Towards a Hydrobromic Acid Splitting Device Using Earth-Abundant Materials

Thesis by
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Abstract

This thesis disembarks from the traditional approach of tailoring a system to the water splitting reaction. As detailed in Chapter 2, this thesis predicts that two silicon photoelectrons connected in parallel are ideally suited to electricity storage in an integrated light collector and chemical storage device driving the splitting of hydrobromic acid (2HBr $\rightarrow$ H$_2$ + Br$_2$). The predicted dual photoelectrode system could potentially obtain high solar-to-hydrogen conversion efficiencies of up to an $\eta_{\text{STH, HBr}}$ of 12 %, whereas an equivalent water splitting system is not possible due to the small band gap of silicon. Unfortunately, silicon possesses low catalytic activity for both the hydrogen evolution half-reaction and the bromide oxidation half-reaction. In the past, the electrocatalysis of silicon has been aided by using Pt/Ir alloys to act as both a protective and electrocatalytic layer. Herein, efforts are detailed to replace these precious metals, where possible, by using only earth-abundant materials to decrease the cost of a module. Our hope is that efforts along this path will aid the field of artificial photosynthesis as a whole.

We begin by further testing a chemical insight previously noted within our group and discover a surprisingly high activity electrocatalyst for the hydrogen evolution reaction by cobalt phosphide (CoP) nanoparticles, detailed in Chapter 3. Falling on a traditional technique of increasing the surface area of particular facets, we nanostructured our crystalline CoP to increase its surface area of exposed (111) facets and hoped it would increase our catalytic activity; however, we found that simple structuring resulted in poor adhesion of nanostructures and poorer activity than our multi-faceted CoP nanocrystals (see the appendix to find out more). Our original catalysis efforts spurred a flurry of activity in the literature, and consequently, alternative devices that are more scalable arose. We detail the developments occurring since our work in the last appendix.

Now, with a potential catalyst in hand, comes the difficulty of balancing the delicate interplay between light absorption and catalysis, as detailed in Chapter 4. While CoP is active for HER, our particles possess a relatively low turnover frequency compared to hydrogenase or platinum, and thus require high mass loadings of material (2 mg/cm$^2$) to obtain competitive extrinsic performance. Planar electrodes are incompatible with our particles because of substantial light absorption by the thick catalyst overlayer. By structuring our photoelectrode, we abnegate our catalyst limitations by exploiting the properties of microwires. High-aspect ratio microwires
have shown promise as potentially low-cost materials for future photovoltaic applications as well as photocathodes functioning as part of an energy storage device. We discuss how to integrate our materials with silicon microwires (the wires were grown by an unscalable process to serve in place of functional CVD wires with radial emitters) to prototype a candidate photocathode. While a parasitic resistance limited the overall efficiency of the photocathode candidate, it still had promising stability. The parasitic resistance was addressed by electrodepositing the cobalt phosphide, thereby giving us a promising efficiency limited by the quality of the p-n junction.

While high-catalytic activity for the HER in acidic solutions using earth-abundant materials represents a significant advance, the photocathode is just one component of what is necessary for a complex system of splitting hydrobromic acid. Silicon, by its virtue of being a small band gap material, is easily passivated in aqueous solutions by the formation of a silicon oxide. In the past, our colleagues had shown that a monolayer of graphene could occasionally provide protection in a test solution, but batch-to-batch variability provided a considerable challenge. The putative hypothesis offered for the degradation argued defects in the crystalline graphene at grain-boundaries were the culprit. In Chapter 5 we present a method to passivate defects in the graphene crystal by light fluorination and observe a considerable enhancement in stability relative to typical graphene-protected silicon photoanodes. We had hoped that catalysis for bromide oxidation would be aided by the near-perfect graphene liquid junction, but electrodeposited Pt was required to effect photoxidation. A cursory stability test shows promising stability for one-half of an hour, but we would like to avoid using Pt. Finally, we also turned our attention to protecting silicon surfaces from oxidation by exploiting covalent silicon surface chemistry, accessible via a two-step chlorination/alkylation procedure, and explored the deposition of potentially protective thin-film metal oxides (see the appendix).
Published Content and Contributions


(2) C. W. Roske, J. W. Lefler and A. M. Muller, *J. Colloid Interface Sci.*, 2016, **00**, 00, (used in Appendix I) CWR participated in the characterization and writing of the manuscript.

(3) A. C. Nielander, A. C. Thompson, C. W. Roske, J. A. Maslyn, Y. Hao, N. T. Plymale, J. Hone and N. S. Lewis, *Nano Lett.*, 2016, **16**, 4082–6, (used in Chapter 5) CWR participated in the conception of the project and performed experiments relating to hydrobromic acid.

(4) C. W. Roske, E. J. Popczun, B. Seger, C. G. Read, T. Pedersen, O. Hansen, P. C. Vesborg, B. S. Brunschwig, R. E. Schaak, I. Chorkendorff, H. B. Gray and N. S. Lewis, *J. Phys. Chem. Lett.*, 2015, **6**, 1679–83, (used in Chapter 4) CWR conceptualized the project, performed all the major experiments, and wrote the manuscript.


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Chapter 1

Introduction

1.1 Motivation

The world population increased from 3 billion in 1959 to 6 billion in 1999.¹ Projections indicate that we can expect 9 billion souls by 2044.¹ Prominent among the challenges we will face is elevating their standard of living — one key way to do this is by energy equality. Today the average American demands energy at a rate of 9.5 kW per capita, whereas for other rapidly growing countries, such as an India national, 0.74 kW per capita is more typical.² The world rate of primary energy consumption is about 17.5 TW, totaling $5.52 \times 10^2$ EJ per year, with the United States accounting for about 17 % of the demand despite having 4.4 % of the world population.² If every living person today consumed at comparable levels, then worldwide energy consumption would soar to $2.2 \times 10^3$ EJ per year today and $2.8 \times 10^3$ EJ per year by 2044. If we aim to elevate our fellow (wo)man with energy equality, then there are massive resource challenges along the path ahead.

Today, the world’s primary energy production portfolio consists of oil (32.9 %), natural gas (23.8 %), coal (29.2 %), nuclear (4.44 %), hydro (6.79 %), and renewables (2.78 %).² We convert approximately two-thirds of this supply to usable energy, while the other third is lost to entropy.³ This supply includes all transportation (27.6 %), industrial (29.1 %), residential and commercial (34.6 %), and raw material (8.83 %) consumption of primary energy.⁴ Fossil fuels, constituting more than 85 % of the supply,² fundamentally originate from plants and animals that lived hundreds of millions of years ago.

Photosynthetic organisms captured energy from sunlight and stored it in chemical
bonds that were, occasionally, prevented from oxidizing back to CO\textsubscript{2} after becoming trapped in anaerobic conditions, thereby leaving a finite supply through geological processes. While the same formation processes exist today, their slow rates are unhurried compared with our rapid rate of extraction.\textsuperscript{†} This fossil fuel supply is used in two ways: chiefly as an energy carrier and secondly as a chemical feedstock. After the discovery and extraction of crude materials, refining occurs on a massive scale (Figure 1.1). As stewards of this planet, it is our responsibility to carefully consider the benefits and costs to extraction at elevated rates. This first chapter is dedicated to the larger picture of the energy landscape, and motivated the rest of this thesis work. First, an estimate of reduced carbon is taken from Wurfel.\textsuperscript{5} Hubbert’s model is used to show an estimate of the time left until resource exhaustion.\textsuperscript{6} Third, a toy model reflecting the physical mechanism by which fossil fuel emissions can change the temperature of a planet as inspired by others is presented and then energy sources are compared as discussed by others.\textsuperscript{7} Finally, a technical solution is argued so as to mitigate climate change as adopted by our cohort (including Lewis\textsuperscript{8} and Gray\textsuperscript{9}).

\textsuperscript{†}Consider that if the total stored reduced carbon energy is \(1.60 \times 10^{25} \text{ J}\) and this has formed since the great oxygenation event 2.3 billion years ago, then the rate of formation is an estimated: 
\[
\frac{1.60 \times 10^{25} \text{ J}}{7.25 \times 10^{9} \text{ a}} \approx 220 \times 10^6 \text{ W} = 220 \text{ MW}.
\]
1.2 Limits of Fossil Fuels

It is instructive to estimate the total stored solar energy in terms of reduced carbon and then frame the present trajectory of resource depletion. We begin by determining the mass of carbon created by life,* then we calculate the total energy stored and consider our extraction progress in the best possible recovery case. Finally, we incorporate estimates from the energy industry to make a projection using proven reserves.

Mass of Carbon Reserves

Free oxygen, making up 21% of today’s atmosphere, is considered biogenic in origin as a product of photosynthesis. Otherwise, photolysis of water to O₂ and H₂ with gaseous escape is the expected abiotic process slowly leading to, for example, the oxidized surface of Mars.¹⁰ However, this inorganic process contributes negligibly compared to photosynthesis because of UV protection afforded by our atmosphere. We are estimating carbon reserves as dictated by the photosynthetic reaction, which produces reduced carbon from carbon dioxide and water:

\[
6 \text{CO}_2 + 6 \text{H}_2\text{O} \xrightarrow{\text{Light}} \text{C}_6\text{H}_12\text{O}_6 + 6 \text{O}_2.
\]

Therefore, the mass of carbon, \(m_C\), can be estimated from the mass of oxygen, \(m_{O_2}\), in the air:

\[
m_C = \frac{12}{32}m_{O_2}.
\]

Using a simplified atmospheric makeup (79% N₂ and 21% O₂) we infer \(m_{O_2}\) from

---

*We assume that materials not properly stored revert back to CO₂ or are returning at a slow rate.
the mass of air, $m_{\text{air}}$:

$$m_{\text{O}_2} = \frac{21}{100} m_{\text{air}}$$

We determine $m_{\text{air}}$ as the product of air pressure ($P_{\text{atm}} = 101325 \text{kg} \cdot \text{m/m}^2$), the reciprocal of the gravitational acceleration constant ($g^{-1} = \frac{s^2}{9.8 \text{m}}$), and the surface area of earth ($4\pi R_{\text{earth}}^2$, where $R_{\text{earth}} = 6371 \times 10^3 \text{m}$):

$$m_{\text{air}} = P_{\text{atm}} \times g^{-1} \times 4\pi R_{\text{earth}}^2.$$  

Thus, $m_C$ is computed:

$$m_C = \frac{12}{32} \times \frac{21}{100} P_{\text{atm}} \times g^{-1} \times 4\pi R_{\text{earth}}^2$$

$$= \frac{12}{32} \times \frac{21}{100} (101325 \text{kg} \cdot \text{m/m}^2) \times \frac{s^2}{9.8 \text{m}} \times 4\pi (6371 \times 10^3 \text{m})^2$$

$$= 4.2 \times 10^7 \text{kg of carbon.}$$

**Total Chemical Energy of Stored Carbon**

Determining the total stored energy requires finding the estimated mass of fossil fuels, then using an approximate specific energy⁴ to obtain an energy reserve total. The specific chemical makeup will vary substantially from one resource to another (even site to site), and hence the H/C molar ratio will vary between 1 (for coal) to 4 (for natural gas). Assuming the average H/C ratio is 3 (giving CH$_3$ with 15 g mol$^{-1}$) the mass of fossil fuels, $m_{\text{ff}}$, can be calculated as

$$m_{\text{ff}} = \frac{15}{12} m_C.$$

⁴Specific energy is J kg$^{-1}$. 
Obtaining the specific energy requires calculating the enthalpy of combustion for:

\[ 4 \text{CH}_3 + 7 \text{O}_2 \xrightarrow{\Delta} 4 \text{CO}_2 + 6 \text{H}_2\text{O}. \]

As defined, there is a half C–C bond with a bond dissociation energy (BDE) of approximately \(\frac{337}{2} \text{kJ/mol}\) and three C–H bonds with a BDE of \(430 \text{kJ/mol}\). The enthalpy of the reaction is calculated by \(\Sigma(\text{energy of bonds broken}) - \Sigma(\text{energy of bonds formed})\), which in this case results in:

\[
\Delta H = \frac{1}{4}(4(\frac{337}{2} + 3 \times 430) + 7 \times 500) - \frac{1}{4}(4 \times 2 \times 749 + 6 \times 2 \times 428) = -448.5 \text{kJ mol}^{-1}.
\]

Our desired expression of specific energy, \(\rho_E\), is best represented as:

\[
\rho_E = 448.5 \text{kJ mol}^{-1} \times \frac{1 \text{mol}}{15 \text{g}} \times \frac{1000 \text{mol}}{1 \text{kg}} \times \frac{10^3 \text{J}}{1 \text{kJ}} \times \frac{1 \text{MJ}}{10^6 \text{J}} = 30 \text{MJ} \text{kg}^{-1}.
\]

Now we can calculate an upper-bound of the available energy, \(Q_{\text{max}}\), from reduced carbon with:

\[
Q_{\text{max}} = \rho_E \times m_{\text{ff}} = \rho_E \times \frac{15}{12} m_{\text{C}} = 30 \frac{10^6 \text{J}}{\text{kg}} \times \frac{15}{12} \times 4.2 \times 10^{17} \text{kg} = 1.6 \times 10^7 \text{EJ} = 16 \text{YJ}.
\]

**Progress in Logistic Consumption of Fossil Fuels**

We are in a position to make a comparison of our historical fossil fuel extraction with the total reserves as well as track our progress along a relevant model. In light of exponential growth of consumption in the face of finite resources, the logistic growth function is aptly invoked:
\[ Q(t) = \frac{Q_{\text{max}}}{1 + ae^{-bt}}, \]

where \( Q(t) \) denotes the cumulative production at some time, \( a \) controls the peak production time, \( b \) controls the rates of depletion, and \( Q_{\text{max}} \) is the the maximum supply reserve. While this nonlinear function is useful for producing a familiar result used in ecology models, the derivative \( \left( \frac{dQ}{dt} \right) \) is exploited for our purposes in tracking peak production:

\[ \frac{dQ}{dt} = \frac{abQ_{\text{max}}e^{bt}}{(a + be^{bt})^2}. \]

A toy model incorporating historical consumption and projecting total supply exhaustion is depicted in Figure 1.2. At a glance these fuels are seemingly inexhaustible, but a large proportion of this total stored energy is in the form of kerogen, which may require expending more energy retrieving the fuel than it produces in combustion. Therefore, this model does not reflect total recoverable fossil fuel energy because that depends on economical and technological considerations.

There is a large abundance of reduced carbon on Earth, but it is impractical to burn the entire reserve because many of these reservoirs are difficult to discover, extract, and refine. As such, predictions of imminent resource exhaustion refer not to the total possible reduced carbon energy supply, but to conventionally proven sources that are more readily recovered and converted into usable energy. Table 1.1 illustrates the proven potential reserve energies. The results from a model reflecting proven reserves and their consumption are shown in Figure 1.3. This estimate only accounts for known geological repositories that can be mined and processed using standard industrial techniques, but history shows (beyond the discovery of new reserves) innovation and demand will turn some unconventional sources to
Figure 1.2: Historical data on total world fossil fuel energy supply obtained from BP\textsuperscript{11} are fitted using \( Q_{\text{max}} = 1.6 \times 10^7 \text{EJ} \) to give \( a = 2.167 \times 10^{19} \) and \( b = 1.886 \times 10^{-2} \). The shaded area under the curve is our progress in extraction to date, \( Q_{\text{used}} = \int_0^{2016} \frac{ahQ_{\text{max}}e^{bt}}{(a+e^{bt})^2} \, dt = 24\,002.1 \text{EJ} \).

It is unclear when the cost of production will exceed demand. As Figure 1.3 reflects by 2044 (when the world population reaches 9 billion) we will either have: (1) delayed the inevitable exhaustion or (2) significantly modified our energy portfolio. In any case, known reserves are unable to solely provide energy equality either today (\( 2.2 \times 10^3 \) EJ per year) or by 2044 (\( 2.8 \times 10^3 \) EJ per year) without substantially decreasing our energy consumption per capita.

<table>
<thead>
<tr>
<th>Resource Type</th>
<th>Potential Energy (EJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>( 1.0 \times 10^4 )</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>( 3.9 \times 10^2 )</td>
</tr>
<tr>
<td>Coal</td>
<td>( 2.2 \times 10^4 )</td>
</tr>
<tr>
<td>Total</td>
<td>( 3.2 \times 10^4 )</td>
</tr>
</tbody>
</table>

Table 1.1: Potential energy of fossil fuel resources from proven reserves.\textsuperscript{2}
Figure 1.3: Using a more realistic projection based on the data in Table 1.1, we assume that all energy from fossil used to date is $2.4 \times 10^4$ EJ and that total proven reserves reach $3.2 \times 10^4$ EJ. Thus, $Q_{\text{max}} = 5.7 \times 10^4$ EJ. Nonlinear fitting resulted in $a = 1.37 \times 10^{32}$ and $b = 3.64 \times 10^{-2}$ for the logistic growth model. The red area under the curve reflects our progress of exhaustion to date. This model predicts that by 2034 we will have peaked in production per year and that by 2044 declining performance can be expected.

1.3 Greenhouse Gas Effects

Fossil fuels are poised to meet our current prosaic energy demands for the next 18 years using known geological repositories and standard techniques, although they are insufficient as the sole provider for a world with energy equality. While further geological discoveries or high demands may open additional avenues for extraction, an important penalty to fossil fuel combustion is worth mentioning: we appear to be changing the atmospheric composition as a result of our emission products. We weakly justify the mechanism of the greenhouse effect with simple models to demonstrate the magnitude of the effect at the scale of a planet as presented by others. More exhaustive efforts are found elsewhere.

Black Body Surface Temperature

The surface temperature of a planet, $T_p$, is determined by an equilibrium between the power entering and exiting a planet, $P_{\text{in}} = P_{\text{out}}$. Of course, the power entering a planet from a sun is determined by a simple modification to the Stefan-Boltzmann law that incorporates the surface area of the sun $(4\pi R_{\text{sun}}^2)$, the distribution of power.
over a sphere with a radius from the sun to a given planet \((4\pi R_d^2)\), the cross-sectional area of the planet \((\pi R_p^2)\), and the imperfect absorption of radiation by the planet as represented by the albedo \((1 - \alpha)\),

\[
P_{\text{in}} = \frac{\sigma T_{\text{sun}} \times 4\pi R_{\text{sun}}^2}{4\pi R_d} \times \pi R_p^2 (1 - \alpha),
\]

where \(\sigma\) is the Stefan-Boltzmann constant, \(T_{\text{sun}}\) is the temperature of the sun, \(R_{\text{sun}}\) is the radius of the sun, \(R_d\) is the average distance between a planet and sun, \(R_p\) is the radius of a planet, and \(\alpha\) is the surface albedo of a planet.

Likewise, black body emissions from a planet are predicted by,

\[
P_{\text{out}} = \sigma T_p^4 \times 4\pi R_p.
\]

Finally, setting \(P_{\text{in}} = P_{\text{out}}\) and rearranging the equality furnishes the desired result:

\[
\frac{\sigma T_{\text{sun}} \times 4\pi R_{\text{sun}}^2}{4\pi R_d} \times \pi R_p^2 (1 - \alpha) = \sigma T_p^4 \times 4\pi R_p
\]

\[
T_p = T_{\text{sun}} (1 - \alpha)^{1/4} \sqrt{\frac{R_{\text{sun}}}{2R_d}}.
\]

Table 1.2 shows the tabulated parameters, results, and a comparison between observed surface temperatures and atmospheric pressures for Mercury, Venus, Earth, and Mars. A cursory glance reveals that this simple relationship reliably estimates the temperatures of Mercury and Mars (both have low atmospheric pressures), but the model grossly fails to predict the average temperatures of Venus and Earth (both planets have considerably higher atmospheric pressures). We ascribe the difference in errors to the greenhouse effect, because we hypothesize atmospheric species introduce additional corrections to our simple model. Below, we incorporate infrared
gas absorptions into an improved model.

<table>
<thead>
<tr>
<th>Planet</th>
<th>( \alpha )</th>
<th>( R_d ) (m)</th>
<th>( T_p ) (K)</th>
<th>( T_{\text{obs}} ) (K)</th>
<th>( \Delta T_{\text{obs}} ) (%)</th>
<th>( P ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>0.119</td>
<td>( 5.91 \times 10^{10} )</td>
<td>430</td>
<td>440</td>
<td>2.3</td>
<td>( 10^{-15} )</td>
</tr>
<tr>
<td>Venus</td>
<td>0.750</td>
<td>( 1.08 \times 10^{11} )</td>
<td>232</td>
<td>735</td>
<td>68</td>
<td>92</td>
</tr>
<tr>
<td>Earth</td>
<td>0.306</td>
<td>( 1.50 \times 10^{11} )</td>
<td>254</td>
<td>288</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Mars</td>
<td>0.250</td>
<td>( 2.29 \times 10^{11} )</td>
<td>210</td>
<td>215</td>
<td>2.5</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 1.2: Data obtained from NASA. The planet bond albedo, \( \alpha \), and distance from sun to planet, \( R_d \), are used in conjunction with sun temperature (\( T_{\text{sun}} = 5870 \text{K} \)) and radius (\( R_{\text{sun}} = 6.96 \times 10^8 \text{m} \)) to predict equilibrium temperatures, \( T_p = T_{\text{sun}} (1 - \alpha) \frac{1}{4} \sqrt{\frac{R_{\text{sun}}}{2R_d}} \). The observed surface temperature, \( T_{\text{obs}} \), is compared with the predicted temperature, \( T_p \), and the atmospheric pressure for each planet is noted, \( P \).

**Hot-House Effect on Surface Temperature**

At the surface, incoming power from the sun, \( P_{\text{in, sun}} \), will heat the surface and the energy will be re-emitted by the surface, \( P_{\text{out, sun}} = \sigma T_{\text{surf}}^4 4\pi R_p^2 \), back into the atmosphere. Now we consider an atmospheric layer that imperfectly (\( \epsilon \)) absorbs power, \( P_{\text{in, atm}} \), isotropically emitting power back to the planet surface (\( \epsilon \sigma T_{\text{atm}}^4 4\pi R_p^2 \)) and into space, (\( 1 - \epsilon \))\( \sigma T_{\text{surf}}^4 4\pi R_p^2 + \epsilon \sigma T_{\text{atm}}^4 4\pi R_p^2 \). Balancing this flux requires distinguishing between the atmospheric and black body emissions. Let \( P_{\text{in, sun}} = \sigma T_{\text{sun}}^4 4\pi R_{\text{sun}}^2 \times \pi R_p^2 (1 - \alpha) \) represent the absolute incoming power reaching a planet’s surface from a sun. A planet surface will have a temperature, \( T_{\text{surf}} \), and the atmosphere will have another temperature, \( T_{\text{atm}} \), with an imperfect emissivity of \( \epsilon \) (note that \( \epsilon = 1 \) for a perfect black body, while \( \epsilon = 0 \) for a perfect white body). Thus for the planet’s surface,

\[
P_{\text{in, surf}} = P_{\text{out, surf}}
\]

\[
P_{\text{in, sun}} + \epsilon \sigma T_{\text{atm}}^4 (4\pi R_p^2) = (1 - \epsilon)\sigma T_{\text{surf}}^4 (4\pi R_p^2).
\]

Correspondingly for the atmosphere,
\[ P_{\text{in, atm}} = P_{\text{out, atm}} \]

\[ P_{\text{in, sun}} - \varepsilon \sigma T_{\text{atm}}^4 (4\pi R_p^2) = (1\varepsilon) \sigma T_{\text{surf}}^4 (4\pi R_p). \]

By the addition method, the relations for the surface and atmosphere are combined and solved for \( T_{\text{surf}} \):

\[ 2P_{\text{in, sun}} = (1 - \varepsilon) \sigma T_{\text{surf}}^4 (4\pi R_p^2) \]

\[ 2\left( \frac{\sigma T_{\text{sun}} \times 4\pi R_{\text{sun}}^2}{4\pi R_d} \times \pi R_p^2 (1 - \alpha) \right) = (2 - \varepsilon) \sigma T_{\text{surf}}^4 (4\pi R_p^2) \]

\[ T_{\text{surf}} = \frac{\sqrt{\frac{2\left( \sigma T_{\text{sun}} \times 4\pi R_{\text{sun}}^2 \times \pi R_p^2 (1 - \alpha) \right)}{(2 - \varepsilon) \sigma}}}{(4\pi R_p^2)} \]

\[ T_{\text{surf}} = T_{\text{sun}} \sqrt{\frac{R_{\text{sun}}}{R_d}} \sqrt{\frac{1 - \alpha}{2(2 - \varepsilon)}}. \]

Using values for Earth and \( \varepsilon = 0, 1.00, 0.780 \), we get \( T_{\text{surf}} = 254, 302, 288 \) K, which accounts well for the surface temperatures on Earth with or without an atmosphere full of heat-absorbing gases.‡

**Estimates on the Effect of Atmospheric Gases on Surface Temperature of Earth**

Early on (1896) the potential effects of heat-absorbing gases in the atmosphere on the surface temperature of the planet were recognized.14 We use Planck’s law to estimate the black body emissions of Earth, and then demonstrate the effect of gas absorptions by either water or CO\(_2\) on the emissivity of a planetary atmosphere.

‡An astute reader might test this model against Venus, obtaining \( T_{\text{surf}} = 232 \) and 276 K for \( \varepsilon = 0 \) and 1.0, which fails to account for \( T_{\text{obs}} = 735 \) K. Our previous model relies on a simple atmosphere surrounding a planet with sunlight arriving at the surface, but the Venustian atmosphere is more complex owing to the higher pressure at its surface and as a result little sunlight directly reaches the surface, hence model failure. A refined approach would consider several layers of atmosphere, each with coupled radiative energy balances and absorptions. We will also not succeed at predicting the temperature of gaseous giant planets, such as Saturn and Jupiter, because of internal heating from gravitational compression or being unable to define the “surface” of a gas giant.
Planck’s law readily calculates spectral irradiance of a black body:

\[
B(\lambda(m), T(K))(\text{Wm}^{-2}\text{nm}^{-1}) = \frac{2\pi hc^2}{10^9\lambda^5(\exp(\frac{hc}{k_B\lambda T_{surf}}) - 1)},
\]

where \( h \) is the Planck constant, \( c \) is the speed of light, \( \lambda \) is the wavelength, \( k_B \) is the Boltzmann constant, and \( B(\lambda, T) \) is the spectral irradiance. A plot of the wavelength (nm) versus the spectral irradiance for Earth is depicted in Figure 1.4 with colored areas under the emission curve representing infrared transitions of water and carbon dioxide. (The profile for the sun as seen outside the atmosphere is obtained by appropriate scaling and temperature, \( B(\lambda, T) \times (\frac{R_s}{R_d})^2 \).)

![Figure 1.4: Black body emissions of Earth with \( T = 288 \) K is the curve in blue. Yellow area under the curve reflects water infrared transitions and the red area is from CO\(_2\) transitions. \( \int_0^{\infty} B(\lambda, T) \, d\lambda = 388 \) Wm\(^{-2}\). The area corresponding to water vapor totals 265 Wm\(^{-2}\) and the area for CO\(_2\) equals 37.1 Wm\(^{-2}\).]

In Figure 1.4, a perfectly behaving black body atmosphere would be represented, \( \epsilon = 1 \), with an area completely filling an entire emission curve area; in this way, our \( \epsilon \) is a ratio of the power adsorbed relative to the total emission of a planet, therefore to crudely estimate\(^\text{8}\) the planetary emissivity we sum contributions for

\(^8\)Indeed, this approximation is rough since we do not capture the full shape of each vibrational transition at each pressure and temperature in the atmosphere; account for the variation in the concentration of these gases at different altitudes; avoid double-counting shared areas between H\(_2\)O and CO\(_2\) transitions (we argue it is fair because of underestimates elsewhere); regard different oscillator strengths; include considering other species such as ozone and methane; or use a litany of other factors considered in a full treatment.
each component relative to the total area and obtain

\[
\epsilon = \frac{\int \text{ (area H}_2\text{O transitions) } + \int \text{ (area CO}_2\text{ transitions) } \int_0^\infty B(\lambda, T) \, d\lambda}{388 \text{ W/m}^2} = \frac{265 \text{ W/m}^2 + 37.1 \text{ W/m}^2}{388 \text{ W/m}^2} = 0.779.
\]

Our estimated value of \( \epsilon = 0.78 \) matches our earlier estimate, but most importantly this toy model captures the core behavior of the natural system. Accounting for vibrational features of gases in the atmosphere roughly explains the atmospheric emissivity. Granted that water is the most potent greenhouse gas, but CO\(_2\) should not be undervalued (\( \epsilon = 0.68 \) without CO\(_2\) or \( T_{\text{surf}} = 282 \text{ K} \)).

**Estimates on Radiative Forcing of CO\(_2\)**

One of the last considerations is the effect of CO\(_2\) concentration on the emissivity. We do not fully detail a derivation of the simplified expression used, but the general sense of the relationship between [CO\(_2\)] and the area under the curve (called the radiative forcing) is developed in Figure 1.5. Briefly, at low concentrations, the concentration and radiative forcing are linearly related; at intermediate concentrations, they are related by the square root; and at high concentrations the relationship becomes logarithmic.

![Figure 1.5](image_url)

**Figure 1.5:** (Left) Depicts different concentrations of a gaseous species, at high enough concentrations saturation occurs when transmittance is 0 %. Further gains in the integrated area of a peak occur in the “wings” of a peak. (Right) Shows how the relation between the area and concentration changes dependence on the regime. Low concentrations are fit well to a linear equation; intermediate concentrations have a square-root dependence; and at high concentrations the relationship is logarithmic.

The IPCC estimates that the CO\(_2\) forcing is best represented as,\(^{12}\)
\[ F = 5.35 \ln\left(\frac{[\text{CO}_2]}{[\text{CO}_2]_0}\right), \]

where \([\text{CO}_2]\) represents the current concentration of CO\(_2\) (402 ppmv) and \([\text{CO}_2]_0\), represents an initial concentration, typically taken as the pre-industrial era value of 280 ppmv.\(^{12}\)

We should then roughly expect the influence of human combustion of reduced carbon to give an emissivity of:

\[
\epsilon = \frac{\int \text{(area H}_2\text{O transitions}) + \int \text{(area CO}_2\text{ transitions}) + 5.35 \ln\left(\frac{[\text{CO}_2]}{[\text{CO}_2]_0}\right)}{\int_0^\infty B(\lambda, T) \, d\lambda}
= \frac{265 \text{ W m}^{-2} + 37.1 \text{ W m}^{-2} + 5.35 \ln\left(\frac{402 \text{ppmv}}{280 \text{ppmv}}\right) \text{ W m}^{-2}}{388 \text{ W m}^{-2}} = 0.784.
\]

Accordingly, the difference in temperature from pre-industrial levels to today’s concentrations should be on the order of 0.30 K, which is only a factor of three from IPCC’s prediction of 0.85 K. Nonetheless, IPCC’s value incorporates the effects of CO\(_2\), methane, N\(_2\)O, among feedback systems, whereas ours only roughly accounts for CO\(_2\).\(^{12}\) This means our rather simple discussion here demonstrates some of the essential principles of the formidable work undertaken by IPCC. In particular, it highlights how human-made emissions are occurring at a scale large enough to shift the surface temperature of the planet. As a final note on this particular discussion, the amount of shift our civilization can tolerate is uncertain because we depend on past climate behavior as part of our risk management strategy. So, seemingly small changes move us into uncharted territory. As such, there is considerable interest in developing energy systems that do not contribute to climate change and can simultaneously help make a world with energy equality possible.
**Emissions of CO\(_2\) from Anthropogenic Sources**

Now we estimate the magnitude in change of CO\(_2\) concentration in the atmosphere, \(\Delta[\text{CO}_2]\), from emissions relative to the total air to see if anthropogenic sources can account for the magnitude of change observed from the pre-industrial era level (280 ppmv) to now (402 ppmv). First we calculate the total volume of CO\(_2\) produced by humans and then ratio to the total volume of air in the atmosphere.

Figure 1.2 used \(2.4 \times 10^4\) EJ as the total fossil fuel energy spent; if we further assumed the entire resource was burnt then this means that the total volume of CO\(_2\) is obtained as:

\[
V_{\text{CO}_2} = 2.4 \times 10^4 \times 10^{18} \text{J} \left(\frac{1 \text{kg}}{30 \times 10^6 \text{J}}\right) \times \frac{44}{15} \times \frac{1 \text{m}^3}{1.98 \text{kg}} = 1.2 \times 10^{15} \text{m}^3.
\]

Similarly, the total volume of the atmosphere is determined:

\[
V_{\text{air}} = 101325 \frac{\text{kg} \cdot \text{m}}{\text{m}^2} \times \frac{1 \text{s}^2}{9.8 \text{m}} \times 4\pi (6471 \times 10^3 \text{m})^2 \times \frac{1 \text{m}^3}{1.225 \text{kg}} = 4.3 \times 10^{18} \text{m}^3.
\]

Thus,

\[
\Delta[\text{CO}_2] = \frac{V_{\text{CO}_2}}{V_{\text{air}}} \times 10^6 = \frac{1.2 \times 10^{15} \text{m}^3}{4.3 \times 10^{18} \text{m}^3} = 280 \text{ppmv}.
\]

Our estimated \(\Delta[\text{CO}_2]\) is approximately double than what is measured because CO\(_2\) becomes trapped in the carbon cycle, with about half the CO\(_2\) ending up in photosynthetic organisms or the ocean. In the ocean, one of the largest reservoirs in the carbon cycle, the formation of carbonic acid from equilibration with CO\(_2\) vapor has led to ocean acidification and detrimental effects seen on the growth of corals.
1.4 Low CO₂ Emission Energy Systems

Any future where humanity expels less CO₂ as part of the operation of modern life will require a mixed portfolio of energy sources, each with positive and negative attributes, tailored to the region of generation and consumption. This future economy will also leverage fossil fuels strictly as a chemical feedstock instead of wasting precious materials on thermal energy. Among the many choices that will be available, a select few are highlighted below due to their immense promise and potential. We will also mention some of their undesirable properties. While it may be obvious fusion and fission rely on the energetic balance of nuclear forces, it is less intuitive that many other sources of energy (including wind and solar) indirectly rely on the sun, a natural nuclear reactor; for this reason, we distinguish between direct and indirect nuclear sources.

Direct Nuclear

Both nuclear options make clear the large difference in specific energy available from nuclear reactions compared to less energetic chemical transformations. Fusion remains a technical challenge ever out of reach, while fission reactors have been available for decades but struggle to gain relevance to electrical companies who would build more power stations. Unlike other renewable options, nuclear systems appear well suited to supplying baseload power, but the economics of fission seem to demonstrate that these power stations are not amenable to a distributed power generation scenario. Instead, these options appear to work best in a centralized power scheme.

Fusion

The oft dreamed future energy source is fusion. A challenging criteria for this brand of energy conversion is the so-called ignition point, which is when the nuclear
reactions become self-sustaining. Humans have transiently achieved ignition in the D-T reaction used by thermonuclear weapons:

\[ ^2\text{H} + ^3\text{H} \rightarrow ^4\text{He} + ^1\text{n}. \]

We can estimate the energy released by Einstein’s mass-energy equivalence relationship, \( E = mc^2 \):

\[
E = (\Delta m)c^2 \\
= (m_{^2\text{H}} + m_{^3\text{H}} - m_{^4\text{He}} - m_{^1\text{n}})c^2 \\
= (3.34 + 5.01 - 6.65 - 1.67) \times 10^{-27} \text{kg} (3.00 \times 10^8 \text{m/s})^2 \\
= 2.70 \times 10^{-12} \text{J}
\]

A more useful metric of comparison requires converting to the specific energy of an equimolar mixture of deuterium and tritium gas, the fuel, to:

\[
\rho_E = \frac{\text{1 kg}}{1 \text{kg}} \times \frac{1000 \text{g}}{1 \text{kg}} \times \frac{4 \text{mol}}{(4.03 + 6.03) \text{g}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{mol}} \times \frac{2.70 \times 10^{-12} \text{J}}{2 \text{ atoms}} = 3.23 \times 10^{14} \text{ J/kg}
\]

\[
= 32.3 \times 10^7 \frac{\text{MJ}}{\text{kg}}.
\]

Recall that the specific energy of all reduced carbon on Earth works out to be about \( 30 \frac{\text{MJ}}{\text{kg}} \) which pales in comparison to \( 32 \times 10^7 \frac{\text{MJ}}{\text{kg}} \), reflecting the enormous potential of fusion. Unfortunately, we have never harnessed this reaction aside from displays of destruction or laboratory experiments.* Overcoming electrostatic repulsion, material compatibility with high neutron fluxes, and generating sufficient tritium are some of the major challenges facing development of the D-T reactor. We

---

*To frame the challenge, consider that the “spark” required to “ignite” is a fission explosion in a thermonuclear weapon.
are unlikely to achieve fusion by the same pathway as the Sun, the p-p pathway, because of a considerably lower ($10^{-24}$) nuclear cross section,\(^\dagger\) but there are other fusion reactions available with different properties.

**Fission**

Fission accounts for 4.44 % of all energy converted today. Natural uranium ore is 99.3 % $^{238}$U and 0.7 % $^{235}$U. Of the naturally occurring isotopes, only $^{235}$U is fissile, meaning a nuclear reaction with a thermal neutron can lead to fission chain reactions. Typically, isotopic enrichment is performed to increase the ratio of $^{235}$U/$^{238}$U for use as a fuel in a light water nuclear reactor, while heavy water reactors can use natural abundance uranium. Among the many different fission reaction pathways that occur, here is an example of a reaction representing the average fission fragment masses and energy:

$$^{235}\text{U} + ^1\text{n} \rightarrow ^{236}\text{U} \rightarrow ^{140}\text{Xe} + ^{94}\text{Sr} + 2^1\text{n}.$$  

The specific energy for pure natural abundance uranium is calculated similarly to our fusion example above,

$$\rho_E = \frac{1\text{kg}}{1\text{kg}} \times \frac{0.7}{100} \times \frac{1000\text{g}}{1\text{kg}} \times \frac{1\text{mol}}{235\text{g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{1\text{mol}} \times \frac{3.12 \times 10^{-11}\text{J}}{1\text{atom}} = 56 \times 10^6 \text{MJ/kg}.$$  

The specific energy of this fission reaction is poorer than our fusion example by a factor of ten but greater than that obtained from fossil fuels by about two million.

The energy conversion of a nuclear power plant is limited by Carnot efficiency. As an aside, there is an example of a natural nuclear reactor that occurred in the Oklo region of central Africa millions of years ago when $^{235}$U natural abundance was considerably higher, thereby allowing natural water to serve as a neutron moderator.

\(^\dagger\)The nuclear cross section is the probability of nuclear fusion reaction rather than scattering.
for a system that released about 0.4 EJ over thousands of years.\textsuperscript{15}

Fission power plants have a capacity factor of around 0.90. The availability of uranium is of no immediate concern and a plethora of positive attributes of fission energy plants can be found detailed elsewhere,\textsuperscript{16} but there are significant hurdles that prevent increased adoption in the US, such as high capital cost, construction delays, uncompetitive electricity pricing, engineering failures that erode the public’s trust, no long-term storage of waste, and concerns about the proliferation of nuclear weapons. It is our opinion that additional reactors will be built in a free market when investors believe there is a profit to be made, which seldom appears to have been the case in recent memory, even with substantial government subsidies in place, such as the Price-Anderson Nuclear Industries Indemnity Act.

**Indirect Nuclear**

Power from wind has been practiced for more than a century, recently undergoing a renaissance and quickly gaining relevance as major player in electricity generation. Whereas, solar energy transformation with the use of photovoltaics has steadily accumulated momentum, and as a result, it is moving toward becoming a competitor with traditional electricity sources. One major problem with both options is their inherent intermittency, but they are not capital intensive to construct at a small scale; this naturally lends to possible inclusion in distributed power generation scenarios. The advantage of a decentralized grid is that small pieces can be brought together over a wide area (lowering transmission losses and hour-by-hour intermittency), but distributed power will encounter power conversion losses on the order of $< 10\%$. Centralized power, on the other hand, will suffer from transmission losses likely on the order of $< 10\%$. Without storage, there are concerns the stability of the grid will be negatively impacted by large scale integration of intermittent power stations.\textsuperscript{17}
Wind

As sunlight unevenly heats the surface of Earth, mass transfer through convective processes creates wind. Wind electricity generation depends on wind with a density, \( \rho \), a velocity, \( v \), passing through a turbine with a radius, \( r \), and cross-sectional area, \( \pi r^2 \). The product of the kinetic energy and wind velocity gives the power:

\[
P_{\text{wind}} = \frac{1}{2} \pi r^2 \rho v^3.
\]

The power conversion is fundamentally limited by Betz’s law to \( \eta = 16/27 \) but more practically reaches \( \eta = 0.30 \). Wind power complements raw solar energy because it peaks at night while solar peaks during the day. The altitude, blade size, and location all change the characteristics of the wind power that can be collected. Generally speaking, the capacity factor \( (C_f = P_{\text{average}}/P_{\text{maximum}}) \) is around 0.30. Another constraint is that wind turbines need to be spaced approximately \( 3 \times (2r) \) from one windmill to another. Among renewable energy sources, wind is one of the fastest growing in number of installations because it has already reached cost parity with natural gas in a variety of locations. Currently wind contributes to 4.7% of total electricity generation within the United States.\(^\text{18}\)

We can calculate the energy intensity of wind per day by,

\[
\frac{E_{\text{daily, wind}}}{\text{area day}} = \frac{P_{\text{wind}} \times \eta \times C_f \times t}{\pi (3 \times (2r))^2} = \frac{\rho v^3 \eta C_f \times t}{72}.
\]

For instance, in north-eastern Montana an average wind velocity, \( v \), of 7.00 m/s at a height of 30 m can be assumed,\(^\text{19}\) giving:

\[
\frac{E_{\text{daily, wind}}}{\text{area day}} = \frac{(1.23 \text{ kg/m}^3)(7.00 \text{ m/s})^3 \times 0.30 \times 0.30 \times (60^2 \times 24) \text{s}}{72} = 4.56 \times 10^4 \frac{\text{J}}{\text{m}^2\text{day}}.
\]
Solar Photovoltaics

Figure 1.6 compares the black body emission of the sun (attenuated by distance) and an AM0 spectrum. As we might expect, the irradiance reaching the Earth fairly matches a black body emission. Integration of AM0 tells us that $1.37 \times 10^3 \frac{W}{m^2}$ travels to the planet; therefore, for our surface-area illuminated we must receive:

$$P_{\text{arriving}} = (\int AM0) \times 2\pi R^2_{\text{earth}} = (1.37 \times 10^3 \frac{W}{m^2}) 2\pi (6.37 \times 10^6 m)^2 = 5.56 \times 10^{16} W$$

$$= 3.49 \times 10^5 \text{ TW.}$$

As such, in about half an hour we receive all the energy the world demands in a year at current rates (552 EJ) and in about two hours we would have enough for a world with energy equality ($2.2 \times 10^3$ EJ). There are additional constraints on a real-world system. More specifically, the power available per unit area is limited by the abledo; therefore, $((1 - 0.306)(1.37 \times 10^3 \frac{W}{m^2})) = 951 \frac{W}{m^2}$ is roughly what we expect at the surface.

Figure 1.6: The black body emission is calculated as mentioned earlier, $B(\lambda, T) \times \left(\frac{R}{R_s}\right)^2$. The AM0 spectrum is provided by NREL. $20 \int_0^{10000} AM0(\lambda) d\lambda = 1.37 \times 10^3 \frac{W}{m^2}$.

Naturally, we do not expect to cover the entire surface of our planet with solar cells,
but some fraction could prove to be an important addition to our future energy portfolio. We will more closely examine the thermodynamic limits of photovoltaics (PV) in the next chapter, although commercial panels can reach $\eta = 0.20$ today and advanced multijunction cells are approaching $\eta = 0.50$.\textsuperscript{21} One of the largest drawbacks hampering deployment of photovoltaics is the capacity factor for these power systems, which is about 0.30 for excellent installations using a single-axis tracking system. Considering these factors, the real energy intensity that can be converted on a daily basis is easily calculated from,

$$\frac{E_{\text{daily}}}{\text{area day}} = P_{\text{sun}} \times \eta_{PV} \times C_p \times t,$$

where $E_{\text{daily}}$ is the daily energy converted per unit area, $P_{\text{sun}}$ is the power of sunlight at the Earth’s surface, $\eta_{PV}$ is the efficiency of a solar cell, $C_p$ is the capacity factor, and $t$ is the number of seconds in a day. Now we can use values available today to estimate modern, $\frac{E_{\text{modern, PV, daily}}}{\text{area day}}$, and future, $\frac{E_{\text{future, PV, daily}}}{\text{area day}}$, energy intensities for PV:

$$\frac{E_{\text{modern, PV, daily}}}{\text{m}^2\text{day}} = 951 \frac{W}{\text{m}^2} \times 0.20 \times 0.30 \times (60^2 \times 24) \text{s} = 4.93 \times 10^6 \frac{\text{J}}{\text{m}^2\text{day}},$$

$$\frac{E_{\text{future, PV, daily}}}{\text{m}^2\text{day}} = 951 \frac{W}{\text{m}^2} \times 0.50 \times 0.30 \times (60^2 \times 24) \text{s} = 1.23 \times 10^7 \frac{\text{J}}{\text{m}^2\text{day}}.$$

As a point of comparison, the Palo Verde Nuclear Generating Station, the largest operating complex in these United States, harnesses 3.94 GW with $C_f = 0.98$ over $1.53 \times 10^7 \text{ m}^2$ or

$$\frac{E_{\text{nuclear, daily}}}{\text{m}^2\text{day}} = \frac{3.94 \times 10^9 \times 0.98 \times (60^2 \times 24)}{1.53 \times 10^7 \text{m}^2} = 2.18 \times 10^7 \frac{\text{J}}{\text{m}^2\text{day}}.$$

Thus, the energy intensity of nuclear is a factor of four better than modern high-
density PV and only a factor of two better than future PV, which suggests that in certain regions with proper solar insolation PV may be viable under a number of different scenarios, such as when land is low cost or the area is on a rooftop. Not surprisingly, PV must cover this area cheaply in order to compete economically. As a consequence, the components must also be affordable to make the economics favorable. Within a short period of time, solar’s total share has crept up to 0.6% of the total US electricity generation total.\textsuperscript{18}

An essential hypothesis is that no single source will necessarily dominate the immediate future energy landscape (aside from fossil fuels), but cooperation among different systems could enable a shift in energy holdings before our untimely exhaustion of these valuable supplies. In light of the massive potential of solar energy, in terms of what is available from the sun and its relatively high energy intensity, we focus the rest of this thesis on advancing PV.

1.5 Theme of Thesis: Intermittent Energy Storage

The architecture of traditional electrical grids relies on large dispatchable centralized power stations with high capacity factors. These grids have virtually no storage, and their supply is synchronized in tune with demand. Intermittent supplies, such as solar and wind, are a key challenge facing large-scale integration of renewable energy sources.\textsuperscript{17,22} Consequently, there is considerable interest in storing this energy. There are some promising methods of electrical storage, such as pumped hydro or compressed air, but they rely on relatively specific geological features. Thermal and chemical energy storage are largely location insensitive, but chemical storage takes the center stage of our focus.

Among the chemical storage options are traditional batteries, such as lead-acid or lithium-ion; unconventional batteries, such as redox-flow; and chemical fuels, by means of water splitting or carbon dioxide reduction.
Chemical storage largely falls within the field of electrochemistry. The specific properties of a battery depend on the chemistry involved, and some chemistries are better suited for specific applications than others. Lead-acid batteries offer cheap storage with a specific energy around $9 \times 10^4$ J/kg. This makes them great for small applications (as in a car starter), but as weight becomes important, larger densities as in electric cars are required. For that reason, expensive lithium-ion batteries, offering $4.5 \times 10^5$ J/kg, become more attractive.

The key properties for grid-level electricity storage are high-cycle lifetimes (both Pb-acid and Li-ion suffer in this regard), the speed of charging or discharging, scalability (instead of depending on modules, tanks can be easily fitted to change the volumes in a reservoir), and low cost. Redox-flow batteries are promising systems to use in this application.

More broadly, energy storage has more stringent requirements than the chemistry used in electrical storage. This is where the field of artificial photosynthesis sits. In the best case, we could reduce CO$_2$ to liquid fuels, such as methanol, with renewable power plants, and then, use existing infrastructure to transport stored energy for use in a traditional combustion engine. Unfortunately, the chemistries are fiendishly difficult. From a chemical point of view, water splitting is more tractable, and as a chemical fuel, H$_2$, has attractive qualities.

The principal focus of this thesis sits at the boundary between redox-flow batteries and artificial photosynthesis. We argue that electrical storage is a goal we are closer to realizing, but we hope that advancements made toward our goal will also simultaneously benefit the field of artificial photosynthesis as a whole.

Our goal of supplanting fossil fuels with alternative energy sources is challenging. Solar PVs are capable as supplemental sources during peak hours of sunlight, and large installations are already being deployed across the globe, but we must move
faster and a way to do this may be by enabling the storage of intermittent electricity.

Specifically, we (in Chapter 1) explore the limits of fossil fuels as a sole provider of energy in a world with energy equality; show how human emissions of CO\textsubscript{2} occur at a large enough scale to shift the temperature of the planet; explore the landscape of renewable energy sources while focusing our attention on solar photovoltaics due to its immense potential; and explain why we are focused on using redox-flow chemistry to store solar energy for electricity consumption. After understanding our broad goal, we outline our specific device goals (in Chapter 2) for our system with a photocathode and photoanode and we model device efficiencies for different configurations of our system. By Chapter 3 we introduce a cathode catalyst, which displays promising activity. We integrated this newly developed material with silicon microwire arrays in Chapter 4. Chapter 5 details efforts towards a photoanode. Inside Chapter 6, we provide an overview of where we have come, where we have fell short, and what still needs to be done. Additionally there is also an exploration of our catalyst (in Appendix B), another strategy to protect silicon (Appendix C), the synthesis of complex nanominerals by PLAL (Appendix D), and the academic impact our work has had (Appendix E).

