Hg(Xe) arc lamp fitted with a water filter to cut off the infrared radiation. Using a Newport OSM-400 spectrophotometer, the power density at the surface of the sample was measured to be ~5.6 mW/cm² over wavelengths shorter than 365 nm, which corresponds to a photon flux of ~ 3.65×10^{17} photons/s. The gaseous reaction products were monitored at 10 min intervals by an online gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD).

Materials Characterization. Powder X-ray diffraction (XRD) patterns were acquired using a Bruker-AXS D8 Advance diffractometer with Cu Ka radiation and a LynxEye 1-D detector. The CrystalMaker / CrystalDiffract software package was used to simulate XRD patterns for MnP-type FeP. Microscopy samples were prepared by dropcasting 0.7 µL of dispersed FeP 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 that was operated at an accelerating voltage of 80 kV. A JEOL JEM-2010F microscope equipped with an EDAX solid-state X-ray detector was used to collect high-resolution TEM (HRTEM) images at an accelerating voltage of 200 kV, as well as scanning transmission-electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) data. ES Vision software (Emispec) was used for EDS and STEM-EDS data processing, with the Fe Kshell and P K-shell transitions chosen for quantitative EDS analysis. X-ray photoelectron spectroscopy (XPS) analysis was performed on a monochromatic Al Ka source Kratos Axis Ultra operating at 14 kV and 20 mA for an X-ray power of 280 W. XPS spectra were acquired with a photoelectron takeoff angle of 90° from the sample surface plane and were referenced to the C_{1s} peak with a binding energy of 285 eV. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were acquired using a Bruker IFS 66/s spectrometer (Bruker Optics, Billerica, MA). KBr powder was used to dilute the nanoparticle samples for analysis and DRIFT spectra were processed with OPUS 6.0 (Bruker Optics, Billerica, MA). The catalyst loadings on TiO₂ were verified using a Shimadzu AA-7000 atomic absorption spectrophotometer.

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4.5 References

- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis. *Chem. Rev.* 2010, *110*, 6446.
- (2) H. B. Gray. *Nature Chem.* **2009**, *1*, 7.
- B. Hinneman, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, L. B.
 Chorkendorff, J. K. Nørskov. J. Am. Chem. Soc. 2005, 127, 5308.
- Y Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai. J. Am. Chem. Soc. 2011, 133, 7296.
- (5) I. A. Raj, K. I. Vasu. J. Appl. Electrochem. **1990**, 20, 32.
- (6) D. Kong, H. Wang, Z. Lu, Y. Cui. J. Am. Chem. Soc. 2014, 136, 4897.
- (7) M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding, S. Jin. J. Am. Chem. Soc. 2014. 136, 10053.
- (8) E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis, R. E. Schaak. J. Am. Chem. Soc. 2013, 135, 9267.
- (9) L. Feng, H. Vrubel, M. Bensimon, X. Hu. Phys. Chem. Chem. Phys. 2014, 16, 5917.
- E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak. Angew. Chem., Int. Ed. 2014, 53, 5427.

- (11) J. Tian, Q. Liu, A. M. Asiri, X. Sun. J. Am. Chem. Soc. 2014, 136, 7587.
- J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis, R. E. Schaak. *Chem. Mater.* 2014, 26, 4826.
- (13) P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J-Y. Wang, K. H. Lim, X. Wang. *Energy Environ. Sci.* 2014, 7, 2624.
- (14) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak. *Chem. Commun.* 2014, 50, 11026.
- (15) Z. Huang, Z. Chen, Z. Chen, C. Lv, H. Meng, C. Zhang. ACS Nano, 2014, 8, 8121.
- (16) D. Kong, J. J. Cha, H. Wang, H. R. Lee, Y Cui. *Energy Environ. Sci.* 2013, *6*, 3553.
- (17) H. Vrubel, X. Hu. Angew. Chem., Int. Ed. 2012, 51, 12703.
- (18) W. Chen, J. T. Muckerman, E. Fujita. *Chem. Commun.* **2013**, *49*, 8896.
- B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic, P. G. Khalifah. J. Am. Chem.
 Soc. 2013, 135, 19186.
- (20) U.S. Geological Survey, *Metal Prices in the United States through 2010*. Retrieved from <u>http://pubs.usgs.gov/sir/2012/5188/</u>
- S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. Meyer-Klaucke, E. Warkentin, R. K. Thauer, U. Ermler. *Science*. 2008, *321*, 572.
- (22) Y. Xu, R. Wu, J. Zhang, Y. Shi, B. Zhang. Chem. Commun. 2013, 49, 6656.
- (23) C. D. Giovanni, W. Wang, S. Nowak, J. Greneche, H. Lecoq, L. Mouton, M. Giraud, C. Tard. ACS Catal. 2014, 4, 681.
- (24) E. Muthuswamy, P. R. Kharel, G. Lawes, S. L. Brock. ACS Nano 2009, 3, 2383.
- (25) X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa. Angew. Chem., Int. Ed. 2014, 53, 4372.

- M. Cargnello, V. V. T. Doan-Nguyen, T. R. Gordon, R. E. Diaz, E. A. Stach, R. J. Gorte, P. Fornasiero, C. B. Murray. *Science* 2013, *341*, 771.
- (27) Q. Xiang,; J. Yu,; M. Jaroniec. J. Am. Chem. Soc. 2012, 134, 6575.
- (28) C. Wang, H. Yin, S. Dai, S. Sun. Chem. Mater. 2010, 22, 3277.

Chapter 5

Solution Synthesis of Metal Silicide Nanoparticles

5.1 Introduction

Intermetallic compounds of the transition metals and silicon constitute an important and diverse family of inorganic solids that are of interest for their fundamentally interesting structures and properties, as well as for their technological applications.¹⁻³ Depending on their constituent metals, stoichiometries, and crystal structures, metal silicides can exhibit a range of electronic, magnetic, optical, catalytic, and mechanical properties.³ Metal silicides are typically synthesized using high-temperature methods.⁴ However, such methods do not produce nanostructures, which are needed for studying size- and dimension-dependent properties and for integrating into nanoscale devices, or colloidal particles, which are useful for solution processing and for producing high surface area materials.^{2,3,5} For these purposes, lower temperature synthetic methods are highly desirable, as they can minimize sintering and grain growth while permitting control over the growth process and therefore the size and morphology of the product.^{3,5,6}

Metal silicide nanostructures have been produced using methods that include chemical vapor transport, chemical vapor deposition, ball milling, and high temperature and pressure reduction of metal oxide and metal salt precursors.^{2,3,5,7} Solution routes have been used to grow metal silicide nanostructures off of substrates,⁸ as well as to synthesize colloidal iron silicide nanoparticles.⁶ However, it remains challenging to produce colloidal metal silicide nanoparticles using all-solution, ambient-pressure routes. Such solution routes, by analogy to capabilities for other families of intermetallic compounds,⁹ constitute a powerful low-temperature approach for synthesizing high surface area nanostructures. Such methods also offer an alternative, non-mainstream platform for the exploratory synthesis and discovery of new compounds, complementing strategies used by John Corbett to synthesize metal silicides and other intermetallic compounds throughout his distinguished career.^{4,10}

Accordingly, here we report a lower-temperature solution route to colloidal metal silicide nanoparticles. Colloidal metal nanoparticles serve as reagents that transform into their corresponding metal silicides upon injection of monophenylsilane (MPS) in trioctylamine (TOA) at 375 °C. MPS is sometimes used in the synthesis of Si nanowires, often *via* higher-temperature seed-mediated vapor-liquid-solid growth processes.¹¹ Our prototype system for demonstrating this approach is Pd₂Si, because this metal silicide is known to form readily from the interdiffusion of Pd and Si in electronic devices¹² and because it has also been demonstrated to be catalytically active for selective hydrogenation reactions.¹³ We then generalize this approach to the Cu_3Si and Ni_2Si systems. Leveraging heterogeneous catalysis as a key application that benefits from the high surface areas afforded by nanoparticles, we also show that these metal silicides function as catalysts for the hydrogen evolution reaction (HER). The HER, which involves the electrochemical reduction of aqueous protons to produce molecular hydrogen, is implicit in the function of water electrolyzers and solar fuel cells and is typically catalyzed most effectively by noble metals such as platinum.¹⁴

5.2 Results and Discussion

The Pd₂Si nanoparticles were synthesized by reacting Pd nanoparticles, which were produced by heating Pd(acac)₂ in trioctylphosphine and oleylamine at 250 °C (Figure 5-1),¹⁵ with MPS in TOA at 375 °C.



Figure 5-1: Top: TEM images of Pd, Cu, and Ni nanoparticle precursors that were reacted with MPS to form transition metal silicide nanoparticles. Bottom: Corresponding XRD patterns. The Cu sample also contains Cu_2O (black simulated pattern) due to unavoidable oxidation during work-up and storage.

Briefly, the Pd nanoparticles were dispersed in TOA and then injected into a solution of squalane at 375 °C, followed by injection of MPS in TOA. The Pd₂Si product was then washed with a mixture of chloroform and methanol and redispersed in ethanol. To remove any adventitious SiO₂, the particles were also washed with 1 M NaOH in water. Figure 5-2 shows a powder X-ray diffraction (XRD) pattern for the Pd₂Si particles, along with a simulated XRD pattern for Fe₂P-type Pd₂Si for comparison. The lattice

parameters for the Pd₂Si product are a = 6.489 Å and c = 3.435 Å, which match well with literature values (a = 6.497 Å and c = 3.432 Å).¹⁶ Scherrer analysis of the XRD peak widths indicates an average grain size of approximately 15 nm, which is indicative of nanocrystallinity.



Figure 5-2: Powder XRD data for Pd₂Si nanoparticles. Bottom (black), simulated. Top (red), experimental. Indexing corresponds to Fe₂P-type Pd₂Si.

A transmission electron microscopy (TEM) image of the Pd₂Si product, along with the corresponding selected area electron diffraction (SAED) pattern and the energydispersive X-ray spectrometry (EDS) spectrum, is shown in Figure 5-3. The TEM image (Figure 5-3a) indicates that the Pd₂Si particles are nanoscopic and discrete, with a mixture of pseudospherical and multi-faceted morphologies that have diameters ranging from approximately 15–45 nm. The average grain size of approximately 15 nm that was observed by Scherrer analysis of the XRD data is smaller than the majority of the particles observed by TEM, suggesting that the particles are polycrystalline. The SAED pattern (Figure 5-3b) shows diffraction spots that are consistent with the peaks expected for Fe₂P-type Pd₂Si, matching well with the bulk XRD data. The EDS data in Figure 5-3c indicate an approximate Pd:Si ratio of 63:37, which is consistent with the expected Pd₂Si stoichiometry.



Figure 5-3: (a) TEM image with corresponding (b) SAED pattern and (c) EDS spectrum for Pd₂Si nanoparticles. The Cu signal in (c) originates from the Cu TEM grid.

To demonstrate the potential generality of the method, two other metal silicides were synthesized. Upon reacting Cu nanoparticles (Figure 5-1) with MPS at 375 °C, Cu₃Si nanoparticles formed. Similarly, Ni₂Si nanoparticles formed from the reaction of Ni nanoparticles (Figure 5-1) with MPS at 375 °C. Figure 5-4 shows XRD data and TEM images for the Cu₃Si and Ni₂Si products. The XRD pattern for the Cu₃Si nanoparticles matches well with that expected for η -Cu₃Si (Figure 5-4a). For Ni₂Si, the XRD pattern matches well with that expected for Co₂Si-type Ni₂Si (Figure 5-4b). The Cu₃Si and Ni₂Si nanoparticles appear pseudospherical by TEM (Figures 5-4 and 5-5), and the SAED patterns confirm their phase assignment (Figure 5-5).



Figure 5-4: Powder XRD and TEM data for (a) Cu3Si and (b) Ni2Si nanoparticles. The bottom XRD patterns are simulated data and the top patterns are experimental data. Minor Cu0.83Si0.17 and NiSi impurities are sometimes observed.



Figure 5-5: SAED patterns and TEM images for Cu₃Si and Ni₂Si nanoparticles, showing characteristic diffraction spots.