1.6 References


(17) B. Sovacool, *Util Policy*, 2009, **17**.


System Concept

A prominent role for solar energy in the future requires technical solutions to its intermittent nature and cost. An integrated light collector and storage system could rise to the challenge if it takes advantage of the distributed nature of solar energy. Widespread adoption requires covering a large area with cheap components, which must have reversible chemical reactions, affordable light absorbing materials with high quantum yields, and utilization of abundant electrocatalysts with high activities. What differs from many strategies herein is that we propose using redox-flow chemistry to store the electricity. Instead of splitting water, as would be needed for energy storage, we will split hydrobromic acid for distributed electricity storage by using only light provided by the sun as an input into an integrated device. We begin by reviewing historical efforts on this path, and then, estimate device thermodynamic limits. Finally, we outline our idealized device construction, and describe specific challenges facing our path towards efficient HBr splitting.

2.1 Project Illinois

Among factors that precipitated the 1970s energy crisis, declining oil production within the United States in 1970 made her particularly susceptible to the effects of the OPEC oil embargo of 1973. As a result of the change in trade, prices of oil rapidly increased throughout the country with significant effects. The fact that oil was limitless had been taken for granted, and so this shock initiated a surge of interest in developing alternatives to fossil fuels, culminating in the installation of rooftop thermal solar panels on the White House in 1979 by President Jimmy Carter.
During this time period, rationing of retail gasoline was commonplace,* in addition to federal measures, such as a mandated maximum speed limit of 55 mph that was meant to curb consumption.¹

Simultaneously, Jack Kilby — co-inventor of the integrated circuit — took a leave of absence from Texas Instruments (TI) in 1970 to pursue independent inventing.² Perhaps sensing an opportunity in the growing energy crisis, Kilby initiated conceptual work on a solar electricity storage system using hydrogen iodide in 1973. By 1975 he had refined his idea with Jay Lathrop (former researcher at TI and then professor of electrical engineering) and Arthur Porter (former researcher at TI and then professor at nearby Texas A&M), resulting in a series of patents they filed on the concept.³⁻⁵ They extended earlier efforts within TI and made high-quality spherical solar cells from cheap polysilicon.

Initial experimental work occurred at Texas A&M, but then TI brought this work into their Central Research Laboratory under the code name “Project Illinois” (for Kilby’s undergraduate alma mater) in 1976. Scientists within the company characterized the project as risky, but technically sound. By 1978, TI had further refined the concept to include a roof-top residential installation with spherical, hydrogen-bromide-splitting solar cells, which were internally equipped with a fuel cell to generate electricity. To make this idea a reality, TI sought outside funding from the Department of Energy (DOE) because of significant investments elsewhere in the company, such as in personal computing. John Deutch, then Director of Energy Research at the DOE, immediately recognized the significance of the program and supported the formation of a cooperative agreement between TI and the DOE in 1978.

The terms of the agreement were unusual for the time but necessary in light of the significant energy crisis. Over four years, TI would supply $4 million (14.8 million

*An even/odd number of a leading digit on license plate indicated on what days (even/odd) the consumer could purchase automobile fuel.
inflation adjusted 2016 dollars), and the DOE would provide $14 million (51.8 million) for the development of an economical system. In the event a commercial product was brought to market, the $14 million would have been repaid as a portion of the proceeds. With this agreement in hand, the TI Solar Energy System (TISES) development was underway. By 1980, the first TISES development module was completed; in 1981 the first prototype system module was demonstrated.

TISES used four components: the solar chemical converter (SCC), a metal-based hydrogen storage unit, a fuel cell to produce electricity from the stored chemical potential, and a heat exchanger. After exposing the system with solar energy, both electrical and thermal energy would be available for output to a residence. We focus only on the component relevant to this thesis, the SCC. The solar-to-hydrogen efficiency ($\eta_{\text{STH,HBr}}$) achieved by their highest functional cell was $\eta_{\text{STH,HBr}} = 9.5\%$. We begin ascertaining the limits of this value in the next section.

The SCC array consisted of spherical silicon micro-sized crystals embedded in a glass matrix and immersed in the aqueous electrolyte. These microcrystals were chosen to bring down the costs of the light absorber. The spheres were either n$^+$-on-p or p$^+$-on-n type for the cathode and anode, respectively. The sphere tops, when exposed to the solution, were coated by a Pt/Ir alloy acting as a protective and electrocatalytic film, while ohmic back-contact was provided by a thin metal film (see Figure 2.1 for a cross-sectional diagram of the component). Another important piece was the membrane, Nafion, that separated the anode and cathode half-reactions and prevented self-discharge. The fuel cell subsystem releases electricity by running the reverse reaction of the SCC. The chemistry of the SCC is straightforward and facile.
As light hits the photoanode, oxidation of bromide to bromine takes place:

\[ 2 \text{HBr} + \text{Light} \rightarrow \text{Br}_2 + 2 \text{H}^+ + 2 \text{e}^- . \]

And at the photocathode, reduction of protons occurs with light:

\[ 2 \text{H}^+ + 2 \text{e}^- + \text{Light} \rightarrow \text{H}_2 . \]

These two half-reactions contribute to an overall reaction of

\[ 2 \text{HBr} + \text{Light} \rightarrow \text{Br}_2 + \text{H}_2 . \]

Figure 2.1: Cross section of TISES Solar Chemical Converter. (Used with permission from W. McKee, IEEE Transactions on Components, Hybrids, and Manufacturing, 1982, 5(4), pp 336-341. Copyright 1982 IEEE.

By 1981, an oil glut appeared under the first term of President Ronald Reagan.\(^7\) This signaled the end of the 1970s energy crisis.\(^7\) The Reagan Administration substantially reduced energy research outlays by 50 %.\(^7\) As a result, the DOE had to revisit the TI cooperative agreement for the 1981 and 1982 fiscal years; instead, the DOE provided $5.3 million, and TI provided $12.5 million for Project Illinois, totaling $17.8 million (65.3 million, factoring in inflation). By the end of the project (1983), the team had succeeded in all technical aspects, and the system was ready for
further development at the pilot-plant level. Due to declining interest in alternative energy, from the uncertainties in the economics and marketability, TI divested from this project by 1985, although spherical solar cells were pursued for some time thereafter. Symbolically marking the end of a chapter in our history, the Reagan administration removed solar panels from the White House in 1986.

Among commercial endeavors, TISES was one of the largest industrial research projects using semiconducting components for electrical storage. Another smaller effort was made between 2009 and 2014 by a start-up called Sun Catalytix, which raised a total of $14.5 million. As a part of a pivot from unsuccessful water splitting, Sun Catalytix briefly investigated electricity storage using haloacids, such as HBr, before the company was acquired by Lockheed Martin for their patented technology on redox-flow batteries using metal-ligand coordination compounds.\(^8\) Reportedly, they are trying to scale up this technology for grid-level electricity storage applications.

### 2.2 Limits of Solar Energy Power Generation

This section of the chapter focuses on building a thermodynamic foundation from which to determine the limits of solar-to-chemical power generation. The upper-limit of efficiency observed by TI was \( \eta_{\text{STC, HBr}} = 0.095 \), but we would like to ascertain the theoretical upper-limits to this conversion for different devices to make an informed choice of configuration and materials. In this chapter we perform calculations using theoretical estimates on optimized systems not yet constructed, but that are perhaps within reach in the coming decade. For a single light absorber, the oxidation and reduction reactions happen on the same material, but as we have predicted here efficiencies will be lower than a more complex system using two semiconductors. When using two light absorbers, we can either configure them in series or in parallel. For the parallel system, the efficiency is slightly better than a
We borrow a simple theoretical approach, refined by Ross, to our specific case.\textsuperscript{9,10} Practically, we would like to understand the factors that control the magnitude of $\eta_{\text{power}}$, where $\eta_{\text{power}} = \frac{\text{extracted power}}{\text{incoming power}}$. The incoming power, of course, is determined by photons of the correct energy from the sun and passing from space through the atmosphere, ultimately reaching the semiconductor surface — see Figure 2.2 for the photon flux density versus wavelength at the surface, according to a standard used in the testing of solar devices. To determine the maximum power attainable a considerable discussion will follow. We start from values that are out of reach and then subsume different parasitic losses until we have the minimum number of necessary parameters needed to describe efficiencies for a wide range of materials and configurations.

Figure 2.2: Photon flux density of AM1.5D spectrum,\textsuperscript{11} which refers to the number of photons arriving at each wavelength that have passed through the atmosphere of Earth when the sun’s zenith is 48.2° and the surface is tilted at 37°, representing average conditions, directly illuminating the light absorber.
**Apparent Power Yield**

The statistical distribution of quasi-particles in a semiconductor is perturbed by incoming photons with an energy greater than the band gap \(E_g\), that is the difference in energy between the ground state (valence band) and excited state (conduction band) of the semiconductor. Moreover, there is an absorption of light with an energy greater than \(E_g = \frac{hc}{\lambda_g}\). It is important to point out that both the valence and conduction bands represent a continuum of states and that we care about both the valence band maximum energy, called the valence band edge, and the conduction band minimum energy, called the conduction band edge. One real key to the operation of a PV solar cell is spatially separating the excited-state electrons from the holes left behind in the valence band before they can recombine; another key is exploiting carefully tuned interfacial energetics so that electrons and holes can be shuttled through an external circuit where power can be extracted.

The rate of excitation, \(J_e\), is calculated by,

\[
J_e = \int \sigma I_s d\lambda,
\]

where \(I_s\) is the photon flux density of sunlight reaching the installation, and \(\sigma\) is the absorption cross section of the material. Roughly speaking, we say that \(\sigma = 1\) for \(hc/\lambda > E_g\), and \(\sigma = 0\) for \(hc/\lambda < E_g\). In a real material a distribution — reflected in the natural line width of absorption spectra — exists at the boundary, but we neglect this to simplify analysis.

The absorption of a photon with sufficient energy results in the excitation of an electron from the valence band to the conduction band. For photons with energies greater than the band gap, energy is lost in the form of phonons (eventually heat) — this process occurs on the timescale of picoseconds \((10^{-12}\text{ s})\) until the electron reaches the conduction band edge where it can rest for milliseconds \((10^{-3}\text{ s})\). Thus,
any excited-state electrons will have an energy determined by the band gap, $hc/\lambda_g$.

Naively one might calculate the apparent power yield, $P_{\text{yield}}$, in the vain of obtaining a reasonable estimate on the extractable power. This power yield is calculated as the product of the excitation rate and the associated energy of the band gap:

$$P_{\text{yield}} = J_e \frac{hc}{\lambda_g}.$$ 

As will soon become clear, this quantity does not represent useful power. The maximum power extractable from the system is governed by thermodynamics and commensurately depends on a detailed balance. Our balance must account for gains and losses; therefore, in our next case, energy is lost through the form of light emission from the semiconductor.¹³

**Semiconductor Light Emission**

We follow the energy balance by determining the entropy for photons exiting and entering a semiconductor. More importantly, we keep in mind the fact that the entropy change, $\Delta S$, is related to the change in energy, $\Delta E$, at a constant temperature, $T$, by way of a simple relationship, $\Delta S = \frac{\Delta E}{T}$. In addition, the energy of a photon is related to the wavelength, $\lambda$, simply as, $E = \frac{hc}{\lambda}$. Recall that the black body photon flux density is calculated from Planck’s law by,¹²

$$I_{BB,SC} = \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{k_B T_{sc} \lambda}\right) - 1} \frac{\lambda}{hc}.$$ 

Solving for the reciprocal temperature of the semiconductor ($T_{sc}^{-1}$) gives:

$$T_{sc}^{-1} = \frac{\lambda k_B}{hc} \ln \left( \frac{2c}{I_{BB,SC} \lambda^4} + 1 \right).$$ 

To find the entropy for every photon departing the electromagnetic field, the entropy
per photon \((-\partial S/\partial N = (hc/\lambda)/T)\) is set equal to the black body intensity of the semiconductor,

\[-\frac{\partial S}{\partial N} = \frac{hc/\lambda}{T} = k_B \ln \left(\frac{2c}{I_{BB,SC}\lambda^4} + 1\right) .\]

Now we utilize the fact that the chemical potential difference between the band edges, \(\mu\), controls the resulting entropy change per absorbed photon within the semiconductor at temperature, \(T_{sc}\), in order to formulate:

\[\frac{\partial S}{\partial N} = \frac{hc/\lambda - \mu}{T_{sc}} .\]

Equating the entropy changes for the electromagnetic field and the semiconductor, and then solving for \(I_{BB,SC,\mu}\) results in:

\[-k_B \left( \ln \left(\frac{2c}{I_{BB,SC,\mu}\lambda^4} + 1\right) \right) = \frac{hc/\lambda - \mu}{T_{sc}} \]

\[I_{BB,SC,\mu} = \frac{2c}{\lambda^4} \left[ \exp \left( \frac{hc/\lambda - \mu}{T_{sc}k_B} \right) - 1 \right]^{-1} .\]

Now, we use the insight that the term “\(-1\),” above, corresponds to stimulated emissions and therefore, is neglected to give:

\[I_{BB,SC,\mu} = \frac{2c}{\lambda^4} \left[ \exp \left( \frac{hc/\lambda - \mu}{T_{sc}k_B} \right) \right]^{-1} \]

\[= \frac{2c}{\lambda^4} \exp \left( \frac{\mu - hc/\lambda}{T_{sc}k_B} \right) \]

\[= \frac{2c}{\lambda^4} \exp \left( \frac{\mu}{T_{sc}k_B} \right) \exp \left( -\frac{hc/\lambda}{T_{sc}k_B} \right) .\]

Recognizing that the rate of radiative emission, \(J_r\), from the semiconductor is the
integrated product of the intensity and surface area results in:

\[ J_r = \int \sigma I_{BB, SC, \mu} d\lambda \]

\[ = \exp\left( \frac{\mu}{T_{sc} k_B} \right) \int \sigma \frac{2c}{\lambda^4} \exp\left( \frac{-hc}{\lambda T_{sc} k_B} \right) d\lambda \]

\[ \approx \exp\left( \frac{\mu}{T_{sc} k_B} \right) \int \sigma I_{BB, SC} d\lambda . \]  \hspace{1cm} (2.2)

**Maximum Potential Power**

We use the expression from 2.2 for the rate of emission from the semiconductor to balance incoming and outgoing fluxes of photons.* The maximum potential, \( \mu_{\text{max}} \), is less than the apparent band gap due to entropic losses, and it is calculated by letting the flux of photons entering and exiting a semiconductor equal one another \((J_e = J_r)\):

\[ \mu_{\text{max}} = k_B T_{sc} \ln \left( \frac{\int_0^{\lambda_0} I_S d\lambda}{\int_0^{\lambda_0} I_{BB} d\lambda} \right) . \]  \hspace{1cm} (2.3)

This has given us the tools required to express a power smaller than the apparent yield, based on the maximum potential:

\[ P_{\text{potential}} = J_e \mu_{\text{max}} . \]

This relationship does not capture losses due to the quantum yield of the electronic processes occurring within the material, so it should be unsurprising the that maximum power will be lower still.

---

*The maximum chemical potential, or Gibbs free energy, is by definition a reversible process: thus an equal rate of excitation and radiative recombination (emission) must occur.
Maximum Power

The maximum extractable power, $P_{\text{power}}$, depends on the product of the chemical potential, rate of excitation, and internal losses (i.e., not contributing to the extracted work in a resistive circuit or a chemical transformation):

$$P_{\text{power}} = \mu_{\text{power}} J_e (1 - \phi_{\text{loss}}).$$

where $\phi_{\text{loss}}$ accounts for both radiative ($J_r/J_e$) and nonradiative losses ($\alpha$) in the form of

$$\phi_{\text{loss}} = \alpha \frac{J_r}{J_e}.$$  \hfill (2.4)

Plugging in equation 2.2, expression 2.1, and equality 2.3 into the formula 2.4 results in:

$$\phi_{\text{loss}} = \alpha \exp \left( \frac{\mu_{\text{power}}}{k_B T_{\text{sc}}} \right) \frac{\int \sigma I_{BB} d\lambda}{\int \sigma I_S d\lambda},$$

$$\ln (\phi_{\text{loss}}) = \ln (\alpha) + (\mu_{\text{power}}/k_B T_{\text{sc}}) + \ln \left( \frac{\int \sigma I_{BB} d\lambda}{\int \sigma I_S d\lambda} \right) + k_B T_{\text{sc}} \ln \left( \frac{\int \sigma I_{BB} d\lambda}{\int \sigma I_S d\lambda} \right)$$

$$\mu_{\text{power}} = k_B T_{\text{sc}} \ln (\phi_{\text{loss}}) - k_B T_{\text{sc}} \ln (\alpha) + k_B T_{\text{sc}} \ln \left( \frac{\int \sigma I_{BB} d\lambda}{\int \sigma I_S d\lambda} \right)$$

recognize that $\mu_{\text{max}} = k_B T_{\text{sc}} \ln \left( \frac{\int_0^{I_{BB}} I_S d\lambda}{\int_0^{I_{BB}} I_{BB} d\lambda} \right)$

$$\mu_{\text{power}} = \mu_{\text{max}} + k_B T_{\text{sc}} \ln (\phi_{\text{loss}}) - k_B T_{\text{sc}} \ln (\alpha).$$

A plot comparing the energy conversion efficiency for the yield ($\eta_{\text{yield}} = \frac{P_{\text{yield}}}{\text{incoming power}}$), potential ($\eta_{\text{potential}} = \frac{P_{\text{potential}}}{\text{incoming power}}$), and extractable power ($\eta_{\text{power}} = \frac{P_{\text{power}}}{\text{incoming power}}$) for different band gap materials is shown in Figure 2.3. Silicon, with $E_g = 1.12$ eV, has an estimated efficiency of around $\eta_{\text{power}} = 0.319$, which is equivalent to the Shockley-Queisser limit. As silicon is perched near the maximum, it is should be
unsurprising to find that silicon solar cells are ubiquitous. The theory just described is used as a foundation for what we call the “$\mu$power” approximation in Appendix A.

Figure 2.3: Different estimates of the efficiencies depend on the band gap of the semiconductor for the $\eta_{\text{yield}}$ (blue), $\eta_{\text{potential}}$ (red), and $\eta_{\text{power}}$ ($\alpha = 1$, yellow) assuming illumination by AM1.5D.

2.3 Basis Set of Parameters to Model Solar Cells

In this section we discuss the basis set of metrics used for the characterization of a solar cell. An important expression to describe solar cell behavior is the ideal diode equation:

$$J = J_0[\exp(-\frac{qV}{nk_BT_{sc}}) - 1] - J_L,$$

where $J$ represents net current density flow, $J_0$ is the dark saturation current density (reflecting recombination occurring within the material), $q$ is the electron charge, $n$ is the ideality factor, $V$ is the applied voltage across the cell, and $J_L$ is the photocurrent. Simple demonstrations of this equation reveal important metrics used in performance assessments of solar devices.

Setting $J = 0$ and solving for $V$ reveals:

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_L}{J_0} + 1\right),$$
where we call $V_{oc}$ the open-circuit potential, which represents the maximum potential the system can produce. We use the theory described in the previous section to estimate this value, letting $V_{oc} = \frac{\mu_{\text{power}}}{q}$. A plot of the band gap versus the $V_{oc}$ for $\alpha = 1$ or $\alpha = 2$ or $\alpha = 320$,* shown in Figure 2.4, gives a $V_{oc}$ of 0.751 V, 0.733 V, and 0.601 V for silicon solar cells.

![Figure 2.4: Predicted $V_{oc}$ vs band gap for two cases, $\alpha = 1$ (green) and $\alpha = 2$ (blue) to represent idealistic and future values, respectively. Purple reflects obtainable values where $\alpha = 320$.](image)

If we let $V = 0$ in the ideal diode law, then $J = J_{\text{sc}} = J_L$. We call $J_{\text{sc}}$ the short-circuit current density. The photocurrent, or short-circuit current density, can be calculated from the excitation rate by way of:

$$J_L = J_{\text{sc}} = \beta \int_0^{\lambda_0} q J_e \, d\lambda,$$

where $\beta$ represents (as we define for semi-empirical analysis) the probability of absorbing photons and includes realistic losses such as reflection. In Figure 2.5 we plot the band gap versus $J_{\text{sc}}$. This tells us that for silicon we should be able to reach 43.8, 41.6, and 35.1 mA/cm$^2$ for $\beta = 1.0$, $\beta = 0.95$, and $\beta = 0.80$.

The $J_0$ parameter reflects the rate of recombination processes occurring in a solar cell. A full treatment would require a more realistic theory that reflects the micro-

*Recall that we use $\alpha$ as a semi-empirical parameter that reflects losses in a semiconductor.
scopic structure of a photodiode, but in our simpler treatment here we rely on our other parameters to estimate $J_0$ by:

$$J_0 = \frac{J_L}{\exp\left(\frac{\mu_{max} q n T}{\eta \eta_T}\right) - 1}.$$  

Now we are in a position to simulate a $J$–$V$ curve for a solar cell (drawn in Figure 2.6 is a silicon solar cell example). This is a natural point to illustrate how to determine another metric. In the Figure 2.6 there is a green box that represents the maximum power obtainable from the system. Graphically, this factor is found by using the maximum power point ($\frac{dP}{dV} = 0$), which has a corresponding voltage ($V_{MP}$) and power ($P_{MP}$). The rectangle starts at the origin with its width determined by $V_{MP}$ and its height determined by finding the corresponding current for $V_{MP}$, which we call the maximum power point current ($J_{MP}$). This metric is aptly called the fill factor (when ratioed to the total incoming power):

$$ff = \frac{V_{MP} J_{MP}}{V_{oc} J_{sc}}.$$  

Our final value of interest is the solar-to-electricity efficiency ($\eta_{PV}$), a value calcu-
lated by way of:

\[ \eta_{PV} = \frac{V_{oc} J_{sc} ff}{P_{in}}. \]

We demonstrate our simulated metric values for silicon compared to a series of research cells in Table 2.1. Our idealistic simulated silicon solar cell \((\alpha = 2, \beta = 0.95)\) is slightly better than demonstrated champion research cells but should be in reach within the decade. The realistic simulated silicon solar cell \((\alpha = 320 \text{ and } \beta = 0.80)\) is within reach today.

![Figure 2.6: Predicted silicon solar cell J–V curve. Blue line represents the solar cell characteristic according to the diode equation. The orange line represents the power \((V \times J)\) and at its maximum is the maximum power point, the green rectangle represents the maximum power the solar cell can supply to a resistive load.](image)

<table>
<thead>
<tr>
<th>Silicon Solar Cell</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>ff (%)</th>
<th>(\eta_{PV}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated (Ideal)</td>
<td>0.733</td>
<td>41.6</td>
<td>87.5</td>
<td>26.7</td>
</tr>
<tr>
<td>Simulated (Realistic)</td>
<td>0.601</td>
<td>35.1</td>
<td>82.8</td>
<td>17.5</td>
</tr>
<tr>
<td>SunPower</td>
<td>0.737</td>
<td>41.3</td>
<td>82.7</td>
<td>25.2</td>
</tr>
<tr>
<td>Kaneka</td>
<td>0.738</td>
<td>40.8</td>
<td>83.5</td>
<td>25.1</td>
</tr>
<tr>
<td>Fraunhofer</td>
<td>0.718</td>
<td>42.1</td>
<td>83.2</td>
<td>25.1</td>
</tr>
<tr>
<td>UNSW</td>
<td>0.706</td>
<td>42.7</td>
<td>82.8</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Table 2.1: Basis set of solar cell parameters used for the description of performance and comparison of silicon simulated value with high-performing silicon samples.\(^{14}\)
2.4 Butler–Volmer Kinetic Model Effects on Ideal Diode

Our interest in using the solar cell to directly drive an electrochemical engine means that we must consider parasitic voltage losses from electrocatalysis. A central equation used for electrochemical kinetics is the Butler–Volmer model,\(^{15}\)

\[
j = j_0 \left( \exp\left(\frac{\alpha_{CT,a} F \eta_{op}}{RT}\right) - \exp\left(-\frac{-\alpha_{CT,c} F \eta_{op}}{RT}\right) \right),
\]

where \(j\) is the current density, \(j_0\) is the exchange current density (representing the equilibrium rate of reactions), \(\alpha_{CT}\) is the charge-transfer coefficient (which depends on the Tafel slope) for either the anodic or cathodic reaction, \(F\) is Faraday’s constant, \(R\) is the ideal gas constant, \(T\) is the temperature, and \(\eta_{op}\) is the overpotential.

A solar cell in isolation will always have better characteristics than a device driving an electrochemical reaction. Since we are not extracting work the easy way, the voltages for our device are coupled in the following way:

\[
V_{\text{device}}(J_d) = V_{\text{solar cell}}(J_d) + \eta_{\text{catalysis}}(J_d),
\]

where \(V_{\text{device}}(J_d)\) is the voltage of the device and depends on the current of the device \((J_d)\), \(V_{\text{solar cell}}(J_d)\) is the voltage of the solar cell, and \(\eta_{\text{catalysis}}(J_d)\) is overpotential voltage required in the Bulter–Volmer model. \(J-V\) curves for a device are calculated by numerically finding, both, their matching currents and their respective voltages, and then, using the voltage relationship above to eventually find a solution where both boundary conditions are satisfied. The effect of the losses encountered during catalysis is illustrated in Figure 2.7. Simply put, real catalysts impose additional voltage requirements on the overall process, in addition to the internal losses we

\[\text{\textsuperscript{*You may notice some vague similarities in form of the ideal diode law to this model, and this is no coincidence because it results from the similar underlying physical models used to describe the two phenomena.}}\]
account for in the last section.

Figure 2.7: Predicted silicon solar cell $J-V$ curve with catalysis. Orange line represents the ideal diode response while the blue line incorporates losses due to the voltage losses from the kinetics of catalysis. In this case we are assuming a single absorber is poorly carrying out both catalysis for the oxidation and reduction half-reactions for HI splitting.

Our model, outlined in the previous sections, captures the core behavior of a semiconductor driving an electrochemical reaction and allows estimations of the magnitude of the effect different parameters have on an overall device efficiency. However, there are several limitations of the simulations used in our discussion below. Among the many factors our model does not include are:

- Light absorption by the solution (this becomes significant as Br$_2$ concentrations increase);
- Membrane resistance (membranes, such as Nafion, introduce a transport resistance);
- Solution resistance (real liquid electrolytes have a non-zero resistance);
- Internal solar cell resistance (often, real devices have shunt and series resistance components);
- Recombination is being explicitly modeled (explicit modeling of the kinetics for recombination will yield more accurate results);
• Exact device cell geometry is considered for mass transport purposes (the specific construction of a device has a real impact on the resulting performance);

• Mass transport limitations in the Bulter–Volmer model.

2.5 Comparison of Estimated Device Efficiencies for HBr and H\textsubscript{2}O Splitting

Now that we are equipped to estimate solar-to-hydrogen efficiency ($\eta_{\text{STH}}$) for a device, we define this efficiency as:

$$\eta_{\text{STH}} = \frac{J_{\text{MP, BV}} \times E_f}{P_{\text{in}}},$$

where $J_{\text{MP, BV}}$ is the current density maximum power point for a diode limited by Bulter–Volmer overpotentials, and $E_f$ is the difference in the formal potentials between the two-half reactions for either HBr splitting (1.09 V) or H\textsubscript{2}O splitting (1.23 V), resulting in either $\eta_{\text{STH,HBr}}$ or $\eta_{\text{STH,H\textsubscript{2}O}}$, respectively. We consider three different device configurations and their attributes. The first system uses a single semiconductor while the second system exploits two semiconductors sitting side-by-side, and the third system has two semiconductors in a stacked structure, where the top material absorbs and transmits light to the bottom semiconductor, as determined by the band gap. In Table 2.2 we list the parameters used for devices developed in the future (“idealistic”) and for devices that could be made today (“realistic”). Former results are in the next section while the latter results are given in Appendix A.
Table 2.2: Parameters used in simulations of efficiency for solar devices driving either water or hydrobromic acid splitting. The “idealistic” values for the PV are obtained from Table 2.1 while the Butler–Volmer parameters come from a fit of experimental data\(^{16}\) (this same source also documents an excellent analysis of water splitting) for the hydrogen evolution reaction and oxygen evolution reaction (the HBr anode will have similar characteristics to the HER). The “realistic” values for the PV are obtained from a semiempirical fit of $\alpha$ and $\beta$ to the best values observed in our laboratory.

### Single Absorber

Figure 2.8: The red “+” represents the efficiency for HBr splitting and the blue circles represent H$_2$O splitting using a single light absorber. Used with permission from C. Roske.

In Figure 2.8, $\eta_{\text{STH}}$ is determined for a range of band gaps driving either HBr or H$_2$O splitting. Significant voltage losses are encountered for the oxygen-evolving half-reaction due to sluggish kinetics; therefore, a material with a 2.20 eV band gap is required to provide a sufficient driving force for water splitting at $\eta_{\text{STH,H$_2$O}} = 12.3\%$. The anodic half-reaction for HBr splitting is considerably more facile and hence higher efficiencies are possible for a 1.80 eV band gap material of $\eta_{\text{STH,HBr}} = 22.3\%$. Cu$_2$O with a band gap of 2.17 eV might be desirable for water splitting in this scheme. One candidate material for HBr splitting would be CdSe, with a band
gap of 1.74 eV. The results from simulations with realistic parameters are shown in Figure A.1. The beauty of this configuration is that it only requires a single absorber although the sensitivity of the ultimate efficiency highly depends on the quality and band gap of the specific material.

**Dual Light Absorbers: Side-by-Side**

![Figure A.1: Results from simulations with realistic parameters.](image)

Figure 2.9: This calculation shows the solar-to-hydrogen efficiency ($\eta_{\text{STH}}$) for two equivalent devices consisting of side-by-side semiconductors connected in parallel using A) HBr splitting and B) H$_2$O splitting.

In Figure 2.9, we consider two semiconductors sitting side-by-side and connected in parallel at their back-contact. Here, considerably higher efficiencies are possible compared with a single-absorber, especially for water splitting using a wider range of materials. The optimum system for H$_2$O splitting has two 1.30 eV band gap semiconductors working at $\eta_{\text{STH,H}_2\text{O}} = 19.5\%$ while, for HBr splitting the ideal system is two 1.10 eV materials sitting side-by-side producing $\eta_{\text{STH,HBr}} = 22.8\%$.

For the water splitting system, this might be InP (1.35 eV) or GaAs (1.43 eV) while for hydrobromic acid splitting silicon (1.12 eV) or MoS$_2$ (1.23 eV) may be optimal. Realistic results are shown in Figure A.2. One of the benefits to the side-by-side
configuration is its wide accommodation of different materials, including those with the same band gap.

**Dual Light Absorbers: Tandem**

In Figure 2.10, our two systems are configured with a light absorber on top and bottom of a stack. These efficiencies are considerably higher than other competing configurations. For H$_2$O splitting, a 1.70 eV top and 1.00 eV bottom configuration could give $\eta_{\text{STH,}H_2O} = 26.2\%$, and for HBr splitting, a 1.50 eV top and 0.700 eV bottom could give $\eta_{\text{STH,}HBr} = 30.0\%$. An example of a system for water electrolysis would be a CdSe top and a Cu$_2$SnS$_3$ bottom. While for our haloacid, a Zn$_3$P$_2$ top and a Ge bottom could be optimal. Realistic results are shown in Figure A.3. While the tandem, stacked, configuration has the best absolute performance for a well-optimized system, it also has considerable specific challenges, listed below.

1. The band gaps of the two layers must be different for any non-zero efficiency, so in other words, two high-quality semiconductors are needed in a single device.

2. Growing two dissimilar semiconducting materials epitaxially remains a very difficult endeavor, although there are common ways around this.

3. Minimizing mass transport limitations requires careful engineering for tandem structures.

4. Manufacturing complexity increases considerably.
2.6 Proposed Device Layout

While the tandem structure is the ultimate envisioned device, it has been very hard in practice to build in our laboratories. The single absorber is promising, but we do not have expertise with the materials most suitable for either water or hydrobromic acid splitting. This leaves us with the side-by-side configuration. For HBr splitting, silicon (a material we have a strong understanding of and expertise in handling) would work as both a photocathode and photoanode; therefore, this is the configuration and material we pick. An ultimate efficiency of $\eta_{\text{STH, HBr}} = 22.8\%$ is the theoretical upper-limit, but in our hands $\eta_{\text{STH, HBr}} = 11.0\%$ is more likely to be obtained as reflected by our “realistic” simulation.

In Figure 2.11 the proposed device layout is depicted. It consists of a photoanode and photocathode made of silicon microwires embedded in a glass matrix (to protect the underlying metal back-contact and provide mechanical stability to the wires). Ideally, above the glass matrix is where the electrocatalysts would sit, hopefully avoiding parasitic light absorption by using a reflective layer coating of TiO$_2$ particles. Above
Table 2.3: This table uses either (I)dealistic or (R)ealistic parameters (defined in Table 2.2). The first six rows represent the maximum efficiencies for those scenarios and the respective band gaps. The realistic value for H$_2$O splitting compare well with the literature.\textsuperscript{16}

<table>
<thead>
<tr>
<th>Idealistic/Realistic</th>
<th>Configuration</th>
<th>$\eta_{\text{STH, HBr}}$ (%)</th>
<th>$\eta_{\text{STH, H}_2\text{O}}$</th>
<th>$E_g$ HBr (eV)</th>
<th>$E_g$ H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$S^a$</td>
<td>22.3</td>
<td>12.3</td>
<td>1.80</td>
<td>2.20</td>
</tr>
<tr>
<td>I</td>
<td>SBS$^b$</td>
<td>22.8</td>
<td>19.5</td>
<td>1.10/1.10</td>
<td>1.30/1.30</td>
</tr>
<tr>
<td>I</td>
<td>T$^c$</td>
<td>30.0</td>
<td>26.2</td>
<td>1.50/0.70</td>
<td>1.70/1.00</td>
</tr>
<tr>
<td>R</td>
<td>$S^a$</td>
<td>16.2</td>
<td>8.6</td>
<td>1.80</td>
<td>2.30</td>
</tr>
<tr>
<td>R</td>
<td>SBS$^b$</td>
<td>17.2</td>
<td>14.2</td>
<td>1.20/1.20</td>
<td>1.70/1.70</td>
</tr>
<tr>
<td>R</td>
<td>T$^c$</td>
<td>22.2</td>
<td>19.3</td>
<td>1.60/0.900</td>
<td>1.80/1.20</td>
</tr>
<tr>
<td>R</td>
<td>SBS$^b$</td>
<td>11.0</td>
<td>–</td>
<td>1.10/1.10</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ S is for (S)ingle light absorber.

$^b$ SBS is for (S)ide-(B)y-(S)ide configuration.

$^c$ T is for (T)andem or stacked configuration.

all, the light absorbers are cheap and high-quality silicon microwires. Between the anode and cathode sits a membrane separator, likely Nafion. At the photoanode oxidation occurs, producing bromine, free protons, and electrons (shuttled to the photocathode). At the photocathode, free protons and electrons are consumed to yield H$_2$(g). In essence, this would be a modern rendition of the TISES, but we would like to lower the costs of the materials even further with earth-abundant materials and microwires more readily manufactured at scale.
Figure 2.11: In the presence of aqueous hydrobromic acid, hydrogen and bromine will be generated upon irradiation of the integrated photosystem:

\[ 2 \text{HBr} + \text{Light} \rightarrow \text{H}_2 + \text{Br}_2. \]

### 2.7 Challenges Facing HBr Splitting

The outline of what we must accomplish is as follows:

1. We need high quality microwires of silicon as a light absorber for both a cathode and anode;

2. We must stabilize the photoanode;

3. We must stabilize the photocathode at its resting state;

4. We need an earth-abundant cathode catalyst that has a low overpotential for the hydrogen evolution reaction in acidic media;

5. We need an earth-abundant anode catalyst that has a low overpotential for halide oxidation;

6. We will assess the stabilities of the resulting components;

7. We would need to integrate both components in a complete system.
2.8 Conclusions

One promising strategy to break the world from its dependence on fossil fuels is by massive solar energy conversion. Successful implementation of large-scale solar energy capture may require driving chemical reactions. Semiconductors are suitable materials to capture and convert sunlight into usable power with high efficiency. We suggest that an integrated device capable of collecting solar energy and storing it in chemical potential is a worthwhile goal. In this scheme, a careful choice is required when selecting a compatible combination of materials (for light absorption) and chemical reactions (for storing energy as chemical potential). Silicon has an ideal band gap (1.12 eV) for solar absorption, but silicon cannot drive water splitting (\(2 \text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2\)) because its electronic structure prevents generation of a sufficient photovoltage. Instead, two silicon electrodes connected in parallel can carry out hydrobromic acid splitting (\(\text{HBr} \rightarrow \text{H}_2 + \text{Br}_2\)). Modeling with realistic parameters suggests that the ultimate solar to hydrogen conversion \(\eta_{\text{STH}}\) is optimized for a device with a band gap of 1.1 eV to 1.2 eV would be ideal for HBr splitting in a side-by-side configuration, with a potential to make between 11% to 17%. Silicon, with a band gap of 1.12 eV has the potential to make \(\approx 12\%\) in this scenario. Unfortunately, earlier efforts by TI used precious metals to catalyze the two half-reactions and protect the silicon. Our device needs to use earth-abundant materials to both catalyze the relevant half-reactions and protect the underlying silicon electrodes at low cost. In Chapter 3 we introduce a candidate cathode catalyst compatible with strongly acidic solutions. Then, in Chapter 4, we integrate this catalyst with a silicon photocathode. Finally, in Chapter 5 we introduce a method to protect a silicon photoanode from oxidation, but ultimately fail to catalyze the anodic half-reaction without a Pt catalyst.
2.9 References


Chapter 3

Highly Active Electrocatalysis of the Hydrogen-Evolution Reaction by Cobalt Phosphide Nanoparticles


3.1 Abstract

Nanoparticles of cobalt phosphide, CoP, have been prepared and evaluated as electro-catalysts for the hydrogen evolution reaction (HER) under strongly acidic conditions (0.50 M H$_2$SO$_4$, pH 0.3). Uniform, multi-faceted CoP nanoparticles were synthesized by reacting Co nanoparticles with trioctylphosphine. Electrodes comprised of CoP nanoparticles on a Ti support (2 mg/cm$^2$ mass loading) produced a cathodic current density of 20 mA/cm$^2$ at an overpotential of −85 mV. The CoP/Ti electrodes were stable over 24 h of sustained hydrogen production in 0.50 M H$_2$SO$_4$. The activity was essentially unchanged after 400 cyclic voltammetric sweeps, suggesting long-term viability under operating conditions. CoP is therefore amongst the most active, acid-stable, earthabundant HER electrocatalysts reported to date.

3.2 Introduction

The hydrogen-evolution reaction (HER), which generates molecular hydrogen through the electrochemical reduction of water, underpins many clean-energy technologies. Platinum, the most widely used HER catalyst, requires very low overpotentials to generate large cathodic current densities in the highly acidic solutions that are used for water electrolysis in proton-exchange membrane systems.\textsuperscript{1–3} However, Pt is expensive and relatively scarce in the Earth’s crust, limiting the utility of Pt in
energy systems deployed at global scale. Active, acid-stable alternative HER electrocatalysts include the molybdenum-based MoS\textsubscript{2},\textsuperscript{2,4} MoB,\textsuperscript{5} Mo\textsubscript{2}C,\textsuperscript{5,6} NiMoN\textsubscript{x},\textsuperscript{7} and Co\textsubscript{0.6}Mo\textsubscript{1.4}N\textsubscript{2} systems,\textsuperscript{8} as well as several first-row transition metal dichalcogenides.\textsuperscript{9} Alloys of Ni–Mo,\textsuperscript{10} Ni–Mo–Zn,\textsuperscript{11} Ni–Fe,\textsuperscript{12} and Ni–P,\textsuperscript{13} along with Ni/NiO/CoSe\textsubscript{2} nanocomposites,\textsuperscript{14} are active HER electrocatalysts, but are not stable in acidic solutions.

Recently, nanoparticulate films of Ni\textsubscript{2}P, comprised of inexpensive and earth-abundant elements, have been reported to show high HER activity, requiring an overpotential of $\eta = -130 \text{ mV}$ to produce cathodic current densities of $-20 \text{ mA/cm}^2$ in 0.50 M H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{15} Like MoS\textsubscript{2},\textsuperscript{2,16} Ni\textsubscript{2}P is also a hydrodesulfurization (HDS) catalyst,\textsuperscript{17,18} which suggests that other known HDS catalysts may also be active HER catalysts.

We report herein that CoP, a known metal phosphide HDS catalyst that is structurally and compositionally distinct from Ni\textsubscript{2}P,\textsuperscript{18} is a highly active and acid-stable HER catalyst, exhibiting an overpotential ($\eta$) of $-85 \text{ mV}$ at a current density ($j$) of $-20 \text{ mA/cm}^2$ (at a mass loading of 2 mg/cm\textsuperscript{2}), as well as stability over 24 h of operation in 0.50 M H\textsubscript{2}SO\textsubscript{4}.

### 3.3 Materials and Methods

To synthesize the CoP nanoparticles, 9 ± 1 nm diameter spherical nanoparticles of $\epsilon$-Co (Figure B.1) were prepared by the decomposition of Co\textsubscript{2}(CO)\textsubscript{8} in 1-octadecene (ODE), oleylamine (OLAM), and nonanoic acid (NA) at 230 °C, followed by addition of oleic acid (OLAC).\textsuperscript{19} To form CoP, the $\epsilon$-Co nanoparticles were then reacted for 1 h at 320 °C with trioctylphosphine (TOP) in ODE and OLAM. (See Supporting Information for full experimental details.)

### 3.4 Results and Discussion

Figures 3.1a and 3.1b show representative transmission electron microscope (TEM) images of the CoP nanoparticles, which were quasi-spherical, multi-faceted, uni-
form, and hollow, with an average diameter of 13 ± 2 nm. The hollow morphology is the result of a nanoscale Kirkendall effect, which often occurs for metal phosphide nanoparticles that have been synthesized by reaction of the metal nanoparticle templates with TOP.20–24

Selected-area electron-diffraction (SAED) (Figure 3.1c) showed that the nanoparticles adopted the MnP structure type expected for CoP,25 whereas energy dispersive X-ray spectroscopy (EDS) (Figure B.2) indicated a 45:55 Co:P ratio, which is consistent within experimental error with the expected 1:1 stoichiometry of CoP. The powder X-ray diffraction (XRD) pattern (Figure 3.2a) confirmed that the bulk sample consisted of high-purity MnP-type CoP. Scherrer analysis of the peak widths of the XRD pattern for the CoP nanoparticles indicated an average grain size of 12 nm, which is consistent with the particle diameters observed by TEM, and suggests that the particles were largely single crystalline. HRTEM (Figure 3.1d) confirmed that the CoP particles were single crystalline, with observed lattice spacings of 2.4 Å that intersected in a manner consistent with expectations for the closely spaced (102) and (111) planes of MnP-type CoP (Figure 3.1e).

The HER electrocatalytic activity of the CoP nanoparticles was evaluated in 0.50 M H2SO4. Working electrodes were prepared by applying CoP nanoparticle samples to 0.2 cm2 titanium supports with CoP loading densities of 0.9 and 2 mg/cm2, respectively. Ti electrodes were chosen because Ti is not an active HER catalyst and because Ti promoted adhesion of the CoP nanoparticle catalysts, while remaining chemically inert. The Ti/CoP electrodes were heated at 450 °C in H2/Ar to remove the organic ligands, and the powder XRD pattern (Figure 3.2b) confirmed that the nanocrystalline CoP phase persisted after this treatment. Figure 3.3a shows polarization data for representative Ti/CoP electrodes at two distinct mass loadings, along with polarization data obtained under identical conditions for uncoated Ti foil electrodes as well as for Pt, which is a benchmark HER electrocatalyst. Ten
Ti/CoP electrodes, from several different CoP nanoparticle samples, were tested and showed highly consistent HER activities. The CoP nanoparticles produced a cathodic current density of $-20 \text{ mA/cm}^2$ at an overpotential of $-95 \text{ mV}$ for a mass loading of 0.9 mg/cm$^2$ (i.e. $\eta_{-20\text{mA/cm}^2} = -95 \text{ mV}$) and exhibited $\eta_{-20\text{mA/cm}^2} = -85 \text{ mV}$ for a mass loading of 2 mg/cm$^2$. In contrast, the Ti foil electrode was not an active HER catalyst, as expected, under these conditions.

These overpotentials compare favorably to the values reported at similar current densities and mass loadings for other acid-stable, Earth-abundant HER electrocatalysts, including Ni$_2$P ($\eta_{-20\text{mA/cm}^2} = -130 \text{ mV}$), Mo$_2$C on carbon nanotubes ($\eta_{-10\text{mA/cm}^2} = -152 \text{ mV}$), and MoS$_2$ ($\eta_{-20\text{mA/cm}^2} = -175 \text{ mV}$), and also compare favorably to, but are somewhat larger than, the behavior exhibited by the Pt control electrode ($\eta_{-20\text{mA/cm}^2} = -25 \text{ mV}$). The overpotentials exhibited by the CoP nanoparticles are also comparable to that of Ni–Mo nanopowder ($\eta_{-20\text{mA/cm}^2} = -80 \text{ mV}$), which is not stable under acidic conditions when Ni$^{2+}$
Figure 3.2: Powder XRD patterns for (a) as-synthesized CoP nanoparticles (top, experimental; bottom, simulated) and (b) a CoP/Ti electrode annealed at 450 °C (top, experimental; bottom, simulated for CoP and Ti). In (b), peaks marked with an asterisk (*) correspond to the Ti substrate.

is formed, and the $\eta_{-20mA/cm^2}$ for CoP is significantly smaller than $\eta_{-20mA/cm^2}$ for comparable catalytic systems that are unstable in acid, including Ni/NiO/CoSe$_2$ nanocomposites ($\eta_{-20mA/cm^2} \approx -120$ mV).$^{14}$ Porous nanosheets of isostructural FeP have been reported to catalyze the HER, but at significantly higher overpotentials ($\eta_{-20mA/cm^2} \approx -300$ mV for 0.28 mg/cm$^2$) than that of CoP, with unknown acid stability.$^{26}$ Ni$_5$P$_4$, as bulk pellets of nanocrystalline powders, also has been recently reported to be a highly active HER electrocatalyst in both acidic and alkaline solutions.$^{27}$

The slope of the Tafel plot [overpotential vs. log(cathodic current density)] for the Pt control (Figure 3.3b) was $\approx 30$ mV/decade, which is consistent with that expected for the known HER mechanism on Pt. In contrast, the Tafel slope for representative CoP/Ti electrodes (Figure 3.3b) was $\approx 50$ mV/decade, independent of mass loading. This value does not correspond to one of the standard HER Tafel slopes (29, 38, and 116 mV/decade),$^{28}$ indicating that the mechanism of the HER on CoP/Ti is different from that on Pt. However, similar Tafel slopes have been reported for other non noble-metal catalysts, such as MoS$_2$ (50 mV/decade),$^{29}$ Mo$_2$C (55 mV/decade),$^{29}$ and Ni$_2$P (46 mV/decade).$^{15}$ The HER exchange current density of
the CoP nanoparticle catalysts was $\approx 1.4 \times 10^{-4}$ A/cm$^2$, which is comparable to that exhibited by Ni$_2$P nanoparticles as HER electrocatalysts under acidic conditions.\textsuperscript{15}

![Figure 3.3: (a) Polarization data in 0.50 M H$_2$SO$_4$ for CoP nanoparticle electrodes at mass loadings of 0.9 and 2 mg/cm$^2$, along with a Ti foil and Pt for comparison. (b) Corresponding Tafel plots for the CoP and Pt electrodes](image)

To determine the faradaic yield for hydrogen evolution, a CoP/Ti working electrode was held at $-20$ mA/cm$^2$ for 6.94 h. The amount of H$_2$ collected over 6.94 h was consistent with the amount of charge passed through the system (100 C), indicating essentially 100% faradaic efficiency for the HER. The amount of hydrogen produced also compared favorably with that produced by a Pt control cathode over the same time period. Complete decomposition of the catalyst would have produced gaseous byproducts that would account for less than 1% of the gas volume that was observed experimentally. This stable chemical behavior, coupled with the observed long-term acid stability of the material (confirming that significant degradation did not occur), therefore indicates that the CoP nanoparticle catalyst is capable of sustained electrocatalytic H$_2$ production in acidic media.

The CoP nanoparticles had a measured Brunauer-Emmett-Teller (BET) surface area of 59.1 m$^2$/g. Using this surface area, the turnover frequency (TOF) was calculated to be 0.046 s$^{-1}$ at $\eta = 100$ mV. As a benchmark, the upper limit of the surface area was estimated based on average particle geometry and size (e.g. 13 nm spheres) to be 71.9 m$^2$/g, and this procedure yielded a TOF of 0.038 s$^{-1}$. (See Supporting Information for detailed calculations.) These TOF values are estimates because the
specific active sites are not known and because the calculations do not account for porosity or for surfaces that are inaccessible because of contacts between particles. However, the TOF values estimated based on both the experimental and theoretical surface areas are mutually comparable and compare favorably to the TOF values at $\eta = -100$ mV for Ni$_2$P nanoparticles ($0.015$ s$^{-1}$) and Ni-Mo nanopowder ($0.05$ s$^{-1}$).$^{10,15}$

To evaluate the stability of the CoP nanoparticles during repeated cycling in acidic solutions, accelerated degradation studies were performed on representative CoP/Ti electrodes having mass loadings of 0.9 mg/cm$^2$. As shown in Figure 3.4a, the CoP nanoparticles exhibited no measurable loss of activity after 400 cyclic voltammetry (CV) sweeps between $+5$ mV and $-140$ mV (vs. the reversible hydrogen electrode potential, RHE). The production of a current density of $-20$ mA/cm$^2$ initially required an overpotential of $-95$ mV, whereas the overpotential changed to $\approx -90$ mV after 400 cycles, demonstrating high stability under strongly acidic conditions. In addition to the accelerated degradation studies, galvanostatic measurements at a current density of $-20$ mA/cm$^2$ in a pre-electrolyzed solution indicated that the overpotential increased in magnitude only slightly (25 mV) over 24 h (Figure B.3) of continuous operation. Some particle desorption from the substrate (and therefore a slight decrease in mass loading) is the likely cause of this small increase in overpotential.

X-ray photoelectron spectroscopy (XPS) survey data (Figure B.3) indicated that the surface of the as-prepared CoP/Ti electrode consisted primarily of carbon and oxygen, as expected from the organic surface-stabilizing agents. Co, P, and Ti were also present. After annealing the CoP/Ti electrode at 450 °C, the carbon signal nearly disappeared, consistent with the expected removal of the capping ligands. High-resolution XPS data for the annealed CoP/Ti electrode showed two characteristic Co 2p peaks, with binding energies consistent with those expected for Co(II). Following
3.4 Conclusion

In conclusion, nanoparticles of CoP are highly active HER electrocatalysts, with < 100 mV overpotentials at low mass loadings and operationally relevant current densities of −20 mA/cm². In addition, CoP nanoparticles are exceptionally stable in acidic solutions, showing no evidence of significant degradation over 24 h of H₂ production in 0.50 M H₂SO₄. These results further establish that HDS electrocatalysts comprised of inexpensive and Earth-abundant elements provide interesting and important candidate materials for obtaining high activity and stability for the HER in acidic media.
3.6 Acknowledgements

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3.7 References

Chapter 4

Comparison of the Performance of CoP-Coated and Pt-Coated Radial Junction n⁺p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water to H₂(g)

Adapted with permission from C.W. Roske; E.J. Popczun; B. Seger; C.G. Read; T. Pedersen; O. Hansen; P.C.K. Vesborg; B.S. Brunschwig; R.E. Schaak; I. Chorkendorff; H.B. Gray; N.S. Lewis. J. Phys. Chem. Lett., 2015, 6, 1679-1683. Copyright 2014 American Chemical Society.

4.1 Abstract

The electrocatalytic performance for hydrogen evolution has been evaluated for radial-junction n⁺p-Si microwire (MW) arrays with Pt or cobalt phosphide, CoP, nanoparticulate catalysts in contact with 0.50 M H₂SO₄(aq). The CoP-coated (2.0 mg/cm²) n⁺p-Si MW photocathodes were stable for over 12 h of continuous operation, and produced an open-circuit photovoltage (Vₜ) of 0.48 V, a light-limited photocurrent density (Jₚₜ) of 17 mA/cm², a fill factor (ff) of 0.24, and an ideal regenerative-cell efficiency (ηIRC) of 1.9 % under simulated 1-Sun illumination. Pt-coated (0.5 mg/cm²) n⁺p-Si MW array photocathodes produced Vₜ = 0.44 V, Jₚₜ = 14 mA/cm², ff = 0.46, and η = 2.9 % under identical conditions. Thus the MW geometry allows the fabrication of photocathodes entirely composed of earth-abundant materials that exhibit performance comparable to that of devices that contain Pt. Increased performance, η = 2.71 %, is obtained upon electrodeposition of CoP onto Si MWs with TiO₂ scattering particles.
4.2 Introduction

One of the challenges to the development of a sustainable and globally scalable solar-driven water-splitting system is the discovery and development of materials and architectures that allow for the replacement or minimal use of scarce elements.\textsuperscript{1–4} The most active catalysts for water splitting in an acidic environment are Pt and IrO\textsubscript{2}. Pt operates at a very low (< 30 mV) overpotential to catalyze the reduction of H\textsubscript{2}O to H\textsubscript{2}(g) in acidic or alkaline media at cathodic current densities of > 10 mA/cm\textsuperscript{2}. Recently, significant progress has been made in the development of earth-abundant catalysts for the hydrogen-evolution reaction (HER) in both acidic and alkaline media. Overpotentials for the HER comparable to those for Pt (albeit at higher mass loadings) have been observed in alkaline media by use of Ni-Mo and related Ni-based alloys,\textsuperscript{5–7} whereas transition-metal sulfides and phosphides have emerged as robust, active electrocatalysts for the HER in acidic media,\textsuperscript{8–17} with FeP yielding overpotentials as low as 60 mV to produce cathodic current densities of 10 mA/cm\textsuperscript{2}.\textsuperscript{11} Moreover, a sensitivity analysis has shown that further reduction in the HER overpotential from 60 mV to < 50 mV at a cathodic current density of 10 mA/cm\textsuperscript{2} would yield little further gain in overall efficiency for an optimally designed solar-driven water-splitting system.\textsuperscript{2,18}

The HER activity is, however, only one important factor in assessing whether an electrocatalyst is well-suited for incorporation into a fully integrated solar-driven water-splitting device.\textsuperscript{1} At the mass loadings needed to provide low overpotentials under 1 Sun illumination, the catalyst must not significantly absorb incident light, and optimally, any light reflected by the catalyst should be directed toward the photoelectrode to produce additional photocurrent. The electrocatalyst must also remain active when integrated with an appropriate semiconducting photoelectrode, while preserving the photovoltage and photoactivity of the light absorber. In general for a tandem structure in a full solar-driven water-splitting configuration, for at least one
of the photoelectrode/electrocatalyst assemblies the light must be incident through the catalyst. Hence the approach described herein is advantageous when light is incident on such a catalyst-coated wire-array photoelectrode. Herein we examine whether the mass loadings required for HER electrocatalysis at low overpotentials using CoP nanoparticles can be accommodated without adversely affecting the overall performance of a microwire-array photocathode. Specifically, the performance of radial-junction n$^+$p-Si microwire (MW)-array photocathodes loaded with nanoparticulate CoP is compared to that of otherwise identical photocathodes loaded with smaller amounts of Pt.

### 4.3 Results and Discussion

Detailed experimental procedures are provided in the Supplementary Information. Briefly, Si microwires (unoptimized in dimensions for light absorption) were fabricated by reactive-ion etching of a (100)-oriented p-Si wafer. The microwires were 4 $\mu$m in diameter, 50 $\mu$m in length, spaced in a hexagonal grid with an 11 $\mu$m pitch, and were nearly completely vertically oriented with respect to the underlying 14.6 ohm-cm resistivity Si(100) substrate. Vapor diffusion of phosphorous at 900 °C for 10 min produced a radial emitter over the surface of the MW array that was estimated to be 100 nm thick at the base of the structure. Similar planar electrodes were also fabricated. The Pt nanoparticles were synthesized by ascorbic acid reduction and were determined to have an average diameter of $\approx$ 3 nm, based on analysis of transmission-electron microscope (TEM) images (See Figure C.1). The CoP nanoparticles were synthesized by the thermal decomposition of octacarbonyl dicobalt(0) to first produce Co nanoparticles, and were then transformed to CoP by reaction with trioctylphosphine.$^9$ X-ray powder diffraction and TEM data (Figure C.2) confirmed the formation of crystalline CoP nanoparticles having diameters of $\approx$ 13 nm. The Pt and CoP nanoparticles were loaded onto the Si MW arrays using
centrifugation. Figure 4.1 shows SEM images of a bare n\(^{+}\)p-Si MW array and of n\(^{+}\)p-Si MW arrays loaded with either 2.0 mg/cm\(^2\) of CoP nanoparticles or with 0.50 mg/cm\(^2\) of Pt nanoparticles. The CoP particles deposited primarily at the base of the Si MW array and consisted of aggregates of the \(\approx 13\) nm particles. The clusters of CoP completely covered the base of the array, with some of the CoP nanoparticles on the top of the Si microwires and a small amount along the length of each wire. The Pt nanoparticles deposited predominantly at the base of the wire arrays, also aggregated and with some adsorbed particles near the tops of the wires and others sparingly present along the length of the wire, similar to the deposited CoP nanoparticles.

![SEM images of radial-junction n\(^{+}\)p-Si microwire arrays. The microwires were 50 µm in length, 4 µm in diameter, and were spaced on an 11 µm pitch. (Left) A bare microwire array. (Center) A microwire array coated by centrifugation of CoP nanoparticles. The CoP loading was 2.0 mg/cm\(^2\). (Right) A microwire array coated with Pt nanoparticles at a loading of 0.50 mg/cm\(^2\). The scale bars indicated in the images above are each 70 µm.](image)

The photoelectrochemical performance of the n\(^{+}\)p-Si planar and MW-array photocathodes was evaluated in contact with H\(_2\)(g)-saturated 0.50 M H\(_2\)SO\(_4\)(aq). Figure 4.2 shows the current density versus potential (\(J-E\)) behavior of n\(^{+}\)p-Si planar, as well as Si MW-array photocathodes with adsorbed Pt or CoP catalysts, and Table C.1 summarizes the relevant \(J-E\) parameters for the n\(^{+}\)p-Si electrodes.

Under 1 Sun (100 mW/cm\(^2\)) of simulated Air Mass (AM) 1.5G illumination, planar electrodes in the absence of deliberately added catalysts showed a light-limited
Figure 4.2: Effect of catalyst loading on the current-density versus potential behavior of n⁺p-Si planar photocathodes in contact with H₂(g)-saturated 0.50 M H₂SO₄(aq) and under 100 mW/cm² of AM1.5G simulated solar illumination. The black curve shows a representative scan in the dark. The red curve shows the behavior of a bare, planar n⁺p Si sample. The orange and purple curves show the behavior of microwire arrays loaded with 0.10 mg/cm² and 0.20 mg/cm² of adsorbed Pt, respectively. The blue and magenta curves show the behavior of microwire arrays loaded with 0.050 mg/cm² and 0.10 mg/cm² of CoP, respectively. These data were collected using a scan rate of 5.0 mV s⁻¹.

Current density, $J_{ph}$, of 30 mA/cm². Pt loadings of 0.10 mg/cm² on a planar electrode reduced $J_{ph}$ by 24 % (23 mA/cm²) and gave fill factors (ff) of 0.40. Comparable (0.050 mg/cm²) mass loadings of CoP on planar electrodes yielded $J_{ph}$ values 20 % higher than for the Pt-coated photocathodes (28 mA/cm²) but yielded significantly lower fill factors (ff = 0.15), as expected based on the lower HER activity of CoP relative to Pt. Increasing the mass loadings (2.0 mg/cm²) of CoP on planar Si electrodes increased the fill factor to ff = 0.54, which is comparable to and slightly larger than that observed for Pt at a mass loading of 0.20 mg/cm² (ff = 0.49). However, the light-limited photocurrent density produced by the highly loaded CoP-Si planar photocathodes ($J_{ph} = 0.19$ mA/cm²) was significantly lower than $J_{ph}$ for 0.20 mg/cm² of Pt ($J_{ph} = 12$ mA/cm²) or for the bare planar Si photocathode ($J_{ph} = 30$ mA/cm²). As such, $J_{ph}$ decreased from that of the bare planar photoelectrode by a factor of $\approx 150$ due to the increased loadings of CoP, consistent with significant losses associated with the reflection and/or absorption of incident photons by the electrocatalyst.
Figure 4.3 and Table C.1 show the effects of different levels of the light intensity on the $J–E$ behavior of n$^+$/p-Si MW-array photocathodes coated either with Pt or CoP electrocatalysts. For light intensities $\leq 100$ mW/cm$^2$ of simulated AM1.5 illumination, the $J_{ph}$ and $V_{oc}$ values observed for deposition of 2.0 mg/cm$^2$ (of projected electrode area) of CoP were comparable to those obtained for deposition of 0.50 mg/cm$^2$ of Pt. At 100 mW/cm$^2$ of simulated sunlight, n$^+$/p-Si MW/Pt photocathodes yielded $J_{ph} = 14$ mA/cm$^2$, $V_{oc} = 0.44$ V, and $ff = 0.46$, whereas n$^+$/p-Si MW/CoP photocathodes produced $J_{ph} = 17$ mA/cm$^2$, $V_{oc} = 0.48$ V, and $ff = 0.24$. At higher light intensities, the CoP-loaded Si MW electrodes showed significantly lower ff values than the Pt-loaded Si MW electrodes, reflective of the lower intrinsic HER activity of CoP relative to Pt.

The open-circuit voltages of all of the photocathodes were similar, as expected for a buried n$^+$/p junction that could be used for construction of a photovoltaic (PV)-biased electrosynthetic water-splitting cell.$^{19}$ A significant apparent series resistance was present in the CoP-loaded MW array system (Figure 4.3), which may be indicative of poor electrical contact either between nanoparticles or between the solution and the particles or most likely between the silicon and the nanoparticles. All issues could
presumably be improved by embedding the nanoparticles in a conductive matrix such as Ketjenblack. The CoP mainly was present at the base of the wire arrays, in contrast to the Pt-coated array, which had a significant number of particles along the length of the wires (as seen in the SEMs of Figure 4.1). The resistance of electrons in the radial emitter, calculated assuming the measured doping density of the emitter and the measured emitter thickness is 0.005 Ω (see Supporting Information for details), as compared to the observed resistance of 285 Ω. The longer distance that charge carriers must travel along the wires in the CoP case thus does not contribute significantly to the observed series resistance. Due to the difference in the placement of the catalyst materials, the restricted mass transport of protons from the bulk solution may occur within the internal volume of the microwire structure.20 The Si microwire array morphology has an 8:1 ratio of its internal surface area relative to its geometric area, and thus a given incident photon flux (per projected electrode area) yields a photogenerated charge-carrier density at the internal surfaces of the Si MW array electrode that is on the order of 8-10-fold lower than that of a planar Si electrode producing the same $J_{ph}$ value. This reduced charge-carrier flux results in a lower overpotential requirement for the electrocatalyst, and thus narrows the difference in the kinetic overpotentials and consequently in the fill factors between the Si MW array photoelectrodes loaded with Pt vs those loaded with CoP.

Figure C.3 shows the external quantum yield, $\Phi_{\text{ext}}$, as a function of the wavelength of incident light for the bare and catalyst-coated MW-array photocathodes, respectively, for the same loadings as shown in Figure 4.3. For the Pt-covered Si MW array, the maximum $\Phi_{\text{ext}}$ value was 0.40, which is comparable to values of $\Phi_{\text{ext}}$ observed previously on similar chemical-vapor deposition (CVD)-grown Si microwire-array devices of 0.30.6,21 For the Pt-coated device under 100 mW/cm² of simulated AM1.5G illumination, the photocurrent density per wavelength integrated to $J_{ph} = 12$ mA/cm², while the data for the CoP-coated Si MW device integrated to a value
of \( J_{\text{ph}} = 9.2 \text{ mA/cm}^2 \). The mutually similar \( J_{\text{ph}} \) values expected for the CoP-loaded and Pt-loaded Si MW arrays are in accord with observations (Figure 4.3, Table C.1), and the differences in absolute values of \( J_{\text{ph}} \) between expectation and observation are likely due to spectral mismatch between the ELH-type W-halogen lamp and the solar spectrum.

Figure 4.4 presents the angular dependence of \( J_{\text{ph}} \) for planar and microwire-array Si photocathodes, respectively, to establish minimal contribution of light absorption by the photoactive substrate in the microwires. The CoP-loaded planar Si and Si MW electrodes exhibited a different dependence of \( J_{\text{ph}} \) on angle of illumination. For the planar electrodes \( J_{\text{ph}} \) reached a maximum of 27 mA/cm\(^2\) at an angle of 0° relative to the surface normal, and \( J_{\text{ph}} \) decreased monotonically with increasing angles of incidence. In contrast, the Si MW array photocathode exhibited a dependence of \( J_{\text{ph}} \) that peaked at 21.8 mA/cm\(^2\) at an angle of \( \approx 35^\circ \) relative to normal incidence. Microwire arrays show a minimum in photocurrent under standard test conditions with the illumination at normal incidence. Furthermore, Table S1 shows the behavior of a planar Si electrode coated with 2.0 mg/cm\(^2\) CoP, indicating that little photocurrent was observed. Thus \( J_{\text{ph}} \) for the Si MW array is dominated by light absorption in the Si microwires as opposed to absorption in the underlying p-Si substrate.\(^{22}\)

Figure 4.4 displays the stability of an n\(^+\)p-Si MW/CoP electrode during \( \text{H}_2(\text{g}) \) evolution. Over 12 h of continuous operation under potentiostatic control at \(-0.40 \text{ V vs a reversible hydrogen electrode (RHE)}\), the light-limited current density of a n\(^+\)p-Si MW/CoP (2.0 mg/cm\(^2\)) photocathode in 0.50 M \( \text{H}_2\text{SO}_4(\text{aq}) \) at 100 mW/cm\(^2\) illumination intensity was stable at 16.3 ± 0.45 mA/cm\(^2\). \( J-E \) data collected at the beginning and end of the experiment showed negligible degradation in the fill factor or \( J_{\text{ph}} \) over the 12 h period of operation. CoP electrocatalysts deposited on Ti metal supports have been reported to exhibit < 25 mV increase in overpotential during 24 h of continuous operation at cathodic current densities of 20 mA/cm\(^2\),\(^{9}\) suggesting
that the performance and stability limits of the Si/CoP system were not reached in the experiment shown in Figure 4.4.

Figure 4.5 shows n⁺p-Si MWs coated with electrodeposited CoP. At 30, 100, 330 mW/cm² the apparent series resistance has disappeared, reflecting improved contact between the catalyst and the light absorber. Correspondingly, markedly improved performance is observed at 100 mW/cm² obtaining ηIRC of 2.71 %, $V_{oc} = 0.472$. $J_{ph} = 12.6$ mA/cm². This underscores the importance in obtaining intimate contact between the light absorber and electrocatalyst.

Figure 4.4: Voltammetric sweeps under 100 mW/cm² illumination intensity before (black) and after (red) the photocathode was maintained under potentiostatic conditions (left) at −0.40 V vs RHE for 12 h at the same light intensity. The potential for the chronoamperometric experiment was chosen to maintain the light-limited current throughout the experiment in the event of significant degradation within the power-producing region of the sweep. In a tandem structure, the photocathode would presumably be operating at less negative potentials, and thus would produce lower current densities than the light-limited current density at which the stability evaluation was performed. The corresponding chronoamperometric data are displayed on the right under the conditions described for the left panel.

The globally optimized morphology and catalyst placement that simultaneously optimizes optical absorption, carrier collection, reactant access, and product egress while operating during formation of bubbles of H₂(g) requires further investigation. For instance, although the optimum diameter for carrier collection purposes of Si wire arrays is when the wire diameter is approximately equal to the minority-carrier collection length, the exact structure of the material, and whether uniform geometry
Figure 4.5: 100 mC of CoP were deposited from a known procedure\textsuperscript{23}. Several illumination (0, 30, 100, 330 mW/cm\textsuperscript{2}) intensities illuminate the resulting n\textsuperscript{+}p-Si/MWs coated with a TiO\textsubscript{2} scattering particle underlayer\textsuperscript{24} and electrodeposited CoP.

Microwires are preferred relative to more branched nanoscale structures or relative to asymmetric structures that will funnel light into the microwires or nucleate bubble formation and growth at the wire tips requires further investigation.

\textbf{4.4 Conclusion}

Due to the lower turnover frequency of CoP relative to Pt,\textsuperscript{9} higher mass loadings of CoP are required to produce similar geometric area-based HER activities as those obtained from Pt. Microwire arrays, compared with planar surfaces, therefore can beneficially accommodate the higher CoP mass loadings and provide comparable performance to Pt at 30 mW/cm\textsuperscript{2} to 100 mW/cm\textsuperscript{2} illumination intensities. Even at \textlessthan 2 Suns of simulated Air Mass (AM) 1.5 illumination, the $J$–$E$ behavior of an n\textsuperscript{+}p-Si MW/CoP photocathode was comparable to that observed for an n\textsuperscript{+}p-Si MW/Pt photocathode. Since a photocathode in a tandem water-splitting device would operate at \approx 8 mA/cm\textsuperscript{2} for a device having a solar-to-hydrogen energy-conversion efficiency of 10 \%,\textsuperscript{2,3} earth-abundant CoP is therefore an attractive candidate for use as a catalyst for the HER in a functional, intrinsically safe, integrated solar-driven water-splitting system.\textsuperscript{2,3}
4.5 Acknowledgements

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4.6 References


Lightly Fluorinated Graphene as a Protective Layer for n-Type Si(111) Photoanodes in Aqueous Electrolytes


5.1 Abstract

The behavior of n-Si(111) photoanodes covered by monolayer sheets of fluorinated graphene (F–Gr) was investigated under a range of chemical and electrochemical conditions. The electrochemical behavior of n-Si/F–Gr and np⁺-Si/F–Gr photoanodes was compared to hydride-terminated n-Si (n-Si–H) and np⁺-Si–H electrodes in contact with aqueous Fe(CN)₆³⁻/⁴⁻ and Br₂/HBr electrolytes as well as in contact with a series of outer-sphere, one-electron redox couples in nonaqueous electrolytes. Illuminated n-Si/F–Gr and np⁺-Si/F–Gr electrodes in contact with an aqueous K₃(Fe(CN)₆)/K₄(Fe(CN)₆) solutions exhibited stable short-circuit photocurrent densities of −10 mA/cm² for 100 000 s (> 24 h), in comparison to bare Si electrodes, which yielded nearly a complete photocurrent decay over ≈ 100 s. X-ray photoelectron spectra collected before and after exposure to aqueous anodic conditions showed that oxide formation at the Si surface was significantly inhibited for Si electrodes coated with F–Gr relative to bare Si electrodes exposed to the same conditions. The variation of the open-circuit potential for n-Si/F–Gr in contact with a series of nonaqueous electrolytes of varying reduction potential indicated that the n-Si/F–Gr did not form a buried junction with respect to the solution contact. Further, illuminated n-Si/F–Gr electrodes in contact with Br₂/HBr(aq) were significantly more electrochemically stable than n-Si–H electrodes, and n-Si/F–Gr
electrodes coupled to a Pt catalyst exhibited ideal regenerative cell efficiencies of up to 5% for the oxidation of Br\(^-\) to Br\(_2\).

5.2 Introduction

Several protective coating strategies have been developed to suppress deleterious surface reactions associated with corrosion or passivation of semiconductor photoanodes in aqueous electrolytes.\(^{1,2}\) Nickel oxide (NiO\(_x\)) films prepared by reactive sputtering or amorphous TiO\(_2\) films in conjunction with a NiO\(_x\) based electrocatalyst have produced extended stability for Si photoanodes and allow the electrochemical evolution of O\(_2\)(g) from water under alkaline conditions.\(^{3,4}\) Thin metallic overlays or transparent conductive metal oxide protective layers often result in relatively low photovoltages due to thermionic emission of majority carriers at Si/overlay Schottky contacts.\(^{3–10}\) Insulating metal oxide barriers must be thin enough (a few nm) to permit conduction by tunneling, and such thin layers are difficult to prepare in a pinhole-free manner over macroscopic areas.\(^{5,11,12}\) Chemical functionalization has led to improved stability of n-Si surfaces, but such methods have not yet yielded stability over extended time periods in aqueous electrolytes.\(^{13–15}\) An ideal protective coating would be transparent, provide low resistance to charge transfer, allow for maximum energy-conversion efficiency for a range of semiconductor/electrolyte contacts, be applied easily to semiconductor surfaces, be capable of uniformly protecting macroscopic electrode areas, and be chemically and electrochemically stable under the relevant conditions. Monolayer graphene can be prepared in large (> 100 cm\(^2\)), pinhole-free layers and transferred to any arbitrary planar surface, and it has been shown to inhibit oxidation of metals both in air and in aqueous solution.\(^{16–21}\) Graphene is chemically inert, optically transparent, can be deposited onto surfaces at room temperature. Illuminated Si photoanodes coated by polycrystalline, CVD-grown graphene and in contact with neutral pH aqueous electrolytes
have demonstrated stability for over 1000 s while providing desirable photoelectrochemical performance.\textsuperscript{22–25} However, the graphene does not completely protect the Si photoanodes from oxidation, and the devices exhibit partial Fermi-level pinning, which limits their energy-conversion efficiency. The incomplete protection and Fermi-level pinning are consistently ascribed to reactive sites near grain boundaries in the polycrystalline graphene produced by chemical-vapor deposition (CVD), and to the presence of mid-gap electronic states introduced at the n-Si/Gr interface as a result of the graphene electronic structure, respectively. Relative to unfluorinated graphene, fluorination of graphene should reduce the density of states near the Fermi level, thus reducing Fermi level pinning effects, and should passivate reactive graphene defect sites via fluorine capping.\textsuperscript{26–28} Accordingly, we report herein an investigation of the stability and photoelectrochemical behavior of fluorinated-graphene-coated Si photoanodes in contact with aqueous electrolytes.

5.3 Materials and Methods

Detailed experimental procedures are provided in the Supporting Information. Briefly, monolayer sheets of lightly fluorinated graphene (<10 atom % F) were fabricated by treating CVD-grown graphene on a Cu foil with XeF\(_2\)\((g)\).\textsuperscript{28} X-ray photoelectron spectroscopy (XPS) of the resulting F–Gr confirmed the fluorination profile, which was consistent with previous reports indicating that low fluorination levels are observed after XeF\(_2\) exposure of CVD grown graphene on copper foil.\textsuperscript{27,28} The F–Gr was further characterized by UV/Vis and Raman spectroscopy (see SI). The fluorinated graphene sheets were transferred to n-type Si and np\(^{+}\)-Si (np\(^{+}\)-Si = Si homojunction with moderately doped n region and degenerately doped p region, see SI) electrodes using standard CVD graphene growth and transfer methods.\textsuperscript{29,30}
5.4 Results and Discussion

Figure 5.1 shows the current-density vs. time ($J–t$) and current density vs. potential ($J–E$) behavior for illuminated ($\approx 33$ mW/cm$^2$ ENH-type W-halogen lamp) n-Si/F–Gr photoanodes in contact with aqueous 50 mM Fe(CN)$_6^{3−}$ - 350 mM Fe(CN)$_6^{4−}$ (aq). The n-Si/F–Gr electrodes exhibited stable current over 100 s while the current density of n-Si–H electrodes decayed to nearly baseline values over the same time period (Figure 5.1a). Furthermore, the current density of the n-Si/F–Gr electrode decayed by less than 1 mA/cm$^2$ over 100 000 s of continuous operation (Figure 5.1b). After correcting for fluctuations in the light intensity impinging on the electrode, greater than 97 % of the expected current density of an ideally stable electrode was observed. Similar results were observed for np$^+$-Si/F–Gr electrodes (see SI). Figure 5.1c depicts the $J–E$ behavior before and after exposure to the conditions in Figure 5.1b. The stable open-circuit potential ($−0.27$ V vs. $E(A/A^-)$) and fill factor (ff, 0.33 before exposure, 0.32 after exposure) attest to the stability of the n-Si/F–Gr interface.

Prior to the stability test, the open-circuit potential ($E_{oc}$) of the n-Si/F–Gr electrode was $−0.27$ V vs. $E(A/A^-)$, approximately 70 mV lower than the reported $E_{oc}$ of $−0.34$ V vs. $E(A/A^-)$ for n-Si coated with a single layer of graphene.$^{22}$ Further, exposure of n-Si/F–Gr to a series of non-aqueous electrolytes of varying electrochemical potential showed a dependence of $E_{oc}$ on $E(A/A^-)$, indicating partial Fermi level pinning of the n-Si surface with respect to the solution potential. The mutually similar fill factors of the n-Si/F–Gr to the np$^+$-Si/F–Gr electrodes in aqueous electrolyte, 0.33 and 0.30 respectively, with the non-ideal fill factor for the np$^+$-Si/F–Gr interface attributable to a series resistance imposed by the Si/F–Gr/Fe(CN)$_6^{3−/4−}$ interface (see SI), suggests that the Si/F–Gr/Fe(CN)$_6^{3−/4−}$ may also be the source of the non-ideal fill factor for the n-Si/F–Gr electrode as well.

Figure 5.2 shows a comparison of the XP spectra of methyl-terminated n-Si elec-
trodies (n-Si–Me) with and without a F–Gr protective layer before and after photoelectrochemical testing in an aqueous \(50 \text{mM Fe(CN)}_6^{3-} - 350 \text{mM Fe(CN)}_6^{4-}\) electrolyte. After passing 1600 \(\text{mC/cm}^2\) of anodic charge on an n-Si–Me electrode, the growth of an oxide peak was observed in the Si 2p XPS region and was consistent with formation of multiple layers of oxide. In contrast, no additional growth of the oxide peak was observed after passing twice the number of Coulombs (3200 \(\text{mC/cm}^2\)) across an n-Si–Me/F–Gr electrode (see SI). As such, F–Gr acts as a physical barrier to oxide formation, preserving the photoelectrochemical behavior of the n-Si–Me/solution interface. Methylated surfaces were used because, in contrast with n-Si–H surfaces, the n-Si–Me surface does not easily oxidize in air nor forms significant oxide upon fabrication of n-Si/F–Gr interfaces, allowing more facile observation of oxide growth in the presence various protective layers, such as F–Gr. F–Gr covered Si surfaces did not form platinum silicide upon evaporation of Pt onto the F–Gr/Si surface, and F–Gr is stable in both aqueous and acidic (pH 0) solutions, suggesting F–Gr also provides as an effective physical barrier to inhibit Pt/Si reactivity and is stable under harsh fabrication and electrolyte conditions (see SI).

Figure 5.3 displays the \(J–E\) behavior of n-Si–H and n-Si/F–Gr electrodes under \(\approx 33 \text{mW/cm}^2\) illumination intensity in contact with 0.4 M \(\text{Br}_2\) - 7.0 M HBr (pH=0), with and without electrochemical deposition of 100 mC/cm\(^2\) of a Pt catalyst, respectively. With the Pt catalyst, the properties of the n-Si/F–Gr/Pt electrode improved to \(E_{oc} (\text{n-Si/F–Gr/Pt}) = 0.26 \text{V}, \text{ff} = 0.52\), and \(J_{sc} = 8.3\ \text{mA/cm}^2\) from \(E_{oc} (\text{n-Si/F–Gr}) = 0.22 \text{V}, \text{ff} = 0.16, J_{sc} = 5.14\ \text{mA/cm}^2\). The improved \(\text{ff}\) can be ascribed to improved catalysis for the \(\text{Br}^-\) to \(\text{Br}_2\) reaction effected by the Pt. The current density of the n-Si–H/Pt electrode under illumination decayed precipitously over two potential sweeps, while the n-Si/F–Gr/Pt electrode showed a stable \(\text{ff}\) and photocurrent density under the same conditions. The n-Si/F–Gr/Pt electrode had an
ideal regenerative cell efficiency ($\eta_{IRC}$) of 3.5 % in contact with the Br$_2$/HBr (aq) electrolyte.\textsuperscript{51} The current density at n-Si/F–Gr/Pt electrodes was stable over 45 min at $E = 0$ V vs. the Nernstian potential of the solution, $E(A/A^-)$ and $\eta_{IRC}$ increased to 5 % over this time (see SI). The improvement in $\eta_{IRC}$ indicates a change in the energetics of the n-Si/F–Gr/Pt interface after electrochemical deposition of Pt. Although lightly fluorinated (C$_x$F, $x > 10$) graphene was used herein, these fluorinated polycrystalline graphene sheets provided superior and more consistent protection against corrosion to the underlying Si relative to the protection routinely imparted by polycrystalline monolayer graphene on n-Si(111) photoanodes (see SI).\textsuperscript{22} These results are consistent with the hypothesis that light fluorination of graphene induces reaction with high-energy defect sites, such as dangling bonds or missing atoms, effectively passivating defects that otherwise would allow oxide formation at the n-Si surface and further degrade the Gr protective layer (see SI).\textsuperscript{28,32} The bonding of a very electronegative atom to the surface may also increase the hydrophobicity of the graphene sheet, which would further reduce deleterious corrosion reactions near pinholes.
Figure 5.1: Current density-time ($J-t$) and current density-potential ($J-E$) behavior of n-Si/F–Gr electrodes in contact with aqueous 50 mM Fe(CN)$_6^{3-}$ - 350 mM Fe(CN)$_6^{4-}$ under $\approx 33$ mW/cm$^2$ of ENH-type W-halogen lamp illumination. (A) Comparison of the $J-t$ behavior of bare n-Si–H and n-Si/F–Gr electrodes over 100 s. (B) The $J-t$ behavior of F–Gr covered n-Si at $E = 0$ V vs. the Nernstian potential of the solution ($E(A/A^-)$) over 100 000 s (> 24 h). The normalized current density is reported to correct for any variation in the intensity of the light source with time. (C) $J-E$ behavior of n-Si/F–Gr (3 scans at 50 mV s$^{-1}$) before and after exposure to the conditions depicted in (B).
Figure 5.2: XP spectra of n-Si–Me and n-Si–Me/F–Gr electrodes. (A) and (B) show the XP spectra of an n-Si–Me electrode before and after passing 1600 mC/cm$^2$ (inset) while passing anodic current in contact with an aqueous 50 mM Fe(CN)$_6^{3−}$ - 350 mM Fe(CN)$_6^{4−}$ electrolyte. (C) and (D) show an n-Si–Me/F–Gr electrode before and after passing 3200 mC/cm$^2$ under similar electrochemical conditions to (A) and (B).

Figure 5.3: Electrochemical behavior of n-Si/F–Gr and n-Si–H electrodes with and without Pt deposition in aqueous 0.4 M Br$_2$ - 7.0 M HBr (pH = 0) electrolyte under 33 mW/cm$^2$ from an ELH-type W-halogen lamp. (A) J–E behavior of n-Si/F–Gr and n-Si–H electrodes with and without Pt deposition. Each cyclic voltammogram was started at 0.4 V vs. $E(A/A^−)$ and swept twice to more negative potentials at 50 mV s$^{-1}$. (B) $J$–$t$ behavior of an n-Si/F–Gr/Pt electrode over 45 min at $E = 0$ V vs. $E(A/A^−)$ (C) J–E behavior of an n-Si/F–Gr/Pt electrode after exposure to conditions described in (B).
5.5 Conclusion

In conclusion, fluorinated graphene forms an effective physical barrier between silicon surfaces and a number of contacting phases, including acidic and neutral pH aqueous electrolyte as well as metallic interfaces. Additionally, Si covered by fluorinated graphene exhibits partial Fermi level pinning in contact with non-aqueous electrolytes. Additional work at higher fluorination levels on both p-type and n-type silicon will elucidate whether a reduction in the density of states near the Fermi level can lead to a fully unpinned interface, and will allow elucidation of the effect of the graphene-based surface dipole on the electrochemical behavior of the resultant photoelectrode.

5.6 Acknowledgements

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5.7 References


Considerable interest in diversifying the world energy supply from finite fossil fuels to renewable sources arose in the 1970s as the result of an energy crisis. After the embargo of trade subsided, attention to energy waned until simultaneous concerns of fossil fuel resource exhaustion and anthropogenic climate change reignited a resurgence of interest.

Among renewable energy sources, collecting light from the sun is promising due to its immense potential. Unfortunately, photovoltaic solar cells produce intermittent electricity that is at odds with baseload generation necessary for large-scale adoption. This thesis peers back into the 1970s and examines a failed commercial endeavor by Texas Instruments (TI) to store electricity by splitting hydrobromic acid using silicon photoelectrodes. We try to advance a modern rendition of the TI system by replacing expensive precious metals with earth-abundant materials to further lower the cost of modules. We encounter a wide range of problems spanning from catalysis to semiconductor interfaces.

While water splitting is attractive for fuel storage, hydrobromic acid storage is promising for electricity storage. In this thesis we see, in agreement with predictions by others, that modern oxidation catalysts for water splitting fall short and will always result in lower solar-to-hydrogen ($\eta_{\text{STH}}$) efficiencies than comparable hydrobromic acid systems. In this thesis, we model different device configurations for the storage of chemical work to tailor the chemical reaction to the material of interest. For a single light absorber, the optimum device converts with an $\eta_{\text{STH, HBr}}$ of 16.2 % for a 1.80 eV band gap material and $\eta_{\text{STH, H}_2\text{O}}$ of 8.60 % for a 2.30 eV band gap material. Two light absorbers sitting side-by-side allow an $\eta_{\text{STH, HBr}}$ of 17.8 % for two 1.20 eV
materials and $\eta_{\text{STH, H}_2\text{O}}$ of 14.2 % for two 1.70 eV absorbers. A tandem system (with the larger band gap material on top of a smaller band gap semiconductor) could produce $\eta_{\text{STH, HBr}}$ of 22.2 % for 1.60 eV:0.900 eV and $\eta_{\text{STH, H}_2\text{O}}$ 19.3 % for 1.80 eV:1.20 eV. In light of the strength of our expertise, we elect to use HBr splitting in a side-by-side configuration where two silicon photoelectrodes ($E_g = 1.12$ eV) could give an $\eta_{\text{STH, HBr}} \approx 12.0 \%$.

In this thesis we develop an acid-compatible proton reduction catalyst for our system. We recognize that due to the similar mechanism between hydrodesulfurization (HDS) and the hydrogen evolution reaction (HER) that a good HDS catalyst may also be an active HER catalyst. We present another such example, cobalt phosphide (CoP) that reduces protons to $\text{H}_2(g)$ with an overpotential ($\eta$) of $-85$ mV at a current density of $-20 \text{ mA/cm}^2$ with promising stability over 24 h.

As part of this thesis, we integrate CoP with silicon microwire photocathodes with radial emitters (to simulate cheaper wires produced by CVD) to demonstrate a prototype photocathode, where we obtain an ideal-regenerative efficiency ($\eta_{\text{IRC}}$) of 1.9 % with promising stability over 12 h. We obtain a higher $\eta_{\text{IRC}}$ of 2.71 % by electrodepositing amorphous CoP thereby improving electrical contact.

Next, a protection strategy for a silicon photoanode is introduced using lightly-fluorinated graphene as an improvement over graphene. With an appropriate catalyst (Pt), we obtain an $\eta_{\text{IRC}}$ of 5 % for Br$^-$ with promising stability over 30 min (we did not continue extended testing because the goal was to use graphene directly, but fluorination appears to have hampered oxidation catalysis).

Then we present an attempt to improve our CoP by increasing the surface area with highly branched crystalline nanoparticles, but find the $\eta$ to be 117 mV for $-20 \text{ mA/cm}^2$. Unfortunately these nanoparticles did not appear to adhere well to the Ti substrate and stability was therefore lacking.
We present a strategy to protect silicon by using covalent molecular monolayers as a first step to control the interface by seeding the growth of metal oxides during atomic layer deposition. Upon deposition of thin metal oxide layers, we find that the surface recombination velocity ($S$) remains low while providing enhanced deposition rates for our aldehyde-terminated surfaces.

Then we present an alternative strategy for controlling the composition of nanoparticles by pulsed laser ablation in liquids by adding select metal salts. This adds an additional knob to enable the synthesis of complex materials by kinetic control, allowing for the selection of future desirable materials.

And finally, we present a review of the general academic impact the metal phosphides have had on the community since their introduction and chart their progress in several aspects.
Efficiency Calculation Matlab Program

A.1 Realistic Calculation Results

Single Absorber

Figure A.1: The “+” (red) represents the efficiency for HBr splitting and the blue circles represents H$_2$O splitting using a single light absorber.

Dual Light Absorbers: Side-by-Side

Figure A.2: This calculation shows the solar-to-hydrogen efficiency ($\eta_{STH}$) for two equivalent devices consisting of side-by-side semiconductors connected in parallel using A) HBr splitting and B) H$_2$O splitting.
A) HBr

B) H₂O

η_{STH} (%)

Figure A.3: This calculation shows the $\eta_{\text{STH}}$ for two equivalent devices consisting of stacked (photoanode on top) semiconductors, using A) HBr splitting and B) H₂O splitting.

Dual Light Absorbers: Tandem

A.2 Script Dependencies

The script detailed performs simple calculations on potential device efficiencies for an integrated solar collector and chemical energy converter. It uses the theoretical outline developed in Chapter 2 to calculate efficiency. It works in the MATLAB (R2015b) environment. Dependencies include the intersections.m script written by Schwarz on Math Works File Exchange as well as a data file saved as data.m which includes a cell called data which is merely obtained as ASTM173.xls from NREL stripped of headers.

A.3 Source Code

Listing A.1: Analysis Program for Efficiency Calculation

```matlab
function A
%the purpose of this script is to estimate the efficiencies of certain PEC
% schemes in different solutions.

% dbstop if error % this flag tells the debugger to kick in if there is an error so I may
% investigate.
% dbstop if warning
%Author:
%Christopher W. Roske (CWR)
%Reviewed by:
%Shane Ardo
%James McKone
% v = ver;
if ~any(strcmp('Parallel Computing Toolbox', {v.Name}));
    warning('you will have a bad time without parallel computing toolbox, but if you so decide
    to proceed without it then change all parfor to for, good luck!')
end
```
%close all

bg=[1:0.025:3]; % band gap(s) of interest in eV

% Volts: standard electrode potential for anodic reaction per 2 photons
a_SEP_V=1.09; % Volts: for cathodic reaction per 2 photons
c_SEP_V=0;

no_photons=1; % no of photons %no_photons=2 is S4, no_photons=1 is S2
betal = 0.95; %light losses from reflection and etc.

%BV parms for anodic reaction
a_ecd_c_mA_cm2=10^(-3)*10^3; % anodic mA/cm^2 this is the exchange current density for a catalyst to be used in Butler-Volmer calculations
a_ctc_a=0.5; % anodic charge transfer coefficient for anodic reaction for BV
a_ctc_c=0.5; % anodic charge transfer coefficient for cathodic reaction for BV

%BV parms for cathodic reaction
a_ecd_c_mA_cm2=10^(-3)*10^3;
c_ecd_c_mA_cm2=10^(-3)*10^3;
c_ctc_a=0.5;
c_ctc_c=0.5;

num_photoabsorbers=2; % Dual=2 or single=1 photoabsorber?
sidebyside = 1; % 1 means they are side-by-side, 0 means stacked

no_e=1; % no. of electrons transferred in
%desired reaction for BV (we just assume this is =1 for simplicity b/c %BV is actually written for the 1 e- case.)

%the instructions below with the different cases of a) single light %absorber doing two half reactions b) two light absorbers side-by-side %doing two half reactions and c) two stacked light absorbers...

TOP{1,1} = 't';
TOP{1,2} = num2str( bg(1) );
TOP{2,1} = 'b';
TOP{2,2} = num2str( bg(1) );
top_or_bottom = TOP; %not important for you the user to set, only important for stacked calculations

if num_photoabsorbers == 1
%if one photoabsorber is carrying out two half-reactions
majority_doping_type='n'; % this may be 'p' for photocathode or 'n' for photoanode.