One advantage of solution-synthesized nanoparticles is that they have high surface areas that maximize exposure of surface sites for heterogeneous catalysis. Metal silicides catalyze several types of reactions, including hydrodesulfurization (HDS),¹⁷ hydrogenation,¹⁸ and hydrogen evolution.¹⁹ In particular, Ni-Si phases are known HDS catalysts,¹⁷ and PdSi, NiSi₂, and Cu₅Si phases are known HER catalysts.¹⁹ This therefore provides an impetus to evaluate the Pd₂Si, Cu₃Si, and Ni₂Si nanoparticles as HER catalysts, because a mechanistic commonality between the HDS and HER processes has been postulated based on the low energetic barrier to binding and dissociating molecular hydrogen.^{14,20}

The metal silicide nanoparticles were deposited onto 0.2 cm² Ti foil supports (1 mg cm⁻²) and heated in 5% H₂/Ar at 450 °C. Figure 5-6 shows polarization data for a bare Ti foil electrode and a Pt mesh control, as well as Pd₂Si/Ti, Cu₃Si/Ti, and Ni₂Si/Ti electrodes. The Ti foil is inactive in the potential range that was surveyed, while Pt is an excellent HER catalyst. Cu₃Si was not an active catalyst for the HER. However, Pd₂Si and Ni₂Si required overpotentials of -192 mV and -243 mV, respectively, to produce a current density of 10 mA cm⁻². The HER overpotentials for Pd₂Si and Ni₂Si revealed by this initial, preliminary evaluation are higher than those of related metal phosphide nanoparticle systems prepared and tested in a similar manner, which require -50 to -110 mV to produce a 10 mA cm⁻² current density.²⁰ However, the HER overpotentials for Pd₂Si and Ni₂Si are comparable to those of other systems, including some molybdenum compounds and carbon-based nanostructures.²¹ While long-term stability remains to be established given the possible reactivity of metal silicides with aqueous acids, FeSi and FeSi₂ were previously found to be highly stable during sustained HER testing in H₂SO₄.²²



Figure 5-6: Polarization data (iR corrected) in 0.50 M H₂SO₄ for Pd₂Si, Ni₂Si, and Cu₃Si nanoparticle films on Ti foil electrodes, as well as Ti foil and Pt mesh controls.



Figure 5-7: Tafel plot of Ni₂Si/Ti, Pd₂Si/Ti, and Pt electrodes showing overpotential vs. log(current density). The Tafel slopes for these materials were ~66, ~131, and ~30 mV/decade respectively. A linear fit was applied to the regions of -100 mV to -200 mV for Ni₂Si, -75 mV to -100 mV for Pd₂Si, and -10 mV to -40 mV for Pt to obtain the slopes. Ni₂Si has a Tafel slope that is comparable to other nanomaterials including Ni₂P (~46 mV/decade to ~81 mV/decade) and CoP (50 mV/decade).⁵ Pd₂Si gave a significantly steep Tafel slope indicating that the mechanism for the HER on this material differs from that of either Pt or Ni₂Si. A Tafel slope of 30 mV/decade is expected for Pt and matches the literature value.⁵

5.3 Conclusions

In conclusion, we demonstrated the solution synthesis of several transition metal silicides – Pd₂Si, Cu₃Si, and Ni₂Si – as colloidal nanoparticles by reacting metal nanoparticles with MPS in TOA at 375 °C. The addition of metal silicides to the list of systems that can be accessed in solution using straightforward adaptations of known colloidal nanoparticle synthetic protocols further expands this synthetic toolbox, as well as the scope of future studies that leverage their solution dispersibility and high surface areas. An initial screening indicates that Pd₂Si and Ni₂Si function as heterogeneous electrocatalysts for the HER and, as such, complement previous studies of metal silicide HER catalysts.¹⁹

5.4 Experimental Details

Chemicals and Materials. Palladium acetylacetonate [Pd 34.7%, Pd(acac)₂, Alfa Aesar, Lot#I092017], oleylamine [tech. 70%, C₁₈H₃₇N, Sigma-Aldrich, Lot #BCBH8493V], trioctylphosphine [TOP, tech. 90%, P(C₈H₁₆)₃, Sigma-Aldrich, Lot #SHBC8966V], copper(I) acetate [99%, Cu(CH₃COO), Strem Chemical, Lot #18804000], n-tetradecylphosphonic acid [TDPA, CH₃(CH₂)₁₃P(O)(OH)₂, PCI Synthesis, Lot #P1-12TDP], nickel acetylacetonate [95%, Ni(acac)₂, Alfa Aesar, Lot #H27Z033], squalane [99%, C₃₀H₆₂, Sigma-Aldrich, Lot #BCBL8628V], monophenylsilane [MPS, C₆H₅SiH₃, Gelest Inc., Lot #3L-21908], trioctylamine [TOA, 98%, (CH₃(CH₂)₇)₃N, Sigma-Aldrich, Lot #MKBG0491V], titanium foil [99.7%, 0.25 mm thickness], and sulfuric acid [99.999%, Sigma-Aldrich] were used as received. High-quality colloidal Ag paint was purchased from SPI Supplies and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr.

Synthesis of Pd Nanoparticles. The synthesis of Pd nanoparticles was modified from a literature protocol.¹⁵ First, Pd(acac)₂ (0.1 g) was dissolved *via* sonication in 1 mL of TOP. In a 50-mL three-necked, round-bottom flask, the Pd-TOP solution was added to 10 mL of oleylamine. The round bottom flask was then equipped with a reflux condenser, a thermometer adapter, a rubber septum, and a stir bar, and heated to 250 °C under Ar with rapid stirring. After 30 min at 250 °C, the heat was turned off and the reaction mixture was allowed to cool to room temperature. The solution was transferred to a centrifuge tube, and then 5 mL of hexanes and 15 mL of ethanol were added followed by centrifugation at 12,000 rpm for 3 min. The centrifugation process was repeated and the isolated Pd particles were redispersed in hexanes for storage until reacting with MPS.

Synthesis of Cu Nanoparticles. Copper nanoparticles were synthesized based on a literature protocol²³ using an identical three-necked glassware apparatus as for the Pd nanoparticles described above. In the three-necked flask, 10 mL TOA was heated under Ar to 130 °C for 30 min with moderate stirring to remove any oxygen or water present. Then, the solution was allowed to cool to 50 °C, and 122 mg Cu(CH₃COO) and 139.2 mg TDPA were added. The mixture was placed back under Ar and rapidly heated to 180 °C for 30 min where the solution turned from green to brown. After the 30 min dwell, the solution was heated to 270 °C for 30 min where the solution turned from brown to red.

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Following the 270 °C dwell, the heat was turned off and the solution was allowed to cool to room temperature. The isolation process for the Cu nanoparticles was identical to the Pd nanoparticles described above. After sitting in hexanes for a few hours, the particles can partially oxidize to form some Cu₂O, although this does not seem to negatively impact the reaction with MPS to form metal silicide particles.

Synthesis of Ni Nanoparticles. The synthesis of nickel nanoparticles was carried out in a 50 mL three-necked round bottom flask with a reflux condenser, thermometer adapter, PTFE-coated stir bar and rubber septum. Based on a literature protocol,²⁴ the particles were synthesized by first adding 250 mg Ni(acac)₂, 10 mL oleylamine, and 0.5 mL TOP to the round bottom flask. The contents were moderately stirred and heated to 120 °C for 20 min under vacuum. Then, the mixture was placed under Ar and rapidly heated to 220 °C. After holding at this temperature for 2 h, the flask was removed from heat and the particles were allowed to cool. The isolation process for the Ni nanoparticles was identical to that for the Pd nanoparticles described above.

Synthesis of Metal Silicide Nanoparticles. [Caution: Decomposition of monophenylsilane (MPS) at high temperatures can yield silane.^{11a} While the amount of silane produced in this reaction would be extremely small, especially since we observe nearly quantitative incorporation of all MPS-derived Si into the silicide nanoparticles and SiO₂ byproducts, this reaction still should be considered to have the potential to be highly flammable and therefore should only be carried out in a small-scale reaction vessel under rigorously air-free conditions by personnel with appropriate training. Procedures for

working with such reactions are provided in work by Korgel et. al.^{11a}] Squalane (10.0 mL) was added to a 50-mL three-necked, round-bottom flask equipped with a reflux condenser, a thermometer adapter, a thermometer, a rubber septum, and a borosilicatecoated stir bar. With moderate stirring, the squalane solution was degassed at 120 °C under vacuum for 30 min, to remove any water or oxygen present. The solution was then placed under Ar and quickly heated to 375 °C. Once the solution reached this temperature, 20 mg of metal nanoparticles redispersed in a few drops of hexanes and 0.5 mL of pre-degassed TOA were rapidly injected into the hot squalane solution. The temperature was observed to drop approx. 10 °C upon injection. As soon as temperature recovered to 375 °C, a mixture of 0.15 mL of MPS in 0.35 mL of pre-degassed TOA was injected. The MPS injection was performed using a 4" needle and inserting it directly into the solution to promote decomposition at the metal nanoparticle surfaces rather than evaporation at the surface of the solution. Also, for Cu₃Si and Ni₂Si, a second injection of the MPS mixture once re-equilibrated at 375 °C helped to maximize phase purity. The reaction mixture was maintained at 375 °C for 1 h. After 1 h, the heat was turned off and the reaction mixture was allowed to cool to room temperature. After transferring the reaction solution to a centrifuge tube, the nanoparticles were collected by adding hexanes (5 mL) and ethanol (15 mL) to the tube, followed by centrifugation (12,000 rpm, 3 min). The particles were then resuspended in hexanes (5 mL), and this process was repeated two additional times. After isolating the product, the particles were redispersed in hexanes and poured into a scintillation vial. To clean the metal silicide particle surface, the particles were twice collected via centrifugation and redispersed in 5 mL of chloroform using methanol as the anti-solvent. The particles were then redispersed in 1

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mL of ethanol and 1 mL of 1 M NaOH in H_2O . This suspension was sonicated for 1 min, followed by dilution with 5 mL of H_2O . Finally, the particles were re-collected using centrifugation and redispersed in hexanes for use.

Preparation of Working Electrodes. Electrodes were prepared similarly to protocols from previous reports.²⁰ First, stock solutions of the NaOH-treated metal silicide particles were prepared in hexanes at a concentration of 10 mg mL⁻¹ for each. The metal silicide nanoparticles were then deposited in 5- μ L increments onto 0.2 cm² pieces of Ti foil, up to a total of 20 μ L. Once dry, the metal silicide-decorated Ti foils were heated at 450 °C in 5% H₂/Ar, then attached to a polyvinylchloride-coated Cu wire. Finally, a two-part epoxy was applied to insulate the conductive surfaces from contact with the electrolyte solution, with the exception of the metal silicide-decorated side.

Electrochemical Measurements. Electrochemical data were acquired using a Gamry Instruments Reference 600 potentiostat. All measurements were performed in $0.50 \text{ M H}_2\text{SO}_4$ using a two-compartment, three-electrode cell. The two compartments were separated by a Nafion® membrane (Fuelcellstore.com) to prevent cross contamination between the contents of the working electrode and the counter electrode solutions. Pt mesh was used as the counter electrode itself while a mercury/mercurous sulfate (Hg/Hg₂SO₄) electrode was used as the reference electrode. Polarization data were acquired using a sweep rate of 1 mV s⁻¹, with rapid stirring using a magnetic stir bar. The Current Interrupt method (a built-in potentiostat feature) was used to account for uncompensated solution resistance in all measurements. Research-grade H₂(g) was

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continuously bubbled through the solution at \sim 1 atm to maintain a constant value for the RHE potential. Measurement of the open-circuit potential of a clean Pt mesh electrode in the electrolyte solution was used to determine the RHE potential after electrochemical characterization of the metal silicide nanoparticles.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using the CrystalMaker / CrystalDiffract software suite. All samples for microscopic analysis were prepared by drop-casting 0.7 µL of dilute, dispersed nanoparticles in hexanes onto a Cu or Ni grid (400 mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmission-electron microscopy (TEM) images were obtained using a JEOL 1200 microscope (80kV) or a JEOL 2010 microscope (LaB₆, 200 kV) and selected area electron diffraction (SAED) patterns were obtained using the JEOL 2010 microscope. The JEOL 2010 microscope was also coupled with an EDAX solid-sate X-ray detector which was used for collecting energy-dispersive X-ray spectroscopy (EDS) data. EDS data were processed using Revolution software.