EFF_A = zeros(1, length(bg));
EFF_B = zeros(1, length(bg));
count = 1;
for i=bg
display(['i ' num2str(count) ' of ' num2str( length(bg) ) ])
[EFF_A(count), EFF_B(count)]=B(i, num_photoabsorbers, sidebyside, majority_doping_type,
a_SEP_V, c_SEP_V, a_ecd_c_mA_cm2, a_ctc_a, a_ctc_c, c_ecd_c_mA_cm2, c_ctc_a, c_ctc_c,
no_e, no_photons, top_or_bottom, betal);
count=count+1;
end

else
%two light absorbers, side-by-side or stacked
majority_doping_type='n';

EFF_A = zeros(1, length(bg));
EFF_B = zeros(1, length(bg));
count = 1;
for i=bg
display(['i ' num2str(count) ' of ' num2str( length(bg) ) ])
[EFF_A(count), EFF_B(count)]=B(i, num_photoabsorbers, sidebyside, majority_doping_type,
a_SEP_V, c_SEP_V, a_ecd_c_mA_cm2, a_ctc_a, a_ctc_c, c_ecd_c_mA_cm2, c_ctc_a, c_ctc_c,
no_e, no_photons, top_or_bottom, betal);
count=count+1;
end
end

figure
plot(bg, EFF_A)
hold on;
plot(bg, EFF_B, 'r')

elseif num_photoabsorbers == 2
% if two photoabsorbers are carrying out two half-reactions
% they can be either 1) side by side
% 2) stacked
if sidebyside == 1
% if they are side by side

% first we compute the photoanode efficiency

% then we compute the photocathode efficiency

% the max efficiency is obtained via 1/2 * ( eta_A + eta_C )
% otherwise we can take the intersection of the J-V curves for the
% photoanode + BV_a and the photocathode + BV_c and take that
% intersection to be the operating point for the device.
% let's do the latter...
% the best use of resources would save the J-V curve for each
% photoanode/photocathode + OP and then to the
% intersection/efficiency calculations after that
% if any(strcmp('Parallel Computing Toolbox', {v.Name}));
% s = matlabpool('size');
% if s == 0 % is the matlabpool open?
matlabpool close; % then close it, we are done with it!
% end
% end
if ~( exist('TheData_temp.mat', 'file') == 2 ) % we save files for long computations, in
the future we will generate these for each particular simulation

a.EFF_A = zeros(1, length(bg)); % preallocating memory
a.EFF_B = zeros(1, length(bg));
c.EFF_A = zeros(1, length(bg));
c.EFF_B = zeros(1, length(bg));

TheData={}; % this is a cell
% defaultProfile = parallel.defaultClusterProfile; % where we take advantage of multi-
cores, if the computer has them
% myCluster = parcluster(defaultProfile);
% matlabpool(myCluster, 'open');
for i = 1 : length(bg) % again, this loop is special in that is it for parallel
processing so its limitations/uses are a bit weird compared with a standard for
loop
  % photoanode
  disp(num2str(bg(i)) ' and ' num2str(i)); % this is really just helpful for
diagnostic purposes in case something gets stuck or is abnormal
majority.doping.type = 'n'; % first we compute for the photoanode
TheData_temp(i).bandgap_n = bg(i); %now we save the outputs to our cells, you’ll notice I am using TheData_temp. We can’t save directly to TheData (defined above) for two reasons 1) it is a cell 2) it was not created within the parfor loop

TheData_temp(i).doping_n = ’n’;
TheData_temp(i).GibbsIncorp_n = Gibbsoutput_a;
TheData_temp(i).Overpotential_n = Overpotential_a;
TheData_temp(i).J_n = J_a;

%photocathode

majority_doping_type = ’p’; %now we run the photocathode

%you will notice that the output of B is variable, i.e., %more vars are saved from the photoanode case than for this %photocathode case: this is programmed behavior
[c.EFF_A(i), c.EFF_B(i), Gibbsoutput_c, Overpotential_c, J_c]=B(bg(i), num_photoabsorbers, sidebyside, majority_doping_type, a_SEP_V, c_SEP_V, a.ecd_c.mA.cm2, a.ctc_c, c.ecd_c.mA.cm2, c.ctc_c, no_e, no_photons, top_or_bottom, betal);
TheData_temp(i).bandgap_p = bg(i); %again, we save the output for the photocathode in a temp variable
TheData_temp(i).doping_p = ’p’;
TheData_temp(i).GibbsIncorp_p = Gibbsoutput_c;
TheData_temp(i).Overpotential_p = Overpotential_c;
TheData_temp(i).J_p = J_c;

end

S=S_temp(1); %we need to save the solar irradiance

save(’TheData_temp’, ’TheData_temp’, ’a.EFF_A_temp’, ’a.EFF_B_temp’, ’c.EFF_A_temp’, ’c.EFF_B_temp’, ’S’) %here we are temporarily saving simulation results, %these contain the raw J-V curves, but next we need do %load-line analysis to obtain efficiencies
end

if (exist(’TheData_temp.mat’, ’file’) == 2) && (~exist(’Temp.mat’, ’file’) == 2) 

%This is actually the computationally intensive process because we must %first generate all the combinations of bandgap materials, draw their J-V %curves and find their intersection to find the operating point of the %device
load(’TheData_temp’) %here we load the temporarily saved file from the parfor loop above
a.EFF_A = a.EFF_A_temp; %this contains the individual efficiencies... in this case they are not STH but power
a.EFF_B = a.EFF_B_temp;
c.EFF_A = c.EFF_A_temp;
c.EFF_B = c.EFF_B_temp;
TheData = TheData_temp; %this contain the J-V curves
S=S(1); %solar irradiance
%now when we calculate these values for a side-by-side, their %J-V curves are saved and we can now load them and calculate %the different combinations to find interesections

%load J-V curves
%all possible combinations

%for i = 1 : length(bg)

TheEff_temp = cell(length(bg), length(bg) ); %preallocating memory
TheEff_eff_wBV=zeros(length(bg), length(bg), 1 );
TheEff_eff_woBV=zeros(length(bg), length(bg), 1 );
clear i
for i = 1 : length(bg) %where again we use parallel processing to split up these jobs
and enable faster computation on multi-core systems

TheEff_temp_eff_wBV = zeros(length(bg),1 ); %unfortunately these variables must
be redeclared each time
TheEff_temp_eff_woBV = zeros(length(bg),1 );

for v = 1 : length(bg) %this insures we are computing all possible combinations

%display( [ num2str(i) ' ' num2str(v) ] ) %this is used for diagnostic purposes
during a run

%where we do the load-line analysis for the photoanode plotted on the RHE
%scale and the photocathode plotted on the RHE scale all happening in the
%same current magnitude and determine at what voltage and current they
%intersect at
[a,c_wBV] = intersections(TheData(i).GibbsIncorp_n+TheData(i).Overpotential_n ,
TheData(i).J_n , TheData(v).GibbsIncorp_p-TheData(v).Overpotential_p ,
TheData(v).J_p);

%the outputs in this case are:
% a  is the Voltage where they intersect at vs RHE
% c_wBV  is the current in mA/cm^2 they intersect at
%for the BV case

%for b) w/o BV case
[a,c_woBV] = intersections(TheData(i).GibbsIncorp_n, TheData(i).J_n ,
TheData(v).GibbsIncorp_p, TheData(v).J_p);
%find efficiencies
% display( [ 'SBS Efficiency for bandgaps (eV): ' num2str(bg(i)) ' and ' num2str(bg(v)) ] )

%there are several possible cases to deal with for the
%output of c_wBV & c_woBV... those are dealt with here.

if any(c_woBV) %if the without BV case has any non-zero elements then
continue
%find max idx of woBV
IndexWOBV = []; IndexWOBV = find(c_woBV); %find the index of the non-zero elements
%now see if multiple indices

if length(IndexWOBV) > 1 %if there is more than one non-zero element then
we want the one which has the largest current
MJ = c_woBV(IndexWOBV(1) ); %first value

for JK = IndexWOBV
if abs(c_woBV(JK) ) > abs(MJ) %if any of the other values have a
higher current than the first one then they are elected to
be the winner
MJ = c_woBV(IndexWOBV(JK) );

end
IndexWOBV = win; %This is the index for the value of the highest
current
end

if any(c_wBV) %now that we know c_wBV is non-zero it is time to find out
if w/BV is non-zero as well
IndexWOBV = find(c_wBV);
if length(IndexWBV) > 1
    MJ = c_wBV(IndexWBV(1));
    win=IndexWOBV(1);
    for JK = IndexWBV
        if abs(c_wBV(JK)) > abs(MJ)
            MJ= c_wBV(IndexWBV(JK));
            win=JK;
        end
    end
    IndexWBV = win;
end
else %if sadly c_wBV is zero then we must empty that variable
    c_wBV = [];
end
else
    %if no nonzero's in the w/o BV case then
    isempty or is nan
    c_woBV=[];
    c_wBV=[];
end
%The folowing actually computes the STH (%):
if ~isempty(c_wBV) %there are two cases, w/BV is empty or it is not empty...
    %if it is not empty then the efficiency can be calculated with that
    current
    TheEff_temp_eff_wBV(v) = abs((a_SEP_V - c_SEP_V)/no_e * c_wBV(IndexWBV) / (2*S) *10 * 100);
else %if it is empty then the efficiency is zero
    TheEff_temp_eff_wBV(v) = 0;
end
if ~isempty(c_woBV)
    TheEff_temp_eff_woBV(v) = abs(( (a_SEP_V - c_SEP_V)/no_e * c_woBV(IndexWOBV) / (2* S) *10 * 100));
else
    TheEff_temp_eff_woBV(v) = 0;
end
plot(TheData(i).GibbsIncorp_n+TheData(i).Overpotential_n, TheData(i).J_n, 'displayname', num2str(i) )
hold on;
plot(TheData(v).GibbsIncorp_p-TheData(v).Overpotential_p, TheData(v).J_p, 'r', 'displayname', num2str(v) )
hold off;
filename = 'Slice.gif';
title(['BG PA: ' num2str(TheData(i).bandgap_n) ' and BG PC: ' num2str(TheData(v).bandgap_p) ' STH%: ' num2str( TheEff_temp_eff_wBV(v) ) ])
ylim([-60 0]);
drawnow
frame = getframe(1);
im = frame2im(frame);
[limind,cm] = rgb2ind(im,256);
if i == 1 && v == 1;
    imwrite(limind,cm,filename,'gif', 'Loopcount',inf);
else
imwrite(imind,cm,filename,'gif','WriteMode','append');

end

display( [ num2str(i) ' of ' num2str(length(bg)) ] ) % this allows the user to keep up with the progress

TheEff_eff_wBV(i,:)=TheEff_temp_eff_wBV;
TheEff_eff_woBV(i,:)=TheEff_temp_eff_woBV;

end

TheEff_eff_wBV=zeros(length(bg), length(bg));
TheEff_eff_woBV=zeros(length(bg), length(bg));

for R = 1 : length(bg)
    for a = 1 : length(bg)
        TheEff.eff_wBV(R,a)=TheEff_eff_wBV(R,a); % we store the variables like this because it is convenient to debug with
        TheEff.eff_woBV(R,a)=TheEff_eff_woBV(R,a);
    end
end

save('Temp')

end

if (exist('Temp.mat', 'file') == 2 )
    load('Temp.mat')
    % put in a nice 3D plot! (well, bg by bg by color)
    for i = 1 : length(bg)
        for d = 1 : length(bg)
            X(i,d) = bg(i);
            Y(i,d) = bg(d);
            if isempty(TheEff.eff_wBV(i,d) )
                TheEff.eff_wBV(i,d) = 0;
            end
            PlotHeatEff_wBV(i,d) = TheEff.eff_wBV(d,i);
        end
    end
    imagesc( bg, bg, PlotHeatEff_wBV, [0 25]);
    axis xy; % this sets the origin
    colorbar;
    set(gcf, 'color', 'white');
    xlabel('band gap (photoanode) eV')
    ylabel('band gap (photocathode) eV')
    title('Side by Side')
end

else sidebyside == 0
    % if they are stacked
    % first we compute the photoanode efficiency
    % then we compute the photocathode efficiency
    % the max efficiency is obtained via eta_A + eta_C
otherwise we can take the J−V curves for the photoanode + BV_a and photocathode + BV_c and take the intersection to be the operating point for the device.

let's do the latter

unlike in the side-by-side case, it does little for us to save each J−V curve and then calculate efficiencies because the light absorption by the top semiconductor changes the J−V curves, so we do not have that luxury here

if any(strcmp('Parallel Computing Toolbox', {v.Name}));
    s = matlabpool('size');
    if s ~= 0 is the matlabpool open?
        matlabpool close; %then close it, we are done with it!
    end
end

if ~( exist('TheData_temp.mat', 'file') == 2 ) %we save files for long computations, in the future we will generate these for each particular simulation
    a.EFF.A = zeros(1, length(bg)); %preallocating memory
    a.EFF.B = zeros(1, length(bg));
    c.EFF.A = zeros(1, length(bg));
    c.EFF.B = zeros(1, length(bg));
    TheData={}; %this is a cell

    defaultProfile = parallel.defaultClusterProfile; %here we take advantage of multi-cores, if the computer has them
    myCluster = parcluster(defaultProfile);
    matlabpool(myCluster, 'open');

    for i = 1 : length(bg) %again, this loop is special in that is it for parallel processing so its limitations/uses are a bit weird compared with a standard for loop
        %photoanode
        disp([ num2str(bg(i)) ' and ' num2str(i) ]); %this is really just helpful for diagnostic purposes in case something gets stuck or is abnormal
        majority_doping_type = 'n'; %first we compute for the photoanode
        TOP=cell(2,2);
        TOP(1,1) = 't';
        TOP(1,2) = num2str( bg(i) );
        TOP(2,1) = 'b';
        TOP(2,2) = num2str( bg(i) );
        top_or_bottom = TOP;
        [a.EFF.A_temp(i), a.EFF.B_temp(i), Gibbsoutput.a, Overpotential.a, J.a, SEP.V.a, SEP.V.c, S.temp(i)]=B(bg(i), num.photoabsorbers, sidebyside, majority_doping_type, a.SEP.V, a.ecd.c.MA.cm2, a.ctc.a, a.ctc.c, c.ecd.c.MA.cm2, c.ctc.a, c.ctc.c, no.e, no.photons, top_or_bottom, beta);
        TheData.temp(i).bandgap_n = bg(i); %now we save the outputs to our cells, you'll notice I am using TheData_temp. We can't save directly to TheData (defined above) for two reasons 1) it is a cell 2) it was not created within the parfor loop
        TheData.temp(i).doping_n = 'n';
        TheData.temp(i).GibbsIncorp.n = Gibbsoutput.a;
        TheData.temp(i).Overpotential.n = Overpotential.a;
        TheData.temp(i).J.n = J.a;
        c.EFF.A_temp.bottom = zeros(1, length(bg)),
c.EFF_B.temp.bottom = zeros(1, length(bg));
a.EFF_A.temp.bottom = zeros(1, length(bg));
a.EFF_B.temp.bottom = zeros(1, length(bg));
TheData.temp.bottom={};
%photocathode
for v = 1 : length(bg)
    TOP{1,1} = 'b';
    TOP{1,2} = num2str( bg(v) );
    TOP{2,1} = 't';
    TOP{2,2} = num2str( bg(i) );
    top_or_bottom = TOP;
    majority.doping.type = 'p'; %now we run the photocathode
    %you will notice that the output of B is variable, i.e.,
    %more vars are saved from the photoanode case than for this
    %photocathode case: this is programmed behavior
    [c.EFF_A.temp.bottom(v), c.EFF.B.temp.bottom(v), Gibbsoutput.c, 
     Overpotential.c, J.c]=B(bg(v), num_photoabsorbers, sidebyside, 
     majority.doping.type, a.SEP.V, a.SEP.V, a.ecd.c.mA.cm2, a.ctc.a, a.ctc.c , 
     c.ecd.c.mA.cm2, c.ctc.a, c.ctc.c, no.e, no.photons, top_or_bottom, 
     betal);
    TheData.temp.bottom(v).bandgap_p = bg(i); %again, we save the output for the 
    TheData.temp.bottom(v).doping_p = 'p'; %again, we save the output for the 
    TheData.temp.bottom(v).GibbsIncorp_p = Gibbsoutput.c;
    TheData.temp.bottom(v).Overpotential_p = Overpotential_c;
    TheData.temp.bottom(v).J_p = J_c;
end

c.EFF_B.Bottom(i,:)=c.EFF.B.temp.bottom;
c.EFF_A.Bottom(i,:)=c.EFF.A.temp.bottom;
TheData.Bottom(i,:)=TheData.temp.bottom;
end

S=S.temp(1); %we need to save the solar irradiance

save('TheData_temp', 'TheData_temp', 'a.EFF_A.temp', 'a.EFF_B.temp', 'S', ' 
  c.EFF.B.temp.Bottom', 'c.EFF.A.temp.Bottom', 'TheData.temp.Bottom') %here we are
%temporarily saving simulation results,
%these contain the raw J-V curves, but next we need do
%load-line analysis to obtain efficiencies
end

if (exist('TheData_temp.mat', 'file') == 2) & & (~exist('Temp.mat', 'file') == 2) )
    %This is actually the computationally intensive process because we must
    %first generate all the combinations of bandgap materials, draw their J-V
    %curves and find their intersection to find the operating point of the
    %device
    load('TheData_temp') %here we load the temporarily saved file from the parfor loop
    above
a.EFF_A = a.EFF.A.temp; %this contains the individual efficiencies... in this case
    %they are not STH but in fact power
a.EFF_B = a.EFF.B.temp; 
% c.EFF.A = c.EFF.A.temp;
% c.EFF_B = c.EFF.B.temp;
TheData = TheData.temp; %this contain the J-V curves for the top case
TheData.B = TheData.temp.Bottom;

S=S(1); %solar irradiance
%now when we calculate these values for a side-by-side, their
%J-V curves are saved and we can now load them and calculate
%the different combinations to find intersections

%load J-V curves
%all possible combinations

for i = 1 : length(bg)
  TheEff_temp = cell(length(bg), length(bg)); %preallocating memory
  TheEff_eff_wBV=zeros(length(bg), length(bg), 1);
  TheEff_eff_woBV=zeros(length(bg), length(bg), 1);
  clear i
  for i = 1 : length(bg) %where again we use parallel processing to split up these jobs
    TheEff_temp_eff_wBV = zeros(length(bg),1 ); %unfortunately these variables must
    TheEff_temp_eff_woBV = zeros(length(bg),1 );
    for v = 1 : length(bg) %this insures we are computing all possible combinations
      display([ num2str(i) ' ' num2str(v) ]) %this is used for diagnostic purposes
        %here we do the load-line analysis for the photoanode plotted on the RHE
        %and the photocathode plotted on the RHE scale all happening in the
        %same current magnitude and determine at what voltage and current they
        %intersect at
      if any( TheData_B(i,v).J_p(:) )
        [a,c_wBV] = intersections(TheData(i).GibbsIncorp_n+TheData(i).Overpotential_n, TheData(i).J_n , TheData_B(i,v).GibbsIncorp_p-TheData_B(i,v).Overpotential_p, TheData_B(i,v).J_p(:) );
      else
        c_wBV =[];
      end
      %the outputs in this case are:

      %a is the Voltage where they intersect at vs RHE
       %c_wBV is the current in mA/cm^2 they intersect at

      %for b) w/o BV case
      if any(TheData_B(i,v).J_p(:) )
        [a,c_woBV] = intersections(TheData(i).GibbsIncorp_n, TheData(i).J_n , TheData_B(i, v).GibbsIncorp_p, TheData_B(i,v).J_p(:) );
      else
        c_woBV = [];
      end
      %find efficiencies
      display("SBS Efficiency for bandgaps (eV): ' num2str(bg(i)) ' and ' num2str(bg(v)) ")

      %there are several possible cases to deal with for the
      %output of c_wBV & c_woBV... those are dealt with here.
   
      if any(c.woBV) %if the without BV case has any non-zero elements then
        continue
        %find max idx of woBV

        IndexWOBV = find(c.woBV); %find the index of the non-zero elements
        %now see if multiple indices

        if length(IndexWOBV) > 1 %if there is more than one non-zero element then
          we want the one which has the largest current
          MJ = c.woBV(IndexWOBV(1) ); %first value

      else
        continue
      end
win=IndexWOBV(1); %at present, the first value is the winner
for JK = IndexWOBV
    if abs(c_wOBV(JK)) > abs(MJ) %if any of the other values have a
        MJ = c_wOBV(IndexWOBV(JK));
        win=JK;
    end
end
IndexWOBV = win; %This is the index for the value of the highest
end

if any(c_wBV) %now that we know c_wOBV is non-zero it is time to find out
    IndexWBV = find(c_wBV);
    if length(IndexWBV) > 1
        MJ = c_wBV(IndexWBV(1));
        win=IndexWOBV(1);
        for JK = IndexWBV
            if abs(c_wBV(JK)) > abs(MJ)
                MJ= c_wBV(IndexWBV(JK));
                win=JK;
            end
        end
        IndexWBV = win;
    end
else %if sadly c_wBV is zero then we must empty that variable
    c_wBV = [];
end

else %if no nonzero's in the w/o BV case then
    %isempty or is nan
    c_wOBV = [];
    c_wBV = [];
end

%The following actually computes the STH (%):
if ~isempty(c_wBV) %there are two cases, w/BV is empty or it is not empty...
    if it is not empty then the efficiency can be calculated with that
current
        TheEff_temp.eff_wBV(v) = abs((a_SEP_V - c_SEP_V)/no_e * c_wBV(IndexWBV)
            / (S) *10 * 100);
    else %if it is empty then the efficiency is zero
        TheEff_temp.eff_wBV(v) = 0;
    end
else %isempty(c.wBV)
    TheEff_temp.eff_wBV(v) = abs((a_SEP_V - c_SEP_V)/no_e * c_wOBV( IndexWOBV) / (S) *10 * 100));
else
    TheEff_temp.eff_wOBV(v) = 0;
end
TheEff_eff_wBV = TheEff_eff_wBV;
TheEff_eff_woBV = TheEff_eff_woBV;

% plot( TheData(i).GibbsIncorp_n+TheData(i).Overpotential_n, TheData(i).J_n )
% hold on;
% plot( TheData(j).GibbsIncorp_p-TheData(j).Overpotential_p, TheData(j).J_p, 'p')

TheEff_eff_wBV= zeros(length(bg), length(bg));
TheEff_eff_woBV = zeros(length(bg), length(bg));

for R = 1 : length(bg)
    for a = 1 : length(bg)
        TheEff_eff_wBV(R,a) = TheEff_eff_wBV(R,a); % we store the variables like this because it is convenient to debug with
        TheEff_eff_woBV(R,a) = TheEff_eff_woBV(R,a);
    end
end

save('Temp')

end

if (exist('Temp.mat', 'file') == 2 )
    load('Temp.mat')
    % put in a nice 3D plot! (well, bg by bg by color)
    for i = 1 : length(bg)
        for d = 1 : length(bg)
            X(i,d) = bg(i);
            Y(i,d) = bg(d);
            if isempty(TheEff_eff_wBV(i,d) )
                TheEff_eff_wBV(i,d) = 0;
            end
            PlotHeatEff_wBV(i,d) = TheEff_eff_wBV(i,d); % this flip is to make sure the photoanode is on the x-axis and photocathode is on the y-axis
        end
    end
    imagesc( bg, bg, PlotHeatEff_wBV, [0 25]);
    axis xy; % this sets the origin
    colorbar;
    set(gcf, 'color', 'white');
    xlabel('band gap (photoanode) eV')
    ylabel('band gap (photocathode) eV')
    title('Stacked')
end
end
end

function [OUTPUT_A, OUTPUT_B, varargout] = B(band_gap_eV, num_photoabsorbers, sidebyside, 
    majority_doping_type, a_SEP_V, c_SEP_V, a_ecd_c_mA_cm2, a_ctc_a, a_ctc_c, c_ecd_c_mA_cm2, 
    c_ctc_a, c_ctc_c, no_e, no_photons, top_or_bottom, betal)

    % note this may be unusual to you for outputs, but 'varargout' gives
    % variables length for the output so I can pass J-V curves to the primary
    % function
%H2O \rightarrow H2 + 1/2 O2 has $E^0 = 1.229$ V per electron... assume two electron
process so 1.229 * 2 is SEP. V... so an S2 will require 1.229 eV per
photon! (as Bolton says)

AM='1.5'; % may be set as 'i' for imaginary sun, '0' for AM 0 data or
'1.5' for AM 1.5 data

Voc_approx='mu_power'; % There are multiple estimates available for Voc, the'
mu_power' approach or 'mindiosat' or 'Sze'

% step size for J-V curve calculations...

% CONSTANTS

hc_eV_micron = 1.23984193; % in eV * micron

band_gap_micron= hc_eV_micron/band_gap_eV; % The bandgap internally is computed in microns. Deal
with it.

Avocado=6.02214129*10^(23);

e_C=1.60217646*10^(-19); % Coulombs

c.m_s = 2.99792458e8; % speed of light m/s

h Js = 6.62608e-34; % Planck constant J * s

kB J_K = 1.38066e-23; % Boltzmann constant J K^−1

R J molK=kB J_K*Avocado; % gas constant with units of J/(mol K)

F=e_C*Avocado; % Faraday constant

hc J um = 1.986446*10^(-19); % J * um

n.refractive = 1; % refractive index of semiconductor for BB calcs

n.idealidityfactor=1; % ideality factor for semiconductor for J, Voc, J calcs

alpha = 2; % internal conversion coefficient for calculating P curve

T K = 300; % Kelvin of semiconductor for BB calcs

T_sun K=5800; % Kelvin of the calculated sun

radius_sun_m=6.955*10^8; % radius of sun in meters

distance_earth_m=1.484*10^11; % distance of earth to sun in meters (on avg)

A mA cm2 K2=1.20*10^5; % free electron value, 120 A cm^−2 K−2... Richardson constant

%COMPUTATIONS

load reqd.mat %This contains NREL data for AM 1.5 spectrum, AM 0 and AMG 1.5
% This loads data, a variable that is important for calculations involving
% AM 1.5

lambda=data(1:end,1)*1/10^3; % this puts the internal data in terms of microns... Why my
obsession with um? Made it easier to compare with literature while writing this.

[rn, index_of_interest]= (min(abs(lambda – band_gap_micron ))); % calculates index of the band gap
we are interested in

%Calculating BB

ratio=radius_sun_m^2/distance_earth_m^2; % recall that light intensity from a pt source follows
the inverse square law

sun=zeros(length(lambda),1);

for i=2:length(lambda)
    sun(i)=2 * pi * h Js * c.m.s^2/lambda(i)^5 * ( 1 / ( exp( h Js * c.m.s/ ( lambda(i)*10^(-6) *

kB J.K * T_sun.K ) )-1 )) * 10^24 * ratio;
end

% This means sun(i) is in units of W/m^2/microns and lambda is in units of
microns
\begin{verbatim}

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\textbf{Calculate E} \textbf{%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%}

\textbf{Disp('Calculating E')}

%The next three if statements are optional switches to make it easy to pick
%between the different scenarios for incoming light flux.
if strcmp(AM, 'i')
    Spectral_Irradiance=sun; %in units of W/m^2/microns from generated BB sun.
end

if strcmp(AM, '0')
    Spectral_Irradiance=data(1:end,2) * 1000; %in units of W/m^2/microns AM 0
end

if strcmp(AM, '1.5')
    Spectral_Irradiance=data(1:end,3) * 1000; %in units of W/m^2/microns AM 1.5
end

S = trapz( lambda, Spectral_Irradiance )*no_photons; %integrated AM 1.5 in W m^-2, of course

if sidebyside == 0
    if strcmp( top_or_bottom{1,1}, 't') % if top
        % do nothing
    elseif strcmp(top_or_bottom{1,1}, 'b') % if bottom
        % remove lambda corresponding to the top, to account for its
        % complete light absorption
        bg_t_eV = str2num( top_or_bottom{2,2} ); %bg of top light absorber to remove
        bg_t_microns = ( bg_t_eV ./ hc_eV_micron )^(-1); %bg of top in microns
        [aa, idx] = min(abs( lambda - bg_t_microns ));
        lance = length([1:idx]);
        Spectral_Irradiance(1:idx) = zeros( lance,1 );
    end
end

I.s = (Spectral_Irradiance./hc_J_um).*lambda; %This converts from spectral irradiance to photon
% flux... should be ~ 5 * 10^21 photons/(s * micron * m^2) around max

J.e = zeros(length(lambda),1); %preallocate memory

sigma = zeros(length(lambda),1); %preallocate memory

for i=1:length(sigma) %This is a temporary placeholder until we decide to incorporate sigma data
    sigma(i) = 1;
end

for i = 2 : length(J.e)
    J.e(i) = trapz( lambda(1:i) , I.s(1:i) * sigma(i) ); % \int I.s(lambda) * sigma(lambda) d(lambda)
    %This is eqn 1 in Ross 1977.
end
\end{verbatim}

We define the energy yield as being the rate of excitation times the
band-gap energy, \( E = J_e \times \frac{(hc)}{\lambda_0} \)

\[
E = \text{zeros(length(lambda),1)}; \quad \text{%preallocate memory}
\]

\[
\text{for } i = 2: \text{length}(E) \quad \text{end}
\]

\[
E(i) = J_e(i) \times \frac{(hc)_{\text{um}}}{\lambda(i)}; \quad \text{eqn 2 in Ross 1977}
\]

\[
\text{end}
\]

this is also called the total incident solar power.

At this point one may plot the ‘\( E \)’ in Fig. 1 of Ross 1977 by the
following:

\[
\text{Sanity check:}
\]

\[
\text{ylabel(gca, 'Yield (W/m^2)')}
\]

\[
\text{xlabel(gca, 'Band gap (nm)')}
\]

\[
\text{plotyy(lambda*1000, E, lambda*1000, E./S) \quad \text{Y axis 1 is YIELD, 2 is}}
\]

efficiency

%this is also called the total incident solar power.

%At this point one may plot the ‘\( E \)’ in Fig. 1 of Ross 1977 by the
%following:

%Sanity check:

%ylabel(gca, 'Yield (W/m^2)')
%xlabel(gca, 'Band gap (nm)')
%plotyy(lambda*1000, E, lambda*1000, E./S) %Y axis 1 is YIELD, 2 is
efficiency

%this is also called the total incident solar power.

%At this point one may plot the ‘\( E \)’ in Fig. 1 of Ross 1977 by the
%following:

%Sanity check:

%ylabel(gca, 'Yield (W/m^2)')
%xlabel(gca, 'Band gap (nm)')
%plotyy(lambda*1000, E, lambda*1000, E./S) %Y axis 1 is YIELD, 2 is
efficiency

%this is also called the total incident solar power.

%At this point one may plot the ‘\( E \)’ in Fig. 1 of Ross 1977 by the
%following:

%Sanity check:

%ylabel(gca, 'Yield (W/m^2)')
%xlabel(gca, 'Band gap (nm)')
%plotyy(lambda*1000, E, lambda*1000, E./S) %Y axis 1 is YIELD, 2 is
efficiency

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Calculate Y %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Calculate Y %%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Calculate Y %%%%%%%%%%%%%%%%%%%%%%%%%

%disp('Calculating Y')

%Now to calculate the open-circuit yield, \( Y \), which is defined as the
%product of the maximum flux and the maximum potential difference.
%This is defined as \( Y = J_e \) and \( \mu_{\text{max}} \)

%we know \( \mu_{\text{max}} \) is equal to \( kT \times \ln (\text{int } I_s/ \text{int } I_{BB}) \)

%Calculate I BB

I_BB=zeros(length(lambda),1);

\[
\text{for } i=1:length(lambda) \quad \text{end}
\]

\[
I_{BB}(i) = 8 \times \pi \times n_{\text{refractive}}^2 \times c_{\text{m.s}} / \lambda(i).^4 \times (1 / ( \exp(h_{\text{Js}} c_{\text{m.s}}/(k_B \times J \times \lambda(i). \times 10^{(-6)} \times T_{K} ) \times 10^{(-18)}) \times 10^{(-18)}; 
\]

%Now we need to integrate I_BB over d lambda from 0 microns to band gap
%microns to obtain the rate of photons absorbed per area per micron

for i = 2:length(lambda)

clear indexofinterest

[m,indexofinterest] = min(abs(lambda-lambda(i)));

int_I_BB(i) = trapz(lambda(1:indexofinterest), I_BB(1:indexofinterest));
\end

%mu_max calculation

mu_max=zeros(length(lambda),1); %preallocate memory

\[
\text{for } i=1: \text{length}(mu_{\text{max}}) \quad \text{end}
\]

\[
\mu_{\text{max}}(i) = k_B \times J \times T \times \text{K} \times \log(J_e(i)/\text{int } I_{BB}(i)); \quad \text{as defined in eqn 8 of Ross 1977}
\]

%what we do here is take total number of absorbed photons then convert it
%to moles of photons then times by \( \mu_{\text{max}} \) which is in terms of J/mol so
%that we get the total J per micron per unit area

\[
Y = \text{zeros(length(lambda),1)};
\]

%for i = 2:length(lambda)
\[ Y(i) = J_e(i) \times \mu_{\text{max}}(i); \quad \text{eqn 10 Ross 1977} \]

\[
% At this point one may plot the 'Y' and 'E' in Fig. 1 of Ross 1977 by the following:
%ylabel(gca, 'Yield (W/m^2)')
%xlabel(gca, 'Band gap (nm)')
%plotyy(lambda*1000, Y, lambda*1000, Y/S)
%plot(lambda*1000, E, 'displayname', 'E')
%hold on;
%plot(lambda*1000, Y, 'displayname', 'Y')
%%%%%%%%%%%%%%%%%%%%%%%%%%Calculate P %%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%
% disp('Calculating P')

% In order to get the net production of photoproduct, it is necessary to lower the potential difference below mu_max. In most photochemical systems, this is achieved by reducing the fraction of absorber molecules that are in the upper electronic state at any instant. The total power production is \( P = J_e \times (1 - \phi_{\text{loss}}) \mu \)
% where \( \phi_{\text{loss}} \) is the fraction of absorbed quanta that are lost from the excited state without yielding a photoproduct.
%\( \phi_{\text{loss}} \approx kT/\mu_{\text{max}} \)

\([\mu = \text{zeros(length(lambda),1); \% preallocate memory}]
\text{for } i = 1:\text{length(lambda)}
\quad \mu_P(i) = \mu_{\text{max}}(i) - k_B J_K \times T.K \times \log( \mu_{\text{max}}(i)/(k_B J_K \times T.K) ) - k_B J_K \times T.K \times \log(alpha) \; ; \quad \text{eqn 15 Ross 1977}
\text{end}
\]

\([\mathbf{J_r} = \text{zeros(length(lambda),1); \% preallocate memory}]
\text{for } i = 1:\text{length(lambda)}
\quad \mathbf{J_r}(i) = \exp(\mu_P(i)/(k_B J_K \times T.K) \times \text{int}_I_{BB}(i); \quad \text{eqn 3 Ross 1977}
\text{end}
\]

\([\phi_{\text{loss}} = \text{zeros(length(lambda),1); \% preallocate memory}]
\text{for } i = 1:\text{length(lambda)}
\quad \phi_{\text{loss}}(i) = \alpha \times \mathbf{J_r}(i) ./ \mathbf{J_e}(i); \quad \text{eqn 12 Ross 1977}
\text{end}
\]

\([P = \text{zeros(length(lambda),1);}
\text{for } i = 2:\text{length(lambda)}
\quad P(i) = \mathbf{J_e}(i) \times \mu_P(i).*(1 - \phi_{\text{loss}}(i)); \quad \text{eqn 11 Ross 1977}
\text{end}
\]

% sanity check:
\%ylabel(gca, 'Yield (W/m^2)')
\%xlabel(gca, 'Band gap (nm)')
\%plotyy(lambda*1000, Y, lambda*1000, Y/S)
\%plot(lambda*1000, E, 'displayname', 'E')
\%hold on;
\%plot(lambda*1000, Y, 'displayname', 'Y')
\%or as efficiency
% figure('Color', [1 1 1])
% plot(lambda*1000, E./S, 'displayname', 'E', 'LineWidth', 4)
% hold all;
% plot(lambda*1000, Y./S, 'displayname', 'Y', 'LineWidth', 4)
% ylabel(gca, 'Efficiency (%)')
% xlabel(gca, 'Band gap (nm)')
% legend('toggle')
% set(gca, 'FontSize', 33)
% ylim([0 0.5]);
% set(findall(gca,'type','text'),'fontSize',33)
% set(findall(gca,'type','LineWidth'),'LineWidth',4)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%Calculate Jsc %%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%disp('Calculating J_sc')
%the implicit assumption is that J_L and J_sc are equal AND J_L is voltage
%independent.
%The following is for finding the short-circuit current density under E
%conditions and then P conditions
%figure
%hold all;

photon_flux_E=E./hc_J_um .*lambda; %takes spectral irradiance of E and turns it into photoflux
and then we make it into current
for i = 2: length(lambda)
current_E(i) = photon_flux_E(i).*e_C/10.*betal;
end
J_sc = current_E;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%Calculate J_0 %%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%There are two possible ways and switches to reflect these different
%assumptions. The first method does not depend on Ross' method, whilst the
%second method does use Ross' method involving mu. The first method gives
%more realistic/conservative estimates and the second method gives more
%ideal estimates.
%disp('Calculating J_0')

%%%%%%%%%% Conservative estimate mindiosat %%%%%%%%%%%
%the minimum value of the diode saturation current is
%J_0 = q/k ( 15 * SBC / pi^4) * T^3 * int from u to infty x^2/(e^x
%-1) dx
%where u = E_g/kT
%more information on this assumption can be found at Solar Energy Materials
%unfortunately evaluation of this integral is very complex and numerical
%integration may suffer in the lim x--> infty due to build up of errors
%over the course of this improper integral... one could pick infinity to be
%something like 6 eV or put this in terms of the Rieman Zeta
%series for convergence, however, numerically 4 eV is easier, which I have
%defined to be the infinite variable.

infinitesimal= 4; % eV for calculation of J_0 in slow algorithm (disabled now)
%SBC is the Stefan-Boltzman constant or $2 \times \pi^5 \times k_B^4/(15 \times h^3 \times c^2)$

\[ SBC = 2 \times \pi^5 \times k_B^4/(15 \times h \times s^3 \times c \times m^2); \]

%The problem with the algorithm below, while it works and is simple to
%implement or understand, is that it is very slow to converge and takes 2 hrs on my
%processor to process all of lambda. Either I can save it as a text-file and load it on demand or
%utilize a more sophisticated method so that it can change whenever a user
%inputs a different variable.

% for i = 1 : length(lambda)
kB_eV_K = kB_J_K /(1.602176565*10^(-19)); %kB in terms of eV
% 1 electronvolt = 1.602E+19 J
% u = (hc/(lambda(i) * e ))/(kB_eV_K * T); %it's very important kB here is in
% terms of eV/K not J/K, otherwise the math explodes due to incompatible
% units.
% x=[u:1:infinite/kB_eV_K*T];
% J_0(i) = e / kB * (15 * SBC / pi^4) * T^3 * trapz( x ,x.^2./(exp(x) -1 ) );
% disp([num2str(i) ' of ' num2str(length(lambda)) ]);%end
% To check sanity:
% semilogy(hc./(lambda(i) * e), J_0)
% xlabel(gca, 'Band gap (eV)')
% ylabel(gca, 'diode saturation current (A/m^2)') %should show a linear line from ~10^0 down to
% 10^-70 A/m^2 at 4 eV
% the basic problem is to compute the integral \int_x^\infty \frac{t^n}{e^{t} -1} dt
% This integral is not trivial to solve.
% its expansion is:
% \sum_k=1^\infty \exp(-k * x} * [ x^n/k + n * x^{n-1}/k^2 +
% (n)(n-1)x^(n-2)/k^3 + ... + n!/k^{n+1}
% courtesy of Abramowitz and Stegun: Handbook of Mathematical Functions
% our case is n=2.
J_0 = zeros(length(lambda),1);
if strcmp(Voc_approx,'mindiosat') %Voc may be calculated from mu_max or mindiosat
CONST_h=e_C / kB_J_K * (15 * SBC /pi^4) * T_K^3;
%This for loop is merely a finite truncation of the infinite series mentioned above.
for i=1:length(lambda)
  x=(hc_J_um/(lambda(i) * e_C))/(kB_eV_K * T_K);
  M= exp(-k * x) * ( x^2 / 2 + x + 1 /k^2 + 2/k^3 ); % new term
  while M > ( 10^(-100) ) %check if new term is larger than some arb. small value, A test
    for i=1:length(lambda)
      J_0 = CONST_h * J_0_int;
    end
end
%sanity check:
%semilogy(hc./(lambda.*e), J_0)
%xlabel(gca, 'Band gap (eV)') %should show a linear line from -10^0 down to 
%ylabel(gca, 'diode saturation current (A/m^2)') %should show a linear line from ~10^0 down to 
%at Voc we have I, q, Voc, nkt and I_L, all we need to do is rearrange to 
%solve.
%(I+I_L)/((exp(q*V/(nkt)) −1) = I_0

%%%%%%%%%%%%%%%%%% Liberal Estimate Based on mu_max %%%%%%%%%%%%%%%%%%
if strcmp(Voc_approx,'mu_power') %Voc may be calculated from mu_max or mindiosat
   for i = 1:length(lambda)
      J_0(i) = J_sc(i)/ ( ( exp( ( 1 * mu_P(i)/e_C ) / (n_idealityfactor * kB_eV_K * T_K) )−1 )
      *100 );
   end
end
if strcmp(Voc_approx, 'Sze')
   for i = 1:length(lambda)
      bH=hc_J_um./(lambda(i).*e_C); %barrier height (eV)
      J_0(i) = A_mA_cm2_K2 * T_K^2 * exp(− bH / (kB_eV_K * T_K)); %pg 156 of Sze
   end
end
if strcmp(Voc_approx, 'IEEE')
% from http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=01486627
   C=17.90;% mA/cm^2 K^3
   for i = 1:length(lambda)
      E_g = hc_J_um./(lambda(i).*e_C);
      J_0(i) = C * T_K^3 * exp(− E_g / (kB_eV_K * T_K) );
   end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Calculate Voc %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Voc may be determined by either the mindiosat method or the mu_max method.
%One is more conservative/realistic than the other.
%disp('Calculating V_oc')
%given as Voc = (n * k * T/ q) * ln ( I.L/ I.0 + 1)
Voc=zeros(length(lambda),1);
The method below is one method.
if strcmp(Voc_approx,'mindiosat')
   for i = 1:length(lambda)
      Voc(i) = n_idealityfactor * kB_eV_K * T_K/e_C * log( J_sc(i)/J_0(i) + 1);
   end
The method below is another method.

```matlab
if strcmp(Voc_approx, 'mu_power')
    for i = 1:length(lambda)
        Voc(i) = mu_P(i) ./ e_C;
    end
end
```

```matlab
if strcmp(Voc_approx, 'Sze') || strcmp(Voc_approx, 'IEEE')
    for i = 1:length(lambda)
        Voc(i) = n_idealityfactor * kB_J_K * T_K / e_C * log( J_sc(i) / (J_0(i)) + 1);
    end
end
```

% sanity check: Voc
plot(hc_J_um/(lambda.*e_C), Voc)
xlabel(gca, 'Band gap (eV)')
ylabel(gca, 'Voc (Volts)')

unrelated to the methods above are these variables:
V_max_u = max(Voc);
V_max_l = -max(Voc);
V_max_u=Voc(index_of_interest);
V_max_l=-Voc(index_of_interest);

they are used to set bounds on the size of later arrays to aid in speeding up computations.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%Calculate J-V curves %%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```matlab
disp('Calculating J-V curves')
```

% IV curve in the first quadrant is given by:
% I = I_L - I_0 [ exp ( q V/ (n k T) ) - 1 ]

```matlab
Voltage=[V_max_l:stp_size:V_max_u];
V迹age=[V_max_l:stp_size:V_max_u];
J = zeros(1, length(Voltage));
```

% the structure of the following statements may not be very intuitive, but
% it was written this way to increase throughput