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5.5 References

- (1) S.-L Zhang, M. Ostling, *Crit. Rev. Solid State Mater. Sci.* 2003, 28, 1.
- (2) Y.-C Lin, Y. Chen, Y. Huang, *Nanoscale* **2012**, *4*, 1412.
- (3) A. L. Schmitt, J. M. Higgins, J. R. Szczech, S. Jin, J. Mater. Chem. 2010, 20, 223.
- (4) Y. Kwon, M. A. Rzeznik, A. Guloy, J. D. Corbett, *Chem. Mater.* **1990**, *2*, 546.
- (5) M. Estruga, S. N. Girard, Q. Ding, L. Chen, X. Li, S. Jin, *Chem. Commun.* 2014, 50, 1454.
- (6) N. Dahal, V. Chikan, *Chem. Mater.* **2010**, *22*, 2892.
- (7) (a) Q. Lu, J. Hu, K. Tang, Y. Qian, G. Zhou, X. Liu, *Solid State Ionics* 1999, *124*, 317. (b) X. Chen, J. Guan, G. Sha, Z. Gao, C. T. Williams, C. Liang, *RSC Adv.* 2014, *4*, 653.
- (8) (a) F. W. Yuan, C. Y. Wang, S. H. Chang, L. W. Chu, L. J. Chen, H. Y. Tuan, *Nanoscale* 2013, *5*, 9875. (b) H. Geaney, C. Dickinson, C. O'Dwyer, E. Mullane, A. Singh, K. M. Ryan, *Chem. Mater.* 2012, *24*, 4319.
- (9) (a) A. K. Sra, T. D. Ewers, R. E. Schaak, *Chem. Mater.* 2005, *17*, 758. (b) R. E. Cable, R. E. Schaak, *Chem. Mater.* 2005, *17*, 6835. (c) N. H. Chou, R. E. Schaak, *J. Am. Chem. Soc.* 2007, *129*, 7339. (d) J. C. Bauer, X. Chen, Q. Liu, T.-H. Phan, R. E. Schaak, *J. Mater. Chem.* 2008, *18*, 275.
- (10) J. D. Corbett, *Inorg. Chem.* **2010**, *48*, 13.
- (11) (a) H. Tuan, D. C. Lee, T. Hanrath, B. A. Korgel, *Nano Lett.* 2005, *5*, 681. (b) A.
 T. Heitsch, C. M. Hessel, V. A. Akhavan, B. A. Korgel, *Nano Lett.* 2009, *9*, 3042.
- (12) (a) R. W. Bower, D. Sigurd, R. E. Scott, *Solid-State Electron*. 1973, *16*, 1461. (b)
 R. K. Joshi, M. Yoshimura, K. Tanaka, K. Ueda, A. Kumar, N. Ramgir, *J. Phys. Chem. C* 2008, *112*, 13901.
- (13) M. Zaheer, G. Motz, R. Kempe, J. Mater. Chem. 2011, 21, 18825.
- (14) C. G. Morales-Guio, L.-A. Stern, X. Hu, Chem. Soc. Rev. 2014, 43, 6555.
- (15) S. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon, Y. W. Kim, *Nano Lett.* **2003**, *3*, 1289.
- (16) B. Aronsson, A. Nylund, Acta Chem. Scand. 1960, 14, 1011.
- (17) X. Chen, X. Liu, L. Wang, M. Li, C. T. Williams, C. Liang, *RSC Adv.* 2013, *3*, 1728.
- (18) (a) J. Panpranot, K. Phandinthong, T. Sirikajorn, M. Arai, P. Praserthdam, J. Mol. Catal. A: Chem. 2007, 261, 29. (b) X. Chen, M. Li, J. Guan, X. Wang, C. T. Williams, C. Liang, Ind. Eng. Chem. Res. 2012, 51, 3604.
- (19) (a) A. K. Vijh, G. Belanger, R. Jacques, *Int. J. Hydrogen Energy* 1990, *15*, 789.
 (b) A. K. Vijh, G. Belanger, *J. Mater. Sci. Lett.* 1995, *14*, 982. (c) M. S. Faber, S. Jin *Energy Environ. Sci.* 2014, *7*, 3519.
- (20) (a) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak, *J. Am. Chem. Soc.* 2014, *53*, 5427. (b) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak, *Angew. Chem. Int. Ed.* 2014, *53*, 5427. (c) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis, R. E. Schaak, *Chem. Mater.* 2014, *26*, 4826. (d) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. G. Read, N. S. Lewis, R. E. Schaak, *Chem. Mater.* 2014, *26*, 4826. (d) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak, *Chem. Comm.* 2014, *50*, 11026. (e) J. C. Callejas, J. M. McEnaney, C. G. Read, J. C. Crompton, J. S. Lewis, R. E. Schaak, J. C. Crompton, J. S. Lewis, J. M. McEnaney, C. G. Read, J. C. Crompton, J. S. Lewis, R. E. Schaak, *Chem. Comm.* 2014, *50*, 11026. (e) J. C. Callejas, J. M. McEnaney, C. G. Read, J. C. Crompton, J. S. Lewis, R. E. Schaak, J. C. Crompton, J. S. Lewis, J. M. McEnaney, C. G. Read, J. C. Crompton, J. S. Lewis, *R. E. Schaak*, J. C. Crompton, J. S. Lewis, *R. E. Schaak*, *Chem. Comm.* 2014, *50*, 11026. (e) J. C. Callejas, J. M. McEnaney, C. G. Read, J. C. Crompton, J. S. Lewis, *R. E. Schaak*, J. C. Crompton, J. S. Lewis, *R. E. Schaak*, J. C. Crompton, J. S. Lewis, *Schaak*, J. S. Lewis, *Schak*, J. S. Lewis, *Schaak*

A. J. Biacchi, E. J. Popczun, T. R. Gordon, N. S. Lewis, R. E. Schaak, *ACS Nano* **2014**, *8*, 11101.

- (21) (a) X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková, T. Asefa, *Angew. Chem., Int. Ed.* 2014, 53, 4372. (b) H. Vrubel, X. Hu, *Angew. Chem., Int. Ed.* 2012, 51, 12703.
- (22) A. K. Vijh, G. Belanger, R. Jacques, Mater. Chem. Phys. 1988, 20, 529.
- (23) L. Hung, C. Tsung, W. Huang, P. Yang, Adv. Mater. 2012, 22, 1910.
- (24) S. Carenco, C. Boissiere, L. Nicole, C. Sanchez, P. Floch, N. Mezailles, *Chem. Mater.* 2010, 22, 1340.

Chapter 6

Crystal Phase Control in Cobalt Sulfide Nanoparticles and Their Preliminary Evaluation as Catalysts for the Hydrogen Evolution Reaction

6.1 Introduction

Metal chalcogenides are an important class of materials with an array of useful properties. For example, lead and cadmium sulfide and selenide quantum dots are efficient materials for solar energy conversion applications.¹ Iron based selenides can exhibit superconducting properties.² The sulfide and selenide nanostructured compounds of molybdenum and cobalt (amongst others) are also important chalcogenide materials with known applications in catalysis.³⁻⁵ Cobalt sulfide nanocrystals are accessible via several colloidal synthesis routes. The previous works have focused on the characterization of synthesized materials but have yet to establish parameters for significant control over the crystal phase and composition of the nanoparticle product. For example, Tuan and co-workers have synthesized gram-scale Co₉S₈ nanocrystals for dye-sensitized-solar-cell applications,⁶ and the Alivisatos group studied the Kirkendall effect as observed in the formation of hollow Co_9S_8 and Co_3S_4 nanoparticles.⁷ It is advantageous to control the phase and composition of nanomaterials as this allows for control over the chemical bonding in the material, thereby influencing the properties and functionality of the material. Once phase and composition control is accessible, critical structure-property relationships can begin to be established.

Herein, we demonstrate the colloidal synthesis of CoS, CoS₂, and Co₉S₈ nanoparticles by systematically altering reaction conditions as well as the ability to convert premade CoS nanocrystals to CoS₂ and Co₉S₈ nanocrystals. Our preliminary evidence suggests that these materials are catalytically active for HER, requiring overpotentials of about -200-300 mV to produce current density of -10 mA cm⁻², which compares adequately with many non-noble metal catalysts (for example, FeS₂ $\eta_{-10mA/cm}^2$ = -260 mV, NiSe₂ $\eta_{-10mA/cm}^2$ = -250 mV, CoSe₂ $\eta_{-10mA/cm}^2$ = -230 mV)⁸ including recent reports of cobalt sulfide materials in the literature (Co-S film $\eta_{-10mA/cm}^2$ = -190 mV,⁹ C@Co₉S₈ $\eta_{-10mA/cm}^2$ = -245 mV¹⁰).

6.2 Results and Discussion

Briefly, cobalt sulfide nanoparticles were synthesized by heating a degassed solution of oleylamine, cobalt chloride, and sulfur powder to a target temperature over 200 °C and maintaining that temperature for 1 h, based on a generalized method for metal sulfide nanocrystals reported previously by Hyeon and co-workers.¹¹ CoS nanoparticles were successfully synthesized using a 1:1.39 molar ratio of Co to S and heating to 220 °C for 1 h (see Experimental Details in Section 6.4 for exact amounts and detailed procedure). Transmission electron microscopy (TEM) of the resulting particles and corresponding powder X-ray diffraction pattern (XRD) are shown in Figure 6-1a and 6-2, respectively. Particles are cauliflower-shaped in morphology and are approximately 15-35 nm in diameter. The reaction temperature was controllably raised and aliquots were taken at 220 °C, 240 °C and 260 °C, yielding a change in the phase of the nanoparticles from CoS to Co₉S₈. Powder XRD patterns for this transition are shown in Figure 6-3. We observed that Co₉S₈ formation is favorable at higher temperatures, and can be made

without CoS impurities by using less sulfur in the reaction (1:0.82, Co to S), and by heating the reaction to 270 °C for 1 h. A TEM image of this product is shown in Figure 6-1b. The Co₉S₈ particles had primarily platelet-shaped morphologies and were approximately 5-25 nm in diameter. By increasing the sulfur content substantially (1:4.17, Co to S molar ratio), and holding at a temperature of 230 °C for 1 h, predominantly CoS₂ nanoparticles were produced (Figure 6-1c). These particles were thin agglomerated cauliflower-shaped structures with approximate diameters of 30-80 nm. The powder XRD patterns for Co₉S₈ and CoS₂ nanoparticles are also shown in Figure 6-2. Impurities cannot be ruled out due to the low signal-to-noise ratio of the XRD patterns, although the data suggests that each sample is predominantly single-phase.



Figure 6-1: Transmission electron microscopy images of, from left to right, CoS (a), Co_9S_8 (b), and CoS_2 (c) nanoparticles.



Figure 6-2: X-ray diffraction patterns of cobalt sulfide nanoparticles as individually synthesized. Simulated patterns for CoS, CoS_2 , and Co_9S_8 are shown as darker colored red, blue, and green line patterns, respectively.



Figure 6-3: XRD pattern of showing aliquot samples of the CoS reaction when heated to 220 °C, 240 °C, and 260 °C. The predominant phase changes from CoS to Co_9S_8 with increasing temperature.

CoS, Co_9S_8 , and CoS_2 nanoparticles were screened for their ability to catalyze the hydrogen evolution reaction in 0.5 M H₂SO₄. This was not an in-depth electrochemical evaluation, and direct comparison of the materials is difficult, since there is a significant difference in the size of the cobalt sulfide nanoparticles. Additionally, we cannot unambiguously determine that the nanoparticles are phase pure, making clear-cut comparisons difficult. The low signal-to-noise ratio in the powder XRD patterns may suggest an amorphous component in the cobalt sulfide nanoparticles. Future work should include longer, fluorescence-suppressed powder XRD scans (cobalt fluorescence increases XRD background). However, the phases were compared for HER activity, in their present state to give a rough idea of whether the predominant phases present in these systems have a profound effect on the activity of the material. Linear scan voltammetry curves (Figure 6-4) show activity for each material. CoS exhibited the highest activity, requiring an overpotential of -200 mV to produce a current density of -10 mA cm⁻². The Co_9S_8 nanomaterial electrodes required -265 mV, and the CoS_2 electrodes required -295 mV to produce a current density of -10 mA cm⁻², respectively. Several electrodes of each material were tested and showed consistent results. This adequately compares with other non-noble metal HER catalysts under acidic conditions in the literature including films of iron, nickle, and cobalt sulfides and selenide (FeS₂ $\eta_{-10mA/cm}^2$ = -260 mV, NiSe₂ $\eta_{-10mA/cm}^2$ = -250 mV, $\text{CoSe}_2 \eta_{-10\text{mA/cm}}^2$ = -230 mV).⁸ However, these activities are significantly below those of many metal phosphide catalysts (Ni₂P $\eta_{-10mA/cm}^2$ = -110 mV, CoP $\eta_{-10mA/cm}^2$ $10 \text{ mA/cm}^2 = -70 \text{ mV}$, amorphous MoP $\eta_{-10 \text{ mA/cm}}^2 = -90 \text{ mV}$, amorphous WP $\eta_{-10 \text{ mA/cm}}^2 = -120 \text{ mV}$ mV).¹² Materials with different compositions are nonetheless important to study despite lower activities, as sulfides may result in a more cost effective catalyst or be more useful

for specific material interfaces. Recent studies have shown comparable activity for cobalt sulfides for the HER (Co-S film $\eta_{-10\text{mA/cm}}^2 = -190 \text{ mV}$, $^9 \text{ C}@\text{Co}_9\text{S}_8 \eta_{-10\text{mA/cm}}^2 = -245 \text{ mV}^{10}$). The main outlier in our data set was CoS₂, which as thin films has since been reported to require -145 mV to -240 mV depending on the synthesis and resulting morphologies to produce a current density of -10 mA cm⁻².^{13,8} In these reported examples, CoS₂ nanowires performed with very high activity ($\eta_{-10\text{mA/cm}}^2 = -145 \text{ mV}$)¹³ whereas microwires and polycrystalline films required higher overpotentials ($\eta_{-10\text{mA/cm}}^2 = -158 \text{ mV}^{13}$ and $\eta_{-10\text{mA/cm}}^2 = -240 \text{ mV}^8$ respectively). It is possible that some feature of the nanoparticles, such as an amorphous impurity, is causing lower activity, but further studies will be required to elucidate the reason for the observed discrepancy.



Figure 6-4: Polarization data in 0.50 M H₂SO₄ for the preliminary evaluation of cobalt sulfide nanoparticles. CoS, CoS₂, and Co₉S₈ nanoparticles at a mass loading of ~1 mg cm⁻² are shown as the red, blue, and green lines respectively.

Additional phase control was demonstrated by first synthesizing CoS nanoparticles, then converting these particles into either Co₉S₈ or CoS₂ by using specific reaction conditions. Briefly, a concentrated solution of CoS nanoparticles (Figure 6-1a) was added to oleylamine and heated with cobalt chloride or sulfur powder, to give Co_9S_8 and CoS_2 , respectively (see Experimental Section 6.4 for complete details). The products were characterized by powder XRD and TEM as shown in Figure 6-5. Importantly, these nanoparticles had similar sizes (between approximately 10-35 nm in diameter), which may be useful for future comparison studies. In order to have a valid comparison of multiple nanoparticle catalysts for the HER, minimizing variables will give the most meaningful results. Phase pure nanoparticles of the same shape, size, and surface area, for example, would allow for the direct comparison of how crystal structure and elemental composition of a material influences the HER activity. This concept is illustrated well in a comparative study between CoP and Co₂P nanoparticles, where the materials were made using similar conditions, resulting in nearly identical size, shape, and surface area.¹⁴ In this study CoP was shown to be statistically more active for the HER than the Co₂P nanoparticles.



Figure 6-5: TEM images and corresponding XRD patterns of CoS nanoparticles (middle) and the converted CoS_2 (left) and Co_9S_8 (right) nanoparticle products. Simulated patterns for each phase are shown in black below each sample XRD pattern.



Scheme 6-1: Reaction scheme outlining the methods used to synthesize the various Co-S nanoparticles described in this chapter.

6.3 Conclusions

In summary, CoS, Co₉S₈, and CoS₂ nanoparticles have been synthesized using colloidal methods by systematically varying reagents and reaction temperatures to control the predominant phase. Each material phase was moderately active for the HER, with CoS showing the highest activity in this preliminary screening of cobalt sulfide nanomaterials. We have successfully demonstrated that CoS nanoparticles can be synthesized and then converted to Co_9S_8 or CoS_2 by adding new precursor material and applying appropriate reaction conditions. The converted cobalt sulfide nanomaterials are of similar morphology and size, and therefore could offer a more direct comparison of catalytic activity, with surface area analysis. Cobalt sulfide materials have significant potential as Earth-abundant HER catalysts which are highly desirable for the global scalability of water electrolysis.

6.4 Experimental Details

Chemicals and Materials. Cobalt(II) chloride hexahydrate [98%, CoCl₂•6H₂O, Alfa Aesar], sulfur powder [-325 mesh, 99.5%, Alfa Aesar], oleylamine [tech. 70%, C₁₈H₃₇N, Sigma-Aldrich], titanium foil [99.7%, 0.25 mm thickness]. High-quality colloidal Ag paint was purchased from SPI Supplies and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr.

Synthesis of Cobalt Sulfide Nanocrystals. CoS nanoparticles were synthesized by first dissolving 142 mg CoCl₂•6H₂O in 10 mL of oleylamine. This mixture was degassed for 20 minutes then heated under argon to 220 °C. Then, 26.6 mg of sulfur

powder, pre-dissolved in 5 mL of oleylamine, was injected into the hot solution and held at 220 °C for 1 h. The solution was then cooled to room temperature and particles were cleaned and collected via centrifugation with hexanes and ethanol (three times for cleaning). Predominately Co_9S_8 and CoS_2 phase nanoparticles were each made using a synthesis parallel to that of the CoS nanoparticles. For Co_9S_8 , 142 mg $CoCl_2 \cdot 6H_2O$ and 16 mg sulfur powder were used and the reaction was heated to 270 °C. For CoS_2 , 142 mg $CoCl_2 \cdot 6H_2O$ and 79.8 mg sulfur powder were used and the reaction was heated to 230 °C. All particles were redispersed in hexanes with sonication for storage.

Synthesis of Co₉S₈ and CoS₂ Nanocrystals from CoS Nanocrystals. CoS

nanoparticles were converted to Co_9S_8 and CoS_2 nanoparticles in a three necked round bottom flask equipped with a reflux condenser, a thermometer adapter, and a rubber septum. The original solution of CoS nanocrystals was cleaned and concentrated to 25 mg/mL hexanes. For each synthesis, CoS nanoparticles (0.25 mg) was added to a 10 mL solution of oleylamine in the round bottom flask. For Co_9S_8 , 50 mg of $CoCl_2 \cdot 6H_2O$ was added to the reaction flask and for CoS_2 , 20 mg of sulfur powder was added. In each case, the reaction solution was heated to 230 °C for 1 h. Particles were cleaned as described above and stored in hexanes for further characterization.

Preparation of Working Electrodes. Electrodes were prepared similarly to protocols from previous reports.⁹ First, stock solutions of the cobalt sulfide particles were prepared in hexanes at a concentration of 10 mg mL⁻¹ for each. The nanoparticles were then deposited in 5- μ L increments onto 0.2 cm² pieces of Ti foil, up to a total of 20

 μ L and allowed to dry. The cobalt sulfide-decorated Ti foils were heated at 450 °C in 5% H₂/Ar, then attached to an exposed Cu wire with a polyvinylchloride coating. Finally, a two-part epoxy was applied to insulate the conductive surfaces from contact with the electrolyte solution, with the exception of the side decorated with nanoparticles.

Electrochemical Measurements. Electrochemical data were acquired using a Gamry Instruments Reference 600 potentiostat. All measurements were performed in 0.5 M H₂SO₄ using a two-compartment, three-electrode cell. The two compartments were separated by a Nafion® membrane (Fuelcellstore.com) to prevent cross contamination between the contents of the working electrode and the counter electrode solutions. Pt mesh was used as the counter electrode itself while a mercury/mercurous sulfate (Hg/Hg₂SO₄) electrode was used as the reference electrode. Polarization data were acquired using a sweep rate of 1 mV s⁻¹, with rapid stirring using a magnetic stir bar. The Current Interrupt method (a built-in potentiostat feature) was used to account for uncompensated solution resistance in all measurements. Research-grade H₂(g) was continuously bubbled through the solution at ~1 atm to maintain a constant value for the RHE potential. Measurement of the open-circuit potential of a clean Pt mesh electrode in the electrolyte solution was used to determine the RHE potential after electrochemical characterization of the metal sulfide nanoparticles.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu Kα radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using the CrystalMaker /

CrystalDiffract software suite. All samples for microscopic analysis were prepared by drop-casting 0.7 μ L of dilute, dispersed nanoparticles in hexanes onto a Cu grid (400 mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmission-electron microscopy (TEM) images were obtained using a JEOL 1200 microscope (80kV).

6.5 References

- (1) P. V. Kamat, Acc. Chem. Res. 2012, 45, 1906.
- L. Sun, X. Chen, J. Guo, P. Gao, Q. Huang, H. Wang, M. Fang, X. Chen, G. Chen, Q.
 Wu, C. Zhang, D. Gu, X. Dong, L. Wang, K. Yang, A. Li, X. Dai, H. Mao, Z. Zhao, *Nature* 2012, 483, 67.
- (3) A. B. Laursen, S. Kegnæs, S. Dahl, I. Chorkendorff, *Energy Environ. Sci.* 2012, 5, 5577.
- M. S. Faber, M. A. Lukowski, Q. Ding, N. S. Kaiser, S. Jin, *j. Phys. Chem. C* 2014, 118, 21347.
- (5) D. Kong, H. Wang, Z. Lu, Y. Cui, J. Am. Chem. Soc. 2014, 136, 4897.
- (6) S. Chang, M. Lu, Y. Tung, H. Tuan, *ACS Nano* **2013**, *7*, 9443.
- (7) Y. Yin, C. K. Erdonmez, A. Cabot, S. Hughes, A. P. Alivisatos, *Adv. Funct. Mater.* **2006**, *16*, 1389.
- (8) D. Kong, J. J. Cha, H. Wang, H. R. Lee, Y. Cui, *Energy Environ. Sci.* **2013**, *6*, 3553.
- (9) Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. R. Long, P. Yang, C. J. Chang, J. Am. Chem. Soc. 2013, 135, 17699.
- (10) L. Feng, G. Li, Y. Liu, Y. Wu, H. Chen, Y. Wang, Y. Zou, D. Wang, X. Zou, ACS Appl. Mater. Interfaces 2015, 135, 980.

- (11) J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang, T. Hyeon, J. Am. Chem. Soc. 2003, 125, 11100.
- (12) (a) E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis, R. E. Schaak. J. Am. Chem. Soc. 2013, 135, 9267. (b) E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak. Angew. Chem., Int. Ed. 2014, 53, 5427. (c) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis, R. E. Schaak. Chem. Mater. 2014, 26, 4826. (d) J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, R. E. Schaak. Chem. Compton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, C. G. Read, N. S. Lewis, R. E. Schaak. Chem. Compton, 2014, 50, 11026.
- (13) M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding, S. Jin, J. Am. Chem. Soc. 2014, 136, 10053.
- J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney, R. E. Schaak, *Chem. Mater.* Just Accepted Manuscript. DOI: 10.1021/acs.chemmater.5b01284. 2015.

Chapter 7

TiO₂ Truncated Bi-pyramidal Nanoparticles: Ag–TiO₂ Hybrid Particles, TiO₂ Chain Formation, and Multilayered Assemblies

7.1 Introduction

Over the past decade, interest has grown significantly in the development of nanostructured materials that are designed to harvest and utilize light energy.¹⁻³ TiO_2 is a semiconductor with appealing photoconductivity, excellent overall chemical stability, minimal environmental health risks, and low cost relative to similar semiconductors.⁴ As such, it is highly attractive for the advancement of many applications, including lightharvesting in nanostructured materials. The ability to spatially control the arrangements unique inorganic domains with specific heterojunctions and functionalities is a defining characteristic in the design of new photoactive nanomaterials.⁵⁻⁸ Specific targets, such as a proposed three domain Pt-TiO₂-IrO₂ nanostructure, are theoretically designed to energetically direct the flow of separated charges from the photoconductive TiO₂ to electron or hole-utilizing metallic domains to promote water photoelectrolysis.⁵ In each three-domain nanostructure, photo-excited electrons in TiO₂ would be directed to the Pt domain which is catalytically active for promoting water reduction to hydrogen, while positively charged holes would be directed to the IrO₂ domain, active for promoting water oxidation to O₂, thereby enhancing the photocatalytic ability of TiO₂. Colloidal synthetic methods have often been utilized to obtain heterostructured nanoparticles similar to this proposed structure.⁹ However, few colloidal strategies exist for obtaining uniform TiO₂ nanoparticles, and fewer still exist for further synthetic manipulations such as ordered assembly or heteroparticle domain growth with such particles. Only recently have more examples of colloidal TiO_2 hybrid particles begun to emerge including the nucleation of Co domains on TiO_2 nanorods by Cozzoli and co-workers.¹⁰

The photocatalytic ability of TiO₂, which is primarily a UV light absorber, can be enhanced by attaching silver metal domains to the semiconductor to utilize visible light as well.¹¹ Dionne and co-workers also demonstrated that controlling the size of silver nanoparticles shifts their plasmonic absorption peak from a wavelength of about 330 nm to nearly 400 nm at particle sizes of 1.7 nm to 11 nm, respectively.¹² Control over light absorption could be used to better utilize wavelengths of the solar spectrum, which reaches a maximum emission in the visible region (400 nm to 700 nm). We herein report a colloidal synthesis of uniform TiO₂ nanoparticles with truncated bi-pyramidal morphology (adapted from a literature protocol)¹³ and the development of synthetic techniques to grow size-controlled silver domains on the TiO₂ nanoparticles. In addition, assembly mechanisms for the TiO₂ particles themselves were developed to obtain chain structures as well as multilayered assembly patterns.

7.2 Results and Discussion

Truncated bi-pyramidal TiO₂ nanoparticles were synthesized via a modified protocol by Dalmaschio and co-workers.¹³ Briefly, TiO₂ nanoparticles were made by mixing titanium butoxide with oleic acid and water before being heated to 250 °C in sealed autoclave for 24 h. Figure 7-1 shows a transmission electron microscopy (TEM) image and the corresponding X-ray diffraction pattern of the as-synthesized particles. Scherrer analysis of the particles indicates that they are approximately 10 nm, which agrees well with the observed particle average length of 7 nm from the TEM image.



Figure 7-1: TEM image of TiO₂ truncated bi-pyramid nanoparticles (left) and corresponding XRD pattern (right).