```matlab
if strcmp(majority_doping_type, 'p')
    for i = index_of_interest % this is written this way so that we may scan just one lambda of interest or all of them
```
[nn, stopV] = min(abs(Voltage-Voc(i))); %we find the Voc

startV = 1;

for j= startV : stopV %we use startV:stopV to limit the number of calls required
    if ((Voltage(j) < Voc(i) ) && (Voltage(j) > V_max_l ))
        J(1,j) = J_0(i) * ( exp( 1 * Voltage(j) / (n_idealityfactor * kB_eV_K * T_K ) )-1 )+100 - J_sc(i);
        if J(1,j) > 0 %when the exponential takes over we don't really care what those
            currents are and so they are ignored.
            J(1,j) = 0;
        end
    end
end

else
    for i = index_of_interest
        [nn, stopV] = min(abs(Voltage-Voc(i)));%nn, stopV = min(abs(Voltage));
        startV = length(Voltage) - stopV;
        if startV == 0
            startV = 1;
        end
        %for j= startV : stopV
        for j = startV: length(Voltage)
            if ((Voltage(j) < V_max_u) && (Voltage(j) > -Voc(i) ))
                J(1,j) = J_0(i) * -( exp( -1 * Voltage(j) / (n_idealityfactor * kB_eV_K * T_K ) ) -1 )+100 + J_sc(i);
                if J(1,j) < 1
                    J(1,j) = 0;
                end
            end
        end
    end
endif

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%Incorporate Butler-Volmer Curves %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
disp('Calculating B-V')

if majority_doping_type == 'p'
    GibbsIncorp.a = Voltage - a_SEP_V/no_photons; %these are corrections necessary to put all our plots on the same x-axis
    GibbsIncorp.c = Voltage - c_SEP_V/no_photons;
end

% if majority_doping_type == 'n'
    GibbsIncorp.a = Voltage/no_photons + a_SEP_V/no_photons;
    GibbsIncorp.c = Voltage/no_photons + c_SEP_V/no_photons;
end
% calculate BV
% edc_c is the exchange current density for a catalyst
% ctc.a is the charge transfer coefficient for anodic reaction
% ctc.c is the charge transfer coefficient for cathodic reaction
% eta is the activation overpotential

\[ j = edc_c \times \left( \exp \left( \frac{ctc_a \times no_e \times F \times \eta}{RT} \right) - \exp \left( \frac{ctc_c \times no_e \times F \times \eta}{RT} \right) \right); \]

J_{BV \_a} = zeros( length(Voltage), 1);
J_{BV \_c} = zeros( length(Voltage), 1);
if majority_doping_type == 'n'
    for i = 1: length(Voltage)
        J_{BV \_a}(i) = (a_{edc_c} \times mA \_cm2 \times ( \exp( (a_{ctc_a} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) )
        - \exp( -(a_{ctc_c} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) ) ));
        J_{BV \_c}(i) = (c_{edc_c} \times mA \_cm2 \times ( \exp( (c_{ctc_a} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) )
        - \exp( -(c_{ctc_c} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) ) ));
        J(1,i) = -J(1,i);
    end
end
if majority_doping_type == 'p'
    for i = 1: length(Voltage)
        J_{BV \_a}(i) = (a_{edc_c} \times mA \_cm2 \times ( \exp( (a_{ctc_a} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) )
        - \exp( -(a_{ctc_c} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) ) ));
        J_{BV \_c}(i) = (c_{edc_c} \times mA \_cm2 \times ( \exp( (c_{ctc_a} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) )
        - \exp( -(c_{ctc_a} \times no_e \times F \times Voltage(i))/ (R_J \_molK \times T \_K) ) ));
        J(1,i) = J(1,i);
    end
end

% plot(Voltage, J_{BV \_a});
% hold on;
% plot(GibbsIncorp, J)
% ylim([-45 1])
% xlim([-1 0])

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%Calculate Efficiency %%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% an important constraint is that overpotentials should only be calculated
% when the efficiency w/o BV effects incorporated is above 0

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%Single Light Absorber %%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

if num_photoabsorbers == 1
    % this is only necessary for the single photoabsorber carrying out two
    % different half-reactions because there is no graphical solution
    % essentially solve the B-V equation for overpotential at each point
    % along the ideal-diode equation (this is computationally expensive)
    % then make a new B-V corrected diode plot that we can then perform a
    % load-line analysis on

if ( majority_doping_type == 'n' ) % photoanode case

    [a, idx] = min(abs(GibbsIncorp.a));
    [V_M, I_M, Power]=MaxPPT(GibbsIncorp.a(1:idx), J(1:idx));
    % [a, idx] = min(abs(GibbsIncorp.a)); % find V=0 for plot w/o BV

    if abs(V_M*I_M/(S)*1000) > 0.01
        % this saves us time because if w/o BF efficiency is 0, then why
        % calculate an overpotential?
        % Calculate the B-V overpotential at each point along the diode
        % equation
        % We actually want to limit the number of expensive computations
        % we need to do. There are two ways to do this: 1) limit the
        % voltage range of interest 2) stop calculating OP after its
        % change reaches a minima
        % We shall try 2) for the time being. We will look at the OP
        % calculated for the previous value, although recall that that
        % they start as NaN or near 0 for a few values initially, change
        % for a bit and then reach a plateau
        Whereabout = Voc(index_of_interest);
        [aa, V_Start] = min(abs(Voltage+Whereabout));

        Output_a = zeros(1, length(Voltage));
        for i = V_Start : length(Voltage)
            if ( i < V_Start+400 )
                Output_a(i) = OP(majority_doping_type, Voltage(i), J(i), a_ecd_c_mA_cm2, no_e,
                        a_ctc_a, a_ctc_c, F, R_J_molK, T_K, J_0(index_of_interest),
                        n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
            elseif ( i > V_Start+400 ) && ( abs(Output_a(i-2)-Output_a(i-1))/abs(Output_a(i-2))*10^{-2} ) > 10^{-2}
                Output_a(i) = OP(majority_doping_type, Voltage(i), J(i), a_ecd_c_mA_cm2, no_e,
                        a_ctc_a, a_ctc_c, F, R_J_molK, T_K, J_0(index_of_interest),
                        n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
            elseif ( i > V_Start+400 ) && ( abs(Output_a(i-2)-Output_a(i-1))/abs(Output_a(i-2))*10^{-2} ) > 10^{-2}
                Output_a(i) = OP(majority_doping_type, Voltage(i), J(i), a_ecd_c_mA_cm2, no_e,
                        a_ctc_a, a_ctc_c, F, R_J_molK, T_K, J_0(index_of_interest),
                        n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
            else
                Output_a(i) = Output_a(i-1);
            end
            end

        Output_c = zeros(1, length(Voltage));
        for i = V.Start : length(Voltage)
            if ( i < V.Start+400 )
                Output_c(i)=OP( majority_doping_type, Voltage(i), -J(i), c_ecd_c_mA_cm2, no_e,
                        c_ctc_a, c_ctc_c, F, R_J_molK, T_K, J_0(index_of_interest),
                        n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
            elseif ( i > V.Start+400 ) && ( abs(Output_c(i-2)-Output_c(i-1))/abs(Output_c(i-2))*10^{-2} ) > 10^{-2}
                Output_c(i)=OP( majority_doping_type, Voltage(i), -J(i), c_ecd_c_mA_cm2, no_e,
                        c_ctc_a, c_ctc_c, F, R_J_molK, T_K, J_0(index_of_interest),
                        n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
            else
                Output_c(i) = Output_c(i-1);
            end
            end
%sanity check
%plot(GibbsIncorp.a+Output.a+Output.c, -J) %check for photoanode case

display(['Efficiency for band gap (eV): ' num2str(band_gap_eV) ' '])

%w/ BV
[a, idx] = min(abs(GibbsIncorp.a+Output.a+Output.c));
if abs((GibbsIncorp.a(idx)+Output.a(idx)+Output.c(idx))) < 10^(-2) %what if the curve isn't anywhere near 0 or exactly zero? Then check to see if value is above zero. i.e., required an external bias to work, within some error
    OUTPUT_A=abs((a_SEP_V)/no_e * J(1, round(idx)) / (S) *10 * 100));
display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' '])
else %clearly this is for when the curve is shifted to the right (non power producing region for photoanode)
    OUTPUT_A=0;
display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' '])
end

%w/o BV
[a, idx] = min(abs(GibbsIncorp.a));
OUTPUT_B=abs((a_SEP_V)/no_e * J(1, round(idx)) / (S) *10 * 100));
display(['w/o BV Efficiency: ' num2str(OUTPUT_B) ' '])

elseif abs(V_M*I_M/(S)*1000) < 0.01
%this is the no-efficiency case, do not calculate B-V overpotential
    display(['Efficiency for band gap (eV): ' num2str(band_gap_eV) ''])
    display(['w/o BV Efficiency: 0 '])
    OUTPUT_A = 0;
    OUTPUT_B = 0;
else (majority_doping_type == 'p')
    [a, idx] = min(abs(GibbsIncorp.a));
    [V-M, I-M, Power]=MaxPPT(GibbsIncorp.a(1:idx), J(1:idx));

    if abs(V_M*I_M/(S)*1000) > 0.01
        %this saves us time because if w/o BF efficiency is 0, then why calculate an overpotential?
        %Calculate the B-V overpotential at each point along the diode equation
        %we actually want to limit the number of expensive computations we need to do. There are two ways to do this: 1) limit the voltage range of interest 2) stop calculating OP after its change reaches a minima
        %we shall try 2) for the time being. We will look at the OP calculated for the previous value, although recall that that they start as NaN or near 0 for a few values initially, change for a bit and then reach a plateau.
        Output.a = zeros(1, length(Voltage));
        Whereabout = Voc(index_of_interest);
        [aa, V_Start] = min(abs(Voltage-Whereabout));
        for i = V_Start-1: -1: 1 %we do we start by going in reverse? This is because our exit command depends on reaching a plateau, this plateau only happens on the trail toward the end (starting from 1 %-> end wastes our computations and our exit condition isn't compatible
            %
if ( i > (V_Start - 400) )
    Output_a(i) = OP(majority_doping_type, Voltage(i), J(i), a.ecd.c_mA.cm2, no.e 
    , a.ctc.a, a.ctc.c, F, R,J.molK, T,K, J,0(index-of-interest), 
    n.ideal.factor, kb.ev.K, J.sc(index.of.interest) );
elseif ( i < (V_Start - 400) ) && ( abs(Output_a(i+2)-Output_a(i+1))/abs(
    Output_a(i+2))*100 > 10^-2 ) %this implements the 
%test to see if the prev two values for OP changed much, 
%if they do then great calculate new OP
    Output_a(i) = OP(majority_doping_type, Voltage(i), J(i), a.ecd.c_mA.cm2, no.e 
    , a.ctc.a, a.ctc.c, F, R,J.molK, T,K, J,0(index.of-interest), 
    n.ideal.factor, kb.ev.K, J.sc(index.of.interest) );
else %if they do not change much, do not calculate and just 
%use prev. value
    Output_a(i) = Output_a(i+1);
end

Output_c = zeros(1, length(Voltage));
for i = V_Start :-1: 1
    if ( i > (V_Start - 400) )
        Output_c(i)=OP( majority_doping_type, Voltage(i), J(i), c.ecd.c_mA.cm2, no.e, 
        c.ctc.c, c.ctc.a, F, R,J.molK, T,K, J,0(index.of-interest), 
        n.ideal.factor, kb.ev.K, J.sc(index.of.interest) );
        %note the distinct difference here is that the BV transfer 
        %coefficients are reversed
        elseif ( i < ( V_Start - 400 ) ) && ( abs(Output_c(i+2) - Output_c(i+1))/abs(
            Output_c(i+2))*100 > 10^-2 )
            Output_c(i)=OP( majority_doping_type, Voltage(i), J(i), c.ecd.c_mA.cm2, no.e, 
            c.ctc.c, c.ctc.a, F, R,J.molK, T,K, J,0(index.of-interest), 
            n.ideal.factor, kb.ev.K, J.sc(index.of.interest) );
        else 
            Output_c(i) = Output_c(i+1);
        end
    end

%sanity check
% plot(GibbsIncorp_a, -J)
% hold on;
% plot(GibbsIncorp_a-Output_a-Output_c, -J, 'r') %check for photoanode case 
% hold off;
Output_c = flipr(Output_c);
Output.a = flipr(Output.a);
display(['Efficiency for band gap (eV): ' num2str(band_gap_eV) ])

%w/ BV

%GibbsIncorp.a-Output.a
[a, idx] = min(abs(GibbsIncorp_c-Output.a-Output_c));
if abs(( GibbsIncorp.a(idx)-Output.a(idx)-Output_c(idx) )) < 10^-2 %what if the 
    curve isn’t anywhere near 0 or exactly zero? Then check to see if value is above 
    zero. i.e., required an external bias to work, within some error
    OUTPUT_A=abs(( (a_SEP_V - c_SEP_V)/no.e * J(1, round(idx)) / (S) *10 * 100));
    display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])
else %clearly this is for when the curve is shifted to the right (non power producing 
    region for photoanode)
    OUTPUT_A=0;
    display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])
end

%w/o BV
[a, idx] = min(abs(GibbsIncorp_c));
OUTPUT_B=abs(( (a_SEP_V - c_SEP_V)/no.e * J(1, round(idx)) / (S) *10 * 100));
display(['w/o BV Efficiency: ' num2str(OUTPUT_B) ' %'])
elseif abs(V_M*I_M/(S)*1000) < 0.01
    % this is the no-efficiency case, do not calculate B-V
    % overpotential
    display(['Efficiency for band gap (eV): ', num2str(band_gap_eV)])
    display(['w/o BV Efficiency: 0 %'])
    OUTPUT_A = 0;
    OUTPUT_B = 0;
end

end

end

if (num_photoabsorbers == 2)
    % we have the stacked and side-by-side cases to deal with
    if (sidebyside == 1) || (sidebyside == 0)
        % yes, it is side by side
        % remember, in a side-by-side case we save each J-V curve so that it
        % may be loaded for analysis later.
        if (majority_doping_type == 'n')
            % is it the photoanode?
            % compute J-V + OP curve

            % before computing OP, we must ask if that is even necessary?
            % i.e., is the w/o BV > 0 % efficiency
            % [a, idx] = min(abs(GibbsIncorp.a)); % find V=0 for plot w/o BV

            [V_M, I_M, Power]=MaxPPT(GibbsIncorp.a, J);
            [a, idx] = min(abs(GibbsIncorp.a));
            [V_M, I_M, Power]=MaxPPT(GibbsIncorp.a(1:idx) , J(1:idx) );

            % if ( abs(( (a_SEP_V - c_SEP_V)/no_e * J(1, round(idx)) / (S*no_photons) +10 * 100) ) > 0.1 )
            % if abs(V_M*I_M/(S)*1000) > 0.01 % verify we are producing some power

            % this is necessary before OP calc if non-negligible
            % efficiency for w/o BV curve

            % now we have to ask about whether or not we have already
            % reached a plateau in OP
            Output_a = zeros(1, length(Voltage));
            Whereabout = Voc(index_of_interest);
            [aa, V_Start] = min( abs(Voltage+Whereabout) );
            for i = V_Start : length(Voltage)
                if (i < 400+V_Start ) % of course, just compute OP
                    Output_a(i) = OP мajority.doping.type,Voltage(i), -J(i), a.ecd.c.mA.cm2, no.e, a.ctc.a, a.ctc.c, F, R.J.molK, T.K, J.0(index.of.interest),

                end
            end
        end
    end
end
n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );

else if (i > 400+V_Start ) && ( abs(Output_a(i-2)-Output_a(i-1))/abs(Output_a
(1-2))*100 > 10^-2 ) %this implements the
%test to see if the prv two values for OP changed much,
%if they do then great calculate new OP
Output_a(i) = OP(majority_doping_type, Voltage(i), -J(i), a_ecd_c_mA.cm2,
no.e, a_ctc_a, a_ctc_c, F, R.IO.molK, T.K, J.0(index_of_interest),
n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );

else %if they do not change much, do not calculate and just
%use prv. value
Output_a(i) = Output_a(i-1);
end

end

display(['Photoanode Efficiency for band gap (eV): ' num2str(band_gap_eV) ])
%w/ BV
% [a, idx] = min(abs(GibbsIncorp_a+Output_a));
%[V_M, I_M, Power] = MaxPPT(GibbsIncorp_a+Output_a, J);
% [a, idx] = min(abs(GibbsIncorp_a+Output_a));
[V_M, I_M, Power] = MaxPPT(GibbsIncorp_a(1:idx) + Output_a(1:idx), J(1:idx));

if abs(( GibbsIncorp_a(idx)+Output_a(idx) )) < 10^-2 %what if the curve isn't
% anywhere near 0 or exactly zero? Then check to see if value is above zero. i
% .e., required an external bias to work, within some error
OUTPUT_A=abs(( V_M(end) * I_M(end)/ (S)*1000));
display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])

else %clearly this is for when the curve is shifted to the right (non power
% producing region for photoanode)
OUTPUT_A=0;
display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])
end

%w/o BV
% [V_M, I_M, Power] = MaxPPT(GibbsIncorp.a);
% [a, idx] = min(abs(GibbsIncorp.a));
[V_M, I_M, Power] = MaxPPT(GibbsIncorp.a(1:idx), J(1:idx) );

OUTPUT_B=abs(( (V_M(end) * I_M(end) / (S)*1000)));
display(['w/o BV Efficiency: ' num2str(OUTPUT_B) ' %'])

elseif (( V.M(end) * I.M(end)/ (S)*1000) < 0.01 )
% %this is the no-efficiency case
% display(['Photoanode Efficiency for band gap (eV): ' num2str(band_gap_eV) ])
% display(['w/o BV Efficiency: 0 %'])
% OUTPUT_A = 0;
% OUTPUT_B = 0;
% Output_a = zeros(1, length(Voltage));
% end

elseif (majority_doping_type == 'p')
%is it the photocathode?
%before computing OP, we must ask if that is even necessary?
% .e., is the w/o BV > 0 % efficiency
[a, idx] = min(abs(GibbsIncorp.c)); %find V=0 for plot w/o BV
[V_M, I_M, Power]=MaxPPT(GibbsIncorp.c(idx:end), J(idx:end) );
%
if ( abs((V_M(1) * I_M(1) / (S)*1000)) > 0.01 )
%this is necessary before OP calc if non-negligible
%efficiency for w/o BV curve

%now we have to ask about whether or not we have already
reached a plateau in OP
Output_c = zeros(1, length(Voltage));
Whereabout = Voc(index_of_interest);
[aa, V_Start] = min( abs(Voltage-Whereabout) );

for i = V_Start : -1 : 1
   Output_c(i)=OP( majority_doping_type, Voltage(i), J(i), c_ecd_c_mA_cm2,
      no_e, c_ctc.a, c_ctc.c, F, R_1.mo1K, T_K, J_0(index_of_interest),
      n_idealityfactor, kB_eV_K, J_sc(index_of_interest) );
   elseif (i < (V_Start - 400)) && ( abs(Output_c(i+2)-Output_c(i+1)))/abs(Output_c(i+2))*10^(-2) > 10^(-2) %this implements the
test to see if the prv two values for OP changed much,
%if they do then great calculate new OP
Output_c(i)=OP( majority.doping.type, Voltage(i), J(i), c_ecd_c_mA_cm2,
      no_e, c_ctc.a, c_ctc.c, F, R_1.mo1K, T_K, J_0(index.of.interest),
      n_idealityfactor, kB.eV.K, J_sc(index.of.interest) );
   else %if they do not change much, do not calculate and just
%use prv. values
   Output_c(i) = Output_c(i+1);
end

Output_c = fliplr(Output_c);

display(['Photocathode Efficiency for band gap (eV): ' num2str(band_gap_eV) ' '])
%w/ BV
[a, idx] = min(abs(GibbsIncorp.c-Output.c));
[V_M, I_M, Power]=MaxPPT(GibbsIncorp.c(idx:end)-Output.c(idx:end), J(idx:end) );

if abs((GibbsIncorp.c(idx)-Output.c(idx ))) < 10^(-2) %what if the curve isn't
   anywhere near 0 or exactly zero? Then check to see if value is above zero. i.e.,
   required an external bias to work, within some error
   OUTPUT_A=abs((V_M(1) * I_M(1) / (S)*1000 ));
   display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])
else %clearly this is for when the curve is shifted to the right (non power
   producing region for photoanode)
   OUTPUT_A=0;
   display(['w/ BV Efficiency: ' num2str(OUTPUT_A) ' %'])
end

%w/o BV
[a, idx] = min(abs(GibbsIncorp.c));
[V_M, I_M, Power]=MaxPPT(GibbsIncorp.c(idx:end), J(idx:end) );

OUTPUT_B=abs(( V.M(1) * I.M(1) / (S)*1000 ));
display(['w/o BV Efficiency: ' num2str(OUTPUT_B) ' %'])

%this is the no-efficiency case

display(['Photocathode Efficiency for band gap (eV): ' num2str(band_gap_eV)])
display(['w/o BV Efficiency: 0 %'])
OUTPUT_A = 0;
OUTPUT_B = 0;
Output.c = zeros(1, length(Voltage));

%output
%output parms

if (majority_doping_type == 'n')
    varargout{1} = GibbsIncorp.a;
    varargout{2} = Output.a;
    varargout{3} = J;
    varargout{4} = a_SEP_V;
    varargout{5} = c_SEP_V;
    varargout{6} = S;
elseif (majority_doping_type == 'p')
    varargout{1} = GibbsIncorp.c;
    varargout{2} = Output.c;
    varargout{3} = J;
end

%compute J-V curve + OP curve
%save to file

function Overpotential=OP(majority_doping_type, V, J, ecd_c, no_e, ctc_a, ctc_c, F, R, T, J_0, n_idealityfactor, kB_eV_K, J_sc)

%now the current densities must be matched up to allow incorporation of
%Butler-Volmer eqn.
%this will go through each point from the diode eqn and find the
%relevant current density from the BV.
%will generate new voltage that takes into overpotential from BV then plot
%diode currents on top of that range.
%we have some J(i,j) and we need to solve the Butler-Volmer eqn
%for that current and obtain the overpotential

%B-V is of the form A = B * ( exp(C * x) - exp(-D * x) )
%there is no closed form solution for x given A,B,C,D
%can numerically calculate answer using Newton-Raphson Method
%where x_(n+1) = x.n - f(x,n)/f'(x.n)
f(x) = B * ( exp(C*x) - exp(-D*x ) )
% f'(x) = B \times ( C \times \exp(C \times x) + D \times \exp(-D \times x) ) 

% FYI:
% f(x) in terms of our equation is
% f(x) = \frac{ecd_c}{(ctc_a \times no_e \times F/(R \times T))} \times \left( \exp\left( \frac{ctc_a \times no_e \times F \times Voltage(j)}{R \times T} \right) - \exp\left( -\frac{ctc_c \times no_e \times F \times Voltage(j)}{R \times T} \right) \right);

B = ecd_c;
C = ctc_a \times no_e \times F/(R \times T);
D = ctc_c \times no_e \times F/(R \times T);

% what is x_0?
% answer: a first estimate.
% assume both C and D are equal:
% then the answer is given by
% x_0 = \left( \frac{R \times T}{ctc_a \times no_e \times F} \right) \times \sinh\left( \frac{J(i,j)}{2 \times ecd_c} \right)^{-1};

% f(i,j) = B \times \left( \exp(C \times x_0) - \exp(-D \times x_0) \right) - J(i,j); % why - J(i,j)? Remember N-R Method only works for finding r when f(r) = 0
% f_x(i,j) = B \times \left( C \times \exp(C \times x_0) + D \times \exp(-D \times x_0) \right);
% the problem with the method just mentioned is that sinh explodes
% very quickly, therefore very high numerical precision is required
% hand therefore a better method must be sought.
% alternatively we can assume that | overpotential | > 118 mV/no_e
% in which case overpotential = -RT/
% (alpha_c \times no_e \times F) \times \ln \left( \frac{-j/j_0,cat}{} \right)

x_0 = \text{real}\left( \left( \frac{R \times T}{ctc_a \times no_e \times F} \right) \times \log\left( \frac{-j}{ecd_c} \right) \right); %initial guess

% if isinf(x_0)
% x_0=0;
% end
% options=optimset('TolX', 1*10^{-1});
% Overpotential(i,j) = fzero( f_, x_0, options);
% waitbar(j/ length(Voltage) )
% elseif isinf(x_0) %x_0 will equal zero when J=0 because log(J) is in approximation

if majority_doping_type == 'n'
    G_=@(x)J_0+(exp(-V/(n_idealityfactor \times kB.eV.K \times T)) - 1)*100+ J_sc - B*(exp(C*x) - exp(-D*x));
elseif majority_doping_type == 'p'
    G_=@(x)J_0*(exp(V/(n_idealityfactor \times kB.eV.K \times T)) - 1)*100- J_sc + B*(exp(C*x) - exp(-D*x));
end
options=optimset('MaxFunEvals', 10^6,'Diagonals','off','Display','off');
[Overpotential, fval, exitflag]=fsolve(G_, x_0, options);
elseif isinf(x_0)
    Overpotential = 0;
end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%% Max Power Point %%%%%%%
function [MaxPPT_V, MaxPPT_J, Power]=MaxPPT(V, J)

    Power = zeros(1, length(V));
    for i = 1 : length(V)
        Power(i) = abs( V(i) * J(i));
    end
    [MaxPPT_J, idx] = max(Power);
    MaxPPT_V = V(idx);
end
Appendix B

Supplementary Information for Highly Active Electrocatalysis of the Hydrogen-Evolution by Cobalt Phosphide Nanoparticles


B.1 Materials and Methods

Chemicals and Materials

Octacarbonyl dicobalt [stabilized with 1-5 % hexane, Co₂(CO)₈], oleic acid [tech. 90 %, C₁₈H₃₄O₂], and nonanoic acid [97 %, C₉H₁₈O₂] (Alfa-Aesar), as well as 1-octadecene [tech. 90 %, C₁₈H₃₆], oleylamine [tech. 70 %, C₁₈H₃₇N], trioctylphosphine [97 %, (C₈H₁₇)₃P], titanium foil [99.7 %, 0.25 mm thickness], and sulfuric acid [99.999 %] (Sigma-Aldrich) were used as received. Ag paint was purchased from SPI supplies, and two-part epoxy [HYSOL 9460] was purchased from McMaster-Carr.

Synthesis of ε-Co nanoparticles

Using an adaptation of a previously reported protocol,¹ 1-octadecene (10 mL, 31.3 mmol), oleylamine (6 mL, 18.2 mmol), and nonanoic acid (2 mL, 11.3 mmol) were added to a 100 mL three-necked round bottom flask containing a polytetrafluoroethylene-coated magnetic stir bar. The flask was then placed in a heating mantle. A thermometer adapter, thermometer, Liebig condenser, and rubber septum were also connected to the flask. The reaction mixture was vigorously stirred and heated to 120 °C for 1 h under vacuum, to remove residual low-boiling solvents, including water. Following degassing, the mixture was heated to 230 °C under Ar. Meanwhile, in an Ar-filled septum-capped vial, octacarbonyl dicobalt (100 mg, 0.29 mmol) was suspended in 1-octadecene (4.5 mL, 14.1 mmol). Following solvation via sonication, the cobalt solution was slowly injected into the reaction flask. After injection of the Co solution, the reaction was held at ≈230 °C for 10 min, followed by rapid injection of degassed oleic acid (2 mL, 6.3 mmol). The reaction was maintained at ≈230 °C for 10 additional min until the contents were allowed to cool by removal of the heating mantle. The resulting cobalt nanoparticle sample was cleaned by adding isopropyl alcohol to the reaction mixture, followed by
centrifugation at 9000 rpm for 5 min. Following centrifugation, the precipitate was resuspended in hexanes, followed by addition of isopropyl alcohol and subsequent centrifugation. The resulting pellet was suspended in hexanes, for characterization purposes, or was suspended trioctylphosphine, for conversion to CoP.

**Synthesis of CoP hollow nanoparticles**

1-octadecene (5 mL, 15.7 mmol), oleylamine (5 mL, 15.2 mmol), and trioctylphosphine (5 mL, 11.2 mmol) were added to a 100 mL three-necked round-bottom flask that contained a borosilicate stir bar. The flask was also equipped with a thermometer adapter, thermometer, Liebig condenser, and rubber septum and placed in a heating mantle. The reaction mixture was degassed at 120 °C for 1 h under vacuum to remove water and other low boiling impurities from the system. The reaction mixture was then heated to ≈320 °C, and allowed to equilibrate for 10 min. Following temperature equilibration, a pre-made suspension of cobalt nanoparticles in degassed trioctylphosphine (2 mL, 4.5 mmol) was slowly injected into the reaction mixture. The resulting mixture was held at 320 °C for 1 h. The reaction mixture was allowed to cool to room temperature by removal of the heating mantle. The resulting CoP nanoparticles were cleaned by addition of the isopropyl alcohol to the reaction mixture. Precipitation of the CoP nanoparticles was performed via centrifugation at 9000 rpm for 5 min. The precipitate was resuspended using hexanes, followed by ethanol to promote flocculation and then centrifugation. This process was then repeated, and for later use the resulting CoP nanoparticles were suspended in hexanes.

**Preparation of Working Electrodes**

To make working electrodes, a stock solution of CoP nanoparticles at 5 mg mL⁻¹ in hexanes was prepared. In 5-10 µL increments, 36 µL of the nanoparticle stock solution was deposited onto 0.2 cm² samples of Ti foil to achieve 0.9 mg/cm² mass loading, or 80 µL was deposited to achieve the 2 mg/cm² mass loading. Following deposition of CoP and drying, the CoP-coated Ti foils were annealed at 450 °C under 5 % H₂/Ar (Air Liquide). The foils were affixed with Ag paint to a polyvinylchloride-coated copper wire that had been threaded through a 6 mm diameter glass capillary. Two-part epoxy was used to cover all surfaces except the CoP-coated side of the Ti electrode.
**Electrochemical Measurements**

All electrochemical measurements were obtained using a Gamry Instruments Reference 600 potentiostat. All measurements were performed in high-purity 0.50 M sulfuric acid, unless otherwise noted. Data were collected using a three-electrode single-compartment cell that contained a mercury/mercury sulfate (Hg/Hg2SO4) reference electrode and a graphite rod counter electrode.

Polarization data were collected at a sweep rate of 5 mV s\(^{-1}\), and rapid stirring from a magnetic stir bar was used to agitate the solution. The current-interrupt method was used to account for any uncompensated resistance (R = 2 ohms, leading to an \(iR\) correction of about 8 mV at 20 mg/cm\(^2\)). Constant bubbling of research-grade H\(_2\) at \(\approx 1\) atm was used to maintain a constant potential for the RHE, with the RHE potential determined by measuring the open-circuit potential of a platinum electrode that was tested following investigation of the behavior of the CoP nanoparticle-coated electrode. Short-term electrochemical stability was measured without correcting for uncompensated resistance by galvanostatically maintaining for 24 h a current density of \(-20\) mg/cm\(^2\). Long-term electrochemical stability measurements were performed by cyclic voltammetric cycling from +0.005 V to –0.140 V without accounting for any uncompensated resistance.

**Quantitative Hydrogen Yield Measurements**

Quantitative measurements of the faradaic H\(_2\) yield were performed in 0.50 M sulfuric acid using a two-electrode cell which had two compartments that were separated by a Nafion membrane (Fuelcellstore.com). The working electrode and counter electrode were identical to those used in the three-electrode measurements described above. An inverted solution-containing graduated cylinder was positioned around the working electrode, and collected the volume of H\(_2\) that was produced by a constant cathodic current density of 20 mA/cm\(^2\) on an electrode having a projected area of 0.2 cm\(^2\). This current density was maintained for 6.94 h, after which the volume of H\(_2\) was recorded and compared to the ideal gas volume expected from the total faradaic charge passed in conjunction with the ideal gas law.

**Materials Characterization**

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker-AXS D8 Advance diffractometer with Cu K\(\alpha\) radiation and a LynxEye 1-D detector operating at room temperature. The CrystalMaker/Crystal Diffract software package was used to simulate the XRD patterns, using published crystallographic parameters for
Transmission electron microscopy (TEM) images were collected using a Phillips 420 microscope operating at an accelerating voltage of 120 kV. A JEOL EM-2010F was used to collect high-resolution bright-field TEM images as well as to obtain energy dispersive X-ray spectroscopy (EDX) measurements at an accelerating voltage of 200 kV. Gatan Digital Micrograph(TM) software was used to measure the lattice spacings from the fast-Fourier transform (FFT) of the HRTEM images. These values, and the corresponding FFT diffraction pattern, were compared to single-crystal diffraction patterns simulated using the CrystalMaker/Single Crystal software. Brunauer-Emmett-Teller (BET) surface area measurements were performed using a Micromeretics ASAP 2020 at liquid nitrogen temperatures, and the data were analyzed using the ASAP 2020 software version 4.0. X-ray photoelectron spectroscopy was performed using a Kratos Ultra XPS with a delay-line detector and a resolution of 0.27 eV as determined by the full-width at half-maximum of the Ag 3d peak on a calibration sample.

Estimation of turnover frequencies

To calculate the turnover frequency (TOF), the density of the sample was first calculated using the CoP unit cell, via the CrystalMaker software suite. Theoretical surface areas were estimated using 13 nm spherical, solid CoP nanoparticles. The measured BET surface areas were used as the “actual” surface area values in the calculations. As was done for Ni$_2$P and Ni–Mo$_3$, the turnover frequencies are reported as turnovers per second per surface atom. Co and P surface atoms were counted separately, as opposed to per hydrogen binding site. An example of the procedure used to perform these calculations is provided below:

The molar mass (89.907 g mol$^{-1}$), density (6.416 g/cm$^3$), molar volume (14.01 mL mol$^{-1}$), volume of a 13 nm sphere (1.15 $\times$ 10$^{-18}$ cm$^3$), surface area of a 13 nm sphere (5.31 $\times$ 10$^{-12}$ cm$^2$), and current density at $\eta = -100$ mV (for 0.032 mg/cm$^2$ $\eta = -5.04$ $\times$ 10$^{-4}$ A/cm$^2$, for 0.9 mg/cm$^2$ $\eta = -2.53$ $\times$ 10$^{-2}$ A/cm$^2$, and for 2.02 mg/cm$^2$ $\eta = -4.30$ $\times$ 10$^{-2}$ A/cm$^2$). The surface area per gram of a 13 nm sphere (BET value = 595 cm$^2$/g) is calculated as:

$$\frac{5.31 \times 10^{-12} \text{ cm}^2}{1 \text{ particle}} \times \frac{1 \text{ particle}}{1.15 \times 10^{-18} \text{ cm}^3} \times \frac{1 \text{ cm}^3}{6.416 \text{ g}} = 719 \text{ cm}^2/\text{mg}.$$

The average surface atoms per 1 square centimeter (used for BET-based calculations
also) is found by:

\[
\left( \frac{2 \times 6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{14.0 \text{ cm}^3} \right)^{2/3} = 2.45 \times 10^{15} \text{ atoms/cm}^2.
\]

Using the surface atoms per tested area at 0.9 mg/cm\(^2\) (BET value = 1.31 \times 10^{18} \text{ atoms/foil}): 

\[
\frac{0.9 \text{ mg}}{1 \text{ cm}^2} \times \frac{7.19 \times 10^2 \text{ cm}^2}{\text{mg}} \times \frac{2.45 \times 10^{15} \text{ atoms}}{1 \text{ cm}^2} = 1.65 \times 10^{18} \text{ atoms/test}.
\]

Values calculated for the 0.032 mg/cm\(^2\) loading for theory is 5.65 \times 10^{16} \text{ atoms/foil} and a BET value of 4.67 \times 10^{16} \text{ atoms/foil}. At 2.02 mg/cm\(^2\) loading the values for theory give 3.57 \times 10^{18} \text{ atoms/foil} with a BET value of 2.95 \times 10^{18} \text{ atoms/foil}.

Finally, the turnover frequency at 100 mV overpotential is calculated (per surface atom) as:

\[
\frac{1 \text{ turnover}}{2e^-} \times \frac{2.53 \times 10^{-2} \text{ A}}{1 \text{ cm}^2} \times \frac{1 \text{ mol}}{96,485 \text{ C}} \times \frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol}} \times \frac{1 \text{ text}}{1.65 \times 10^{18} \text{ atoms}} = 0.048 \text{s}^{-1} \text{atom}^{-1}.
\]

For 0.032 mg/cm\(^2\), the theoretical value gives 0.028 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.034 s\(^{-1}\) atom\(^{-1}\). For 0.9 mg/cm\(^2\), the theoretical value gives 0.048 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.060 s\(^{-1}\) atom\(^{-1}\). For 2.02 mg/cm\(^2\), the theoretical value gives 0.038 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.045 s\(^{-1}\) atom\(^{-1}\).

**B.2 Supporting Data**

![TEM and powder XRD data for \(\epsilon\)-Co nanoparticles.](image.png)

Figure B.1: TEM and powder XRD data for \(\epsilon\)-Co nanoparticles.
Figure B.2: EDS data for CoP nanoparticles. The Cu is from the TEM grid and the Si is present in the background samples, originating from the column.

Figure B.3: XPS data for a CoP/Ti electrode: (top) survey scans showing spectra obtained pre-anneal, post-anneal, and after electrolysis (inset: enlarged C 1s region pre-anneal and post-anneal) and (bottom) high-resolution scan of the Co 2p region, also showing spectra obtained pre-anneal, post-anneal, and after electrolysis.

B.3 References


Appendix C

Supplementary Information for Comparison of the Performance of CoP-Coated and Pt-Coated Radial Junction n⁺p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water to H₂(g)


C.1 Methods

Electrode Preparation

Reactive ion etching of Si(100) substrate (B-doped, resistivity of 14.6 ohm-cm) was used to form 4 µm diameter Si microwires (MWs) at an 11 µm pitch, with the wires being 50 µm in length. Radial n⁺ junctions on the p-Si microwires were formed by vapor-phase P diffusion from phosphoryl chloride (POCl₃) at 900 °C. Ohmic contacts to the back of the Si(100) substrates were made by electron-beam evaporation of 150 nm of Al, followed by a 5 min anneal at 800 °C under forming gas (5 % H₂(g) in N₂(g)). The Si MW arrays were etched for 10 s in 0.5 M HF(aq) (Transene, Inc.) and were dried under a stream of Ar(g). Centrifugation was then promptly performed in 25 mL falcon tubes in a swinging-head centrifuge, with the tubes filled with ≈ 15 mL of polydimethylsiloxane (PDMS, Dupont). The PDMS was cured overnight while centrifuging at 3000 rpm. Si MW arrays were then loaded into the bottom of the falcon tubes and centrifugation of the particles was performed at 3000 rpm with a suspension of the CoP nanoparticles (0.2 mg mL⁻¹) in hexane for 5 min (the suspension was sonicated immediately prior to application of 15 µL for a 0.1 cm² sample). A Cahn microbalance was used to determine the geometric mass loading (mg/cm²) by weighing samples before and after deposition of particles. After deposition of the particles, the catalyst was activated by annealing at 450 °C for 30 min under forming gas. Ga-In eutectic was scratched onto the back side of the wire arrays, and Ag paint (SPI) was then applied to the back side of the arrays. A Cu wire was affixed to the array using Ag paint. The Cu wire was then threaded through a glass tube. Hysol 9460 epoxy was used to adhere the glass tube
to the back side of the electrode and to seal the back and sides of the electrode. The epoxy was cured overnight. Synthesis of Pt nanoparticles: A solution of 0.10 mM H$_2$PtCl$_6$ (Sigma, ACS Reagent), 0.10 mM sodium polyacrylate ($M_w$ 2100, Aldrich), and 0.50 mM ascorbic acid (Sigma, ACS Reagent) was prepared in 250 mL of degassed, deionized H$_2$O with a resistivity of $\approx$ 18.2 M$\Omega$ – cm obtained from a Barnsted Nanopure column. The solution was stirred for 1 h under N$_2$(g), prior to cooling overnight with the subsequent addition of 2.0 g of NaOH. The suspension was left overnight, centrifuged, and then washed with deionized H$_2$O three times before suspending the particles in isopropanol. Synthesis of CoP nanoparticles: synthesized and characterized as previously reported.$^1$

**Electrochemical Measurements**

Photoelectrochemical measurements were performed in 0.50 M H$_2$SO$_4$(aq). Experiments were performed in a Pyrex electrochemical cell in a conventional three-electrode configuration, with a Ag/AgCl reference electrode (BASi) in saturated KCl(aq) and a high-purity carbon cloth counter electrode (FuelCellStore). During a typical acquisition with a Gamry Reference 600 potentiostat, H$_2$(g) was constantly purged into the solution (except for the H$_2$ determination case), to maintain a constant, reversible (H$^+$/H$_2$) Nernstian potential in the solution. The solution was rapidly stirred with a magnetic stir bar, to minimize mass-transport limitations and to minimize any effects due to bubble formation. Potentially detrimental oxidative processes were minimized by limiting the scans to potentials that were negative of the open-circuit potential. The cell was illuminated with an ELH-type W-halogen lamp equipped with a dichroic rear reflector. The light intensity was calibrated using a Si photodiode (Thorlabs UDT UV-005) that had been mounted in the same orientation as the Si working electrodes. The Si photodiode was calibrated, in turn, against a NIST-traceable secondary standard Si cell that had been calibrated and produced a specified short-circuit current density under 100 mW/cm$^2$ of illumination by Air Mass 1.5 G sunlight. Prior to data collection, trace metal impurities were removed by soaking the cell overnight in aqua regia, then thoroughly rinsing the cell with 18 M$\Omega$ – cm resistivity H$_2$O. After each set of experiments, a Pt electrode was used to determine the reversible hydrogen potential, and thereby to calibrate the reference electrode. We have not extended the measurement time nor have we compared the stability of the Si/Pt system to that of the Si/CoP system for extended time periods.
Spectral Response
Photoelectrochemical spectral response measurements were performed using illumination from a 150 W Xe lamp that was passed through an Oriel monochromator (0.50 mm slits), then chopped at 30 Hz, and focused to a beam spot that illuminated a portion of the electrode area in solution. A calibrated Si photodiode (Thorlabs UDT UV-050) was used to measure the light intensity incident on the electrode. Another Si photodiode was used to measure the beam-split portion of the illumination, with this Si photodiode providing a continuous calibration of the light intensity from the monochromator. A Gamry G 300 potentiostat was used to maintain the potential of the Si working electrode at $-0.20 \, V \text{ vs RHE}$ and to record the current produced by the sample. The signal components were measured by use of independent lock-in detection of the sample channel and the calibration channel.

Characterization
Scanning-electron microscopy (SEM) was performed using a Phenom Pro (Phenom World) electron microscope. The substrate was affixed to the sample chuck using Cu tape. A FEI model TF30ST transmission-electron microscope with 300 kV field emission, equipped with a HAADF STEM detector and a CCD camera, was used to image Pt nanoparticles that were dispersed on a copper mesh supported by a Cu grid. Although the images in Figure 4.1 are displayed with different tilt angles for convenience of viewing, when these images were loaded into software such as ImageJ, with the appropriate calibration indicated by the scale bar, the diameters and lengths of the wires were found to be the same in all three cases. The CoP nanoparticles were monodisperse (Figure C.2), whereas the Pt nanoparticles (Figure C.1) were dispersed in a carbonaceous conductive matrix that may more readily adhere to a hydrophobic Si–H surface than the CoP. These factors may contribute to the differences in the distributions of the Pt and CoP nanoparticle on the MW arrays (Figure 4.1).

In some cases, i.e. with a highly resistive radial emitter or with no emitter present, a more uniform distribution of catalyst on the tops, sides, and bottoms of the wire arrays would be more optimal than deposition only at the bottoms of the wire arrays as described herein. Electrodeposition could be used to obtain a more uniform placement of the electrocatalyst onto microwire arrays.²

H₂ Faradaic Yield
H₂(g) generation was determined by quantitative volumetric collection of the gas
evolved in the catholyte chamber in a two-electrode setup consisting of an H-tube made from volumetric burets. The gas formed at the cathode was collected after passage of \(-100 ^\circ\text{C}\) with the electrode held at a current density of \(-10 \text{ mA/cm}^2\). The electrode area was 0.050 cm\(^2\). The volume of the collected gas was in excellent agreement with the amount of H\(_2\)(g) expected assuming 100 % Faradaic efficiency for H\(_2\)(g) production. The counter electrode was an IrO\(_x\)-coated Ti wire.

**Calculation of Photocathode Efficiency**

The ideal regenerative-cell efficiency was calculated by using the measured three-electrode characteristics of the photoelectrode in conjunction with an ideally non-polarizable counterelectrode operating at the Nernstian potential E(O\(_2\)/H\(_2\)O). As such, \(\eta_{IRC} = \frac{ff \cdot V_{oc} \cdot J_{sc}}{P_{in}}\), where \(P_{in}\) is the input solar power, \(V_{oc}\) is the difference between the open-circuit potential and \(E(O_2/H_2O)\), \(J_{sc}\) is the current density observed at \(E(O_2/H_2O)\), and the fill factor is calculated as fractional maximum power with respect to the quantity \(V_{oc} \cdot J_{sc}\).

**Comparison Between Calculated Resistance and Measured Series Resistance**

The sheet resistance of 100 \(\Omega \ \square^{-1}\) for a 100 nm (\(t\)) thick emitter yields a calculated resistivity of 0.001 \(\Omega \ \text{cm}\) (\(\rho\)). The resistance for a single wire of radius 2 \(\mu\)m (\(r\)) along the radial emitter on a 50 \(\mu\)m (\(L\)) tall wire is 398 \(\Omega\) (\(R_{\text{wire}} = \frac{\rho L}{2\pi rt}\)). For an entire wire array, the total resistance decreases by the number of parallel resistors (\(R_{\text{array}} = \frac{R_{\text{wire}}}{N_{\text{wires}}}\)). A 0.1 cm\(^2\) geometric array on an 11 \(\mu\)m pitch (8.26 \(\times\) \(10^5\) wire cm\(^{-2}\)) therefore produces a total calculated emitter-based resistance of 0.0048 \(\Omega\).

The measured series resistance was determined by the measurement of the area \((A = \int_{0}^{J_{sc}} V \, dJ)\) under the \(J-E\) data,\(^3\) yielding \((R_{S,J} = 2(V_{oc} - \frac{A}{J_{sc}^2} - \frac{n k_B T}{q} \times \frac{1}{J_{sc}}))\) a value of 285 \(\Omega\).

C.2 **Supplementary Data**
Figure C.1: Transmission-electron micrographs of ≈ 3 nm mean diameter crystalline Pt nanoparticles, with diameters ranging from 1 to 8 nm. The scale bar on the left image is 2 nm, whereas the bar on the right indicates 10 nm.

Figure C.2: Powder x-ray diffraction (left) and transmission-electron micrograph (right) of ≈ 13 nm diameter crystalline CoP nanoparticles. The scale bar indicates 100 nm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (mg/cm²)</th>
<th>$J_{ph}$ (mA/cm²)</th>
<th>ff</th>
<th>$V_{oc}$ (V vs. RHE)</th>
<th>Illumination (mW/cm²)</th>
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<tbody>
<tr>
<td>Bare (planar)</td>
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<td>-</td>
<td>0.44</td>
<td>100</td>
</tr>
<tr>
<td>Pt (planar)</td>
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<td>0.40</td>
<td>0.43</td>
<td>100</td>
</tr>
<tr>
<td>Pt (planar)</td>
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<td>0.49</td>
<td>0.48</td>
<td>100</td>
</tr>
<tr>
<td>Pt (MW)</td>
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<td>0.37</td>
<td>30</td>
</tr>
<tr>
<td>Pt (MW)</td>
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<td>0.46</td>
<td>0.44</td>
<td>100</td>
</tr>
<tr>
<td>Pt (MW)</td>
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<td>0.43</td>
<td>0.46</td>
<td>330</td>
</tr>
<tr>
<td>CoP (planar)</td>
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<td>28</td>
<td>0.15</td>
<td>0.41</td>
<td>100</td>
</tr>
<tr>
<td>CoP (planar)</td>
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<td>12</td>
<td>0.52</td>
<td>0.49</td>
<td>100</td>
</tr>
<tr>
<td>CoP (planar)</td>
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<td>0.54</td>
<td>0.29</td>
<td>100</td>
</tr>
<tr>
<td>CoP (MW)</td>
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<td>0.35</td>
<td>0.45</td>
<td>30</td>
</tr>
<tr>
<td>CoP (MW)</td>
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<td>17</td>
<td>0.24</td>
<td>0.48</td>
<td>100</td>
</tr>
<tr>
<td>CoP (MW)</td>
<td>2.0</td>
<td>21</td>
<td>0.23</td>
<td>0.52</td>
<td>330</td>
</tr>
</tbody>
</table>

Table C.1: $J–E$ parameters for n$^+$p-Si planar and microwire photocathodes.
Figure C.3: Spectral response for bare (top), Pt-coated (middle), and CoP-coated (bottom) n⁺p Si MW arrays in contact with H₂(g)-saturated 0.50 M H₂SO₄. The data points that were acquired near complex Xe arc-lamp spectral features were omitted due to artifacts.

Figure C.4: Dependence of photocurrent on the angle of illumination. The blue data were obtained using a CoP-coated planar n⁺p Si photocathode (0.050 mg/cm² mass loading), whereas the red data were obtained using a CoP-coated n⁺p Si microwire-array photocathode (2.0 mg/cm² mass loading), both at 1 Sun of simulated AM1.5G solar illumination in 0.50 M H₂SO₄.
C.3 References


Appendix D

Supplementary Information for Lightly Fluorinated Graphene as a Protective Layer for n-Type Si(111) Photoanodes in Aqueous Electrolytes


D.1 Methods

Materials

Single-crystalline, Czochralski grown, (111)-oriented, planar, 380 µm thick, phosphorus doped, 1.1 Ω – cm resistivity (doping density, \( N_D \approx 5 \times 10^{15} / \text{cm}^3 \)) single-side polished n-type silicon wafers were obtained from University Wafer, Inc. Single-crystalline, (100)-oriented, planar, 380 µm thick, boron doped, 1 Ω – cm to 10 Ω – cm resistivity single-side polished p-type silicon with 300 nm thermal oxide (SiO\(_2\) on Si substrate) were also obtained from University Wafer, Inc. Silicon wafers with an np\(^+\) homojunction (np\(^+\)-Si) was fabricated using a previously reported procedure (Yang et. al) via room temperature ion implantation on n-Si at a 7° incident angle using \(^{11}\)B accelerated to 45 keV with a dose of \(1 \times 10^{14} / \text{cm}^2\), and then at 32 keV with a dose of \(5 \times 10^{14} / \text{cm}^2\).\(^1\) To reduce the contact resistance, the back sides of the wafers were implanted with \(^{31}\)P at 140 keV with a dose of \(1 \times 10^{14} / \text{cm}^2\), and then at 75 keV with a dose of \(5 \times 10^{14} / \text{cm}^2\). Dopant activation, both for the junction p\(^+\) layer and the back-surface field (BSF) n\(^+\) layer, was achieved via rapid thermal annealing at 1000 °C for 15 s under a flow of N\(_2\)(g). Water was obtained from a Barnstead Nanopure system and had a resistivity \(\geq 18.0 \text{M} \Omega – \text{cm}\). Copper Etch Type CE - 100 (FeCl\(_3\)-based, Transene Company, Inc., Danvers, MA), and buffered HF improved (aq) (semiconductor grade, Transene Company, Inc., Danvers, MA) were used as received. Acetone (HPLC grade, Sigma-Aldrich) was used as received. Acetonitrile (99.8 % anhydrous, Sigma-Aldrich) used in electrochemical measurements was dried over Al\(_2\)O\(_3\) prior to use. Ferrocene (Fc, bis(cyclopentadienyl)iron(II), 99 %, Strem), cobaltocene (CoCp\(_2\), bis(cyclopentadienyl)cobalt(II), 98 %, Strem), and acetylferrocene (AcFc, (acetylcyclopentadienyl)-cyclopentadienyl iron(II), 99.5 %, Strem) were purified via sublimation. Ferrocenium tetrafluoroborate (Fc\(^+\)[BF\(_4\)]\(^-\),
bis(cyclopentadienyl)iron(III) tetrafluoroborate, technical grade, Sigma-Aldrich) was recrystallized from a mixture of diethyl ether (ACS grade, EMD) and acetonitrile (ACS grade, EMD) and dried under vacuum. Cobaltocenium hexafluorophosphate (CoCp$^{2+}$, bis(cyclopentadienyl)cobalt(III) hexafluorophosphate, 98%, Sigma-Aldrich) was recrystallized from a mixture of ethanol (ACS grade, EMD) and acetonitrile (ACS grade, EMD) and dried under vacuum. Acetylferrocenium (AcFc$^+$) was generated in situ via electrochemical oxidation of AcFc$^0$ with the concomitant reduction reaction occurring in a compartment that was separated by a Vycor frit from the working electrode compartment. Potassium ferricyanide (K$_3$[Fe(CN)$_6$], 99.2%, Sigma-Aldrich) and potassium ferrocyanide (K$_4$[Fe(CN)$_6$] trihydrate, ACS Certified, Fisher Scientific) were used as received. LiClO$_4$ (battery grade, Sigma-Aldrich) was used as received. Petri dishes used were Falcon Optilux(TM) branded and were cleaned with water prior to use. All other chemicals were used as received unless otherwise noted.

**Electrode/Sample fabrication**

Monolayer graphene was grown by chemical vapor deposition (CVD) of carbon on Cu.$^2$ Additional CVD-grown monolayer graphene on Cu was purchased from Advanced Chemical Supplier Materials (Medford, MA). A 2.5 cm × 1 cm piece of monolayer graphene on Cu (from either source) was fluorinated using a home-built XeF$_2$ pulse chamber, with one pulse of XeF$_2$(g) at 2 torr for 90 s with a base pressure of < 1 mtorr. The fluorinated graphene samples on Cu were then coated with 495K A4 polymethyl methacrylate (PMMA, MicroChem) by spinning at 2000 rpm (500 rpm s$^{-1}$ acceleration) for 60 s, followed by a 5 min bake at 185 °C. This procedure was repeated twice to increase the PMMA thickness. This process yielded a PMMA/F–Gr/Cu stack. PMMA/Gr/Cu stacks were obtained using nominally the same spin coating method but without graphene exposure to XeF$_2$.

Smaller pieces were cut from the PMMA/F–Gr/Cu and floated in FeCl$_3$ solution until complete removal of the Cu (≈ 1 h) was observed. To remove the etchant residue, each stack was transferred between five consecutive ≥ 18 MΩ – cm resistivity water baths. N-type Si was etched for 30 s in buffered HF improved to yield n-Si–H surfaces. SiO$_2$ on Si substrates were cleaned using a modified SC1/SC2 cleaning method. SC-1 consisted of soaking the Si wafers in a 5:1:1 (by volume) solution of H$_2$O, NH$_4$OH (≈30 wt. %, J.T. Baker) and H$_2$O$_2$ (≈35 wt. %, Sigma) for 10 min at 75 °C. After washing with H$_2$O, SC-1 cleaned wafers were exposed to SC-2 conditions, which consisted of soaking the Si wafers in a 5:1:1 (by volume)
solution of H\textsubscript{2}O, HCl (11.1 M, Sigma) and H\textsubscript{2}O\textsubscript{2} (≈35 wt. %, Sigma) for 10 min at 75 °C. A clean PMMA/F–Gr stack was then transferred gently onto the appropriately prepared Si wafer (HF etched Si for electrode fabrication, SC1/SC2 cleaned SiO\textsubscript{2} on Si substrate for chemical stability interrogation via Raman spectroscopy) from the water bath and dried with a stream of N\textsubscript{2}(g) to remove any remaining water between the Si wafer and the graphene sheet. The final PMMA/F–Gr/wafer stack was baked at 80 °C for 10 min in air. The majority of the PMMA was detached with a 10 min acetone soak and the remaining PMMA residue was removed by an anneal (H\textsubscript{2}:Ar v:v 5:95) for 2 h at 350 °C, leaving an F–Gr/Si stack. Gr/Si stacks were prepared by nominally identical procedures using pristine graphene. Generally, 5-10 electrodes were made at the same time from the same PMMA/F–Gr/Cu or PMMA/Gr/Cu stack, respectively.

N-Si/F–Gr electrodes were fabricated using Ga:In (75:25) eutectic as an ohmic back contact. The wafers were attached to a Cu wire with Ag paint (high purity, SPI Supplies). All surfaces except the F–Gr layer were covered with insulating epoxy (Loctite Hysol 9460). Monolayer graphene-covered Si(111) electrodes were fabricated using an analogous procedure in which all of the above steps were executed with the exception that the graphene was not exposed to the XeF\textsubscript{2}(g). CH\textsubscript{3}-terminated Si(111) wafers were prepared using a previously reported procedure and were not etched with HF prior to use in electrode fabrication. Graphene-free, H-terminated Si(111) electrodes were etched with HF(aq) immediately before use.

**Instrumentation**

X-ray photoelectron spectroscopic (XPS) data were collected at ≈ 5 × 10\textsuperscript{−9} torr using a Kratos AXIS Ultra DLD with a magnetic immersion lens that consisted of a spherical mirror and concentric hemispherical analyzers with a delay-line detector (DLD). An Al Kα (1.486 keV) monochromatic source was used for X-ray excitation. Ejected electrons were collected at a 90° angle from the horizontal. The CASA XPS software package v 2.3.16 was used to analyze the collected data. Raman spectra were collected with a Renishaw Raman microscope at λ =532 nm through an objective with numerical aperture=0.75. The laser power was ≈ 3 mW.