Ag-TiO₂ hybrid nanoparticles were synthesized based on a modified protocol for the growth of silver off of Fe₃O₄ nanoparticles.⁹ In a typical synthesis, 7 mg of TiO₂ nanoparticles in a toluene stock solution was dispersed in 10 mL of toluene. In a typical reaction, 10 mg silver acetate and 0.5 mL oleylamine were added to the solution, stirred, and heated to 60 °C for 16 h (see Experimental Details in Section 7.4). The TEM image in Figure 7-2 shows the resulting Ag-TiO₂ hybrid nanoparticles. The particles consisted of a single TiO₂ domain surrounded by up to five visible silver domains of 1-2 nm in size. By varying the amount of silver acetate and the amount of oleylamine, the approximate size of the silver domains could be controlled as shown in Figure 7-3 (powder XRD patterns shown are in Figure 7-4). Modifying the synthetic protocol by the addition of more silver acetate (12.5 mg) and more oleylamine (0.75 mL) resulted in larger silver domains, up to approximately 8 nm in size. Using less silver acetate (6.25 mg) and less oleylamine (0.375 mL), Ag domains were limited to less than 1 nm in size. It has been established that the size of Ag nanoparticles has a direct impact on their plasmonic resonance and ability to absorb specific wavelengths of light.¹² In theory, by appropriately controlling the size of silver domains on the TiO_2 surface, the light harvesting ability of the overall material could be optimized; however, further studies will be required to validate this, as these materials were not tested for visible absorption.



Figure 7-2: TEM showing Ag nanoparticles as small dark domains grown on TiO_2 bipyramidal nanoparticles.



Figure 7-3: TEM images showing Ag size control on TiO_2 nanoparticles. The largest Ag domains are on the left and the smallest are on the right.



Figure 7-4: TEM images showing size control of silver domains grown on TiO₂ nanoparticles with corresponding XRD patterns.

Originally, the synthetic protocol that we adapted for making truncated bipyramidal TiO₂ nanoparticles also called for sodium fluoride as a reagent.¹⁴ In this reported synthesis, oleic acid and the fluoride ion of sodium fluoride collectively controlled the shape of the TiO₂ particles as they grew to form nanocrystalline bipyramids. The particles form somewhat better defined edges than without NaF for the truncated bi-pyramidal shape as shown in Figure 7-5; however, silver was not able to nucleate and grow well on these particles. Instead of nucleating on the TiO₂ surfaces in these synthetic attempts, silver would preferentially nucleate into separate particles (Figure 7-6). We suspect this effect was due to inhibition by or reaction with stillattached fluoride ions on the TiO₂. Similarly, Murray and co-workers found that an NaOH treatment of TiO₂ nanoparticles was required to remove fluoride ions to allow for successful photodeposition of Pt when the TiO₂ particles were synthesized from TiF₄.¹⁵



Figure 7-5: TEM (left) and HRTEM (right) images of TiO₂ truncated bi-pyramid nanoparticles synthesized with NaF present.



Figure 7-6: TEM image showing silver nanoparticle nucleation and growth separate from TiO_2 nanoparticles when the TiO_2 was synthesized with fluoride ions present.

Using a literature protocol for a ligand exchange procedure¹⁶ on the TiO₂ nanoparticles that were synthesized with sodium fluoride and oleic acid present, the particles were transferred to a polar H₂O solution and then back to a nonpolar solution containing only toluene and oleylamine, to determine if the presence of oleic acid was inhibiting Ag nanoparticle growth. As expected, silver nanoparticles did not preferentially grow on TiO₂ after ligand exchange. Interestingly, the ligand exchange procedure and exclusivity of oleylamine as a ligand arranges the TiO₂ bi-pyramidal nanoparticles into chain-like structures shown in Figure 7-7. Such control over the arrangement of TiO₂ may be useful for combining nanoparticles to make nanorods, arrays

of which are known for improving light absorption in photoelectrode applications.¹⁷ This also exemplifies protection of specific facets by either oleylamine or by other particles for adding further complexity to the material.



Figure 7-7: TEM image of TiO₂ bi-pyramidal nanoparticles linked in a chain-like arrangement following ligand exchange to an oleylamine/toluene solution.

The as-synthesized TiO₂ particles made with the NaF reagent are exceptionally colloidally stable, forming a transparent, white-yellow solution in toluene. Notably, by using 7 μ L of the final toluene solution described in the Experimental Details (Section 7.4) which was allowed to dry under ambient conditions on the TEM viewing grid, multilayer assembly "superlattices" of TiO₂ form in the patterns shown in Figure 7-8 with corresponding unique selected area electron diffraction patterns (SAED). Electrons are

deflected in patterns that correspond to the anatase TiO_2 crystal structure as well as to specific patterns of the multilayered assemblies with concentrated areas of diffraction rather than typically observed rings or spots. Alivisatos and co-workers have explained that such patterning of nanomaterials, especially when multi-component, lends to a new type of inorganic structure where colloidal atoms are building blocks that can be spatially organized by controlling interactions between particles.¹⁸ One can imagine the new materials possibilities based on this principle; for example, a magnetic component could be intimately patterned with quantum dots or TiO_2 nanoparticles in a layered structure to yield a layered magnetic photoconductive material. Manipulating the pattern of such a superlattice would likely have a measurable effect of the collective material properties. Thus, TiO_2 nanomaterials with superlattice structuring capabilities have potential to yield exciting materials with opportunities for in-depth study.



Figure 7-8: TEM images of TiO₂ bi-pyramidal nanoparticles assembled in multilayered arrangements with corresponding selected area electron diffraction patterns (inset).



Scheme 7-1: Reaction scheme outlining the methods used to synthesize TiO_2 nanoparticles and further synthetic designs described in this chapter.

7.3 Conclusions and Outlook

Ag nanoparticles were successfully grown on truncated bipyramidal TiO_2 seeds to form colloidal hybrid nanoparticle systems. Changing the amount of silver acetate and oleylamine in the reaction can systematically control the relative sizes of the Ag domains in the Ag-TiO2 heterostructures. The TiO₂ nanoparticles themselves can be oriented as building blocks to form chains as well as multi-layered assemblies via controlled colloidal methods, which may be useful for specific light absorbing applications. Nonpolar ligands enable the colloidal nanostructuring described, but present a significant challenge to the general practicality of this system. Future work will look toward studying UV-vis light absorbing properties of the materials, toward adding complexity to the nanostructuring capabilities demonstrated here, and toward removing or exchanging the surrounding ligands for use of this particle system in polar or solid-state based applications.

7.4 Experimental Details

Chemicals and Materials. Oleic acid [technical grade, 90%, Sigma-Aldrich], titanium(IV) butoxide [97%, Ti(OCH₂CH₂CH₂CH₃)₄, Sigma-Aldrich], sodium fluoride [99.99%, NaF, Alfa Aesar], silver acetate [anhydrous, 97%, AgOOCH₃, Alfa Aesar], oleylamine [70%, C₁₈H₃₇N, Sigma-Aldrich].

Synthesis of TiO₂ Bi-pyramid Nanoparticles. Titanium dioxide nanoparticles were synthesized based on a modified literature protocol¹³ using a 25 mL three-necked round bottom glass equipped with a reflux condenser, thermometer adapter and rubber septum. In the three-necked flask, 9.5 mL oleic acid was heated under vacuum to 120 °C for 30 min with moderate stirring to remove any oxygen or water present. Then, the solution was allowed to cool to 50 °C, and 0.10 mg sodium fluoride was added followed by 1 mL titanium tetrabutoxide. The mixture was stirred for 2 h before adding 0.375 mL distilled water drop-wise over 4 min. This mixture was stirred overnight then transferred to a Teflon-lined autoclave (20 mL inner lining) and heated to 250 °C for 24 h. The resulting product required a specific washing technique to isolate the uniform TiO₂ truncated bi-pyramid nanoparticles as these particles are originally a settled mixture of polydisperse particles and a particle free, supernatant. Eight mL of the yellow supernatant from the Teflon container was removed and discarded, and 5 mL of dry toluene was added to the remaining yellow-white slurry and transferred to a 20 mL vial. This mixture was sonicated and large particles were allowed to settle to the bottom of the vial. At this point, the toluene supernatant contains a high density of colloidally stable TiO₂ truncated bipyramids and the solution could be stored indefinitely. To isolate these particles, 0.75 mL of dry toluene was added to 0.25 mL of supernatant solution in a 2.5 mL centrifugation vial, then 1 mL of dry ethanol or acetonitrile was added and the sonicated mixture was spun in a centrifuge at 12,000 rpm for 30 sec. The white pellet was re-dispersed via sonication in 0.5 mL dry toluene for further characterization. For TiO₂ without fluoride present, which was useful for successful Ag particle growth on TiO₂, sodium fluoride and water are omitted, 0.81 mL titanium tetrabutoxide was used, and the reaction was held in the autoclave for 64 h at 250 °C with only 2 h of total stirring prior to heating in the autoclave (modified from a separate literature protocol¹⁵). All other reaction and particle isolation conditions were identical.

*Synthesis of Ag-TiO*² *Heterostructured Nanoparticles.* Ag nanoparticles were synthesized on TiO² in a 50 mL round bottom flask equipped with a reflux condenser, thermometer adapter, and rubber septum. First, silver acetate (6.25-12.5 mg) and oleylamine (0.375-0.75 mL) were added to 10 mL toluene in the round bottom flask. Higher amounts of silver and oleylamine typically resulted in larger silver domains. The mixture was heated to 60 °C for 18 h. The product was isolated by using ethanol as a anti-solvent and centrifugation at 4000 rpm for 3 min.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using the CrystalMaker / CrystalDiffract software suite. All samples for microscopic analysis were prepared by drop-casting 0.7 µL of dilute, dispersed nanoparticles in hexanes onto a Cu grid (400

mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmissionelectron microscopy (TEM) images were obtained using a JEOL 1200 microscope (80kV).

7.5 References

- M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 2010, *110*, 6446.
- 2) I. Mora-Sero, J. Bisquert, J. Phys. Chem. Lett. 2010, 1, 3046.
- S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* 2011, *334*, 645.
- 4) M. Anpo, H. Yamashita, I. Yuichi, S. Ehara, J. Electroanal. Chem. 1995, 396, 21.
- 5) P. V. Kamat, J. Phys. Chem. Lett. 2012, 3, 663.
- 6) G. I. Koleilat, X. H. Wang, E. H. Sargent, *Nano Lett.* **2012**, *12*, 3043.
- J. B. Gao, C. L. Perkins, J. M. Luther, M. C. Hanna, H. Y. Chen, O. E. Semonin,
 A. J. Nozik, R. J. Ellingson, M. C. Beard, *Nano Lett.* 2011, *11*, 3263.
- 8) B. H. Meekins, P. V. Kamat, J. Phys. Chem. Lett. 2011, 2, 2304.
- 9) M. R. Buck, J. F. Bondi, R. E. Schaak *Nature Chemistry*. 2012, 4, 37.
- M. Casavola, V. Grillo, E. Carlino, C. Giannini, F. Gozzo, E. F. Pinel, M. A.
 Garcia, L. Manna, R. Cingolani, P. D. Cozzoli *Nano Lett.* 2007, *7*, 1386.
- 11) X. Zhou, G. Liu, J. Yu, W. Fan J. Mater. Chem. 2012, 22, 21337.
- 12) J. A. Scholl, J. A. Dionne *Nature* **2012**, *483*, 421.
- 13) C. J. Dalmaschio, E. R. Leite, *Cryst. Growth Des.* **201**, *12*, 3668.
- 14) . C. Chen, R. Hu, K. Mai, Z. Ren, H. Wang, G. Qian, Z. Wang. *Cryst. Growth Des.* **2011**, *11*, 5221.

- T. R. Gordon, M. Cargnello, T. Paik, F. Mangolini, R. T. Weber, P. Fornasiero, C.
 B. Murray J. Am. Chem. Soc. 2012, 134, 6751.
- A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. M. Kikkawa, C. B. Murray J. Am. Chem. Soc. 2011, 133, 998.
- 17) H. Wang, Y. Bai, H. Zhang, Z. Zhang, J. Li, L. Guo J. Phys. Chem. C. 2010, 114, 16451.
- E.V. Shevchenko, J. B. Kortright, D. V. Talapin, S. Aloni, A. P. Alivisatos. *Adv. Mater.* 2007, *19*, 4183.

Chapter 8

Expanding the CO₂ Photoreduction Framework: Highlighting SnO Nanosheets and CuPt Nanospheres on TiO₂

8.1 Introduction

As the manufacturing sector of the global economy expands, CO_2 waste production grows immense. The Carbon Dioxide Information Analysis Center reports global CO_2 pollution emissions now exceed 30 billion metric tons per year, up from 5 billion metric tons in 1950.¹ According to the intergovernmental panel on climate change, CO_2 is the primary greenhouse gas responsible for a surface warming of $0.6^{\circ}C$ over the past century.² Continued pollution and warming may lead to environmental problems such as oceanic flooding due to the melting of the ice caps, increased storm energy and frequency, decreased ocean pH which could lead to mass extinctions, as well as other concerns.² On the other hand, as the world demand for fuels continues to rise, an energy crisis approaches with fewer oil reserves being found each year.³ Producing hydrocarbon fuels by using photocatalysts that are capable of reducing waste CO_2 with water and light is an ideal solution to these carbon pollution problems and the pending energy crisis.

Semiconductor photocatalysts are materials that work by absorbing light to excite electrons into the conduction bands of these materials. The increased potential of the excited electrons leaves positively charged holes in the valence band. After this charge separation, the electrons and holes promote redox reactions at the surface of the catalyst (Figure 8-1). Photocatalysts have been used effectively for a number of applications, including the degradation of organic pollutants, the self-cleaning of surfaces, and the promotion of other photoredox reactions, as well as the reaction of focus in this work: catalytic reduction of CO_2 to form carbonaceous fuels.⁴



Figure 8-1: Representation of electron excitation and hole formation in a photocatalyst and reaction on the surface.

Thermodynamic and kinetic barriers make the photoreduction of CO_2 to methane gas (and other fuels) an unfavorable process.

$$CO_{2(g)} + 2H_2O_{(g)} \xrightarrow{\text{Light}} CH_{4(g)} + 2O_{2(g)}$$
(1)

Carbon dioxide is an exceptionally stable molecule, requiring 799 kJ/mol of energy to break a C-O double bond. When other bond cleavage and bond formation energies are considered, the overall reaction requires 818 kJ/mol, indicative of a highly endothermic reaction. Unless photocatalysts efficiently provide enough energy to overcome any activation energy in addition to this barrier, hydrocarbon yields will be low. Mechanistically, the reaction proceeds through the formation of radical species and subsequent radical recombination on catalyst surfaces.⁵

Proposed CO₂ Reduction Mechanism (2)
Overall:
$$CO_{2(g)} + 8H^+ + 8e^- \longrightarrow CH_{4(g)} + 2H_2O$$

Via: $H_2O + 2h^+ \longrightarrow 1/2O_{2(g)} + 2H^+$
 $H^+ + e^- \longrightarrow H^-$
 $CO_{2(g)} + e^- \longrightarrow CO_2^-$
Radical Recombination

The overall reaction requires a concerted eight electron process which is kinetically demanding due to short lived radicals. The formation of radical species allows for the formation of longer chain hydrocarbon products by facilitating uncontrolled carboncarbon bonding. Controlling this process for the formation of a specific fuel product is important to the application, for example gas stoves run on methane whereas cars can run on ethanol. Therefore, specific CO_2 and H_2O adsorption and product desorption characteristics are required for selective formation of desired products. Designing an appropriate catalytic system is paramount to overcoming these challenges toward the photoreduction of CO_2 .

This chapter is divided into two sections, each designed with a specific approach to help overcome the challenges of CO_2 photoreduction. The first part (beginning at Section 8.2) provides a framework for the photocatalytic evaluation of new nanostructured semiconductor materials, highlighting SnO nanosheets, and the second part (beginning at Section 8.5) expands the methodology for studying novel nanostructured co-catalysts, using a standard photocatalyst substrate, P25-TiO₂, and highlighting CuPt nanospheres. Both parts utilize the methods described in Section 8.8 to test materials photocatalytically, which are an integral part of the overall targeting and testing framework outlined in this chapter.

8.2 Part 1 – Discovery of Photocatalystic Materials for CO₂ Conversion to Selected Fuels: SnO Nanosheets

Since the first report by Inoue and co-workers in 1979, it has been known that CO₂ dissolved in water can be photocatalytically reduced by semiconductors, including ZnO, GaP, CdS, SiC, and TiO₂.⁶ Among these, TiO₂ is the most widely studied photocatalyst because it is comparably efficient, inexpensive, abundant, environmentally friendly, and chemically stable. Thus, there are now over 20,000 TiO₂ related research articles published each year.⁷ Review articles on CO₂ photoreduction indicate that TiO₂ based systems have dominated the field with a majority of examples incorporating TiO₂.⁸⁻¹¹ Despite considerable effort using TiO₂ as a photocatalyst, CO₂ photoreduction product selectivity remains a challenge and product yields remain too low for commercial use. Controlled studies on diverse materials can offer insight into improving activity and selectivity of photocatalysts, though many potentially active materials have been neglected or ignored entirely. Therefore, opportunities remain for exploration of

Two main characteristics are required for a semiconductor material to photocatalytically reduce CO_2 to hydrocarbon and other products: possession of a significantly large band gap and appropriate band edge locations. The reduction of CO_2 to hydrocarbons and other products requires a similar minimal potentials as the reduction of water to hydrogen.⁶ Therefore, materials with a band gap (BG) greater than the

photoactive materials that are useful for this catalytic reaction.

potential required to split water (above 1.23 eV), a conduction band edge (CBE) greater than about -5 eV versus vacuum (which is below but near the reduction potential of $2H^+/H_2$), and a valence band edge (VBE) less than -5.6 eV (above but near the oxidation potential of OH/O₂) are potentially useful for this photoreaction. Xu and Schoonen have reported absolute conduction band and valence band edge locations as well as band gap energies for various oxide and sulfide materials.¹² Several of these materials fit the outlined material requirements for CO₂ photoreduction: these have been illustrated in (Figure 8-2). In addition to the outlined property requirements, ideal new photoreduction catalysts would be composed of earth-abundant materials and be readily screened for trends in activity and selectivity across material families. After preliminary screening of potential readily made photocatalyst nano and micro materials, including CdO, ZnO, SnO, and MnS, which all satisfied these major requirements, SnO gave the highest yields as a CO₂ reduction catalyst and was therefore chosen as an initial material target.



Figure 8-2: Selected examples of potential materials likely able to photocatalytically reduce CO₂.¹² (Adapted with permission from the Mineralogical Society of America)

It is widely believed that the kinetics of radical recombination on a crystalline material are highly influenced by the exposed facets of that material; nanomaterials, which have high surface area to volume ratios, often show higher catalytic activity levels than similar bulk materials. For SnO, this is no exception: according to Sakaushi and coworkers, SnO nanosheets produced by controlled growth on a silica substrate could produce a photocurrent whereas SnO bulk powder did not under the same conditions.¹³ From this, it seems that photocatalysis may be facilitated by using SnO nanomaterials versus bulk SnO. Nanosheets, in particular, were targeted for their high surface area of a single exposed facet. In a single crystal rutile TiO_2 study by Anpo and co-workers, it was found that the (100) face produced CH_4 and CH_3OH in higher total yield than the (110) face, which selectively produced CH₃OH.¹⁴ It was reported that the higher Ti/O atomic surface ratio of the (100) face allowed for more reduction reactions to occur on the surface, thus producing a higher yield and lower selectivity than the (110) face. Conceptually, this demonstrates how the study of one primarily exposed facet at a time is preferable to determine product formation on that surface, and through many of such studies, this will hopefully elucidate how CO_2 photocatalytic reaction selectivity can be controlled via well designed material surfaces under appropriate conditions. We report herein that SnO nanosheets with primarily exposed (001) facets are active with selectively for ethanol production via vapor phase CO₂ photoreduction.

8.3 Results and Discussion: SnO Nanosheets

Using a solution-based methodology, slightly modified from a literature protocol by Men and co-workers, SnO nanosheets were successfully synthesized.¹⁵ Briefly, the SnO nanosheet morphology was accomplished by quenching a reaction of SnCl₂ in oleylamine and 1-octadecene with H_2O at the 140 °C. Transmission electron microscopy images of optimal as-synthesized SnO nanosheets are shown in Figure 8-4. SnO nanosheets were regular square sheets with rounded edges and were between 50-500 nm across. Powder X-ray diffraction was used to confirm the phase purity and evaluate the which surface may be exposed in the SnO nanosheets (Figure 8-3). The pattern from the drop-cast sheets revealed one set of peaks was more intense than the bulk powder reference. This set corresponded to the {001} family of planes. The increased intensity of this set is indicative of preferred orientation in the sheets on the diffraction platform. Furthermore, this data reveals that the primarily exposed facet is (001), as the reflection of this facet would be more pronounced. The (001) plane of SnO is modeled in Figure 8-4. SnO is a layered material; therefore sheet growth along this plane is reasonable.



Figure 8-3: XRD pattern showing preferred orientation in the SnO nanosheets for the (001) equivalent planes.


Figure 8-4: TEM images of SnO nanosheets and a model of their layered crystal structure with the exposed (001) face (inset).

Photocatalytic testing of SnO nanosheets was performed by subjecting the material to a fixed amount of UV-visible light, CO₂, and H₂O for 1 h in a closed apparatus (see Section 8.8 for detailed methods). Products were analyzed by gas chromatography mass spectrometry (GCMS), the results of which are shown in Figure 8-5. GCMS revealed a single large signal to be the major product. While other signals were observed, they were not present in notable amounts. By standardizing major product component signals for our GCMS, it was revealed that ethanol was the major product, and the SnO nanosheets were selective for ethanol production at a rate of 380.1 ppm/g•hr. Bulk SnO powder under these conditions gave several product signals, with an ethanol signal of 43.2 ppm/g•hr. Degussa p25-TiO₂ (a 3:1 mixture of anatase to rutile phases) was tested as a standard for typical hydrocarbon product (and, as with many systems, negligible ethanol production). In literature, other non-noble metal containing catalysts give comparable production rates: TiO_2 nanotube arrays at 10 ppm $CH_4/g \cdot h$,¹⁶ Zn_2GeO_4 nanorods at 3.5 ppm $CH_4/g \cdot h$,¹⁷ and $NaNbO_3$ at 22 ppm $CH_4/g \cdot h$.¹⁸ While these literature values can provide a frame of reference, the batch reactor and conditions used in this report are unique, thus the values obtained herein are primarily for intra-lab comparisons and for those mimicking this reactor set-up.

The SnO nanosheets were cleaned several times via centrifugation with hexanes, followed by heat and vacuum treatment to form a dry powder prior to photocatalytic testing; however, remaining organic ligands may have still influenced the photoreduction. Dong and co-workers have developed a ligand exchange reaction, replacing organic ligands with weakly bound charged ligands (which were subsequently washed away) using NO(BF₄).¹⁹ The ligand exchange was successful as demonstrated by the phase transfer of the SnO nanosheets from a hexanes phase into an H₂O phase with this method. Subsequent photoreduction testing resulted in the increased production of total fuel products though a decreased ethanol production at 236 ppm/g•hr. The major product signal for the ligand exchanged sheets was identified as methanol with 322.7 ppm/g•h produced. To evaluate the effect of ligand exchange on material morphology, a "sheetlike" SnO sample was examined by TEM before and after ligand exchange (Figure 8-6). The images show that the material became porous due to the corrosive ligand exchange process. We propose that the newly exposed surfaces in the pores are disrupting the ethanol selectivity of the primarily exposed (001) sheet surface, though further work would be necessary to confirm these findings.



Figure 8-5: GCMS data for SnO nanosheets before (left) and after (right) ligand exchange. The sheets are originally selective for ethanol. After exchange, methanol becomes the major product.



Figure 8-6: SnO nanosheets before (left) and after (right) ligand exchange. After exchange, the sheets become porous.

8.4 Conclusions and Outlook: SnO Nanosheets

In summary, the as-synthesized, primarily (001) exposed, SnO nanosheets were capable of highly selective formation of ethanol by the photoreduction of CO_2 . By introducing pores into the SnO sheet structure, methanol production and overall hydrocarbon production increase, while selectivity and ethanol production decrease. This result lends to a demonstration of the effect that facet control has on product selectivity for CO_2 photoreduction to fuels. Moving forward, thermogravimetric analysis (TGA) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) should be performed to evaluate the removal of ligands and prove the intrinsic ability of the sheets. Production results should also be normalized for surface area with BET analysis. Importantly, to confirm that SnO is indeed a catalyst and not degrading, evaluation of amounts of O_2 produced as well as stability of catalyst integrity and production amounts is required. This evaluation of SnO nanosheets provides a powerful framework and methodology (Section 8.8) for photocatalytic CO_2 reduction testing which can be applied to other materials with underexplored potential to promote this complex reaction.

8.5 Part 2 – Novel Co-Catalyst Materials for the Enhancement of Hydrocarbon Production from CO₂: CuPt Nanospheres

Electron and hole recombination is a major hindrance to efficiency in photocatalytic materials. In a study on a colloidal solution of TiO_2 , it was found that 90% of excited charge carriers recombine one nanosecond after excitation, leaving a maximum of 10% quantum efficiency for unaltered TiO_2 as a photocatalyst.²⁰ One possible method for reducing this recombination effect is to add a catalytically active metal domain to a

 TiO_2 substrate that acts as an electron sink, trapping conductive electrons in the metal to subsequently be used for catalysis (Figure 8-7). Traditional methods of nano-sized metal deposition on TiO_2 involve photoreduction or chemical reduction of a metal salt directly on TiO_2 . This limits materials to single metals, with minimal control over size, composition, exposed facets, and other features of the co-catalysts. With the ever-expanding methodology towards the synthesis of complex nanomaterials, these features can be intentionally controlled, allowing for the study of new co-catalysts such as metal alloys, intermetallics, and core-shell materials. Thus, the following approach exemplified by CuPt alloy nanoparticles, combined with the testing methodology outlined in Section 8.8, establishes a framework for the study of such new co-catalyst nanomaterials.