UV/Vis transmission spectra were collected with a Cary 5000 absorption spectrometer equipped with an external DRA 1800 attachment. The data were automatically zero/baseline corrected by the instrument before any additional processing was performed.
Scanning electron microscope (SEM) images were obtained using a FEI Nova NanoSEM 450 at an accelerating voltage of 10.00 kV with a working distance of 5 mm and an in-lens secondary electron detector. Electrochemical data were obtained using a Princeton Applied Research Model 273, Biologic SP-250, or a Gamry Reference 600 potentiostat. A Pt wire reference electrode (0.5 mm dia., 99.99 % trace metals basis, Sigma-Aldrich) and a Pt mesh counter electrode (100 mesh, 99.9 % trace metals basis, Sigma-Aldrich) were used for the electrochemical measurements. The cell potentials for the nonaqueous redox species were determined using cyclic voltammetry to compare the solution potential to the formal potential of the redox species. The potential difference between cells was calculated using the difference between the solution potentials for each redox couple in conjunction with standard formal reduction potentials from the literature. The CH₃CN-CoCp²⁺/⁰ solution (CoCp₂ [3 mM]/CoCp³⁺ [50 mM]) was calculated to have a solution potential of $E(A/A^-) = -1.26$ V vs. Fc/Fc⁺, the CH₃CN-Fc⁺/⁰ solution (Fc [55 mM]/Fc⁺ [3 mM]) was calculated to have $E(A/A^-) = -0.10$ V vs. Fc⁺/Fc, and the CH₃CN-AcFc⁺/⁰ solution (pre-electrolysis AcFc concentration = [50 mM]) was calculated to have $E(A/A^-) = 0.40$ V vs. Fc⁺/Fc. The nonaqueous electrochemical solutions each contained 1.0 M LiClO₄. The aqueous 50 mM K₃[Fe(CN)₆] - 350 mM K₄[Fe(CN)₆] solution contained no additional supporting electrolyte due to the high intrinsic salt concentration. The current under forward bias saturated at much larger values in the Fe(CN)₆³⁻/⁴⁻ solution than in the Fe⁺/Fc solution due to the increased concentration of electron-accepting species in the Fe(CN)₆³⁻/⁴⁻ solution. The electrolyte solution was rapidly stirred with a small, Teflon-covered stir bar. Illumination was provided with an ENH-type tungsten-halogen lamp. Illumination intensities were set to provide $\approx 10$ mA/cm² $\approx 1.1$ mA/cm² of light-limited current density. These intensities corresponded to $\approx 1/3$rd Sun at AM1.5G ($\approx 33$ mW/cm²), respectively, as determined through the concurrent use of a Si photodiode (Thor Laboratories) that was calibrated relative to a secondary standard photodetector that was NIST-traceable and calibrated at 100 mW/cm² of AM1.5G illumination. Nonaqueous electrochemistry was performed anaerobically in an Ar(g)-filled glovebox. Aqueous electrochemistry was performed in air. Electrodes were washed with H₂O and dried prior to transfer between electrolyte solutions. Plots of current density vs. time data were smoothed using a 9 point Savitzky-Golay algorithm via data analysis software (Igor Pro 6). Normalized current density was calculated by multiplying the ratio of the light intensity at a time point of interest to the light intensity at $t = 0$ s by the original current density and dividing the resulting value by the current density.
measured at the time point of interest. The current density versus potential data in HBr(aq) were measured using a three-electrode setup with a Si working electrode, a Pt wire pseudo-reference electrode, and a large Pt mesh counter electrode. The electrolyte consisted of aqueous 0.4 M Br$_2$ - 7.0 M HBr (pH=0) electrolyte under rapid stirring, and $\approx 33$ mW/cm$^2$ of simulated solar illumination from an ELH-type W-halogen lamp. Photoelectrochemical deposition of Pt was performed by immersing the electrode into an aqueous solution of 5 mM K$_2$PtCl$_4$ (99.9 %, Alfa Aesar) and 200 mM LiCl. Using a three-electrode setup, with a saturated calomel reference electrode and a Pt mesh counter electrode, galvanostatic control was maintained at $-0.1$ mA/cm$^2$ in a stirred solution until $-100$ mC/cm$^2$ had passed. The samples were then rinsed with deionized water and were dried under a stream of N$_2$(g).

D.2 Supporting Data

Electrochemical behavior of np$^+$-Si/F–Gr electrodes in aqueous solution
Figure D.1: Current density vs. time (J–t) and current density vs. potential (J–E) behavior of np⁺-Si/F–Gr electrodes in contact with aqueous 50 mM Fe(CN)₆³⁻ - 350 mM Fe(CN)₆⁴⁻ electrolyte under ≈ 33 mW/cm² of ENH-type W-halogen illumination. (A) The J–t behavior of np⁺-Si/F–Gr at E = 0 V vs. E(A/A⁻) over 100 000 s (> 24 h). The normalized current density is reported to correct for any variations in the light intensity during the experiment. (B) J–E behavior of np⁺-Si/F–Gr (3 scans at 50 mV s⁻¹) before and after exposure to the conditions depicted in (A). The current density decay in the original chronoamperograms is consistently ascribed to fluctuations in the light source, as well as to decomposition of the Fe(CN)₆³⁻/⁴⁻ under illumination, which produced thin colored film on the electrochemical cell over the course of the experiment depicted in (A).

**Comparison of graphene-imparted stability between graphene and fluorinated graphene electrodes**

The photoelectrochemical stability of pristine graphene-coated n-Si electrodes and of fluorinated graphene-coated electrodes was tested by collecting J-t data for n-
Si/Gr and n-Si/F–Gr electrodes from four different electrode ‘batches’ (two Gr/n-Si and two F–Gr/Gr batches) in contact with aqueous 50 mM Fe(CN)$_6^{3−}$ - 350 mM Fe(CN)$_6^{4−}$ under $\approx 33$ mW/cm$^2$ of ENH-type W-halogen illumination (Figure D.2). These batches of electrodes each mutually consisted of 5-6 electrodes in which each electrode was fabricated from the same section of a larger sheet of Gr or F–Gr, respectively. However, between batches of electrodes, different PMMA/(F-)Gr/Cu stacks or different regions of the same stack were used. The n-Si/Gr from the first graphene electrode batch (batch GrA) exhibited stable current densities for $> 1000$ s (Figure D.2A). Among these electrodes fabricated, all five electrodes were photoelectrochemically stable (5/5 stable, where stability was defined as having a current density at $t=1000$ s of at least 60 % of the current density displayed at $t = 0$ s. This definition was used because some graphene-covered (and F–Gr covered) electrodes displayed an initial decay of current density followed by a subsequent stabilization, as seen in Figure D.3. This behavior is consistent with the hypothesis that any pinholes in the graphene protective coating led to the oxidation at the exposed Si surface, but that stability is observed when the exposed Si is passivated with SiO$_x$. However, the other batch (batch GrC, Figure D.2C) yielded only two n-Si/Gr electrodes out of six that exhibited stable current densities for $> 1000$ s (2/6 stable). The inconsistent behavior in the photoelectrochemical stability imparted by graphene coatings on n-Si electrode was observed over many iterations of graphene growth and electrode fabrication. Conversely, both batches of F–Gr coated n-Si electrodes (batch F–GrB, Figure D.2B and batch F–GrD, Figure D.2D) yielded n-Si/F–Gr electrodes that exhibited stable current densities for $> 1000$ s (5/5 stable in batch F–GrB and 5/5 stable in batch F–GrD). The improved consistency of the photoelectrochemical stability is one of the key attributes of the fluorinated graphene-coated n-Si electrodes relative to the routinely observed behavior of pristine graphene-coated n-Si electrodes.

We also explored the extended stability behavior of the Gr-coated n-Si electrodes as compared to F–Gr-coated n-Si electrodes. Figure D.4 depicts the $J–t$ behavior of the most stable n-Si/F–Gr and n-Si/Gr electrodes. After both starting at an initial current density of $\approx 10$ mA/cm$^2$, the n-Si/F–Gr electrode current density decayed to 9.5 mA/cm$^2$, whereas the n-Si/Gr electrode decayed to 8 mA/cm$^2$. The fluorinated graphene-coated electrode was more stable, but the pristine graphene coated electrode also exhibited reasonable stability, particularly between $t = 20\ 000$ s and $t = 80\ 000$ s. In conjunction with the data depicted in Figure D.2, under ideal conditions for extended (100 000 s) time periods, these observations suggest that
Figure D.2: Representative $J$–$t$ data for n-Si/Gr and n-Si/F–Gr electrodes from four different electrode batches (two Gr/n-Si and two F–Gr/Gr batches, see above) in contact with aqueous 50 mM Fe(CN)$_6^{3–}$ - 350 mM Fe(CN)$_6^{4–}$ under ≈ 33 mW/cm$^2$ of W-halogen illumination. (A) The n-Si/Gr electrodes from the batch GrA exhibited stable current densities for $> 1000$ s (5/5 stable). (B) The n-Si/F–Gr electrodes from batch F–GrB exhibited stable current densities for $> 1000$ s (5/5 stable). (C) The n-Si/Gr electrodes from batch GrC did not consistently exhibit stable current densities for $> 1000$ s (2/6 stable). (D) The n-Si/F–Gr electrodes from batch F–GrD exhibited stable current densities for $> 1000$ s (5/5 stable).

Figure D.3: Representative $J$–$t$ data of an n-Si/F–Gr electrode in contact with aqueous 50 mM Fe(CN)$_6^{3–}$ - 350 mM Fe(CN)$_6^{4–}$ under ≈ 33 mW/cm$^2$ of W-halogen illumination. After an initial decay in current density, the current density stabilized at ≈ 8.5 mA/cm$^2$. 
pristine graphene may be able to provide to n-Si electrodes the same level of stability as that provided by F–Gr coatings. However, some difficult-to-control variable in the growth or transfer of graphene limits the routine observation of such extended stability. This hypothesis is consistent with the supposition that grain boundaries and defect sites on the graphene coatings lead to the observed degradation, and that fluorination of such sites passivates them to further loss of integrity. As such, the inconsistency seen in the graphene electrode stability data can be ascribed to the relative preponderance or dearth of defect sites present on an electrode surface, with fluorination greatly decreasing the effect that such sites have on the photoelectrochemical stability of such systems. Future work involving the targeted study of single crystal graphene sheets or single grains in a polycrystalline graphene sheet are underway to further examine this hypothesis.

Figure D.4: \( J-t \) data of the ‘champion’ n-Si/F–Gr and n-Si/Gr electrodes in contact with aqueous 50 mM Fe(CN)\(_6^{3-}\) - 350 mM Fe(CN)\(_6^{4-}\) under \( \approx 33 \text{ mW/cm}^2 \) of W-halogen illumination. After both starting at an initial current density of \( \approx 10 \text{ mA/cm}^2 \), the n-Si/F–Gr electrode current density decayed to 9.5 mA/cm\(^2\) compared to the n-Si/Gr electrode which decayed to 8 mA/cm\(^2\).

**Stability of fluorinated graphene-covered n-Si electrodes under high light intensity conditions**

Fluorinated graphene-coated and pristine graphene-coated n-Si electrodes were tested for photoelectrochemical stability under approximately 1 sun conditions (\( \approx 100 \text{ mW/cm}^2 \) from an ENH-type W-halogen lamp). Figure D.5 depicts the photoelectrochemical stability over 1000 s for n-Si/Gr and n-Si/F–Gr electrodes in contact with aqueous 50 mM Fe(CN)\(_6^{3-}\) - 350 mM Fe(CN)\(_6^{4-}\) under \( \approx 100 \text{ mW/cm}^2 \) of W-halogen illumination. The current density of the n-Si/F–Gr electrode was effectively constant over this time period, whereas the current density of the n-Si/Gr
electrode decayed from $\approx 25 \text{ mA/cm}^2$ to less than $7 \text{ mA/cm}^2$ over the same time period. This behavior supports the hypothesis that under these conditions fluorinated graphene provides a superior protective layer relative to pristine graphene. Figure D.6 further depicts the photoelectrochemical stability under the same conditions of a F–Gr coated n-Si electrode over 100 000 ks. Although the F–Gr coated electrode was stable over the same time period (100 000 s) under lower light intensity conditions (Figure 5.1), at near 1 sun conditions the current density of the electrode decayed to near baseline conditions over the same time period.

Figure D.5: $J-t$ data for n-Si/Gr and n-Si/F–Gr electrodes in contact with aqueous 50 mM Fe(CN)$_6^{3-}$ - 350 mM Fe(CN)$_6^{4-}$ under $\approx 100 \text{ mW/cm}^2$ of W-halogen illumination over 1000 s.

Figure D.6: $J-t$ data for n-Si/F–Gr electrodes in contact with aqueous 50 mM Fe(CN)$_6^{3-}$ - 350 mM Fe(CN)$_6^{4-}$ under $\approx 100 \text{ mW/cm}^2$ of W-halogen illumination over 100 000 s.

The stability of the fluorinated graphene was tested under acidic, neutral, and alkaline aqueous solutions, respectively. To insure that the same area was examined before and after testing, a small area on the graphene wafer was outlined with Hysol 9460
Figure D.7: Raman and X-ray photoelectron (XP) spectra of fluorinated graphene (F–Gr) before and after annealing. (A) The C 1s region before annealing displayed four peaks at binding energies of 284.8 eV, 285.6 eV, 287.2 eV, and 289.5 eV, respectively. Peaks attributed to carbon bound to fluorine are shown in green; peaks attributed to carbon bound to carbon are shown in blue; and peaks attributed to carbon bound to oxygen are shown in red. (B) The F 1s region displayed two peaks at binding energies of 687.1 eV and 690.0 eV, respectively. (C) The Raman spectra before annealing showed a prominent defect peak at 1350 cm\(^{-1}\). (D) Two additional peaks, at 291 eV and 293.5 eV (inset), attributable to CF\(_2\) and CF\(_3\) groups, were observed in the C 1s XP spectra after annealing. (E) The positions of the peaks in the F 1s region were shifted slightly to 686.1 eV and 689.8 eV, respectively, and decreased in size. (F) The defect peak at 1350 cm\(^{-1}\) broadened after the anneal. These spectra are consistent with a lightly fluorinated (C\(_x\)F, x > 10) graphene surface.\(^5\) The change in fluorination profile after annealing is consistent with a reorganization of the fluorine on the surface, and the XPS spectra demonstrate the expected decrease in fluorine content after a two-hour 350 \(^\circ\)C anneal under a H\(_2\):Ar (5:95) atmosphere.\(^6\) Optical images along with Raman spectra were acquired, and wafers were then placed for 1 h in aqueous solutions at pH 0, pH 7, and pH 14. After carefully rinsing the samples with > 18 MΩ – cm H\(_2\)O and drying the samples with a stream of N\(_2\)(g), optical images along with Raman spectra were obtained from the same areas as before testing. The Raman spectra and optical images of the samples soaked in acidic and neutral solutions showed no change after testing (Figure D.8-D.9). The samples tested in alkaline solutions showed a marked decrease in defect density of the remaining sections of fluorinated graphene, closely mimicking the profile of pristine graphene. Repeated tests of fluorinated graphene in 1 M KOH(aq) showed
Figure D.8: Stability tests of F–Gr in acidic (1 M HCl), alkaline (1 M KOH), and neutral aqueous conditions. (A) Raman spectra of the pristine graphene sheets before fluorination (top) and after fluorination (bottom) showed an increase in the size of the defect peak at 1350 cm$^{-1}$. (B) The 1350 cm$^{-1}$ defect peak remained unchanged after 1 h in acidic or neutral aqueous solutions. In contrast, immersion for 1 h in aqueous alkaline media produced a decrease in the intensity of the defect peak. However, in all three spectra the intensity of the G ($\approx 1580$ cm$^{-1}$) and 2D ($\approx 2680$ cm) peaks are consistent with monolayer graphene.

large-scale delamination of the fluorinated graphene sheet, as observed in the images before and after exposure to the aqueous pH 14 solution.
Figure D.9: Optical images of stability tests of F–Gr in acidic (1 M HCl), alkaline (1 M KOH), and neutral (deionized water) conditions. Arrows indicate points of reference for the corresponding before and after images.

**UV-Vis Spectroscopy of Graphene and Fluorinated Graphene**
Figure D.10: UV/Vis spectra of Gr and F–Gr on glass. Graphene and fluorinated graphene were transferred to borosilicate glass slides using the standard transfer procedures (vide supra). The slightly increased transmission for F–Gr is consistent with the expectation of decreased visible light absorption upon fluorination of graphene.

Inhibition of platinum silicide formation

XP spectra of Si–Me/F–Gr/Pt and Si–Me/Pt surfaces were obtained to investigate the ability of F–Gr to inhibit platinum silicide formation. Pt was deposited at ≈ 3 nm thickness via electron-beam evaporation on both F–Gr covered and bare Si surfaces. The 3 nm Pt thickness was chosen to allow for interrogation of the sample surface to a depth at which both Si and Pt were observable by XPS. Methylated Si surfaces were used to inhibit the formation of Si oxide at the Si/Pt interface during sample fabrication, because Si oxide of sufficient thickness is also capable of preventing silicide formation. Figure D.11a shows the XP spectrum of a pure Pt phase. A thicker Pt layer (20 nm) was used to interrogate only the pure Pt phase. Figure D.11b shows the Pt 4f XP spectrum of CH$_3$-terminated Si with a 3 nm Pt overlayer. The Pt 4f peak shifted to higher binding energy, indicative of platinum silicide formation. The shoulder of the peak at low binding energy is consistent with a pure Pt phase overlayer. Conversely, 3 nm of Pt on F–Gr covered silicon showed essentially no change in the Pt 4f binding energy immediately after fabrication (Figure D.11c or after a 1 h anneal under forming gas at 300 °C (Figure D.11d). The data are thus indicative of little or no platinum silicide formation. Figure D.11e presents an overlay of the spectra in Figure D.11a-D.11d and highlights the difference between the Pt 4f peak positions.
Figure D.11: The Pt 4f XP spectra of Pt on both F–Gr covered and Si surfaces. (A) XP spectrum of a thick (20 nm) layer of Pt on Si. This spectrum is representative of a pure Pt phase. (B) XP spectrum of a 3 nm layer of Pt on Si. The Pt 4f peak shifted to high binding energy (72.2 and 75.6 eV), characteristic of platinum silicide formation. The shoulder to lower binding energy is attributed to a pure Pt phase. (C) XP spectrum of Si–Me/F–Gr/Pt (3 nm). The Pt 4f peak positions (71.0 and 74.3 eV) are consistent with pure Pt. (D) XP spectrum of Si–Me/F–Gr/Pt after annealing at 300 °C under forming gas. (E) Overlay of XP spectra (A)-(D).
n-Si/F–Gr non-aqueous photoelectrochemistry

<table>
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<th>Sample</th>
<th>$E_{oc,CoCp^{2+/0}}$ (V vs. $E(\text{CoCp}_2^{+/0})$)</th>
<th>$E_{oc,Fe^{+/0}}$ (V vs. $E(\text{Fe}^{+/0})$)</th>
<th>$E_{oc,AcFe^{+/0}}$ (V vs. $E(\text{AcFe}^{+/0})$)</th>
</tr>
</thead>
<tbody>
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<td>0.26</td>
<td>0.43</td>
</tr>
<tr>
<td>FGr</td>
<td>0</td>
<td>0.20</td>
<td>0.30</td>
</tr>
</tbody>
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Table D.1: $E_{oc}$ values for n-Si/Gr and n-Si/F–Gr electrodes in contact with non-aqueous redox couples under $\approx 33 \text{ mW/cm}^2$ of W-halogen (ENH) illumination. The Nernstian potential, $E(A/A^-)$, of the contacting non-aqueous electrolytes were measured as follows: $E(\text{CoCp}^{2+/0}) = -1.26$ V vs. $E^{\alpha'}(\text{Fe}^{+/0})$, $E(\text{Fe}^{+/0}) = -0.1$ V vs. $E^{\alpha'}(\text{Fe}^{0+/+})$, $E(\text{AcFe}^{+/0}) = 0.4$ V vs. $E^{\alpha'}(\text{Fe}^{+/0})$.

H-Br stability/efficiency over time

Figure D.12: Current density-potential ($J$–$E$) behavior of an n-Si/F–Gr/Pt photoanode before, during, and after 2400 s of photoelectrochemical stability testing in contact with 0.4 M Br$_2$ - 7.0 M HBr (pH=0) aqueous electrolyte. Photoelectrochemical stability was measured by observing the $J$–$t$ behavior at an initial current density of 10 mA/cm$^2$ over the specified time period (see Figure 5.3). The behavior of the n-Si/F–Gr/Pt electrode improved over 2400 s, with improvements in $E_{oc}$ (0.27 V to 0.37 V), $J_{sc}$ (9.0 mA to 9.5 mA), and $\eta$ (0.51 to 0.59), resulting in an increase in the ideal regenerative cell conversion efficiency from 3.5 % to $\geq 5$ %.

XPS Oxide Analysis

XPS analysis was performed in order to determine the effect of electrochemical oxidation at the Si–Me surface on the oxidation state of the Si photoanode surface (Figure 5.2). Silicon oxide detected before and after electrochemical oxidation was quantified using a simple substrate—overlayer model described by equation D.1:

$$d = \lambda_{ov} \sin \theta [\ln(1 + \frac{I_{Si}^{0}}{I_{ov}^{0}} \times \frac{I_{ov}}{I_{Si}})], \quad (D.1)$$
where $d$ is the overlayer thickness, $\lambda_{ov}$ is the attenuation factor through the oxide overlayer (assumed to be 2.6 nm), the angle from the surface of the sample to the detector (90°), $I_{0_{Si}}/I_{0_{ov}}$ is an instrument normalization factor related to the expected signal for a pure Si and a pure SiO$_2$ sample (taken to be 1.3 for this instrument), $I_{ov}$ is the measured intensity of the silicon, and $I_{ov}$ is the measured intensity of the silicon oxide overlayer. The thickness of a monolayer of oxide was taken to be 0.35 nm. Negligible silicon oxide was detected on the bare methyl-terminated silicon surfaces prior to electrochemical oxidation (Figure D.2a) and an oxide thickness of approximately 0.75 nm, or > 2 monolayers of oxide, was observed after exposure of the Si–Me surface (Figure D.2b) to the electrochemical oxidation conditions described in Figure D.2. An oxide thickness of approximately 0.15 ± 0.05 nm was detected on the Si–Me/F–Gr surfaces prior to electrochemical oxidation (Figure D.2c) and an oxide thickness of approximately 0.17 ± 0.5 nm, was observed after exposure (Figure 5.2d) of the Si–Me/F–Gr surface to the electrochemical oxidation conditions described in Figure 5.2.

**np$^+$-Si Solid State Junction Behavior**
Figure D.13: $J-E$ behavior of an np$^+$-Si/Pt PV cell and an np$^+$-Si/F$^-$Gr/Fe(CN)$_6^{3/-4-}$ photoanode under $\approx$ 33 mW/cm$^2$ of ENH-type W-halogen illumination. For the np$^+$-Si/Pt PV cell, the following photovoltaic metrics were measured: $E_{oc} = -0.40$ V, $J_{sc} = 11.3$ mA/cm$^2$, ff = 0.50. For the np$^+$-Si/F$^-$Gr/Fe(CN)$_6^{3/-4-}$ cell, the following photovoltaic metrics were measured: $E_{oc} = -0.39$ V, $J_{sc} = 11.1$ mA/cm$^2$, ff = 0.30. The similar $E_{oc}$ values with varying fill factors between these two interfaces suggest that the Si/F$^-$Gr/Fe(CN)$_6^{3/-4-}$ interface is the source of an additional series resistance but that the parallel shunt resistances are similar between the np$^+$-Si/Pt and np$^+$-Si/F$^-$Gr/Fe(CN)$_6^{3/-4-}$ interfaces. A similar parallel shunt resistance is also consistent with the use of the same buried photoactive junction at each interface. The np$^+$-Si/Pt PV cell was prepared by evaporating 15nm of Pt onto the freshly HF etched p$^+$ surface of an np$^+$-Si chip and scribing a Ga:In eutectic onto the backside of an n-doped surface. For the np$^+$-Si/Pt PV cell, the $(E(A/A^-))$ referenced on the x-axis refers to the potential of the Pt contact.

Analysis of fluorine atom concentration relative to defect site carbon concentration

A key hypothesis of this work is that the fluorination of CVD-grown graphene leads to passivation of defect sites present in CVD graphene. Assuming a carbon-carbon bond length of 0.142 nm and the hexagonal structure of graphene, the area of each hexagonal unit in a graphene sheet is 0.052 nm$^2$ and encompasses two carbon atoms. Therefore, a 1 cm$^2$ sheet of pristine graphene will include $\approx 1 \times 10^{15}$ carbon atoms. A rigorous evaluation of the density and total number of carbon atoms in a polycrystalline graphene sheet is challenging, due to the presence of a variety of defect types, including point and line defects, with various geometries, and also due to a variable number of defects that may be produced by fabrication of the graphene-covered electrode.$^{12}$ For simplicity, we consider only the line defects associated with grain boundaries. These line defects have a variety of geometries and can be composed of alternating 5- and 7-membered carbon rings. Assuming
that the density of carbon atoms at a line defect and in the defect-free graphene sheet are equivalent, and further that the density of carbon atoms in a polycrystalline CVD graphene sheet is equivalent to that in a single crystalline graphene sheet, allows calculation of the percentage of total carbon atoms at defect sites in the graphene sheet. The grain size of the graphene used in this work is 0.2 µm to 5 µm on a side. The grains are generally amorphously shaped, but are approximated herein for simplicity as hexagons for simplicity. Assuming hexagonal grains with side length of 0.2 µm (area of 0.10 µm²) implies \( \approx 10^9 \) grains in a 1 cm² sheet of graphene, and a total length of \( 8 \times 10^8 \) µm of grain boundary area. If the width of these boundaries is equal to the width of a single hexagonal unit of the graphene lattice (\( \approx 0.28 \) nm), and assuming that the carbon density is the same as that of a single hexagonal unit, the total number of defect carbon atoms at grain boundary line defects is \( \approx 10^5 \) C atoms per 1 cm² area of graphene. Thus \( (10^5/10^{15}) \), i.e., 1 defective carbon atom is present for every \( 10^{10} \) pristine carbon atoms in the polycrystalline graphene sheet. This ratio is significantly smaller than the ratio of F atoms to C atoms found via XPS analysis (\( 10 > F/C > 0.01 \)). In conjunction with the knowledge that the defect sites on a graphene sheet are significantly more reactive than the pristine carbon sites, this XPS F/C ratio suggests that most or all of the defect carbon atoms are capped with fluorine. Further studies using electron microscopy methods are underway to confirm this hypothesis.

SEM of Pt electrodeposition on n-Si/F–Gr surfaces Assuming 100 % faradaic yield for charge transfer to platinum during the photoelectrochemical deposition of Pt from an aqueous solution of 5 mM \( K_2PtCl_4 \) and 200 mM LiCl, in conjunction with \( 2 e^- \) per Pt atom deposited, and a conformal deposition, a charge density of \(-100 \) mC/cm² should result in the deposition of an \( \approx 50 \) nm thick of Pt layer on the n-Si/F–Gr electrodes. SEM images were obtained on n-Si/F–Gr surfaces before photoelectrochemical deposition and after 10 mC/cm² or 100 mC/cm² of cathodic charge density was passed during electrodeposition (Figure D.14-D.16). Figure D.15 indicates that the Pt deposited stochastically across the F–Gr surface, in contrast to previous reports of metal deposition via other methods on graphene, which produced preferential metal deposition at grain boundaries.\(^{12}\) This difference in behavior may be due to passivation of highly reactive grain boundary sites by the XeF₂ treatment. The incomplete electrochemical stability observed in Figure D.3 for the n-Si–H/Pt electrode may be related to imperfect conformal deposition, consistent with the observations of Figure D.16.
Figure D.14: SEM image of a fluorinated graphene-covered n-Si surface prior to photoelectrochemical deposition of Pt metal from an aqueous solution of 5 mM K$_2$PtCl$_4$ (99.9 %, Alfa Aesar) and 200 mM LiCl electrolyte solution.

Figure D.15: SEM image of a fluorinated graphene-covered n-Si surface after passing 10 mC/cm$^2$ charge during photoelectrochemical deposition of Pt metal from an aqueous solution of 5 mM K$_2$PtCl$_4$ (99.9 %, Alfa Aesar) and 200 mM LiCl electrolyte solution.
Figure D.16: SEM image of a fluorinated graphene-covered n-Si surface after passing 100 mC/cm² charge during photoelectrochemical deposition of Pt metal from an aqueous solution of 5 mM K₂PtCl₄ (99.9 %, Alfa Aesar) and 200 mM LiCl electrolyte solution.
D.3 References


Highly Branched Cobalt Phosphide Nanostructures for Hydrogen-Evolution Electrocatalysis


E.1 Abstract
CoP nanostructures that exposed predominantly (111) crystal facets were synthesized and evaluated for performance as electrocatalysts for the hydrogen-evolution reaction (HER). The branched CoP nanostructures were synthesized by reacting cobalt(II) acetylacetonate with trioctylphosphine in the presence of trioctylphosphine oxide. Electrodes comprised of the branched CoP nanostructures deposited at a loading density of ≈ 1 mg/cm² on Ti electrodes required an overpotential of 117 mV to produce a current density of −20 mA/cm² in 0.5 M H₂SO₄. Hence the branched CoP nanostructures belong to the growing family of highly active non-noble-metal HER electrocatalysts. Comparisons with related CoP systems have provided insights into the impact that shape-controlled nanoparticles and nanoparticle–electrode interactions have on the activity and stability of nanostructured HER electrocatalysts.

E.2 Introduction
Transition metal phosphides have recently emerged as an important family of highly active electrocatalysts that facilitate the production of molecular hydrogen from acidic aqueous solutions, which is important for clean-energy technologies such as water electrolyzers and solar fuels generators. For example, phosphides of nickel,¹⁻³ cobalt,⁴⁻¹² iron,¹³,¹⁴ copper,¹⁵ molybdenum,¹⁶⁻¹⁸ and tungsten¹⁹ have been found to electrocatalytically generate H₂(g) with low overpotentials at operationally relevant current densities for solar-driven water splitting systems, while exhibiting high stability under strongly acidic conditions. Metal phosphides therefore offer an Earth-abundant and inexpensive alternative to platinum, which serves as the benchmark catalyst for the hydrogen-evolution reaction (HER). The relationship between the electrocatalytic activity and the exposed crystal face has not yet been elucidated
for the transition metal phosphides, which are generally studied as nanocrystals. The (001) surface of Ni$_2$P contains proximate phosphorus and nickel sites that are hypothesized to work cooperatively to facilitate moderate binding of the intermediates and products to the catalyst surface.$^{20}$ The other metal phosphides that have been identified as HER catalysts have related crystal structures which also contain proximate metal and phosphorus structural motifs on their low-index surfaces. This structural feature suggests that metal phosphide nanostructures that preferentially expose different crystal facets would be expected to exhibit different activities for HER catalysis. The CoP system, which has been studied extensively, exhibits high HER activity across a diverse group of morphologies, characteristic grain sizes, support materials, and synthetic preparations. For example, nominally comparable activity has been observed for multi-faceted single-crystalline hollow CoP nanoparticles on Ti foil,$^{4}$ electrochemically deposited CoP films,$^{9}$ CoP nanocrystals on carbon nanotube$^7$ and carbon cloth supports,$^{10}$ porous CoP nanowires on carbon cloth$^5$ and Ti substrates,$^6$ CoP nanosheets on a Ti plate,$^8$ porous template-grown CoP nanowires,$^{11}$ and a collection of morphologically variant CoP nanoparticles on glassy carbon electrodes.$^6$ The primary methods used to synthesize these CoP nanostructures include reaction of pre-made Co nanoparticles with trioctylphosphine, or phosphidation of cobalt oxide and related nanostructured templates.$^4$–$^8$ Although these results collectively demonstrate the high inherent HER activity of CoP nanostructures, a direct comparison of the activities and performance is difficult for samples made by different methods and for electrodes prepared in different laboratories, because of unavoidable differences in the electrode preparation methods, mass loadings, and accessible surface areas. Additionally, the HER-active CoP nanostructures reported to date have been polycrystalline or multi-faceted, without statistically relevant differences in the proportions of the different crystal facets that have been exposed and accessible. An important first step toward the goal of better understanding the origin of the high HER activity in CoP and related nanostructured metal phosphate systems is to synthesize and study high quality, morphologically distinct samples. CoP is ideally suited for such an approach, because multi-faceted single-crystalline CoP nanoparticles have amongst the highest activities and acid stabilities of the metal phosphate family of HER catalysts.$^4$ Also, using closely related chemical strategies, methods exist for synthesizing CoP and related metal phosphate nanostructures to produce materials of the same chemical composition and structure but with different morphologies. Accordingly, we report herein the synthesis of highly branched CoP nanostructures with single-crystal CoP nanorod
protrusions that expose a high density of accessible (111) facets. The electrocatalytic HER performance of the branched CoP nanostructures was evaluated and compared to that of multi-faceted CoP nanocrystals. These observations provide a starting point for the identification of the key parameters that impact the HER performance of morphologically distinct nanostructures in the same materials system.

E.3 Experimental
Chemicals and Materials.
1-Octadecene [tech. 90%, C_{18}H_{36}], oleylamine [70%, C_{18}H_{37}N], trioctylphosphine [TOP, 97%, (C_{8}H_{17})_3P], trioctylphosphine oxide [TOPO, 99%, (C_{8}H_{17})_3PO], titanium foil [99.7%, 0.25 mm thickness], and sulfuric acid [99.999%] were purchased from Sigma-Aldrich, and cobalt(II) acetylacetonate [Co(acac)_{2}] was purchased from Alfa Aesar. All chemicals were used as received. Silver paint was purchased from SPI supplies, and two-part epoxy [HYSOL 1C] was purchased from McMaster-Carr.

Synthesis of highly branched CoP nanostructures. Co(acac)_{2} (256 mg, 1 mmol) was introduced into a three-necked round bottom flask that contained oleylamine (6.4 mL, 19.4 mmol), TOPO (3.8 g, 9.8 mmol), TOP (0.5 mL, 1.1 mmol), and a magnetic borosilicate-coated stir bar. The flask was placed into a heating mantle and was equipped with a mercury thermometer with a thermometer adapter in the first port, a Liebig condenser with gas inlet adapter in the second port, and a glass pennywise stopper in the final port. The reaction mixture was heated to 120 °C for 1 h under vacuum to remove water and other low-boiling impurities. Following degassing, an Ar(g) blanket was introduced to the reaction flask while the temperature was raised to 355 °C to 360 °C and then maintained for 3 h. Following heating, the reaction flask was cooled rapidly by removing the heating mantle. Upon reaching 80 °C, the flask was opened to the atmosphere and ≈10 mL of toluene was added to the reaction to avoid solidification of the TOPO. To isolate the nanoparticles, the reaction solution was separated into centrifuge tubes, with each tube being ≈1/3 full. An equal volume of isopropyl alcohol was added to the centrifuge tubes to promote precipitation. The tubes were sealed and then centrifuged at 7000 rpm for 3 min. The resulting supernatant was discarded and the particles were resuspended by addition of hexanes. The particles were then flocculated by addition of excess isopropyl alcohol and centrifuged again. This entire process was repeated two additional times. The resulting oily residue that contained the nanoparticle precipitate was resuspended in 0.50 M H_{2}SO_{4} and centrifuged to collect the final CoP powder, which was suspended in hexanes for storage.
Preparation of Working Electrodes.

Working electrodes were prepared by first making 10 mL of a CoP nanostructure stock solution in hexanes (10 mg mL\(^{-1}\)). To this suspension, \(\approx 5\) \(\mu\)L of oleylamine was added to help promote particle adhesion to the electrode surface. To a 0.2 cm\(^2\) piece of titanium foil, 20 \(\mu\)L of the CoP nanostructure stock solution was deposited in 5 \(\mu\)L increments to achieve a loading density of \(\approx 1\) mg/cm\(^2\). The resulting CoP-decorated Ti foils were annealed under H\(_2\)(5 %)/Ar(95 %) at 450 \(^\circ\)C for 30 min. The loading densities were validated experimentally using a microbalance, by taking the difference between the mass of the annealed foils and the mass of the initial foil. The back sides of the nanostructure-loaded Ti foils were attached to polyvinylchloride-coated Cu wires with Ag paint. The wires were placed through a 6 mm-diameter glass capillary and two-part epoxy was used to cover all exposed surfaces except the front of the Ti foil, onto which the CoP nanostructure sample was deposited.

Electrochemical Characterization.

Electrochemical data were collected using a Gamry Instruments Reference 600 potentiostat. All measurements were performed in 0.50 M H\(_2\)SO\(_4\), unless otherwise noted. A single-compartment cell was used with a graphite rod counter electrode and mercury-mercury sulfate (Hg/Hg\(_2\)SO\(_4\)) reference electrode.

Polarization data were collected at a scan rate of 2 mV s\(^{-1}\), with the solution agitated using a magnetic stir bar. The data were corrected for uncompensated resistance (\(\approx 6\) \(\Omega\)) using the current-interrupt method that was built into the Reference 600 potentiostat software suite. The reversible hydrogen electrode (RHE) potential was maintained by continuous bubbling of \(\approx 1\) atm of research-grade H\(_2\) (g) into the electrochemical cell. To determine the RHE potential, the open-circuit potential of a platinum mesh electrode was determined following the completion of any experiments involving CoP, to avoid Pt contamination. To test the short-term stability, the potential was held at a current density of \(-10\) mA/cm\(^2\) for 18 h of continuous galvanostatic testing. To test the long-term stability, accelerated degradation studies were performed using cyclic voltammetry from 5 mV to \(-160\) mV vs. RHE for 500 cycles at a scan rate of 100 mV s\(^{-1}\).

Materials Characterization.

Transmission-electron microscopy (TEM) images were collected using a JEOL 1200 microscope operating at an accelerating voltage of 80 kV. A JEOL JEM-2010F was used to collect high-resolution bright-field TEM images as well as to
obtain energy-dispersive X-ray spectroscopy (EDX) data at an accelerating voltage of 200 kV. Gatan Digital Micrograph software was used to measure the lattice spacings from the fast-Fourier transform (FFT) of the HRTEM images. These values, and the corresponding FFT diffraction patterns, were simulated using the CrystalMaker/SingleCrystal software package. Scanning-electron microscopy (SEM) images were collected using a FEI Nova NanoSEM 630 at a working distance of 1.5 mm and an accelerating voltage of 2.00 kV. 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 operating at room temperature. The CrystalMaker/ CrystalDiffract software package was also used to simulate the XRD patterns, using previously published crystallographic parameters for MnP-type CoP. Brunauer-Emmett-Teller (BET) surface area measurements were performed using a Micromeretics ASAP 2020 at liquid-nitrogen temperatures, and the data were analyzed using the ASAP 2020 software version 4.0.

### E.4 Results and Discussion

Figure E.1 shows TEM images for the highly branched CoP nanostructures that formed upon heating Co(acac)₂, TOP, TOPO, and OLAM at 360 °C for 3 h. A majority of the CoP nanostructures consisted of a central core with multiple nanorod protrusions that grew outward. The nanorod protrusions had an average diameter of 14 ± 3 nm and the average diameter of the complete nanostructures was 390 ± 70 nm. The SEM image in Figure E.2 confirmed the three-dimensional branched morphology of the CoP nanostructures, as well as their uniformity. HRTEM images of both the core (Figure E.3a) and the branches (Figure E.3b,c,d) indicated that both regions were crystalline and that the branches appeared to be single-crystalline. The majority of the nanorods that protruded from the core predominantly exposed the (111) lattice plane of CoP, with a lattice spacing of 2.4 Å.

Figure E.4 shows powder XRD data for a bulk sample of the CoP branched nanostructures, with a SAED pattern and an EDS spectrum that both correspond to the TEM image shown in Figure E.1a included in Figure E.1c and Figure F.1, respectively. The experimental powder XRD pattern in Figure E.4 matches well with that expected for MnP-type CoP, with no observable crystalline impurities. The agreement between the relative peak intensities that were observed experimentally vs. those that are expected for an isotropic sample indicates that no significant preferred orientation was present in the sample. Strong preferred orientation would be expected for nanorods, but not for the branched nanostructures with three-dimensionally pro-
Figure E.1: a,b) TEM images and c) corresponding SAED pattern of a representative sample of highly branched CoP nanostructures. The indexing in (c) corresponds to MnP-type CoP.

![Figure E.1](image1)

Figure E.2: SEM image of a sample of highly branched CoP nanostructures.

![Figure E.2](image2)

truding nanorods, which cannot align along a preferential crystal direction upon deposition onto a flat substrate. The lack of preferred orientation in the bulk powder XRD sample is therefore consistent with the morphology observed by TEM and SEM. Scherrer analysis of the peak widths indicated an average grain size of 17 nm,
which is, within expected experimental error, consistent with the average diameter of the single-crystalline nanorod protrusions as observed by TEM.

The SAED pattern in Figure E.1c is also consistent with MnP-type CoP, and therefore matches well with that observed for the bulk sample by powder XRD. The EDS spectrum in Figure F.1, acquired for an ensemble of particles, indicated a Co:P ratio of 50:50, which matches with that expected for CoP. Taken together, the XRD, SAED, and EDS data therefore confirm the assigned composition and crystal phase, and indicate that the CoP branched nanostructures formed with high purity. Although highly branched colloidal CoP nanostructures have not apparently been synthesized previously, morphologically similar Co$_2$P nanostructures have been reported. 22 To access highly branched Co$_2$P nanostructures, Zhang and Robinson thermally decomposed cobalt (II) oleate in the presence of pure TOPO, which was
the lone phosphorus source. Our protocol for synthesizing highly branched CoP nanostructures also used TOPO, but we observed that TOPO alone did not produce CoP. Instead, OLAM and TOP were required to form CoP, suggesting that TOP is the primary phosphorus source under our conditions. TOPO is required to generate the highly branched CoP nanostructures, however, rather than the morphologically distinct pseudo-spherical particles that formed when only TOP was used. When TOPO was used as a co-solvent, the highly branched CoP nanostructures form reproducibly, suggesting that TOPO is involved in directing the growth of the nanorod protrusions and/or stabilizing the predominantly exposed facets.

The branched CoP nanostructures were highly crystalline and exposed predominantly single-crystal (111) facets, as compared to the multi-faceted CoP nanoparticles that have been synthesized previously. Furthermore, the surface areas, as measured by Brunauer, Emmett, and Teller (BET) analysis, are comparable for the two different morphologies, with the branched CoP nanostructures having a BET specific surface area of 66 m$^2$/g and the multi-faceted CoP nanoparticles having a BET specific surface area of 59 m$^2$/g.

The similar BET areas for the two different CoP nanostructures provides an opportunity to evaluate the role of morphology on the HER performance of an earth-abundant HER electrocatalyst. Hence electrodes coated with the branched CoP nanostructures were prepared in an analogous manner to the multi-faceted CoP nanoparticles studied previously. Briefly, the highly branched CoP nanostructures were deposited onto $\approx 0.2$ cm$^2$ Ti substrates from a hexanes dispersion that contained $\approx 0.1$ vol % oleylamine. The mass loadings were $\approx 1$ mg/cm$^2$, and the electrodes
were annealed under H\textsubscript{2}(5 \%)/Ar(95 \%) to remove the surface ligands. The SEM and XRD data in Figure F.2 indicate that both the morphology and crystal phase of the CoP nanostructures remained largely unchanged during the electrode preparation and annealing steps, although a small Co\textsubscript{2}P impurity was observed. The Ti electrode containing the branched CoP nanostructures exposed a high density of accessible (111) lattice planes, as shown schematically in Figure E.5.

Figure E.5: Schematic highlighting the high density of exposed (111) facets on the Ti electrodes that contain the highly branched CoP nanostructures.

Figure E.6 shows the polarization (current density vs potential, $J$–$E$) data that correspond to the HER activity in 0.50 M H\textsubscript{2}SO\textsubscript{4} of the highly branched CoP nanostructures. The HER activity of the branched CoP nanostructures was lower than that of the multi-faceted CoP nanoparticles reported previously (Figure S3), despite the mutually comparable surface areas for the two different CoP electrocatalyst morphologies. The overpotentials required to produce a (cathodic) current density of $-20$ mA/cm\textsuperscript{2} were $-117$ mV and $-100$ mV for the branched nanostructures and multi-faceted nanoparticles, respectively, despite their similar loading densities on analogous Ti substrates. Additionally, the material outperforms previously reported Co\textsubscript{2}P nanostructures ($= -167$ mV), suggesting that the small Co\textsubscript{2}P impurity does not play a significant role in the observed activity of the branched CoP nanorods. A quantitative Faradaic yield of H\textsubscript{2}(g) was observed for both types of CoP catalytic systems (see Supplementary Information). A Tafel analysis, shown in the inset to Figure E.6, revealed Tafel slopes of 29 mV/decade and 123 mV/decade for the Pt mesh and Ti foil controls. Both of these values are consistent with values expected based on literature reports.\textsuperscript{1,4,23} The Tafel slope for the branched CoP nanostructures was 48 mV/decade, which is comparable to the 50 mV/decade Tafel slope observed previously for the multi-faceted pseudo-spherical CoP nanoparticles.\textsuperscript{4} The comparable values suggest a similar mechanism for the HER on the branched CoP nanostructures and on the CoP nanoparticles.
Figure E.6: Polarization data in 0.50 M H₂SO₄ for 6 distinct electrodes of the branched CoP nanostructures on Ti foil substrates at mass loadings of ≈1 mg/cm², along with Ti foil and Pt mesh electrodes for comparison. Inset: Tafel plots for the Ti and Pt electrodes, as well as a representative branched CoP/Ti electrode. Tafel slopes, denoted by the grey dashed lines, were calculated using the following linear regions: −60 mV > η > −125 mV for CoP, −10 mV > η > −60 mV for Pt, and −250 mV > η > −400 mV for Ti.

Given the different activities of the branched CoP nanostructures vs. the CoP nanoparticles, the turnover frequency (TOF) values are necessarily quite different. (See the Supplementary Information for TOF calculations.) The branched CoP nanostructures exhibited a TOF of 0.019 s⁻¹ at an overpotential (η) of −100 mV. This TOF value is lower than that of CoP nanoparticles, which showed a TOF = 0.060 s at η = −100 mV.⁴ The branched CoP nanostructures, however, still provided exceptionally high activity for the HER, performing comparably to many other non-noble-metal HER catalysts in acidic solutions, based on evaluation metrics reported in the literature. Examples include MoS₂ (η = −175 mV),²⁴ Mo₂C (η = −152 mV),²⁵ CoS₂ (η = −145 mV),²⁶ CoSe₂ (η = −155 mV),²⁷ MoP (η = −110 mV),¹⁷ WP (η = −110 mV)¹⁹ and Ni₂P (η = −130 mV).¹ However, the long-term stability of the branched CoP nanostructures on a Ti electrode was inferior to that of the CoP nanoparticles, presumably due to poor adhesion of the branched CoP nanostructures to the Ti electrode surface.⁴ Specifically, under galvanostatic conditions (holding at −10 mA/cm² for 18 h), the particles physically detached from the electrode surface, and the overpotential increased from −113 mV to −174 mV over this time period (Figure S4a). Likewise, 500 cycles between −160 mV and 5 mV (vs. the relative hydrogen electrode, RHE), which simulated multiple catalytic start/stop cycles, re-
resulted in an increase in overpotential at $-10 \text{ mA/cm}^2$ from $-115 \text{ mV}$ to $-135 \text{ mV}$ (Figure S4b). The instability is therefore attributed to poor adhesion and is not reflective of the behavior of the catalytic CoP nanostructures themselves. Typically, differences in activities among morphologically distinct nanostructures of the same compound are routinely attributed to inherent differences in the activities of the exposed crystal facets. However, the complexity of such nanostructured materials and their electrodes makes it difficult to unambiguously determine the reason(s) for the inferior performance of the branched CoP nanostructures relative to their nanoparticle analogues. Indeed, the (111) surface could inherently be less active for the HER than one or more other surfaces that are simultaneously exposed and accessible on the CoP nanoparticles. However, the lower HER activity of the branched CoP nanostructures could also result from poorer adhesion and/or a lower density of direct CoP-Ti contacts on the electrode surface. Despite this issue, the present study is a first step toward evaluating the relative HER activities of distinct nanostructured catalysts of the same material that are of high morphological quality and uniformity. As such, these results begin to place empirical boundaries on the range of overpotentials that are observed for similarly prepared materials and electrodes. The branched CoP nanostructures nevertheless offer exceptionally high HER activity, exceeding that of most other non-noble-metal systems. These results suggest that nanostructuring to expose specific facets may not be necessary to achieve high HER performance. Indeed, comparable HER activity has been observed by several groups for CoP materials that span a range of morphologies, synthetic protocols, accessible surface areas, and support materials. A key finding of this work is that the activities are largely the same, regardless of morphology or preparation method, underscoring the high intrinsic activity of CoP. The intrinsic HER activity of CoP makes it a highly viable candidate for practical applications, regardless of morphological details, and this study reinforces that hypothesis. However, establishing trends in activity that can be correlated to specific crystal facets, surface areas, and electrode materials is still important for furthering the understanding of the origin of the HER activity in these systems, and these results represent a step toward this goal.

E.5 Conclusion

Highly branched nanostructures of CoP, with single-crystal nanorod protrusions that predominantly expose (111) facets act as an active HER electrocatalyst. Moreover, the activity of such samples, while not as high as that of comparable multi-faceted
pseudospherical CoP nanoparticles, is still excellent among the growing family of non-noble-metal nanostructured HER electrocatalysts, producing current densities of $-10\, \text{mA/cm}^2$ and $-20\, \text{mA/cm}^2$ at overpotentials of $-100\, \text{mV}$ and $-117\, \text{mV}$, respectively. These results further establish the high intrinsic activity of CoP as an electrocatalyst for the HER and provide important insights into some of the factors that influence its performance, including exposed crystal facets and nanoparticle-electrode interactions.

E.6 Acknowledgements

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E.7 References


Supplementary Information for Highly Branched Cobalt Phosphide Nanostructures for Hydrogen Evolution Electrocatalysis


F.1 Additional Experimental Details

Quantitative Hydrogen Yield Measurements

Quantitative H$_2$ yield measurements were performed in 0.50 M H$_2$SO$_4$ in a two-electrode experiment using a two-compartment cell. The two compartments, for the working and counter electrode, respectively, were separated by a Nafion(R) membrane (Fuelcellstore.com). A graduated cylinder was inverted above the working electrode to collect the H$_2$(g) produced during the experiment. A constant (cathodic) current of −10 mA was maintained for 50 min (3000 s) on a ≈ 0.2 cm$^2$ electrode. The amount of H$_2$(g) produced was 3.92 mL, as compared to the theoretical yield of 3.92 mL, as calculated with Faraday’s law, Dalton’s law of partial pressures and the ideal gas law. In a control experiment, a platinum electrode produced an identical quantity of H$_2$(g) when the same amount of charge was passed through the cathode.

Estimation of Turnover Frequencies

The turnover frequency was calculated using an established method.$^{1-3}$ First, the density of the sample was calculated using the CoP unit cell. Using the measured BET surface areas, the turnover frequencies are reported as turnovers per second per surface atom, analogous to prior reports for Ni-Mo,$^1$ N$_2$P,$^2$ and CoP hollow nanoparticles.$^3$ The Co and P surface atoms were counted separately.

Calculation of TOF values

The molar mass (89.907 g mol$^{-1}$), density (6.416 g/cm$^3$), molar volume (14.01 mL mol$^{-1}$), volume of a 13 nm sphere ($1.15 \times 10^{-18}$ cm$^3$), surface area of a 13 nm sphere ($5.31 \times 10^{-12}$ cm$^2$), and current density at $\eta = -100$ mV (for 1.0 mg/cm$^2$ $\eta = -1.03 \times 10^{-2}$ A/cm$^2$. The average surface atoms per 1 square centimeter is found
by:

\[
\left( \frac{2 \times 6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{14.0 \text{ cm}^3} \right)^{2/3} = 2.45 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2}.
\]

Using the surface atoms per tested area at 0.9 mg/cm² (BET value = \(1.31 \times 10^{18}\) atoms/foil):

\[
\frac{0.9 \text{ mg}}{1 \text{ cm}^2} \times \frac{6.65 \times 10^2 \text{ cm}^2}{\text{mg}} \times \frac{2.45 \times 10^{15} \text{ atoms}}{1 \text{ cm}^2} = 1.63 \times 10^{18} \frac{\text{atoms}}{\text{test}}.