Figure 8-7: Representation of electron recombination with a hole within a photocatalyst (left) and the trapping of an electron with a co-catalyst on a photocatalyst to reduce recombination (right).

Platinum and copper have been shown to be outstanding co-catalysts on TiO_2 for the photocatalytic formation of CH_4 from CO_2 and $H_2O.^{8,11,21}$ Unfortunately, platinum is an expensive and rare noble metal, limiting its widespread use. Varghese and co-workers reported that together, copper and platinum deposition on TiO_2 nanorods out-perform either platinum or copper alone for the production of hydrocarbons.¹⁶ Nano-sized copper, however, is susceptible to significant surface oxidation, which likely hinders or at least alters co-catalytic performance.²² Alloying Cu with an oxidation resistant noble metal such as platinum can inhibit this oxide layer formation.²³ We report herein that uniform, colloidally synthesized, copper platinum (CuPt) alloyed nanospheres are highly active as co-catalysts on p25-TiO₂ for the photoreduction of CO₂ to methane.

8.6 Results and Discussion: CuPt Nanospheres

The CuPt nanoparticles were synthesized based on a protocol by Schaak and coworkers which results in the synthesis of both CuPt nanospheres and nanorods.²⁴ Briefly, platinum(II) acetylacetonate and copper(II) acetylacetonate were added to a mixture of oleic acid, oleylamine, 1-octadecene, and 1,2-hexadecanediol in a round bottom flask and heated to 225 °C with for 30 minutes under argon (See Section 8.8 for Experimental Details). The as-synthesized mixture of particles is shown in the TEM, Figure 8-8a. The two particle shapes can be physically separated via size-selective centrifugation of the larger rods Figure 8-8b from the supernatant which contained uniform nanospheres with an average diameter of 4.6 nm (Figure 8-8c). Scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS) indicated that the elemental composition of Cu to Pt in the nanospheres was 31:69. For direct co-catalyst comparison, Pt nanospheres (shown in Figure 8-9) were also synthesized with an average diameter of 4.9 nm via a thermal reduction of Pt(acac)₂ with Fe(CO)₅ in 1-octadecene.²⁵



Figure 8-8: TEM images of as-synthesized CuPt alloy nanoparticle mixture (a) and the resulting shape-selected CuPt nanorods (b) and CuPt nanospheres (c).



Figure 8-9: TEM images of comparably sized (~5 nm) Pt nanospheres and CuPt alloy nanospheres.

Prior to photocatalytic testing, all particles were cleaned via centrifugation with hexanes and ethanol, then dropcast onto p25-TiO₂ as a 0.5%, 1%, and 5% co-catalyst loading (dried under vacuum at 40°C overnight). For ligand removal, TiO₂ supported CuPt and Pt particles synthesized with oleylamine ligands could be purged of organic ligands by a mild 185°C heat treatment under flowing air, as demonstrated by Li and co-workers.²⁶ The CuPt and Pt co-catalysts appeared identical on the TiO₂ substrates and there was no observed change in particles from the mild ligand removal treatment (Figure 8-10).



Figure 8-10: TEM images CuPt nanoparticles on TiO₂ before (left) and after (right) 185 °C ligand removal treatment. Pt-TiO₂ appeared identical.

Photocatalytic testing of the CuPt-TiO₂ and Pt-TiO₂ photocatalyst systems was performed by subjecting each material to a fixed amount of UV-visible light, CO₂, and H₂O for 1 h in a closed apparatus (see Section 8.8). Products were analyzed by gas chromatography mass spectrometry (GCMS). For each of these systems, methane was by

far the major product, though less significant quantities of other hydrocarbons were observed. Figure 8-11 shows methane production plotted as a function of catalyst loading for each of the two systems. As expected, methane production increased with CuPt loading initially, before approaching a production plateau at higher loadings (from 480 ppm/g•h at 0.5% loading to 3410 ppm/g•h at 5% loading). Surprisingly, the inverse was true for Pt-TiO₂, as the methane production decreased with increased loading (from 1920 ppm/g•h at 0.5% loading to 2300 ppm/g•h at 5% loading). It is also interesting to note that 0.5%, 1%, and 5% CuPt loadings gave 65 ppm/g•h, 150 ppm/g•h and 485 ppm/g•h ethane evolution, respectively, whereas Pt was very selective for CH₄ production over other hydrocarbons. The experiment was repeated giving similar results, thus verifying the observed trends. We considered that the inverse activity with loading increase for Pt may be an effect stemming from catalyst overloading. Overloading of a co-catalyst may block light from reaching the semiconductor or provide too many different paths for a limited number of photon-excited electrons to flow, thereby reducing activity. If this were true of Pt, however, CuPt would be expected to follow a similar trend, which was not the observed result. Alternatively, it is possible that increased concentrations of platinum may shift evolution to selectively produce other undetected products, such as H₂ or CO. Jaramillo and co-workers have developed a method for the detection of many such products for CO₂ photoreduction, resulting in a nearly faradaic yield for metallic surfaces.²⁷ The adaptation of this would be an important addition to the overall nanosynthesis and testing framework outlined in this chapter.



Figure 8-11: Plot of methane production as a function of CuPt loading (red) and Pt loading (blue) on TiO_2 after 1 h of UV-Vis illumination. The maximum production shown is 3412.6 ppm/g•h for 5% loading of CuPt nanospheres. Pt methane production decreased with increased loading.

8.7 Conclusions and Outlook: CuPt Nanospheres

In summary, the CuPt nanosphere alloy-P25 TiO_2 system is capable of a higher hydrocarbon production rate than a Pt-P25 TiO_2 control system under the photocatalytic conditions used. In addition to the relatively high methane yield, the alloy system also produced significant amounts of ethane. As loading increased from 0.5% to 5%, methane production increased for the CuPt system and decreased for the Pt system. The decreased methane production in the Pt system with increased loading points to the formation of other non-hydrocarbon products such as H_2 and CO, which will need to be detected and quantified in the future along with O_2 for each system to get a complete dataset of product formation and verify catalytic behavior. For further studies, as CuPt nanoparticles can enhance the production of hydrocarbons from CO₂, the prospect of replacing platinum entirely is an attractive goal. To this end, future studies will look to controllably synthesize and test other copper-metal alloy nanoparticles as well as to alter metal concentrations in CuPt nanospheres.

Just as catalyst facet exposure can influence the activity and selectivity of photocatalysts, it should also influence the properties of co-catalysts. Zhang and co-workers reported that the {100} facet of Pt was more active toward the thermal oxidation of CO to CO₂ than the {111} facet, using shape controlled Pt nanoparticles.²⁸ CuPt and Pt nanocubes bound by (100) facets have been prepared in syntheses by Fang and co-workers.^{29,30} This precedent of expanding colloidal nanosynthetic control combined with the presented framework for testing co-catalyst materials (details in Section 8.8) provides a powerful means for evaluating novel co-catalysts for CO₂ photoreduction.

8.8 Experimental Details

Photocatalytic Reactor and Methodology. Traditional photocatalysis systems have used liquid water saturated with CO_2 , though it is known that CO_2 has very poor solubility in water. Therefore gas phase CO_2 with water vapor from a gas line bubbler was chosen for our reaction setup. Secondly, while interest has increased for visible activation of photocatalysts (with an emphasis on enhancing TiO₂), many materials with wider band gaps appropriate for CO_2 photoreduction have yet to be studied. Our system uses a broad spectrum Xe arc lamp, allowing both UV and visible-light active materials to be tested.

Finally, the setup offers a simple design (portrayed in Figure 8-12) with high throughput for testing samples which is ideal for any catalysis set-up.



Figure 8-12: System and chamber design for photocatalysis testing. The quartz lens allows UV and visible light to reach the sample. Gas control valves allow the chamber to be purged and backfilled with CO_2 and H_2O . This reactor setup was designed by Dr. Su-II In of the Schaak group.

To test a material for photocatalytic capability, a sample (~50 mg) is loaded into an in-house photocatalysis vessel, which is shown schematically in Figure 8-12. The sample chamber is sealed, then CO₂ gas is bubbled through deionized H₂O and into the chamber. After flow ceases, the chamber is evacuated and left under vacuum for several minutes. This loading and evacuation process is repeated five times until finally refilling with CO₂ and H₂O. This chamber is then illuminated under a 300 W Xe arc lamp for broad range UV and visible light for one hour. Finally, a (50 uL) sample of the reaction gas is taken from the chamber head space and injected into a Shimadzu GC-2014 equipped with a Restek Rt-Q-Bond column for hydrocarbon separation and detection via flame ionization. The temperature ramp rate used is adjusted for the separation and clear resolution of methane through heptane hydrocarbon chains, using a standard gas sample tank containing 1000 μ mol/mol concentrations of each. Using such a standard where μ mol/mol is equivalent to ppm, a ppm/g•h production value of each sample can be calculated.

It should be noted that the production values obtained are at the level of other photocatalytic batch reactors, though are not among the highest seen in literature. The higher product values are due to the use of flow reactors, which use far more CO_2 and H_2O reactants, maximizing product yields. Therefore, due to the unique and small scale features of the batch reactor, and without quantum efficiency measurements, the values obtained are primarily for intra-lab comparisons, rather than for comparison with other reported values in the literature. However, while flow reactors are ideal for evaluation of a few products, each gas assumed to be produced must be standardized by the GC separately. As we are studying new materials, presuming which products would be obtained is not ideal, so the batch reactor is more appropriate. After possible products have been established, upgrading to a continuous flow reactor to maximize yield is a suggested, engineering based, future option.

Chemicals and Materials. Oleylamine [tech. 70%, C₁₈H₃₇N, Sigma-Aldrich], 1octadecene [90%, C₁₈H₃₆, Sigma-Aldrich], tin(II) chloride [anhydrous, 99%, SnCl₂, Alfa-Aesar], oleic acid [technical grade, 90%, Sigma-Aldrich], 1,2-hexadecanediol [technical grade, 90%, CH₃(CH₂)₁₃CHOHCH₂OH, Sigma-Aldrich], platinum(II) 2,4-pentanedionate [Pt 48.0% min, C_{10} , $H_{14}O_4Pt$ Alfa-Aesar], copper(II) acetylacetonate [99.9%, C_{10} , $H_{14}O_4Cu$, Sigma Aldrich], pentacarbonyliron [99.5%, Fe(CO)₅, Alfa-Aesar]

Synthesis of SnO nanosheets. Tin oxide nanosheets were synthesized by modifying a previous literature protocol.¹⁵ The reaction was carried out using a Schlenk apparatus with a 25 mL 3-neck round bottom flask equipped with a thermometer, reflux condenser, and a rubber septum. Oleylamine (4.7 mL), and 1-octadecene (2.3 mL) were added to the flask then degassed under vacuum, with stirring, at 120 °C for 20 min. The solution was allowed to cool to 60 °C, then 0.303 g of finely ground SnCl₂ was added. The mixture was heated to 140 °C and 40 μ L distilled H₂O was quickly injected, forcing the nanosheet morphology. The reaction was held at 140 °C for 10 min and quenched with dry toluene (10 mL) to room temperature. SnO nanosheets were collected with ethanol and spun in a centrifuge at 4000 rpm. The pellet was redispersed in hexanes with sonication, then spun two additional times using ethanol as the anti-solvent. Particles were stored in hexanes in a 20 mL scintillation vial until characterization and further evaluation.

Synthesis of CuPt nanospheres. Copper-platinum alloy nanoparticles were synthesized based on a previous literature protocol.²⁴ Oleic acid (0.6 mL), oleylamine (0.8 mL), 1-octadecene (5 mL), 1,2-hexadecanediol (105 mg), platinum(II) 2,4-pentanedionate (43 mg), and copper(II) acetylacetonate (24 mg) were added to a 50 mL 3-neck round bottom flask equipped with a thermometer, reflux condenser, and a rubber septum. This mixture was stirred and purged by switching between vacuum and argon

flow 3 times, followed by heating the mixture under argon to 120 °C for 20 min. The transparent green solution was then heated to 225 °C for 30 min. The resulting product was a mixture of rod shaped particles and spheres which can be physically separated. Particles were separated via centrifugation at 1500 rpm for 5 min by using 5 mL of product solution, 2.5 mL hexanes and 12.5 mL ethanol. The product that crashes out is primarily CuPt nanorods. The supernatant contains both rods and spheres. To collect spheres, 2.5 mL of the original product solution was mixed with 1.25 mL hexanes, and 6.25 mL ethanol and spun at 7000 rpm. The resulting supernatant for this procedure is primarily the CuPt nanosphere product. Once conformations were collected, the individual products were cleaned again by faster centrifugation with excess ethanol as a anti-solvent to hexanes. Particles were stored in hexanes in a 20 mL scintillation vial until characterization and further evaluation.