\]

Finally, the turnover frequency at \(-100\text{ mV}\) overpotential is calculated (per surface atom) as:

\[
\frac{1 \text{ turnover}}{2 \text{e}^-} \times \frac{1.3 \times 10^{-2} \text{ A}}{1 \text{ cm}^2} \times \frac{1 \text{ mol}}{96485 \text{ C}} \times \frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol}} \times \frac{1 \text{ text}}{1.65 \times 10^{18} \text{ atoms}} = 0.019 \text{ s}^{-1} \text{atom}^{-1}.
\]

For 0.032 mg/cm², the theoretical value gives 0.028 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.034 s\(^{-1}\) atom\(^{-1}\). For 0.9 mg/cm², the theoretical value gives 0.048 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.060 s\(^{-1}\) atom\(^{-1}\). For 2.02 mg/cm², the theoretical value gives 0.038 s\(^{-1}\) atom\(^{-1}\) with a BET value of 0.045 s\(^{-1}\) atom\(^{-1}\).

### F.2 Supplementary Figures

Figure F.1: Representative EDS spectrum of a sample of highly-branched CoP nanostructures. The Co/P ratio was 1/1. The Cu and Si impurities are due to the TEM grid and column, respectively, and were present in control samples of blank TEM grids.
Figure F.2: (Left) Powder X-ray diffraction data for a sample of highly branched CoP nanostructures deposited onto Ti foil then annealed at 450°C under H₂ (5 %)/Ar (95 %) for 30 min. Simulated XRD patterns for Ti and CoP are shown for comparison. The asterisks indicate a small Co₂P impurity that was observed after annealing. (Right) SEM images of the same sample prior to and after annealing. We did not observe any crystallographic relationships between the interior cores and the branches. It is also difficult to capture the relevant early stages of the reactions that produce the branched CoP nanostructures because of the high temperatures involved.

Figure F.3: Three distinct linear sweep voltammograms for hollow, pseudospherical CoP nanoparticles deposited on Ti foil at a loading density of ≈ 0.8 mg/cm² in 0.5 M H₂SO₄. The electrodes consistently required an overpotential of −100 mV to produce a current density of −10 mA/cm². This value is lower than the overpotential of −117 mV required for the branched CoP nanostructures.
Figure F.4: (a) Plot of overpotential vs. time, held at $-10 \text{ mA/cm}^2$ for 18 h, for a Ti foil electrode containing the highly branched CoP nanostructures. (b) Cyclic voltammetric cycles used to simulate the long-term stability of a comparable CoP/Ti electrode in 0.50 M H$_2$SO$_4$ when cycled between 50 mV and $-160 \text{ mV}$ at a scan rate of 100 mV s$^{-1}$. 
F.3 References


Appendix G

Use of Mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) Functionality to Control Interfacial Chemical and Electronic Properties During the Atomic Layer Deposition of Ultrathin Oxides on Si(111)


G.1 Abstract

Silicon surfaces terminated with a mixed monolayer containing both a propyl aldehyde functionality and methyl groups were prepared and used to control the interfacial chemical and electronic properties of Si(111) surfaces during atomic layer deposition (ALD) of Al$_2$O$_3$ or MnO. Si(111) surfaces functionalized only with the aldehyde moiety exhibited surface recombination velocities, $S$, of 2500 ± 600 cm s$^{-1}$ whereas the mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces displayed $S = 25$ ± 7 cm s$^{-1}$. During the ALD growth of either Al$_2$O$_3$ or MnO, both the HC(O)CH$_2$CH$_2$–Si(111) and CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces produced increased metal oxide deposition at low cycle number, relative to H–Si(111) or CH$_3$–Si(111) surfaces. As detected by X-ray photoelectron spectroscopy after the ALD process, the CH$_3$– and mixed CH$_3$–/HC(O)CH$_2$CH$_2$– functionalized Si(111) surfaces exhibited less interfacial SiO$_x$ than was observed for ALD of metal oxides on H–Si(111) substrates.

G.2 Introduction

Atomic-layer deposition (ALD) is of interest as a conformal, scalable method for the deposition of ultrathin oxides on semiconductor surfaces.$^{1-3}$ For example, ALD has been used to deposit Al$_2$O$_3$, ZrO$_2$, and HfO$_2$ for high-permittivity gates on Si,$^{4-6}$ and is of interest for high-permittivity memory capacitor dielectrics, ferroelectrics, and deposition of metals and nitrides for electrodes and interconnects.$^{7-9}$ Very thin, conformal metal oxide films grown by ALD have produced increased stability of Si photoanodes during water oxidation,$^{10}$ and relatively thick (≈100 nm) films of conductive TiO$_2$ deposited by ALD recently have been shown to stabilize Si, GaAs, and GaP photoanodes for the oxidation of water at pH 14.$^{10}$
ALD precursors are generally transition-metal alkoxides or organometallics that yield initiation and control of film growth by undergoing self-limiting reactions with reactive surface groups. The functionality on the semiconductor surface is thus critical to achieving control over the uniformity of film deposition, the minimization of induction periods, and to provide control over the chemical and electrical properties of the resulting semiconductor/ALD-oxide interfaces. In the case of Si, reaction with the metal precursor oxidizes the hydrogen-terminated Si surface obtained by etching, and is critical to the subsequent growth of the metal oxide layer. Although functionalization of the Si surface via hydrosilylation has been previously demonstrated as a route for initiation of the ALD process that beneficially decreases the amount of silicon oxide (SiOₓ) formed during the growth process, hydrosilylation leaves electronically defective interfaces on Si surfaces, and requires functionalization with long-chain alkanes (> C₁₀) to produce ordered monolayers. We demonstrate herein that aldehyde groups can be introduced to Si surfaces via a chlorination-alkylation reaction sequence designed to terminate all of the Si surface atoms with Si–C bonds. This approach allows the introduction of ALD-initiating functional groups onto the Si surface while maintaining molecular-level control over the chemical and electronic properties of the silicon/ALD-oxide interface.

G.3 Materials and Methods
Films of Al₂O₃ or MnO were grown by ALD through sequential exposure of Si(111) surfaces to trimethyl aluminum (TMA) or bis(ethylcyclopentadienyl)manganese(II) ((EtCp)₂Mn) and water, at 80 °C or 150 °C respectively. The Si(111) samples used for ALD growth were terminated either by: a) H–Si, from etching the Si(111) in NH₄F(aq); b) CH₃–Si, prepared by a two-step chlorination/alkylation process; c) a propyl aldehyde (HC(O)CH₂CH₂–) functionality; d) a mixed monolayer consisting of the propyl aldehyde functionality with methyl groups “back-filling” the remaining reactive Si surface sites of a HC(O)CH₂CH₂–Si functionalized surface; or e) etching the Si surface with a “piranha etch” (3:1 H₂SO₄:H₂O₂(aq) v/v ) after an NH₄F(aq) etch produced terraces on the Si surface. The aldehyde functionality was obtained by functionalization of Cl–Si(111) with (1,3-dioxan-2-ylethyl)magnesium bromide, with subsequent deprotection of the aldehyde with dilute HCl(aq)
G.4 Results and Discussion

Figure G.2 shows the Al 2p and Si 2p regions of the X-ray photoelectron (XP) spectra obtained after 5 deposition cycles of TMA/H$_2$O onto these various functionalized Si(111) surfaces at 80°C. The HC(O)CH$_2$CH$_2$–Si(111) and mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces clearly showed greater film growth than the CH$_3$–Si(111) or H–Si(111) surfaces (Figure G.2A, Table G.4). In addition, the CH$_3$–Si(111) and mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces showed small amounts of SiO$_x$ at 102.5 eV (Figure G.2b), whereas significant SiO$_x$ was observed for the H– terminated Si(111) surface. The position of the Si 2p peak was different for surfaces modified with different functional groups due to effects of band banding and dipoles at the surface.\textsuperscript{19} Table G.4 presents the estimated coverages of the Al$_2$O$_3$ and SiO$_x$ calculated by application of the XPS data to the substrate overlay model.

<table>
<thead>
<tr>
<th>Surface</th>
<th>0-cycles</th>
<th>5 cycle</th>
<th>20 cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S$ (cm s$^{-1}$)</td>
<td>$S$ (cm s$^{-1}$)</td>
<td>Al$_2$O$_3$ (ML)</td>
</tr>
<tr>
<td>H</td>
<td>39</td>
<td>510</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>17</td>
<td>19</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>CH$_3$/HC(O)CH$_2$CH$_2$</td>
<td>25</td>
<td>73</td>
<td>1.8 ± 0.9</td>
</tr>
<tr>
<td>HC(O)CH$_2$CH$_2$</td>
<td>2500</td>
<td>1700</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>SiO$_x$</td>
<td>4000</td>
<td>46</td>
<td>3.7 ± 1.7</td>
</tr>
</tbody>
</table>

Table G.1: Surface recombination velocity and Al$_2$O$_3$ and SiO$_x$ surface coverage by surface functionality and ALD cycle number.\textsuperscript{1} indicates measured in air.

Analogous behavior was observed on these four types of Si(111) surfaces for deposition of MnO. Specifically, the CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surface showed greater MnO deposition than the H–terminated surface (Figure G.3a), but approximately half of the MnO deposition of the piranha-cleaned surface. The mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surface contained little interfacial SiO$_2$, even after
Figure G.2: X-ray photoelectron spectra of CH$_3$– (blue), H – (green), and CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) (orange) surfaces after 5 cycles of TMA/H$_2$O deposition. (A) Al 2p spectral region (offset for clarity). The H– terminated spectrum was taken at a different scan step size. All other factors are equal, so the comparison of counts per second is valid. (B) Si 2p spectral region (offset for clarity) showing the development of SiO$_x$ ($\approx 102.5$ eV) after 5 cycles of TMA/H$_2$O deposition on H–Si(111) surfaces.

ALD, as detected by XPS (Figure G.3b). By this method, an abrupt Si/M$_x$O$_y$ interface was formed, whereas ALD at H–terminated Si or piranha-etched Si results in a Si/SiO$_x$/M$_x$O$_y$ interface.

The electrical properties of the metal oxide-coated functionalized surfaces were probed by measurement of the lifetime of photogenerated charge carriers under conditions for which the carrier lifetime was dominated by interfacial rather than bulk recombination. In this process, a high-carrier-lifetime, float-zone grown, double-side polished Si(111) sample (4 k$\Omega$ to 8 k$\Omega$) was exposed simultaneously on both sides to all of the wet chemical functionalization and ALD process steps. Time-resolved microwave conductivity methods, described elsewhere, were then used to probe the minority-carrier lifetimes of the various samples. The minority-carrier lifetime was related to the surface recombination velocity, $S$, using conventional relationships. H–Si(111) surfaces have extremely low $S$ values, $< 10 \times 10^{-2}$ cm s$^{-1}$, when measured in a stabilizing environment such as H$_2$SO$_4$, but these values increase substantially upon even brief exposure to air, due to the formation of undesirable Si oxides. In contrast to H–Si(111) surfaces, the CH$_3$–Si(111) surface retains a low $S$ value for over a month of air exposure, due to essentially
complete termination of Si atop sites by unreactive Si–C bonds. Although pristine H–Si(111) surfaces have very low electronic defect densities, after 1 cycle of TMA/H$_2$O exposure, the photogenerated carrier lifetime decreased significantly. The HC(O)CH$_2$CH$_2$–Si(111) surface exhibited a rapid photogenerated carrier decay, and consequently high S value (2500 ± 600 cm$^{-1}$) as synthesized and at the low ALD cycle numbers investigated herein (Figure G.4). In contrast, the as-synthesized, mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surface, had a low S value of 25 ± 7 cm$^{-1}$, similar to that of the CH$_3$–Si(111) surface, in accord with previous reports of mixed monolayer functionalized Si(111) surfaces.$^{18,22}$ After 5 cycles of TMA/H$_2$O deposition, the CH$_3$– and mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces showed little change in their photogenerated carrier decay profiles (Figure G.4b). Previous work has shown that ALD initiation at H–Si(111) proceeds via Si–M formation,$^{15}$ which is consistent with the development of electronic defects at the interface, as observed herein on surfaces that were not extensively terminated with Si–C bonding.

Figure G.5 shows the progression of the Al 2p:Si 2p XP intensity ratio and S with the number of TMA/H$_2$O ALD cycles. Up to ≈ 5 cycles, the Al 2p:Si 2p ratio correlated with the presumed density of reactive surface sites, in the order H– ≈ CH$_3$– < mixed CH$_3$–/HC(O)CH$_2$CH$_2$– < HC(O)CH$_2$CH$_2$– < piranha cleaned (Figure G.5a). After 5 exposure cycles, deposition at the H–terminated surface increased significantly (with increased variance), therefore exhibiting behavior sim-
Figure G.4: Photogenerated carrier-decay profiles measured by time-resolved microwave conductivity for H–terminated, piranha-cleaned, and chemically functionalized Si(111) surfaces (A) as synthesized (B) and after 5 cycles of TMA/H$_2$O deposition. The CH$_3$–Si(111) and mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces retained long carrier lifetimes after the ALD cycles.

ilar to what has previously been described as an “initiation period” due to poor ALD nucleation.$^{3,13,23–25}$ As shown in Figure G.5b, the HC(O)CH$_2$CH$_2$–Si(111) surface exhibited a high $S$ value even at 20 ALD cycle numbers. For the H-terminated surface, $S$ increased substantially with the first ALD cycle, and then slowly increased as cycle number increased. The behavior is consistent with literature reports of deposition initiation via Si–M formation.$^{15}$ The CH$_3$– and mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) surfaces, however, exhibited low $S$ values at all ALD cycle numbers tested. Interestingly, the piranha-cleaned Si(111) surface showed a decrease in $S$ after deposition of Al$_2$O$_3$, which may be due to fixed charge generation and consequent development of a surface field, rather than ‘repair’ of the electronic defects present at the Si/SiO$_x$ interface. However, the thickness of the oxide left after piranha cleaning adds to the overall oxide thickness and to the electrical resistance across the Si interface.

Figure G.6 shows the topography of the Al$_2$O$_3$ films formed after 20 TMA/H$_2$O cycles on the CH$_3$–Si(111), CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111), HC(O)CH$_2$CH$_2$–Si(111), and piranha cleaned-Si(111) surfaces, respectively. Both the additional Al or Mn in the XP spectra of the Si surfaces, as well as the smoothness of the resulting ALD films, attest to the improved deposition efficiency for the aldehyde-terminated Si(111) surfaces relative to that of the CH$_3$–Si(111) or H–Si(111) surfaces. Due to the chemical inertness of the CH$_3$– groups, ALD likely initiates at structural defects on the surface and progresses as “island growth” in an inhomogeneous process that leads to the loss of the atomic flatness that is characteristic of the CH$_3$–Si(111)
Figure G.5: (A) Al 2p:Si 2p counts per second ratio versus ALD cycle number, indicating a higher deposition efficiency at low cycle number for surfaces with a high density of initiation points (–OH groups at piranha-cleaned surfaces and aldehyde groups at HC(O)CH₂CH₂–Si(111) surfaces). Slow growth was observed at unreactive and stable CH₃–Si(111) surfaces, whereas delayed initiation was observed at H–Si(111) surfaces. (B) High $S$ values were observed at HC(O)CH₂CH₂–Si(111) surfaces, independent of ALD cycle number. Increasing $S$ values were observed with increasing ALD cycle numbers for H–Si(111) surfaces, indicating the formation of electronic defect states as the film growth proceeded.

Initiation is likely to occur more homogeneously at aldehyde-terminated and SiOₓ surfaces, which have high densities of surface bound –OH or –C(O)H groups, and therefore produces smooth Al₂O₃ films even at low cycle numbers.

Figure G.6: Tapping-mode AFM images of (A) CH₃–Si(111) (rms roughness = 0.320 nm), (B) mixed CH₃–/HC(O)CH₂CH₂–Si(111) (0.259 nm), (C) HC(O)CH₂CH₂–Si(111) (0.360 nm), and (D) piranha-cleaned SiOₓ on Si(111) (0.171 nm) surfaces after ALD 20 cycles of TMA/H₂O exposure. All topographs (Digital Instruments Multi-Mode AFM-2 with a Nanoscope IIIa controller) are 500 × 500 nm, and the height profile follows the line depicted in the corresponding image. Height scales are 4 nm.
G.5 Conclusion

In summary, mixed monolayer formation and functionalization with a protected aldehyde allowed for the synthesis of a low electronic defect-density, high functionality aldehyde-terminated Si(111) surface. Low surface recombination velocities (41 ± 18 cm s\(^{-1}\) for 1-20 cycles) were observed at very low ALD cycle numbers and without subsequent thermal treatment, which is in contrast to reports of surface passivation by the introduction of fixed negative interfacial charge within Al\(_2\)O\(_3\) ALD films.\(^{27}\) No additional thermal annealing step or ozone addition during ALD was required to produce the observed low surface recombination velocities. The ALD growth of Al\(_2\)O\(_3\) or MnO proceeded with higher efficacy on the aldehyde-functionalized Si(111) surface than on the low S CH\(_3\) – Si(111) surface, with lower interfacial recombination velocities and controlled interfacial chemistry obtained from the aldehyde-terminated surfaces. Furthermore, the resulting Si/M\(_x\)O\(_y\) interfaces were abrupt and free of detectable interfacial SiO\(_x\). As such, these chemically modified Si surfaces have allowed for molecular level control over the film uniformity as well as for beneficial control over the interfacial chemical and electronic properties of ALD-deposited oxides on Si surfaces.

G.6 Acknowledgements

This work was supported by the National Science Foundation (CHE-1214152) and the Molecular Materials Research Center of the Beckman Institute at the California Institute of Technology. This work was additionally supported by BP and the Gordon and Betty Moore Foundation. The Link Foundation Energy fellowship (L. E. O.), the NSF ACC-F (CHE-1042006, N. C. S.), and the NSF-GRFP (C. W. R.) are gratefully acknowledged for graduate and postdoctoral fellowship support. The authors thank Judith Lattimer for assistance with XPS data, and Ron Grimm for H-terminated silicon data.

G.7 References


Appendix H

Supplementary Information for Use of Mixed CH$_3$–/HC(O)CH$_2$CH$_2$–Si(111) Functionality to Control Interfacial Chemical and Electronic Properties During the Atomic Layer Deposition of Ultrathin Oxides on Si(111)


H.1 Calculation of Surface Coverage from X-ray Photoelectron Spectra

The average oxide thickness was measured using quantitative XPS and AFM was not used for thickness measurements. The oxide coverage on the Si surfaces was calculated according to published methods using the following equations:

$$
\Phi_A = Q_{AB} \frac{I_A/I_A^{\text{inf}}}{I_B/I_B^{\text{inf}}}
$$

$$
Q_{AB}^X = \left[ \frac{\lambda_A E_A \cos \theta}{a_A} \right],
$$

where $\Phi_A$ is the fractional coverage of monolayer A over the substrate B. $Q_{AB}^X$ is the monolayer matrix factor for XPS. $I_A/I_A^{\text{inf}}$ is an intensity ratio. $\lambda_A$ is the inelastic mean free path in nm (IMFP). $\theta$ is the electron take-off angle from surface-normal. $a_M$ is derived from $1000 \rho N a_M^3 = A_M$ where, in turn, $\rho$ is the density (in kilograms per cubic meter), $N$ is Avogadro’s Number and $A_M$ is the mean atomic weight.

The full form of the equation is:

$$
\Phi_A = \left[ \frac{\lambda_A \cos \theta}{\sqrt{\frac{\lambda_A}{1000 \rho N}}} \right] \left( \frac{I_B^{\text{inf}}}{I_B} \right) \left( \frac{I_A}{I_A^{\text{inf}}} \right).
$$

$\lambda_A$ can theoretically be obtained from multiple-angle XPS experiments. Elastic scattering effects are presumed negligible, so this is taken to be equal to the inelastic mean-free path. We know that this expression is incomplete because $\lambda_{\text{SiO}_2}$ and $\lambda_{\text{Al}_2\text{O}_3}$ are not necessarily equal, however, we used $\lambda = 2.1$ nm following a published
procedure.\textsuperscript{2}

On the Kratos we measured \( \frac{I_{\text{Si}}}{I_{\text{SiO}_2}} = 1.3 \) and \( \frac{I_{\text{Si}}}{I_{\text{Al}_2\text{O}_3}} = 2.0 \).

For aluminum oxide:

\[
\sqrt[3]{\frac{A_A}{1000\rho N}} = \frac{101.9 \text{ g mol}^{-1}}\left(\frac{1000 \text{ g}}{\text{T kg}}\right) \times 6.023 \times 10^{23} \text{ mol}^{-1} \times 3950 \frac{\text{kg}}{\text{m}^3} \left(\frac{1 \text{ m}}{10 \times 10^9 \text{ nm}}\right)^3 = 3.5 \text{ nm}.
\]

On the Kratos \( \theta = 0^\circ \), \( \cos 90 = 1 \).

Using standard methods for propagation of errors, assumed errors on the relative sensitivity ratio to be 20 %. For \( a_A \) and \( \lambda_A \) the assumed the relative error is 30 %.

**H.2 Microwave Conductivity Measurements**

The SRV measurement was conducted in air, and the time taken to make the measurement prior to ALD deposition would have allowed for oxidation and a chemical change in the H–terminated Si(111) surface. A measurement of the recombination velocity for H–terminated Si surfaces prior to ALD is included in Table G.4 (0-cycle column).

**H.3 Supporting Data**
Figure H.1: Atomic-force microscopy images of various surfaces after five cycles of atomic-layer deposition using TMA and H$_2$O. The starting surfaces were (a) H–Si(111), (b) aldehyde-functionalized Si(111), (c) methyl-functionalized Si(111), (d) piranha cleaned Si(111), and (e) Si(111) modified by a mixed monolayer containing aldehyde and methyl functional groups.

H.4 References


Appendix I

Complex Nanomineral Formation Utilizing Kinetic Control by PLAL

C.W. Roske, J.W. Lefler, A.M. Muller. (Submitted)

I.1 Abstract
We used pulsed-laser ablation in liquids (PLAL) of Cu or Zn foil targets in water or in aqueous Cu or Zn salt solutions. PLAL in neat water generated mixtures of metal and (thermodynamically preferred) metal oxide nanomaterials, whereas the availability of select dissolved anions predictably led to the fabrication of more complex phase-pure nanominerals. PLAL of Cu foil in aqueous CuCl\(_2\) solution produced nanoparatacamite, Cu\(_2\)Cl(OH)\(_3\), whereas nanorouaite, Cu\(_2\)(NO\(_3\))(OH)\(_3\), was formed in aqueous Cu(NO\(_3\))\(_2\) and NH\(_4\)OH solution. Likewise, we synthesized simonkolleite, Zn\(_5\)(OH)\(_8\)Cl\(_2\)·H\(_2\)O, or layered zinc hydroxide nitrate, Zn\(_5\)(OH)\(_8\)(NO\(_3\))\(_2\)·2H\(_2\)O, nanoparticles by PLAL of Zn targets in aqueous ablation liquids with added ZnCl\(_2\) and NH\(_4\)OH or Zn(NO\(_3\))\(_2\), respectively. Bimetallic zincian paratacamite resulted from PLAL of Cu foil in aqueous Cu and Zn chloride solution. Our results show that kinetic control exceeded thermodynamic product formation during nanosecond ultraviolet PLAL.

I.2 Introduction
Pulsed laser ablation in liquids (PLAL) has emerged as an innovative technique for the fabrication of nanomaterials with tailored properties. Henglein and Fojtik pioneered the method when they prepared Au, Ni, and C colloids in the early 1990s.\(^1\) Since then, PLAL has been successfully applied to the controlled generation of numerous metal, alloy, oxide, semiconductor, ceramics, and carbon nanoparticles.\(^2\)–\(^4\) Specifically, PLAL of Cu targets in water yielded crystalline particles of Cu and/or CuO with diameters ranging from 2 to 100 nm.\(^5\)–\(^8\) Other phases, such as Cu\(_2\)O, were accessible at high pulse energies.\(^9\) Similarly, PLAL of Zn targets in water has been shown to produce crystalline Zn or ZnO particles with diameters ranging from 5 to 100 nm.\(^10\)–\(^14\) PLAL offers many tunable experimental parameters and is capable of producing nanomaterials with unique electronic and catalytic properties. Very high temperatures, pressures, and atom densities exist in the liquid confined plasma formed from precursors during PLAL, thus permitting exploration
of extreme regions of materials’ phase diagrams. Control of nanoparticle size, polydispersity, and composition is achieved by choice of laser pulse energy and the chemical nature of the solid target or liquid medium. Nanoparticle catalysts exhibit maximum surface area and introduce additional benefits through the modulation of electronic properties as a result of quantum confinement. Another advantage of PLAL is the ease of handling and collecting the resulting nanoparticles, as they are suspended in the liquid upon synthesis. Analogous to the creation of geological minerals, the PLAL process involves high temperatures and pressures. Rapid cooling and injection of nanoparticles into the liquid that surrounds the plasma quench kinetic products. In nature, the entire periodic system is the toolkit for material formation. Therefore, natural minerals often have complex compositions. We show here that addition of select anions to the ablation solutions led to the fabrication of more complex phase-pure nanominerals (ergo the kinetic products) compared to PLAL of metals in water, which generated mixtures of metallic and (thermodynamically most stable) metal oxide nanomaterials.

I.3 Experimental Section

Materials and Methods

Pulsed laser ablation in liquids was performed in the Beckman Institute Laser Resource Center at California Institute of Technology, X-ray photoelectron spectroscopy in the Molecular Materials Research Center (Beckman Institute at California Institute of Technology), and energy-dispersive X-ray spectroscopy in the California Institute of Technology GPS Division Analytical Facility. Data analysis and graphing were performed with Igor Pro 6.37 (WaveMetrics). All chemicals were used as received. Deionized water was obtained from a Barnstead Diamond Nanopure system and had a resistivity of $\geq 16 \, \text{M}\Omega - \text{cm}$.

Syntheses

Nanomaterials were synthesized by PLAL. A 30 mm diameter metal disk was sonicated for 10 min in 10 % aqueous HCl to remove surface oxides and thoroughly washed with water. The clean disk was placed horizontally on a glass flange in a 30 mL glass beaker, which was filled with 10 mL liquid. All glassware was thoroughly cleaned with aqua regia before use. The disk moved between laser pulses, see next section. The metal disks consisted of Cu (0.15 mm thick, A.J. Oster) or Zn (0.25 mm thick, Alfa); all metal sheets had purities of >99.9 %. For preparation of monometallic materials, the liquid was water or aqueous solutions of
3.4 M CuCl₂·2H₂O, 3.4 M Cu(NO₃)₂·3H₂O, 3.3 M Zn(NO₃)₂·6H₂O (all Sigma-Aldrich), or saturated solutions of Cu(NO₃)₂·3H₂O or ZnCl₂ (EM Science) in 1.0 M aqueous NH₄OH (JT Baker). Cu or Zn foils were used in aqueous Cu or Zn solutions, respectively. Bimetallic nanoparticles were made from Cu foil in an aqueous solution of 2.1 M CuCl₂·2H₂O and 0.7 M ZnCl₂. Each sample was irradiated for 60 min by 150 mJ, 355 nm, 8 ns pulses, which were provided by a frequency-tripled 10 Hz Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series). The laser beam was focused with a 100 mm focal length plano-convex quartz lens 1.0 mm below the surface of the liquid, at the metal disk. The nanoparticle suspensions were transferred into glass vials after synthesis. Dry materials were obtained by centrifugation and washing with water until the supernatant did no longer show any salt absorption. The nanoparticles were dried under vacuum after washing twice with 3 mL acetone (EMD, OmniSolv(R)).

Characterization

X-ray photoelectron spectroscopy (XPS) data were taken with a Surface Science Instruments M-probe surface spectrometer, using monochromatic Al Kα radiation (1486.6 eV) and a vacuum chamber pressure of < 5 × 10⁻⁹ torr. Nanomineral samples were drop-cast from aqueous suspensions on clean Ti foil and dried in ambient air at room temperature. Survey scans were collected to identify the elements present in the materials. Depending on the elemental composition of the nanoparticles, high-resolution spectra were taken in the Cu 2p, Zn 2p, Cl 2s, N 1s, or O 1s regions. Binding energies and peak area quantifications were obtained from Gaussian-Lorentzian peak fits after Shirley background subtraction,¹⁵ using relative sensitivity factors, and were referenced to the C 1s peak arising from adventitious carbon, taken to have a binding energy of 284.8 eV.¹⁶ XPS data analysis was performed with CasaXPS (Version 2.3.16 PR 1.6).

Powder X-ray diffraction (XRD) data were obtained with a Bruker D2 PHASER diffractometer, using monochromatic Cu Kα radiation (1.5418 Å; tube power 30 kV, 10 mA). The instrument resolution was 0.050° in 2θ, and the counting time was 3.0 s per step. Solid samples were mounted with Vaseline (X-Alliance GmbH) on a zero-diffraction silicon plate (MTI Corporation). Background subtraction and XRD pattern matching was performed with the Bruker DIFFRAC.SUITE software. Powder XRD peak assignment was carried out using the International Centre for Diffraction Data (ICDD, 2012) database; powder diffraction file (PDF) numbers are referenced throughout the Results and Discussion section.
Energy-dispersive X-ray spectroscopy (EDX) data were collected to determine the metal ratio in the PLAL-made bimetallic material. We used an Oxford X-Max SDD X-ray Energy Dispersive Spectrometer, which allowed quantitative elemental analysis with a relative accuracy of better than 5% and detection limit of better than 0.5%. A working distance of 8 mm was used to maximize X-ray counts, and analysis was performed with the AZtec software package.

Dynamic light scattering (DLS) data were acquired at room temperature with a Brookhaven ZetaPals instrument. Mean values and size distribution widths ($\sigma$) were calculated from the measured intensity histograms by the built-in software; they were obtained by averaging five 1 min sweeps and had an estimated relative error of $\pm 4\%$. An aqueous solution of 0.27 M cetyltrimethylammonium bromide (CTAB) and 0.1 M sodium chloride was passed through a 0.45 µm Millipore syringe filter three times into a freshly cleaned glass scintillation vial to remove all dust. Nanomaterials were suspended in this solution (5 µg mL$^{-1}$) and sonicated for 30 min.

I.4 Foil Target Setup

Large amounts of thermal energy are generated during PLAL. Efficient heat dissipation in the liquid is crucial to achieve reproducibility since bubble formation and thermal distortions of the laser beam interfere with the ablation process. Flow cell and magnetic stirring methods have been successfully employed in the synthesis of silver colloids from stationary solid targets at pulse energies below 13 mJ.\textsuperscript{2} We previously reported PLAL preparations of transition metal oxide and hydroxide nanoparticles with 355 nm nanosecond pulses with energies ranging from 30 to 210 mJ.\textsuperscript{17} The higher pulse energies necessitated moving the metal target. The simplest (oft-used) solution is target powder swirling in magnetically stirred ablation liquid.

We found that the target powder size mattered. Powder particles had to be small enough that gravity did not interfere with individual particles floating in the stirred liquid through the laser focus, which was located just below the liquid surface. Yet particles needed to be large enough that their surface appeared flat with respect to the focal beam waist, so that the main propagation vector of the shock wave was opposite to the incident light direction. A shock wave originating from a convex surface is less powerful than one from a flat surface, thereby leading to less rapid nanoparticle formation. As such, the optimal powder particle size depends on the density of the solid target, the viscosity of the ablation liquid, the stirring velocity,
and the focal beam waist. While some metals can easily be obtained commercially as powders in the desired size range, PLAL nanomaterial synthesis becomes more versatile if widely available metal foils can be used.

Both the foil target and ablation liquid must move at higher pulse energies, which were employed in the syntheses of metal oxide and hydroxide nanomaterials with 355 nm light. When we placed stationary Cu or Zn foil targets with thicknesses of $\geq 0.1 \text{ mm}$ in magnetically stirred liquids we observed the appearance of holes within minutes after irradiation with focused 90 mJ, 355 nm, 8 ns, 10 Hz repetition rate laser pulses. Therefore, we designed and built a PLAL setup that allowed us to move the target foil within its plane between each laser pulse and to simultaneously agitate the liquid.

Moving the target instead of the laser focus is technologically easier. We placed a metal foil disk on a glass flange in a 30 mL beaker (Figure I.1a), which spun at 50 rpm and simultaneously moved back and forth horizontally; the travel distance was 23 mm so that the convergent vertical laser beam hit only the target and not the beaker walls. Two low-cost electrical motors powered both motions. The glass flange had an outside diameter of 30 mm at the bottom, 20 mm at the top, and its height was 10 mm. The disk was cut from commercially available metal foil such that it just fit horizontally into the beaker. A 4 mm diameter hole in the center of the disk facilitated convection of the liquid above and below the target disk. Two disposable, 4 mm diameter glass balls were placed under the metal foil disk to further agitate the liquid. We note that thin Cu foil (0.05 mm thickness) did not withstand the heat generated during PLAL and crumpled after a few minutes under our conditions. Therefore, we used foil targets of at least 0.1 mm thickness. We found that we succeeded in evenly ablating the metal target with our setup (Figure I.1b).

Our method offers a number of advantages: It is amenable to all target metals that are available as foils of at least 0.1 mm thickness. The glassware is low-cost and commercially available or easily made. All chemicals, including the resulting nanomaterials, come only into contact with thoroughly cleaned glass, preventing inadvertent contaminations. The method’s simplicity allows for operation with any laser system of choice, as the target is moved with respect to the laser focus, eliminating the need for a laser scanner. Finally, the compactness of the setup permits its placement in inert gas atmosphere if desired.
I.5 Results and Discussion

In PLAL, the generated plasma consists of chemical elements from the solid and the liquid. Our work on mixed metal hydroxide nanoparticles has shown that the relative proportion of metals in the generated materials was a function of the concentration of the metal ions that were dissolved in the ablation liquid. At high dissolved ion concentrations the metal composition of the resulting nanomaterials was predominantly governed by the ion species. For example, ferrous and ferric oxides were obtained from metallic Ni powder in aqueous Fe(NO$_3$)$_3$ solutions, whereas PLAL of Fe target powder in 3.0 M aqueous Ni(NO$_3$)$_2$ solution resulted in [Ni$_{0.78}$Fe$_{0.22}$]-layered double hydroxide nanosheets.$^{18}$

We also found that nanomaterial yields were higher when metal ions were present in the ablation liquid, while all other experimental conditions were kept virtually identical. This was also true when the metal target and ion species were comprised of the same element. Syntheses with added metal ions typically yielded about 100 mg per batch, whereas we collected only $< 10$ mg per batch from PLAL in pure water. Select anions of the dissolved salts were incorporated into the prepared nanoparticles, thus forming more complex nanominerals utilizing kinetic control. Syntheses in neat water yielded simple metals or (thermodynamically preferred) metal (hydr)oxides. For a direct comparison of nanomaterial syntheses by PLAL, we used Cu or Zn foil in pure water or with added Cu or Zn salts, respectively. All materials were prepared at virtually the same physical conditions. We identified crystal phases of the PLAL-made nanomaterials by XRD. The bulk Cu/Zn ratio of the bimetallic material was determined by EDX. Surface compositions were probed by XPS. Note that the interrogation depths of XRD and EDX range from a few to a few hundred micrometers, whereas X-ray photoelectrons escape only
from the top few nanometers of solid surfaces. We also assessed nanoparticle size distributions by DLS. Characterization data in tabular form are available in the Supporting Information. Our approach allowed us to investigate if kinetic control transcended the generation of thermodynamic products. The synthesized nanomaterials are summarized in Table I.1 and described in more detail below.

<table>
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<tr>
<th>Foil</th>
<th>Added salt</th>
<th>Obtained material (by XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>None</td>
<td>Cu, CuO</td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl₂ · 2 H₂O</td>
<td>Cu₂Cl(OH)₃</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(NO₃)₂ · 3 H₂O, NH₄OH</td>
<td>Cu₂(NO₃)(OH)₃</td>
</tr>
<tr>
<td>Zn</td>
<td>None</td>
<td>Zn, ZnO</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnCl₂, NH₄OH</td>
<td>Zn₅(OH)₈ · H₂O</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NO₃)₂ · 6 H₂O</td>
<td>Zn₅(OH)₃(NO₃)₂ · 2 H₂O</td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl₂ · H₂O, ZnCl₂</td>
<td>Cu₃(Cu,Zn)Cl₂(OH)₆</td>
</tr>
</tbody>
</table>

Table I.1: Nanomaterials synthesized by PLAL of metal foils in water or aqueous solutions.

**Copper Materials**

We used PLAL to synthesize Cu-containing nanomaterials from Cu foil targets in pure water, or equimolar aqueous solutions of copper chloride or nitrate. Because of its limited solubility in water, we could not use Cu(OH)₂ as a dissolved precursor. Depending on the ablation liquid, we obtained different materials.

PLAL of Cu in water generated a mixture of CuO and metallic Cu nanoparticles. Interestingly, we obtained a more complex nanomineral from PLAL of Cu foil in copper chloride solution: Cu₂Cl(OH)₃ in the paratacamite phase. In contrast, PLAL of Cu foil in an aqueous solution of copper nitrate and ammonium hydroxide led to the formation of rouaite nanoparticles. PLAL of Cu foil in Cu(NO₃)₂ solution without NH₄OH did not yield particles, presumably because a relatively high concentration of hydroxide ions was needed for solid-state material formation. Paratacamite and rouaite are not the thermodynamically most stable phases or compositions of oxidized copper. The preparation of Cu₂Cl(OH)₃ and Cu₂(NO₃)(OH)₃ shows that our PLAL synthesis favored the formation of kinetic products if appropriate anions were present. A reddish-black solid was obtained by PLAL of Cu in water (Figure I.2). XRD data showed two phases consisting of metallic Cu (PDF 01-070-3038) and CuO (PDF 01-078-0428); no other crystal phases were detected. The XP spectra in the Cu 2p region exhibited a doublet with the expected branching ratio of 2:1 and corresponding satellite features. Central binding energies of Cu 2p3/2
peaks were 932.7 and 933.8 eV, consistent with assignment to metallic Cu$^{21}$ and divalent Cu–O$^{22}$, respectively. Relative peak quantitation revealed that the surface ratio of Cu$^{0/2+}$ was 4.0:1. We observed a single O 1s peak at 530.7 eV, attributable to CuO$^{23}$. The nanoparticles had a monomodal size distribution and a hydrodynamic diameter of (225 ± 40) nm.

Figure I.2: (a) XRD data (blue), reported fixed-slit intensities of Cu (PDF 01-070-3038, red) and CuO (PDF 01-078-0428, black), inset: photo of the PLAL-made material; (b) XPS data in the Cu 2p and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

Addition of CuCl$_2$ to the aqueous ablation liquid led to the formation of a green solid (Figure I.3). XRD data confirmed that it consisted of basic copper chloride, Cu$_2$Cl(OH)$_3$, in the paratacamite phase (PDF 01-070-0821). The obtained diffraction pattern matched literature data very well [85] and showed no other crystal phases. XPS data in the Cu 2p region exhibited a doublet with a branching ratio of 2:1 and corresponding satellite features. The peaks with central binding energies of 933.4 and 935.4 eV were assigned to CuO and Cu–Cl 2p$_{3/2}$ components, in accordance with reported data$^{23,24}$ We detected single Cl 2s and O 1s core level peaks with binding energies of 270.0 and 531.5 eV, which we attributed to Cu–Cl and Cu–OH, respectively$^{23}$ The nanoparticles exhibited a monomodal size distribution and a hydrodynamic diameter of (258 ± 43) nm.

Paratacamite is thermodynamically the most stable polymorph of Cu$_2$Cl(OH)$_3$. The mineral crystallizes in the rhombohedral space group$^{26}$ It occurs naturally as an oxidation product of other copper minerals under arid, saline conditions.
Figure I.3: (a) XRD data (blue), reported fixed-slit intensities of paratacamite (PDF 01-070-0821, black), inset: photo of the PLAL-made material; (b) XPS data in the Cu 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

Paratacamite is well studied in the context of archaeological objects and art, since it is a corrosion product of Cu-containing alloys; it is often called “bronze-disease”.\textsuperscript{27,28} We collected a green solid upon PLAL of Cu foil in an aqueous solution of Cu(NO\textsubscript{3})\textsubscript{2} and NH\textsubscript{4}OH (Figure I.4). We deliberately chose NH\textsubscript{4}OH as the hydroxide source, as to not introduce additional chemical elements to the ablation liquid. We identified the material as rouaite, Cu\textsubscript{2}(NO\textsubscript{3})(OH)\textsubscript{3}, by XRD; no other crystal phases were present. The XPS Cu 2p core level region exhibited a doublet with a branching ratio of 2:1 and corresponding satellite features, indicative of Cu\textsuperscript{2+} species. The peak with a central binding energy of 935.3 eV is consistent with Cu–OH and Cu–NO\textsubscript{3} 2p\textsubscript{3/2} components \textsuperscript{84}. We detected an N 1s core level peak with a binding energy of 407.3, which we attribute to Cu–NO\textsubscript{3}.\textsuperscript{23} A minor contribution of a component with a central binding energy of 403.6 eV was also present, consistent with a metal nitrite.\textsuperscript{29} We assigned the two components in the O 1s region with binding energies of 531.5 eV and 532.5 eV to Cu–OH and Cu–NO\textsubscript{3}, respectively.\textsuperscript{30,31} The nanoparticles exhibited a monomodal size distribution and a hydrodynamic diameter of (156 ± 62) nm.

Rouaite is a rare mineral that was only described in 2001;\textsuperscript{32} it was named after its locality of discovery at old Cu mines of Roua, Alpes-Maritimes, south-eastern France.\textsuperscript{33} It is the thermodynamically least stable polymorph of Cu\textsubscript{2}(NO\textsubscript{3})(OH)\textsubscript{3}
minerals; decomposition to CuO occurs upon heating. Copper hydroxide nitrates are well investigated as artificial patinas to restore archaeological copper and bronze surfaces.\textsuperscript{34,35}

\textbf{Zinc Materials}

Analogous to our Cu-based materials, we used PLAL to prepare Zn-containing nanomaterials from Zn foil targets in pure water or in zinc chloride or nitrate aqueous solutions. Addition of Zn(OH)\textsubscript{2} as a precursor was not practical as its solubility in water is less than 0.01 g per 100 mL.\textsuperscript{36} We obtained different materials from the three ablation liquids. PLAL of Zn in water produced a mixture of wurtzite ZnO and metallic Zn nanoparticles, as evidenced by XRD data (Figure I.5). Again, similar to our Cu materials, we generated more complex, but phase-pure nanominerals from PLAL of Zn foil in Zn salt solutions. We predicted that PLAL of ZnCl\textsubscript{2} in basic solution would produce the mineral simonkolleite. For maximum material yield, we prepared a saturated solution of ZnCl\textsubscript{2} in 1.0 M aqueous NH\textsubscript{4}OH and indeed formed Zn\textsubscript{5}(OH)\textsubscript{8}Cl\textsubscript{2} \cdot H\textsubscript{2}O in the simonkolleite crystal phase. In contrast, the anionic clay Zn\textsubscript{5}(OH)\textsubscript{8}(NO\textsubscript{3})\textsubscript{2} \cdot 2 H\textsubscript{2}O was the product of PLAL in aqueous Zn(NO\textsubscript{3})\textsubscript{2} solution. Both complex minerals exist in nature, but are not the thermodynamically most stable compositions or phases of oxidized Zn under standard conditions.\textsuperscript{37–40} As
such, our results further substantiate that kinetic control exceeded thermodynamic product formation during PLAL under our conditions.

Figure I.5: (a) XRD data (blue), reported fixed-slit intensities of Zn (PDF 00-004-0831, black) and wurtzite ZnO (PDF 01-075-6445, red), inset: photo of PLAL-made material; (b) XPS data in the Zn 2p and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

The powder diffraction pattern of the material made by PLAL of Zn in water (Figure I.5) was well matched by two crystalline phases, metallic Zn (PDF 00-004-0831) and wurtzite ZnO (zincite, PDF 01-075-6445). The XP spectra in the Zn 2p region confirmed the presence of metallic Zn and ZnO species at the surface (Figure I.5). The Zn 2p core level region consisted of a doublet with an expected branching ratio of 2:1. The Zn 2p3/2 peaks exhibited binding energies of 1021.2 and 1022.4 eV, allowing assignment to metallic Zn and ZnO, with a surface Zn$^{0/2+}$ ratio of 1.1:1. The particles had a monomodal size distribution and a hydrodynamic diameter of (258 ± 40) nm. We obtained a white solid upon addition of ZnCl$_2$ and NH$_4$OH to the aqueous ablation liquid (Figure I.5). XRD data revealed that the mineral simonkolleite, Zn$_5$(OH)$_8$Cl$_2$·H$_2$O (PDF 00-07-0155), was formed, as we had predicted. No other phases were detected. The XPS Zn 2p region showed a doublet with an expected branching ratio of 2:1; the Zn 2p$_{3/2}$ component had a binding energy of 1022.8 eV, allowing assignment to Zn$\equiv$–OH. The O 1s core level peak consisted of two components at 530.5 and 531.9 eV, assignable to ZnO (presumably from surface oxidation) and Zn–OH, respectively. We detected a single Cl 2s core level peak with a binding energy of 271.0 eV, consistent with Zn–Cl. We measured a narrow monomodal size distribution and a hydrodynamic
diameter of \((318 \pm 14)\) nm. Simonkolleite is a layered hydroxide salt,\(^{42}\) which occurs naturally as a weathering product of zinc-bearing slags.\(^{40}\) It decomposes to ZnO upon heating.\(^{39,43}\) The mineral has recently attracted interest for hydrogen gas sensing \([107]\), supercapacitor \([108]\), catalyst support \([109]\), and photocatalysis applications \([102]\). It has also found use as a nutritional feed additive with high bioavailability and antimicrobial activity to supplement zinc in livestock.\(^{44-47}\)

![Figure I.6](image)

**Figure I.6:** (a) XRD data (blue), reported fixed-slit intensities of simonkolleite (PDF 00-07-0155, black), inset: photo of PLAL-made material; (b) XPS data in the Zn 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

A white solid formed by PLAL of Zn foil in aqueous Zn(NO\(_3\))\(_2\) solution (Figure I.7). XRD data revealed that the material consisted of the layered anionic clay zinc hydroxide nitrate, Zn\(_5\)(OH)\(_8\)(NO\(_3\))\(_2\) \(\cdot\) 2 H\(_2\)O (PDF 01-072-0627); no other phase was detected. The XRD pattern exhibited a strong reflection at \(2\theta = 9.09^\circ\), attributable to the (200) diffraction of monoclinic Zn\(_5\)(NO\(_3\))\(_2\)(OH)\(_8\) \(\cdot\) 2 H\(_2\)O.\(^{48}\) The intensities of the basal (00\(l\)) reflections decreased as \(l\) increased, which is characteristic for layered structures. Minor contributions from SiO\(_2\) stemming from the silicon substrate were also present.

High-resolution XP spectra in the Zn 2p region showed a doublet with an expected branching ratio of 2:1. We observed two Zn 2\(p_{3/2}\) components with binding energies of 1021.4 and 1023.7 eV, consistent with Zn–OH in tetrahedral and octahedral coordination, respectively.\(^{49}\) Monoclinic Zn\(_5\)(OH)\(_8\)(NO\(_3\))\(_2\) \(\cdot\) 2 H\(_2\)O has a hydrotalcite-like structure, which consists of slabs of edge-shared Zn(OH)\(_6\) octa-
hedra and Zn(OH)$_4$ tetrahedra that are located above and below the plane of the octahedrally coordinated Zn ions. The bulk ratio of octahedral to tetrahedral sites is 3:2.\textsuperscript{50} We detected a surface ratio of 2.9:2. The O 1s region exhibited two peaks with binding energies of 531.8 and 533.0 eV, attributable to Zn–OH and Zn–NO$_3$, respectively.\textsuperscript{41} We detected two components in the N 1s core level region, with binding energies of 404.9 and 407.4 eV. We tentatively assigned the lower binding energy peak to N-bound Zn–NO$_2$;\textsuperscript{51} the higher binding energy peak is consistent with a transition metal nitrate.\textsuperscript{23} We obtained a very narrow monomodal size distribution and a hydrodynamic diameter of (178 ± 0.5) nm. Zinc hydroxide nitrate is a layered anionic clay mineral, and consists of Zn$^{2+}$ containing layers, whose net positive charge, stemming from the incorporation of tetrahedrally coordinated Zn$^{2+}$ ions into the crystal structure of otherwise octahedrally coordinated metal ions, is balanced by intercalated nitrate anions [115].\textsuperscript{48} Zinc hydroxide nitrate is an effective heterogeneous catalyst for the esterification of free fatty acids and the transesterification of vegetable oils.\textsuperscript{52}

**Bimetallic Nanoparticles**

Finally, based on the insights we gained in our PLAL syntheses of monometallic materials, we aimed to prepare a mixed-metal nanomineral. We targeted a basic copper-zinc chloride material. Since we had synthesized paratacamite by PLAL of
Cu foil in aqueous CuCl$_2$ solution, we anticipated the formation of a similar mineral upon addition of ZnCl$_2$ to the CuCl$_2$-containing aqueous ablation liquid. A possible candidate was lightly Zn substituted basic copper chloride zincian paratacamite, also called herbertsmithite.

We collected a blue-green solid from PLAL of Cu foil in an aqueous solution of CuCl$_2$ and ZnCl$_2$ in a 3:1 molar ratio (Figure I.8). PLAL of Zn foil in the same ablation liquid was unsuccessful, as the Zn target dissolved during synthesis. XRD data confirmed that we synthesized zincian paratacamite (PDF 00-050-1558), as we had predicted. The material is a naturally occurring mineral with the formula Cu$_3$(Cu, Zn)Cl$_2$(OH)$_6$ which forms rhombohedral, blue-green crystals. Zincian paratacamite has recently gained attention for its quantum spin liquid properties due to its kagomé lattice structure.

PLAL, We note that monometallic and zincian paratacamite crystals exhibit similar powder diffraction patterns, albeit with different reflection intensities. Differences are particularly pronounced in the region of $56^\circ < 2\theta < 58^\circ$ (inset in Figure 8a). For a fair comparison of reflection intensities, we normalized measured XRD data of our mono- and bimetallic paratacamites to the strongest reflections. Clearly, the nanomaterial we synthesized by PLAL of Cu foil in an aqueous solution of CuCl$_2$ and ZnCl$_2$ was better matched by zincian paratacamite.

As with monometallic paratacamite, we observed in the XP spectra a doublet with a 2:1 branching ratio and corresponding satellite features in the Cu 2p region of XPS data. The Cu 2p$_{3/2}$ peak consisted of two components with central binding energies of 933.3 and 935.4 eV, attributable to CuO and Cu–Cl, respectively. We could not detect any peaks in the Zn 2p region, indicating a Cu-rich surface. EDX measurements showed that the bulk contained 0.1 atomic % Zn. We detected single Cl 2s and O 1s peaks at 270.1 and 531.6 eV, consistent with Cu–Cl and Cu–OH, respectively. DLS data showed that our PLAL-made lightly doped zincian paratacamite had a monomodal size distribution and a hydrodynamic diameter of (208 ± 35) nm.
Figure 1.8: (a) XRD data (blue), reported fixed-slit intensities of zincian paratacamite (PDF 00-050-1558, black), insets: left, expanded region in which reflections of mono- and bimetallic paratacamites differ most (blue, zincian paratacamite, PDF 00-050-1558; gray, monometallic paratacamite, PDF 01-070-0821); right, photo of the PLALmade material; (b) XPS data in the Cu 2p, Cl 2s, and O 1s regions (open circles, data; lines, fits); (c) DLS particle size distribution.

I.6 Conclusion

We synthesized mono- and lightly-doped bimetallic Cu and Zn nanomaterials by pulsed laser ablation in aqueous liquids, using 150 mJ, 355 nm, nanosecond pulses and a novel foil target setup. PLAL of Cu or Zn foil in pure water or with added Cu or Zn salts predictably produced different materials, depending on the chemical composition of the ablation liquid. Addition of select anions to the ablation solutions led to the fabrication of more complex phase-pure nanominerals. In contrast, PLAL of metals in neat water generated mixtures of metal and metal oxide nanomaterials. Our results demonstrate that kinetic control transcended thermodynamic product formation during nanosecond ultraviolet PLAL nanomaterials synthesis.

I.7 Acknowledgments

We thank George R. Rossman for helpful discussions. Research was performed in the Laser Resource Center and the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology. This work was supported by the NSF CCI Solar Fuels Program (CHE-1305124) and the Arnold and Mabel Beckman Foundation. C.W.R. thanks the National Science Foundation and Link Energy Foundation for graduate research fellowships.
I.8 References


Appendix J
Supplementary Information for Complex Nanomineral Formation Utilizing Kinetic Control by PLAL

<table>
<thead>
<tr>
<th>Foil target</th>
<th>Added salt</th>
<th>Obtained material</th>
<th>PDF card</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>None</td>
<td>Cu, CuO</td>