Synthesis of Pt nanospheres. Platinum nanoparticles were synthesized based on a previous literature protocol.²⁵ Oleic acid (1 mL), oleylamine (1 mL), 1-octadecene (10 mL), and platinum(II) 2,4-pentanedionate (100 mg) were added to a 50 mL 3-neck round bottom flask equipped with a thermometer, reflux condenser, and a rubber septum. This mixture was stirred and heated to 100 °C for 20 min under argon. The transparent yellow solution was then heated to 190 °C and 0.1 mL of iron pentacabonyl dispersed in 1 mL hexanes was injected into the solution. The solution was heated to 200 and held for 1 h. Particles were collected via centrifugation at 7000 rpm for 3 min by using 2-propanol as a anti-solvent and hexanes to redisperse. This collection and cleaning process was repeated

3 times to remove excess ligands. Particles were stored in hexanes in a 20 mL scintillation vial until characterization and further evaluation.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 Advance diffractometer with Cu K α radiation and a LynxEye 1-D detector. Simulated XRD patterns were produced using the CrystalMaker / CrystalDiffract software suite. All samples for microscopic analysis were prepared by drop-casting 0.7 µL of dilute, dispersed nanoparticles in hexanes onto a Cu grid (400 mesh, coated with Formvar and carbon, Electron Microscopy Sciences). Transmission-electron microscopy (TEM) images were obtained using a JEOL 1200 microscope (80kV). Gas chromatography was performed using a Shimadzu GC-2014 equipped with a Restek Rt-Q-Bond column for hydrocarbon separation and a flame ionization detector.

8.9 References

- T. A. Boden, G. Marland, R. J. Andres, *Global, Regional, and National Fossil-Fuel CO₂ Emissions*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. DOI: 10.3334/CDIAC/00001_V2010.
- Intergovernmental Panel on Climate Change 2001. Climate Change 2001: The Scientific Basis. Cambridge University Press: Cambridge, U.K., 2001.
- 3) Association for the Study of Peak Oil and Gas USA. *Peak Oil 202.* 2012
- 4) D. Jing, L. Guo, *Catal. Commun.* **2007**, *8*, 795.
- 5) P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.* **2006**, *45*, 2558

- 6) T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, 277, 637.
- 7) Web of Knowledge "TiO₂" topic search for 2010-2014 journal years
- 8) D. Uner, M. Oymak, *Catalysis Today*. **2012**, *181*, 82.
- 9) K. Kočí, L. Obalová, Z. Lacný, *Chemical Papers*. **2008**, *62*(1), 1.
- 10) Izumi, Y. Coord. Chem. Rev. 2012, 257, 171.
- 11) S. C. Roy, O. K. Varghese, M. Paulose, C. A. Grimes, ACS Nano 2010, 4, 1259.
- 12) Y. Xu, M. Schoonen, American Mineralogist, 2000, 85, 543.
- 13) K. Sakaushi, Y. Oaki, H. Uchiyama, E. Hosono, H. Zhou, H. Imai, *small.* 2010, 6(6), 776.
- 14) M. Anpo, H. Yamashita, I. Yuichi, S. Ehara, J. Electroanal. Chem. 1995, 396, 21.
- K. Men, J. Ning, Q. Dai, D. Li, B. Liu, W. Yu, B. Zou, Colloids and Surfaces A: Physiochem. Eng. Aspects. 2010, 363, 30.
- 16) O. K. Varghese, M. Paulose, T. J. LaTempa, C. A. Grimes, *Nano. Let.* **2009**, *9*, 731.
- 17) H. Shi, T. Wang, J. Chen, C. Zhu, J. Ye, Z. Zou, *Catal. Lett.* 2011, 141, 525.
- 18) S. Yan, L. Wan, Z. Li, Z. Zou, *Chem. Commun.* **2011**, *47*, 5632.
- A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. Kikkawa, C. Murray, J. Am. Chem. Soc. 2011, 133, 998.
- 20) D. Beydoun, R. Amal, G. Low, S. McEvoy, J. Nanopart. Res. 1999, 439.
- 21) A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garcia, *Energy Environ. Sci.*2012, 5, 9217.
- 22) L. Hung, C. Tsung, W. Huang, P. Yang, Adv. Mater. 2010, 22, 1910.
- Coupland et al. (1981). U.S. Patent No. 4261742. Washington, CD: U.S. Patent and Trademark Office

- 24) Q. Liu, Z. Yan, N. L. Henderson, J. C. Bauer, D. W. Goodman, J. D. Batteas, R. E. Schaak, J. Am. Chem. Soc. 2009, 131, 5720.
- 25) M. R. Buck, J. F. Bondi, R. E. Schaak, *Nature Chemistry*. 2012, 4, 37.
- 26) D. Li, C. Wang, D. Tripkovic, S. Sun, N. M. Markovic, V. R. Stamenkovic, ACS Catal. 2012, 2, 1358.
- 27) T. Hatsukade, K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Phys. Chem. Chem. Phys.* 2014, *16*, 13814.
- B. Zhang, D. Wang, Y. Hou, S. Yang, X. H. Yang, J. H. Zhong, J. Liu, H. F. Wang,
 H. J. Zhao, H. G. Yang, *Sci. Rep.* 2013, *3*(1836), 1.
- 29) D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou, K. Sun, Angew. Chem. Int. Ed. 2009, 48, 4217.
- 30) J. Zhang, J. Fang, J. Am. Chem. Soc. 2009, 131, 18543.

Chapter 9

Summary and Outlook

Throughout this dissertation we have demonstrated and expanded the capabilities of colloidal nanosynthesis to produce novel nanomaterials with interesting catalytic properties. Primary targets of interest were potential hydrogen evolution reaction (HER) catalysts that had been previously identified as hydrodesulfurization catalysts. We synthesized or developed syntheses for specific nanoparticles of transition metal phosphides, silicides, and sulfides then characterized and evaluated each electrochemically for their ability to catalyze the HER. We also explored materials for the photocatalytic reduction of CO_2 .

The research in Chapters 2-6 developed and expanded colloidal nanosyntheses of targeted nanomaterials and evaluated each of these for their ability to catalyze the HER. In Chapter 2, we developed the colloidal nanosynthesis of amorphous MoP nanoparticles with a 1:1 ratio of molybdenum to phosphorous, and electrochemical characterization for the HER showed that they were highly active requiring only -90 mV of overpotential to produce a current density of -10 mA cm⁻². In Chapter 3, analogous synthetic pathways were used to form 1:1 amorphous WP nanoparticles, which were slightly less active requiring -120 mV of overpotential to produce a current density to for overpotential to produce a current density of solutions in 0.5 M H₂SO₄ for both short term and simulated long term stability testing. In Chapter 4, hollow crystalline FeP nanospheres were discovered to be exceptionally active for the HER, requiring only -50 mV to produce this same current density, though the material preliminary instability, which resulted in decreased activity before stabilization. Chapter 5 focused on the solution

synthesis of transition metal silicides, forming previously unstudied colloidal nanoparticles of Ni₂Si, Pd₂Si, and Cu₃Si. Ni₂Si and Pd₂Si were found to be moderately active for the HER, requiring overpotentials of -243 mV and -192 mV respectively to produce a current density of -10 mA cm⁻². Finally, in Chapter 6, colloidal synthetic techniques were developed to form several Co-S phases, including CoS, Co₉S₈, and CoS₂, as nanoparticle products from a cohesive synthetic scheme, each of which also gave moderate HER activity requiring an overpotential range between -200 to -300 mV to produce -10 mA cm⁻².

Hydrogen fuel is among the leading options for clean-energy technologies. Further research is required, however, to push water electrolyzers into profitable competition with conventional energy systems, especially considering industrial and transportation infrastructures for these systems are already in place. It will take a monumental effort to convert the expansive, well established infrastructure to hydrogen based technologies. The benefits to the environment and a reduced dependence on fossil fuels cannot be understated, the realization of which are gradually pushing this effort forward.

Several specific future research directions for solar-water electrolysis may allow this ideal energy source to become a globalized one. For the HER, little is known about the mechanisms and active sites on the surface of many HER catalysts under working electrode conditions. To know what intermediate surface species may or may not play a role in hydrogen formation, and especially to identify what chemical reaction sites are most active on surfaces, will allow researchers and material designers to maximize those active sites and make better, more active catalysts. Also, photoelectrochemical cells should last 1-5 years for practical use. For HER catalysts, significant short term stability and long term simulated stability testing has been done for the phosphide catalysts in this dissertation as well as for other materials in literature with promising results, however, actual long term stability may limit these materials if simulated stability is not representative of reality. Outside of the HER, a major limitation remains for oxygen evolution reaction (OER) catalysts. There are currently no highly active, acid stable OER catalysts that do not contain noble metals. IrO_x is a leading acid stable OER catalyst, though the price and scarcity of Ir may translate poorly to the global scalability of acidic water electrolysis. Therefore, developing a highly active, earth abundant, and acid stable OER catalyst is a high priority.

The research in Chapter 7 involved the colloidal manipulation of previously synthesized truncated bipyramidal TiO_2 nanoparticles. These particles were able to be used as seeds for the growth of Ag domains in non-polar media with sizes controllable from 0.5-8 nm. Silver nanoparticles are able to absorb visible light due to plasmonic resonance, the absorbed wavelengths of which can be tuned by the size of the particles. Thus, a photocatalyst and controllably sized plasmonic nanoparticles are intimately combined as colloidal hybrid particle products for further study. The TiO_2 particles themselves can be organized into chain-like conformations, as well as multilayered assemblies depending on conditions chosen, which are interesting for materials patterning and self-assembly applications.

In Chapter 8, we outlined a strategy for the evaluation of potential photocatalytic and co-catalytic materials for CO_2 photoreduction with H_2O . We highlighted results from testing SnO nanosheets with evidence suggesting that the material surfaces were

selective for ethanol product formation. We also highlighted an evaluation of CuPt nanospheres versus Pt nanospheres as co-catalysts on TiO_2 for methane production. Further testing will be required to determine the extent of the catalytic or otherwise redox-active nature of these materials by also testing for oxygen evolution, hydrogen evolution, and other undetected products.

Future directions for CO_2 photoreduction will likely take a similar route as the HER. Rather than combining the complex problems of light harvesting with catalyzing a thermodynamically and kinetically difficult reaction, research will focus on each problem separately, testing catalysts electrochemically first, then eventually combining catalysts with light harvesting technology. This will reduce complexity at first to identify worthy catalysts, regardless of a photoconductive material and then allow the study of integration issues and charge transfer effects once combined. As CO_2 is a gas with many reduction products of both gas and liquid phases that are difficult to analyze, solution electrochemistry will pose its own problems, but provides an appealing approach nonetheless. For the combined, alternative, gas phase approach described in this dissertation, detection of all major products, especially oxygen from the oxidation half of the overall reaction, will be most important to evaluation of materials as catalysts for CO_2 photoreduction.

Each of the described weaknesses in these fields provides opportunities for further study. Capabilities for colloidal nanochemistry are continually expanding and allowing for more uniquely controllable materials to be synthesized and evaluated as nanomaterial catalysts. The strategies outlined in this dissertation facilitate the continued targeted exploration of new nanomaterial catalysts as well as for fundamental studies on such materials to discover how to improve practical catalytic applications such as water electrolysis and photo-redox reactions. We believe that the research and strategies used herein contribute to the growth and development of colloidal nanochemistry for practical applications and we hope that this work inspires others to continue the advancement of clean-energy technologies.

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Selected Publications

- J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney, R. E. Schaak, Nanostructured Co₂P Electrocatalyst for the Hydrogen Evolution Reaction and Direct Comparison with Morphologically Equivalent CoP. *Chem. Mater.*, 2015, DOI: 10.1021/acs.chemmater.5b01284
- E. J. Popczun, C. W. Roske, C. G. Read, J. C. Crompton, J. M. McEnaney, N. S. Lewis, R. E. Schaak, Highly Branched Cobalt Phosphide Nanostructures for Hydrogen-Evolution Electrocatalysis. *J. Mater. Chem. A*, 2015, DOI: 10.1039/C4TA06642A
- J. M. McEnaney, R. E. Schaak, Solution Synthesis of Metal Silicide Nanoparticles. *Inorg. Chem.*, 2015 DOI: 10.1021/ic502394u
- J. F. Callejas,* J. M. McEnaney,* C. G. Read,* J. C. Crompton, A. J. Biacchi, E. J. Popczun, T. R. Gordon, N. S. Lewis, and R. E. Schaak, Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles. *ACS Nano*, 2014, DOI: 10.1021/nn5048553

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- J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis, R. E. Schaak, Electrocatalytic hydrogen evolution using amorphous tungsten phosphide nanoparticles. *Chem. Commun.*, 2014, DOI: 10.1039/C4CC04709E
- J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, A. J. Biacchi, N. S. Lewis and R. E. Schaak, Amorphous Molybdenum Phosphide Nanoparticles for Electrocatalytic Hydrogen Evolution. *Chem. Mater.*, 2014, DOI: 10.1021/cm502035s