<td>01-070-0338 (Cu), 01-078-0428 (CuO)</td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl₂ · H₂O</td>
<td>Cu₂Cl(OH)₃ (Paratacamite)</td>
<td>01-070-0821</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(NO₃)₂ · 3 H₂O, NH₄OH</td>
<td>Cu₂(NO₃)(OH)₃ (Rouaite)</td>
<td>01-075-1779</td>
</tr>
<tr>
<td>Zn</td>
<td>None</td>
<td>Zn, ZnO (Wurtzite)</td>
<td>00-004-0831 (Zn), 01-075-6445 (ZnO)</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnCl₂, NH₄OH</td>
<td>Zn₅(OH)₈Cl₂ · H₂O (Simonkolleite)</td>
<td>00-07-0155</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NO₃)₂ · 6 H₂O</td>
<td>Zn₅(OH)₈(NO₃)₂ · 2 H₂O</td>
<td>01-072-0627</td>
</tr>
<tr>
<td>Cu</td>
<td>CuCl₂ · H₂O, ZnCl₂</td>
<td>Cu₃(Cu, Zn)Cl₂(OH)₆ (Zincian paratacamite)</td>
<td>00-050-1558</td>
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</table>

Table J.1: X-ray diffraction characterization of nanomaterials synthesized by PLAL of metal foils in neat water or aqueous solutions

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu 2p₃/₂ (eV)</th>
<th>Zn 2p₃/₂ (eV)</th>
<th>O 1s (eV)</th>
<th>Cl 2s (eV)</th>
<th>N 1s (eV)</th>
</tr>
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<tbody>
<tr>
<td>Cu, CuO</td>
<td>932.7 (Cu), 933.8 (CuO)</td>
<td>–</td>
<td>530.7 (CuO)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu₂Cl(OH)₃ (Paratacamite)</td>
<td>933.4 (CuO), 935.4 (Cu–Cl)</td>
<td>–</td>
<td>531.5 (Cu–OH)</td>
<td>270.0 (Cu–Cl)</td>
<td>–</td>
</tr>
<tr>
<td>Cu₂(NO₃)(OH)₃ (Rouaite)</td>
<td>935.3 (Cu–OH &amp; Cu–NO₃)</td>
<td>–</td>
<td>531.5 (Cu–OH)</td>
<td>403.6 (Cu–NO₃)</td>
<td>–</td>
</tr>
<tr>
<td>Zn, ZnO (Wurtzite)</td>
<td>–</td>
<td>1021.2–1022.4 (Zn–OH)</td>
<td>530.5 (ZnO)</td>
<td>407.3 (Zn–NO₃)</td>
<td>–</td>
</tr>
<tr>
<td>Zn₅(OH)₈Cl₂ · H₂O (Simonkolleite)</td>
<td>–</td>
<td>1021.2 (Zn–OH)</td>
<td>530.5 (ZnO), 531.9 (Zn–OH)</td>
<td>407.3 (Zn–NO₃)</td>
<td>–</td>
</tr>
<tr>
<td>Zn₅(OH)₈(NO₃)₂ · 2 H₂O</td>
<td>–</td>
<td>1022 (Zn–OH, tetrahedral and octahedral)</td>
<td>530.8 (Zn–OH), 533.6 (Zn–NO₃)</td>
<td>404.9, 407.4 (Zn–NO₃)</td>
<td>–</td>
</tr>
<tr>
<td>Cu₃(Cu, Zn)Cl₂(OH)₆ (Zincian paratacamite)</td>
<td>–</td>
<td>1021.4, 1023.7 (Zn–OH, tetrahedral and octahedral)</td>
<td>531.6 (Cu–OH)</td>
<td>270.1 (Cu–Cl)</td>
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Table J.2: Central binding energies obtained from X-ray photoelectron spectra of nanomaterials synthesized by PLAL of metal foils in neat water or aqueous solutions. Assignments are in parentheses; details are in the main text.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dₖₑₜ (nm)</th>
<th>σ (nm)</th>
</tr>
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<tbody>
<tr>
<td>Cu, CuO</td>
<td>225</td>
<td>40</td>
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<tr>
<td>Cu₂Cl(OH)₃ (Paratacamite)</td>
<td>258</td>
<td>43</td>
</tr>
<tr>
<td>Cu₂(NO₃)(OH)₃ (Rouaite)</td>
<td>xx</td>
<td>xx</td>
</tr>
<tr>
<td>Zn, ZnO (Wurtzite)</td>
<td>258</td>
<td>40</td>
</tr>
<tr>
<td>Zn₅(OH)₈Cl₂ · H₂O (Simonkolleite)</td>
<td>318</td>
<td>14</td>
</tr>
<tr>
<td>Zn₅(OH)₈(NO₃)₂ · 2 H₂O</td>
<td>178</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu₃(Cu, Zn)Cl₂(OH)₆ (Zincian paratacamite)</td>
<td>208</td>
<td>35</td>
</tr>
</tbody>
</table>

Table J.3: Mean hydrodynamic particle diameters Dₖₑₜ with size distribution widths σ obtained from dynamic light scattering data of nanomaterials synthesized by PLAL of metal foils in neat water or aqueous solutions.

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K.1 Abstract
Hydrogen gas obtained by the electrolysis of water has long been proposed as a clean and sustainable alternative to fossil fuels. Noble metals such as Pt are capable of splitting water at low overpotentials, but the implementation of inexpensive solar-driven water-splitting systems and electrolyzers could benefit from the development of robust, efficient, and abundant alternatives to noble metal catalysts. Transition metal phosphides (MₓPᵧ) have recently been identified as a promising family of Earth-abundant electrocatalysts for the hydrogen-evolution reaction (HER), and are capable of operating with low overpotentials at operationally relevant current densities while exhibiting stability under strongly acidic conditions. In this review, we highlight the progress that has been made in this field and provide insights into the synthesis, characterization and electrochemical behavior of transition metal phosphides as HER electrocatalysts. We also discuss strategies for the incorporation of metal phosphides into integrated solar-driven water-splitting systems and highlight key considerations involved in the testing and benchmarking of such devices.

K.2 Introduction
The development of clean, affordable and sustainable approaches to fuel generation and utilization is a critical global challenge. With a rapidly rising world population the global primary energy-consumption rate is expected to increase from 17 TW in 2010 to 27 TW by 2040.¹ Because of their high energy density and ease of combustion, fossil fuels have remained the primary global energy carriers for the past two centuries, and have played a pivotal role in worldwide industrial and technological development. Even though coal and natural gas could continue to meet the world’s energy demand for the foreseeable future, environmental concerns over the extraction and inefficient combustion of non-renewable fossil fuels have
motivated the search for cleaner and more sustainable energy platforms.¹

Solar, wind, and other renewable energy technologies have emerged as promising alternatives to conventional energy sources. These renewable resources are often intermittent and depend on the time of day and/or weather, requiring batteries and/or other storage technologies to compensate for the intermittency of the resource. The storage of energy as chemical bonds in molecules is a promising approach to facilitate long-term storage and additionally to serve the demands of transportation systems.² Molecular hydrogen, H₂, has a considerably higher specific energy than most hydrocarbons, and is a well-known zero-emission fuel that liberates only water upon combustion. The clean, scalable, and affordable production of hydrogen is also an important requirement for the implementation of fuel-cell technologies on a global scale.³ Functional hydrogen-based fuel-cell modules are commercially available but are economically disfavored relative to traditional combustion engines and batteries because of high costs, storage issues, and limited access to H₂ fuel. The combination of fuel-cell technologies with the clean, widespread, and on-demand production of H₂ thus has the potential to significantly impact the transportation and industrial energy sectors.

Currently, most hydrogen is produced through industrial reforming methods.³ For example, steam-methane reforming involves the reaction between steam (water vapor) and methane over a nickel-based catalyst at temperatures above 700 °C to yield H₂ and CO. The obtained CO is then further reacted with more steam to finally produce CO₂ and more H₂ through the water-gas shift reaction. In addition to high reaction temperatures, industrial reforming requires large amounts of natural gas and adds significantly to rising atmospheric CO₂ levels. Additionally, hydrogen produced by this method often carries sulfur-containing impurities that are of significant environmental concern and that can readily poison fuel-cell catalysts.⁴ Devices that facilitate water electrolysis, including electrochemical and photoelectrochemical cells (PEC), are emerging technologies that have the potential to renewably generate clean hydrogen fuel from water without fossil fuels or harmful byproducts.

Overall water “splitting” is the electrochemical reaction that separates water into molecular hydrogen, H₂(g), and molecular oxygen, O₂(g). With ΔG = 237.2 kJ mol⁻¹ under standard conditions, the water-splitting reaction is highly endothermic and requires 1.23 V per electron transferred. While water splitting can be facilitated in acidic, alkaline, or neutral aqueous solutions, each has unique advantages, disadvantages, and challenges.⁵ Water splitting is favored in strong electrolytes because of
their high ionic conductivities. Efficient, safe electrolyzers are constructed in either acidic or alkaline media so that either protons or hydroxide ions can be transferred between the anolyte and catholyte to avoid a substantial increase in pH gradients as a result of the electrolysis reaction. Electrolysis under pH-neutral conditions is impacted by the formation of substantial pH gradients that can impede the water-splitting process. The formation of pH gradients can be mitigated by use of a single compartment reactor with sufficient mixing, but such systems result in the formation
of explosive mixtures of O\(_2\) and H\(_2\) gases and/or are inefficient. Acidic electrolytes are particularly well suited for the HER, because the reduction of a positively charged proton is more energetically favorable than reduction of a neutral water molecule. Additionally, the extensive availability of highly efficient proton-exchange membranes favors a reactor design in acidic conditions. The water-splitting process can be described by two separate half-reactions: the hydrogen evolution reaction (HER), which involves proton reduction and occurs at the cathode, and the oxygen evolution reaction (OER), which involves water oxidation and occurs at the anode. Shown below are the HER and OER in acidic aqueous solutions, which is the primary emphasis of this review because it is relevant to the conditions under which polymer electrolyte membrane based water electrolysis devices operate.

\[
\text{Water Splitting} \quad 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad E^\circ_{\text{cell}} = 1.23 \text{ V vs. NHE}
\]

\[
\text{OER} \quad 2\text{H}_2\text{O} \rightarrow \text{O}_2^+ 4\text{H}^+ + 4\text{e}^- \quad E^\circ = 1.23 \text{ V vs. NHE}
\]

\[
\text{HER} \quad 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2 + \text{O}_2 \quad E^\circ = 0.00 \text{ V vs. NHE}
\]

Several different design schemes have been proposed for solar-driven electrochemical cells (Figure K.1).\(^5\) The simplest, which consists of a photovoltaic cell or module connected to a water electrolyzer, indirectly converts solar energy into chemical fuel. Integrated photoelectrochemical cells are attractive options for direct solar fuel production because of their projected lower costs and potentially high efficiencies as compared to indirect schemes.\(^8\) One possible configuration, in which several key components are integrated and work synergistically to facilitate overall sunlight-driven water electrolysis, is shown in Figure K.1.\(^9\) The general layout includes two distinct arrays of semiconductor microwires that absorb different portions of the incoming solar spectrum, catalysts that decorate the microwire arrays to facilitate the OER and HER, and a membrane that separates the two compartments while allowing selective proton transport. High-energy photons (> 1.8 eV) are absorbed at the photoanode (shown in red), and the OER catalysts attached to the photoanode’s surface oxidize water and release O\(_2\)(g) and protons. Protons then move across a proton-permeable membrane toward the photocathode, where lower-energy (< 1.2 eV) solar photons are absorbed. Catalysts that facilitate the HER are attached to the photocathode’s surface where the protons combine with electrons to produce H\(_2\)(g). The membrane that separates the two compartments shuttles protons from the photoanode to the photocathode while keeping the H\(_2\)(g) and O\(_2\)(g) products in separate compartments. This avoids the formation of an explosive mixture of
H\textsubscript{2}(g) and O\textsubscript{2}(g) and also prevents the oxidation of H\textsubscript{2}(g) at the anode and reduction of O\textsubscript{2}(g) at the cathode, and recombination of products within the electrolyte. While effective integration of all of the components is required to achieve optimal solar water-splitting performance, the materials themselves are critical since they directly impact the overall efficiency, stability, scalability, and cost of the device. The widespread implementation of water-splitting technologies therefore requires the discovery, development, and integration of robust and Earth-abundant materials for each of these individual components. This review focuses specifically on catalytic materials for the HER, which is one of the key components of the cathode in a full solar-driven water-splitting device.

The HER can be facilitated by a diverse range of catalytic systems. In nature and under mild, benign, and pH-neutral operating conditions, the HER can be carried out by several biological catalysts, including the [FeFe],\textsuperscript{10,11} [FeNi],\textsuperscript{12,13} and [Fe]-only hydrogenases\textsuperscript{14,15} as well as by the [FeMo] nitrogenase.\textsuperscript{16,17} These enzymes often have metal-sulfur clusters as active sites embedded in a complex biological cavity that provides a suitable chemical environment for the HER. Substantial work has been directed towards developing molecular mimics of these enzyme active sites, as well as other homogeneous molecular catalysts that exhibit comparable or even higher rates for HER catalysis than the natural enzymes.\textsuperscript{18} For example, several nickel phosphine complexes with proximal amine groups have been shown to facilitate the HER at very high rates, albeit in acetonitrile solutions.\textsuperscript{19–22} Other examples of HER molecular catalysts include diiron,\textsuperscript{23} iron diglyoxime\textsuperscript{24} and cobalt diglyoxime\textsuperscript{25} complexes, as well as thiomolybdate clusters.\textsuperscript{26–28} Interestingly, model compounds of enzyme active sites often are inactive or are significantly less active than desired for catalytic hydrogen production. When inserted into the proper biological cavity, certain inactive synthetic complexes exhibit catalytic activities comparable to those of naturally occurring enzymes.\textsuperscript{29} From a device perspective, biological and homogeneous systems with exceptional catalytic properties face challenges involving anchoring to and integrating with solid-state systems, as well as stability in chemically harsh, non-neutral electrolytic environments, including many of the proposed devices that require strongly acidic or basic conditions to function efficiently.\textsuperscript{30} One key goal of HER-catalyst development is therefore finding heterogeneous systems that can combine the high activity of biological and molecular catalysts with the superior stability and integration capabilities of solid-state materials.

Platinum is the most widely used heterogeneous catalyst for the HER, due to the
high catalytic activity and durability of Pt under harsh operating conditions.\textsuperscript{31} The low terrestrial abundance and cost of mining Pt has motivated the search for Earth-abundant alternatives.\textsuperscript{5, 9} Molybdenum-based materials have been at the forefront of Earth-abundant hydrogen-evolution catalysis for decades. NiMo alloys were reported by Fogarty and coworkers as highly active HER catalysts in alkaline aqueous solutions.\textsuperscript{32} Other related alloys including CoMo,\textsuperscript{33} FeMo,\textsuperscript{33} and NiMoZn\textsuperscript{34} have also been reported to be active catalysts for the HER. However, despite their high catalytic activity and stability under alkaline conditions, these alloys quickly corrode in acidic environments.\textsuperscript{35} Other Mo-based HER catalysts, including Mo\textsubscript{2}C,\textsuperscript{36–38} MoB,\textsuperscript{36} Co\textsubscript{6}Mo\textsubscript{1.4}N\textsubscript{2},\textsuperscript{38} and NiMoN\textsubscript{x},\textsuperscript{39} have been investigated, and many of these catalysts exhibit extended stability in acidic aqueous solutions.

Using theoretical and experimental methods, Hinnemann and coworkers showed that the edge sites of MoS\textsubscript{2}, which are chemically and structurally distinct from the Mo-based alloys, have chemical environments that can facilitate the HER.\textsuperscript{40} Accordingly, MoS\textsubscript{2} has been the leading Earth-abundant alternative to platinum for catalyzing the HER in acidic aqueous solutions. The HER-active edge sites of MoS\textsubscript{2} have structural commonalities with the active-site clusters in some hydrogenase and nitrogenase enzymes.\textsuperscript{40} Extensive research efforts have been directed towards understanding and maximizing the number of exposed active sites in MoS\textsubscript{2}, and this has led to the development of improved MoS\textsubscript{2}-based HER catalysts that are highly active and acid stable.\textsuperscript{41–43} Ooi\textsuperscript{26} and Besenbacher\textsuperscript{28} have developed [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2–} and [Mo\textsubscript{3}S\textsubscript{4}]\textsuperscript{4+} clusters, respectively, while Chang\textsuperscript{27} has developed molecular-based systems, which all aim to mimic the HER-active MoS\textsubscript{2} edge sites. While such studies of molecular mimics of solid-state catalysts are important for active-site design and activity optimization, they also emphasize the structural and chemical interrelationships among heterogeneous, homogeneous, and biological catalytic systems.

The most highly studied molybdenum-based HER catalysts, including NiMo, Mo\textsubscript{2}C, and MoS\textsubscript{2}, are also well-known catalysts for hydrodesulfurization (HDS).\textsuperscript{44} HDS is the catalytic process by which sulfur impurities are removed from hydrocarbon fuels and feedstocks. Despite being distinct chemical processes, both HDS and HER are regulated by the reversible and dissociative binding of hydrogen molecules on the surface of a catalyst. Computational studies have indicated that both HER and HDS catalysts have active sites that bind atomic hydrogen with intermediate strengths, such that the free energy of adsorbed hydrogen is closely matched to the free energy of the products, leading to $\Delta G^\circ_{H^\ast} \approx 0$.\textsuperscript{45} Hydrogen adsorption energies that are too
high (e.g. strong hydrogen adsorption) would prevent the release of products, which include H₂ for the HER and H₂S for HDS. In contrast, hydrogen adsorption energies that are too low (e.g. weak hydrogen adsorption) will result in slow electron-transfer rates. Both strong and weak hydrogen adsorption, therefore, result in low catalytic rates. Because HDS catalysts have intermediate hydrogen adsorption energies, it has been proposed, by our group and others, that HDS catalyst systems may be fertile ground for the discovery and development of new Earth-abundant HER catalysts.

Among the most highly studied and active HDS catalysts are Ni₂P⁴⁶,⁴⁷ and related transition metal phosphides, including CoP, Fe₂P, MoP, and WP.⁴⁸,⁴⁹ Given the potential mechanistic analogy between the HDS and HER catalytic processes, we hypothesized that Ni₂P and other metal phosphides may indeed be active and Earth-abundant HER catalysts. Additionally, in 2005, Rodriguez and coworkers suggested, based on density functional theory (DFT) calculations, that the (001) surface of Ni₂P combines the favorable H binding present in hydrogenase systems with the thermostability of a heterogeneous catalyst, making it a very promising alternative to Pt for catalyzing the HER.⁴⁵ In 2013, we experimentally validated this prediction, showing that Ni₂P was indeed a highly active HER catalyst in acidic aqueous solution.⁵⁰ Since then, our group and others have demonstrated that the HDS-active metal phosphides comprise a new class of highly active and acid-stable HER catalysts. The field of metal phosphide HER catalysts has rapidly expanded to include a growing number of catalytic systems and preparation methods, demonstrations of integration into functional photocathode systems, mechanistic insights in the catalytic reactions, and guidelines for designing new catalysts and improving the performance of existing catalysts.

This Review article highlights recent developments in transition metal phosphides as an emerging family of highly active and Earth-abundant catalysts for the HER, primarily in acidic conditions that are relevant to proton-exchange-membrane electrolysis systems. The HER performance in pH-neutral and alkaline aqueous solutions is also highlighted due to potential relevance to alternative water-electrolysis systems. We include in this Review a survey of how transition metal phosphides are synthesized across multiple platforms such as bulk crystals, films, and nanoparticles, because collectively these techniques and the materials they produce are relevant for exploratory synthesis and catalyst discovery, optimization of catalytic performance through active-site exposure and surface area maximization, integration into devices, and understanding mechanistic details of the catalytic reactions. Addition-
ally, we discuss aspects of materials and electrochemical characterization that are crucial for fully understanding the materials being studied, accurately attributing catalytic activities to the correct materials features, and benchmarking performance metrics with related systems. We then provide an overview of the properties and performance metrics of transition metal phosphides for HER catalysis, including their integration with light-absorber materials as an important step toward building a practical solar-driven water-splitting device.

K.3 Overview of Metal Phosphides

Metal phosphides, represented by the general formula $M_xP_y$, are solid-state compounds formed from the combination of metallic or semimetallic elements with phosphorus. The crystal structures adopted by the large number of known binary, ternary, and higher-order metal phosphides are diverse (Figure K.2), spanning simple high-symmetry ionic structures such as NaCl-type LaP to more complex structures such as ThCr$_2$Si$_2$-type LaRu$_2$P$_2$ and skutterudite-type LaRu$_4$P$_{12}$. The bonding in metal phosphides is also diverse and, depending on the composition and constituent elements, can be described as ionic, covalent, or metallic. Metal-rich ($x > y$ in $M_xP_y$) or stoichiometric ($x = y = 1$ in $M_xP_y$) metal phosphides are often semiconducting and in some cases even metallic or superconducting due to the presence of significant metal-metal bonding. For instance, TiP and Fe$_2$P exhibit metallic behavior, whereas GaP and InP are well-known semiconductors. Superconducting properties have been observed in various metal-rich phases such as Mo$_3$P$_{51}$ and LaRu$_2$P$_2$.$^{52}$

The relatively strong M–P bonds can impart transition metal phosphides with high thermal stability and hardness, as well as resistance to oxidation and chemical attack. For example, the phosphides of various metals, such as Ti, Ta, Mo, and W, are of interest as oxidation-resistant coatings for high-temperature applications.$^{53,54}$ Importantly for applications such as HER electrocatalysis, many transition metal phosphides are impervious to dilute acids and bases, and some are unaffected even by strongly acidic or alkaline solutions. More ionic phosphides, such as Ca$_3$P$_2$ and Zn$_3$P$_2$, however, readily decompose in water to produce highly pyrophoric and toxic gases, such as phosphines and diphosphines.

In contrast to the metal-rich and stoichiometric phosphides, phosphorus-rich transition metal phosphides ($y > x$ in $M_xP_y$) exhibit significant phosphorus-phosphorus bonding, due to the ability of phosphorus to bond with itself to form various
Figure K.2: Crystal structures of representative types of metal phosphides: NaCl-type LaP, skutterudite-type LaRu$_4$P$_{12}$, ThCr$_2$Si$_2$-type LaRu$_2$P$_2$, and MgAs$_4$-type ZnP$_4$.

oligomers and clusters. For example, a number of MP$_2$ compounds, such as NiP$_2$ and SiP$_2$, adopt the pyrite-type structure in which the phosphorus atoms are arranged in P–P dimers. Other polyphosphides contain various phosphorus oligomers, clusters, chains, and planes. These so-called polyphosphides exhibit characteristics that are markedly different from their metal-rich or stoichiometric counterparts, including lower thermal stabilities, higher reactivities, and softer materials properties that can be classified as significantly less refractory. As a result, many phosphorous-rich phosphides are thermally unstable, disproportioning at high temperatures to elemental phosphorus and more metal-rich phases.

K.4 Synthesis of Metal Phosphides

Metal phosphides can be synthesized using a variety of methods and in various forms, producing single crystals,$^{54–56}$ bulk polycrystalline powders,$^{57}$ films,$^{58,59}$ or nanostructured solids$^{60–66}$ (Figure K.3). Bulk metal phosphides can be prepared through traditional solid-state strategies by direct combination of the elements at high temperatures in an inert atmosphere or under vacuum. Using this approach, many phosphide phases can be routinely accessed in high purity and on a large scale. As is typical for bulk-scale solid-state reactions, high reaction temperatures (> 900 °C) and long reaction times (1-10 days) are generally required. For example, in a representative synthesis of bulk FeP,$^{67}$ stoichiometric amounts of iron metal and red phosphorus are sealed in an evacuated silica tube, which is then
heated to 900 °C for approximately 8 days. Red phosphorus is often used in these direct high-temperature solid-state reactions, although the more reactive white phosphorus allotrope can also be used, as can certain reactive metal phosphides. For example, various phosphide phases, including AlP\textsuperscript{68} and NbP\textsuperscript{69} have been accessed by high-temperature reactions between a metal phosphide of a lower stability, such as Ca\textsubscript{3}P\textsubscript{2} or Zn\textsubscript{3}P\textsubscript{2}, and the appropriate metal powder (> 1000 °C). Because the high-temperature solid-state reactions can produce highly reactive and pyrophoric byproducts, including P\textsubscript{4} and phosphine, properly trained personnel must work under rigorously air-free conditions to perform the reactions safely as well as to isolate the products.

To lower the temperatures required by direct reactions and to expand the palette of accessible phases, molten fluxes have been used extensively in the synthesis of metal phosphides.\textsuperscript{55} In this approach, a nominally unreactive and low-melting metal, such as Sn or Pb, is mixed with the precursor elements and used as a high temperature solvent to enhance the diffusion rate of the solid reagents.\textsuperscript{55} After the reaction, the metal matrix must be separated from the products either mechanically or by dissolution in acid. For example, in a representative flux synthesis of RuP\textsubscript{2},\textsuperscript{70} stoichiometric amounts of ruthenium and red phosphorus powders are placed along with excess tin in an evacuated silica tube, which is sealed and heated to 1200 °C for approximately 3 days. After the reaction, the phosphide product is then recovered from the flux by dissolving the tin in hot concentrated HCl. In many instances, the flux method yields high-quality phosphide crystals (Figure K.3) and provides access to metastable and low-temperature phases that are inaccessible by the use of higher-temperature solid-state reactions, which tend to favor the formation of more thermodynamically stable products. Moreover, phosphide phases like CrP\textsubscript{4},\textsuperscript{71} MnP\textsubscript{4}\textsuperscript{72,73} and Re\textsubscript{2}P\textsubscript{5}\textsuperscript{74} are challenging to obtain through alternative methods without the use of high pressures.

Another approach that has been extensively used in the synthesis of metal phosphides is the phosphidation of metal oxides, hydroxides or other precursors by highly-active phosphorus species. The phosphidation can be obtained either through direct exposure to phosphine gas\textsuperscript{75} or by exposure to related compounds generated in situ through the reduction of phosphate salts by hydrogen\textsuperscript{48} or carbon.\textsuperscript{76} For instance, several phosphide phases, such as Ni\textsubscript{2}P, CoP, and FeP, can be readily obtained by the temperature-programmed reduction (TPR) of the corresponding metal phosphate.\textsuperscript{48,49} In a representative TPR synthesis of CoP,\textsuperscript{77} a stoichiometric mixture of cobalt nitrate and ammonium hydrogen phosphate is calcined in air at 500 °C for ap-
proximately 6 hours to produce a cobalt phosphate precursor, which is subsequently reduced by heating to 1000 °C for 2 h in a H₂-containing atmosphere. Originally developed to produce metal-oxide-supported phosphides for catalytic applications such as hydrodesulfurization or hydrodenitrogenation, the strategy has recently been extended to the production of phosphate materials directly on the surfaces of electroactive substrates, such as conductive carbon paper and metal foams. Electrochemical and electroless deposition methods have also been explored as a way to directly coat electrode surfaces with metal phosphides. However, these approaches tend to yield amorphous Co–P and Ni–P alloys with a wide range of phosphorus contents.

The need for high-surface-area phosphide materials for catalytic and electrocatalytic applications has led to renewed interest in alternative synthetic strategies for the production of metal phosphides. For example, solvothermal reactions, thermal decomposition of single-source organometallic precursors, and the reaction of organometallic compounds or metallic nanoparticles with organophosphine reagents have been used to produce crystalline high-surface-area metal phosphides under reaction conditions that are frequently milder than those found in direct reactions or flux approaches. Furthermore, these methods typically produce metal phosphides in the form of dispersable nanocrystals that can be directly applied by drop-casting or spin-coating onto the surfaces of electrodes. Highly reactive reagents such as white phosphorus (P₄) or P(SiMe₃)₃ can be used as phosphorus sources, but milder reagents such as tri-n-octylphosphine (TOP) have been used as general phosphorus sources for the low-temperature conversion of metals into metal phosphides. Multiple phases such as Ni₂P, Ni₁₂P₅, Ni₅P₄, Cu₃P, Fe₂P, Fe₅P₇, Co₂P, CoP, InP, PtP₂, PdP₂, RhP₂, Au₂P₃, Pd₃P₂, and MnP, as well as mixed-metal solid solutions such as (NiₓFe₁₋ₓ)₂P₆₄, (NiₓCo₁₋ₓ)₂P₉₁, (CoₓFe₁₋ₓ)₂P₂, and metal-organic chemical vapor deposition (MOCVD) (Figure K.3) have been widely used to produce high-quality crystalline and amorphous thin films of several transition metal phosphides,
Figure K.3: Representative types of metal phosphide crystals, films, and nanoparticles. A) A crystal of NdFe₄P₁₂ with the cubic LaFe₄P₁₂-type structure grown from a tin flux. Adapted with permission from ref.⁵⁵. Copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim B) Ni₂P single-crystal rod produced by the floating-zone method. Adapted with permission from ref.⁵⁶. Copyright 2013 The Ceramic Society of Japan. C) Cu metal wire and foil and the wire and foil with a thick Cu₃P coating made by refluxing in trioctylphosphine. Adapted with permission from ref.⁵⁷. Copyright 2007 American Chemical Society. D) SEM images of a Ni₂P film on Ni. Adapted with permission from ref.⁵⁸. Copyright 2016 American Chemical Society. E) SEM image of a thin film showing a mixture of Ni₂P and Ni₀.₈₅Se deposited using CVD. Adapted with permission from ref.⁵⁹. Copyright 2008 American Chemical Society. (F) TEM image of MoP nanoparticle catalysts supported on SiO₂. Adapted with permission from ref. 60. Copyright 2012 Elsevier B.V. (G) TEM image of Zn₃P₂ nanoparticles. Adapted with permission from ref.⁶¹. Copyright 2008 American Chemical Society. (H,I) TEM images of Ni₂P nanoparticles. Adapted with permission from refs.⁶²,⁶³. Copyright 2007 and 2009 American Chemical Society. (J) TEM image of FeₓNi₂₋ₓP nanoparticles. Adapted with permission from ref.⁶⁴. Copyright 2015 American Chemical Society. (K) TEM image of Rh₂P nanoparticles. Adapted with permission from ref.⁶⁵. Copyright 2015 American Chemical Society. (L) TEM image of CoP nanoparticles. Adapted with permission from ref.⁶⁶. Copyright 2011 American Chemical Society.
including InP, GaP, Zn₃P₂, Ni₂P, and TiP among others. Typically in these processes, volatile gaseous precursors such as metal alkyls, metal halides, or in the case of MOCVD, single-source metal-organic compounds, are decomposed at high temperatures over an appropriate substrate. Similarly, physical vapor deposition (PVD) techniques, such as sputtering and pulsed laser deposition (PLD), have also been used to produce metal phosphide thin films on various substrates. However, in most cases the films obtained through these techniques are poorly crystalline or amorphous.

K.5 Characterization of Transition Metal Phosphides for the Hydrogen-Evolution Reaction

In this section we discuss methods for thorough and rigorous characterization of metal phosphides. Such methods allow the establishment of catalytic performance metrics using a common framework that permits both benchmarking and comparisons, and also enable accurate attribution of the observed catalytic properties to the key material features that define the systems of interest.

Characterization of Electrocatalytic Properties

Metal phosphide systems have emerged as highly active HER electrocatalysts and they are being increasingly investigated for this and other catalytic reactions. Accordingly, several recent articles have outlined and reviewed best practices for testing, reporting, and benchmarking such electrocatalytic materials as well as related photocatalyst systems. Figure K.4 shows typical data for various types of benchmark Pt catalysts, which will be discussed in more detail below. Key considerations for appropriate electrocatalytic testing of the metal phosphide systems are briefly outlined below as well.

Materials for HER electrocatalysis are typically evaluated using a three-electrode setup, in which a reference electrode, a counter electrode, and a catalyst-modified working electrode are immersed in an aqueous electrolyte. The electrolyte must be continuously purged with high purity H₂ gas to establish standard conditions. When Pt is used as a counter electrode, a two-compartment cell, separated by a proton exchange membrane, must be utilized to separate the working and counter electrodes and thereby prevent cross-contamination by trace noble metal species, as well as undesired back reactions. When using a single compartment cell, only graphite rods or other inert materials should be used as counter electrodes.

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are commonly used...
to evaluate the HER performance by measurement of the catalytic current as a function of applied potential. The observed catalytic current is typically plotted as the experimentally observed current density, normalized to the geometric area of electrode, to facilitate comparisons among electrodes having different sizes. This approach however does not account for variations in catalyst loading or surface area. Methods to estimate the actual surface area of the catalyst include the use of bulk surface areas obtained through BET analysis or geometric estimates using mathematically-derived surface areas based on average particle sizes and shapes.\textsuperscript{50,101} These estimates are limited by the realization that not all exposed surface sites are catalytically active. Electrochemical measurements of surface area most closely relate to HER operating conditions, but they have been predominately developed for noble metal systems and therefore may not be directly applicable to the metal phosphides. The exact determination of the true electrochemically active surface area may not be possible, so electrocatalytic testing on flat electrode substrates is preferable to best obtain the inherent electrochemical performance of a material. The use of flat substrates prevents artificial enhancement of electrochemical performance through increased surface area effects, thereby facilitating comparisons with other catalysts. Although the development of highly efficient 3D and porous electrodes is an important area of research for electrode design and optimization, such studies are most useful when the high surface area systems can be compared with the catalytic performance on a flat electrode.

When reporting the results of electrocatalytic testing, the overpotential required to reach a specific current density, which can be chosen depending on the target application, allows reliable comparison between catalysts tested under similar experimental

![Figure K.4: Polarization Data for the HER in 0.5 M H₂SO₄ using Pt Electrodes.](image-url)
conditions. The “onset potential,” which is the potential at which catalytic current first appears, is often reported in the literature. However, because the onset potential can be ascribed to the production of an arbitrarily defined current density, the “onset potential” is not a well-defined electrochemical property and hence is not a suitable metric for analytically evaluating or comparing different HER catalysts. Other relevant metrics that are often reported for HER catalysts include Tafel slope, exchange-current density, and turnover frequency (TOF). These parameters in combination are also important for evaluating electrocatalytic performance and have been reviewed in detail in recent articles. Galvanostatic measurements and cyclic voltammetry are typically used to characterize the stability of a catalyst. Galvanostatic measurements maintain an application-relevant current density, such as 10 mA/cm² for photoelectrochemical (PEC) cells, for a sufficiently long time to establish the desired degree of catalyst stability. Galvanostatic testing is particularly useful for evaluating the longevity of a catalyst under device-relevant operating conditions. For catalysts that dissolve slowly under operating conditions, high catalyst mass loadings may result in artificially prolonged stability. For this reason, galvanostatic stability measurements are most useful when performed at low mass loadings or when coupled with sensitive elemental analysis of the electrolyte, such as atomic absorption spectroscopy or inductively coupled plasma mass spectrometry (ICP-MS), to detect dissolution processes. An added benefit of galvanostatic testing is that the current density at which the experiment is conducted can be selected to investigate the HER stability for a wide range of applications and device designs, ranging from PEC’s (−10 mA/cm² to −20 mA/cm²) to electrolyzers (−1 A/cm² to −2 A/cm²). Multiple cyclic voltammetry cycles over an appropriate potential window, such as between 0 V vs RHE and the potential required to reach or exceed a target operational current density, mimic the ramp-up and ramp-down cycles expected for solar-driven water-splitting systems. Additional useful studies include prolonged testing under the open-circuit potential (to simulate the system at rest), tests over longer periods of time (months to years), quartz-microbalance and electrolyte analysis studies to identify and understand slow dissolution processes, and impedance measurements to probe the electrical resistivity of the catalyst.

As mentioned above, catalyst benchmarking is important, and as a result, proper controls and reporting metrics are mandatory. For example, showing electrochemical data for standard Pt electrodes under the same conditions used to evaluate new
catalytic materials provides a necessary baseline for comparison. However, the availability of a wide range of different Pt standards having different surface areas and mass loadings, including flat Pt disks, Pt mesh electrodes, and supported Pt nanoparticles, complicates matters, as such systems exhibit very different catalytic performance (Figure K.4). Pt meshes are particularly desirable because they are commercially available, have high catalytic activity, and offer highly reproducible performance. Ultimately, the most active Pt standards should be used for comparison to new catalysts. The overpotentials for a clean Pt mesh are \( \approx -15 \) mV to \(-20 \) mV at a current density of \(-10 \) mA/cm\(^2\). When reporting the results of electrocatalytic testing, the overpotential required to reach a specific current density (the operationally relevant benchmark current density) allows facile comparison between catalysts tested under similar experimental conditions. Reporting the electrode details is also important for characterizing and comparing catalysts. For example, differences in loading density and surface area can influence the reported metrics, and are important considerations.

**Materials Characterization**

Coupled with electrochemical characterization, it is important to fully characterize the key aspects of catalytic materials that contribute to their performance, including techniques that probe the bulk crystal structure, morphology, and chemical composition, as well as key surface chemistry details (Figure 5). This, coupled with the benchmarking efforts described in the preceding section, facilitates meaningful comparisons among catalytic systems, establishes the relevant parameters, and sets the stage for elucidating structure-property relationships. Ultimately, one should make deliberate and informed choices about which characterization tools will provide the necessary information for adequately evaluating a catalyst at each stage of discovery, development, and detailed understanding. Figure 5 shows conceptually how various materials and surface characterization tools can be used together to study catalytically active materials.

For metal phosphide HER catalysts in nanoparticle, bulk-powder, or thin-film form, powder X-ray diffraction (XRD) data enables the identification of all crystalline phases present in a sample, as well as an estimation of the size of crystalline domains through Scherrer analysis. Because phase diagrams of metal phosphides contain multiple crystalline compounds of different compositions and crystal structures, each of which can have different properties, high-quality XRD data is important for establishing phase formation and purity. Additionally, for particles that are found to
be highly anisotropic or films that contain highly oriented crystallites, the observation of preferred orientation by powder XRD data can confirm that the morphology is characteristic of the bulk sample. Powder XRD cannot, however, unambiguously confirm phase purity, nor can it exclude the possibility that catalytically relevant impurities are present or reveal the presence of amorphous components.

Figure K.5: Representative, non-exhaustive summary of materials-characterization data that can be used to understand the key characteristics that underpin the observed catalytic performance, including important aspects of surface and bulk structure, composition, and morphology. Color-coding shows complementary types of information that are provided by different characterization techniques.

Bulk elemental analysis can be used to compare the overall composition with the crystalline phase and thus to determine whether significant amorphous phases not detectable by powder XRD are present in a sample. For fully amorphous samples that have no long-range crystalline order, characterization can be more challenging. In these cases, rigorous analysis of composition, sample heterogeneity, and oxidation states can be especially important, along with any other microscopic or spectroscopic techniques that are appropriate and available. Because the structure and composition
at the surface of a catalyst may be quite different from that in the bulk, X-ray photoelectron spectroscopy (XPS) can be especially powerful. XPS can be utilized for identification of the oxidation states and chemical composition near the surface, both for crystalline and amorphous materials. However, for some systems, such as CoP and Co₂P, differentiating oxidation states and quantifying their relative ratios is often not possible or straightforward. Synchrotron-based techniques such as X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) analysis offer additional insights into the bulk and local structure of catalytic materials, and can be performed in situ and under operationally relevant conditions.

Electron microscopy, particularly for nanoparticulate and thin-film metal phosphide catalysts, complements the bulk and surface analyses highlighted above. Both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can provide detailed information about the morphological aspects of a catalyst sample, including the distribution of shapes and sizes of the constituent particles or grains, as well as insights into sample heterogeneity. Beyond simply imaging the catalytic materials to characterize their morphological features, TEM data corroborate bulk structural and compositional information. For example, carefully and accurately analyzed lattice spacings, angles, and structural motifs observed by high-resolution TEM (HRTEM) can corroborate the assigned structure and provide knowledge about the facets that are exposed. Comparing the average particle or grain sizes observed by TEM to the grain sizes determined by Scherrer analysis of powder XRD data confirms that the bulk of the sample is comprised of same relative sizes as those observed microscopically. As with all microscopy techniques, only a small fraction of the sample is interrogated using SEM or TEM analysis, so care must be taken when formulating conclusions about the properties of a bulk sample from microscopic data alone.

Electron-diffraction data, both for individual particles and for large ensembles of particles, should match the bulk XRD data and, consequently, further confirm the structural assignment. Compositional analysis by energy-dispersive X-ray spectroscopy (EDS), again for both large ensembles of particles and also for individual particles as needed, can further validate the phase assignment. In conjunction with other types of materials-characterization data, such compositional analysis helps confirm that substantial amounts of amorphous or impurity phases are not present in a sample. SEM is particularly helpful because of the relatively large sample size (compared to TEM) that can be interrogated. For amorphous materials, high-
resolution EDS element maps obtained using TEM are particularly helpful because such maps can identify the presence, amounts, and distributions of the elements within the catalytic material, albeit for only a small region of the sample. For all materials, analysis before and after extended testing allows confirmation that the catalyst is stable under operating conditions. Materials characterization after electrochemical testing can be challenging because the catalyst is anchored directly to an electrode substrate, but surface analysis, as well as bulk analysis of the catalyst after physically detaching it from the electrode substrate, can still provide useful insights. These materials-characterization tools can provide valuable information when used separately, but can be even more powerful when used in a complementary fashion. Specifically, structural information from XRD should be in agreement with electron diffraction and with lattice spacings obtained from HRTEM. Similarly, grain sizes observed by TEM should be in agreement with Scherrer analysis from XRD. Elemental analyses from multiple techniques should match one another and should also match the stoichiometry expected for the assigned phase. Electrocatalysts can be examined both before and after electrocatalytic testing because several techniques can be performed directly on electrode substrates, including SEM, XPS, and XRD. Such analyses enable the identification of structural, compositional, and morphological changes during catalysis that provide important insights into both the true active form of the material and its stability.

K.6 Transition Metal Phosphides for the HER

Despite being well-known catalysts for various hydrotreating processes, such as hydrodesulfurization and hydrodenitrogenation, transition metal phosphides have only recently been explored as catalysts for the HER. Early work by Paseka and Burchardt demonstrated that amorphous alloys of Ni, Co, and Fe with small amounts of phosphorus (1 to 27 wt.%) were able to catalyze the HER at relatively low overpotentials in alkaline electrolytes. In 2005, based on density functional theory (DFT) calculations, Liu and Rodriguez predicted that Ni$_2$P may be a potential alternative to Pt, suggesting that synergistic effects between exposed proton-acceptor and hydride-acceptor centers on the (001) surface of Ni$_2$P could mimic features of the active sites of hydrogenase enzymes to facilitate efficient HER catalysis. In 2013, we experimentally validated this prediction, showing that nanostructured Fe$_2$P-type Ni$_2$P was indeed a highly active HER electrocatalyst in acidic aqueous solutions. Hu and co-workers similarly showed that Ni$_2$P nanopowders prepared through alternative solid-state approaches were also highly-active HER catalysts in
acidic aqueous solutions.\textsuperscript{104} Since then, many groups worldwide have contributed extensively to the advancement of this field, including the discovery of other metal phosphide HER catalysts, the development of new and improved methods for the synthesis and processing of catalytic metal phosphide materials, the interrogation of their electrocatalytic and photocatalytic properties, investigations into the mechanisms by which they function, and demonstrations of their applicability in integrated systems and devices. While transition metal phosphides have also been shown to be active HER catalysts in pH-neutral and alkaline aqueous solutions, in this review we focus primarily on their behavior under acidic conditions that are relevant to proton-exchange-membrane electrolysis systems.

\textbf{Nickel Phosphides}

Table K.6 summarizes the performance of various nickel phosphide HER catalysts synthesized under different conditions and evaluated in 0.5 M H\textsubscript{2}SO\textsubscript{4}. The first Ni\textsubscript{2}P materials studied experimentally as HER catalysts were nanoparticles synthesized by reacting trioctylphosphine (TOP) and nickel(II) acetylacetonate in 1-octadecene and oleylamine at 320 °C for 2 h.\textsuperscript{50} Several synthetic routes to colloidal Ni\textsubscript{2}P nanoparticles have been reported. For example, work by the groups of Brock,\textsuperscript{47} Chiang,\textsuperscript{62} Hyeon,\textsuperscript{105} Robinson,\textsuperscript{106} and Tracy,\textsuperscript{62} along with our group,\textsuperscript{57,89} demonstrated that high-quality Ni\textsubscript{2}P nanocrystals could be readily obtained in solution by the co-reaction of organophosphine reagents such as TOP with nickel complexes or premade Ni nanoparticles. The Ni\textsubscript{2}P particles initially evaluated as HER catalysts were synthesized using the method reported by Tracy and co-workers because it produced a high yield of monodisperse, phase-pure Ni\textsubscript{2}P nanocrystals through a simple one-pot reaction.\textsuperscript{63} As shown in Figure 6, the as-synthesized Ni\textsubscript{2}P particles were monodisperse, hollow, multi-faceted and single-crystalline, with an average diameter of 20 nm. The hollow morphology is the result of the nanoscale Kirkendall effect, which is caused by differences in the inward vs. outward diffusion rates of the constituent elements during the reaction. Kirkendall voids are commonly observed in metal phosphide nanoparticles synthesized by the decomposition of trioctylphosphine. Working electrodes of the Ni\textsubscript{2}P material were prepared by applying the as-made nanoparticles to Ti foil substrates, followed by annealing at 450 °C in H\textsubscript{2}(5 %)/N\textsubscript{2}(95 %) to remove the organic ligands that capped the surface of the nanoparticles. The resulting nanoparticulate Ni\textsubscript{2}P films required an overpotential of only −116 mV to produce an operationally relevant current density of −10 mA/cm\textsuperscript{2} ($\eta_{-10\text{mA/cm}^2} = -116$ mV) in a strongly acidic electrolyte (0.50 M H\textsubscript{2}SO\textsubscript{4}), while
also demonstrating good stability and quantitative Faradaic efficiencies over 2 h of sustained hydrogen production.\textsuperscript{50} Hu and co-workers similarly demonstrated that Ni\textsubscript{2}P nanoparticles made using a bulk-scale reaction between NaH\textsubscript{2}PO\textsubscript{2} and NiCl\textsubscript{2} \cdot 6 H\textsubscript{2}O showed excellent activity and stability in both acidic and alkaline solutions, requiring overpotentials of approximately $\eta_{-10mA/cm^2} = -125 \text{ mV}$ and $\eta_{-10mA/cm^2} = -230 \text{ mV}$ in acidic and alkaline conditions, respectively.\textsuperscript{104} The observed catalytic performance placed Ni\textsubscript{2}P amongst the best non-noble-metal HER electrocatalysts in acidic aqueous solutions reported up to that point, including MoS\textsubscript{2},\textsuperscript{40–42} NiMoN,\textsuperscript{38} MoB,\textsuperscript{35} and Mo\textsubscript{2}C catalysts.\textsuperscript{35,36}

Figure K.6: A) TEM image of Ni\textsubscript{2}P nanoparticles. B) HRTEM image of a representative Ni\textsubscript{2}P nanoparticle highlighting the exposed Ni\textsubscript{2}P(001) facet and the 5.2 Å lattice fringes that correspond to the (010) planes. C) Experimental powder XRD pattern for the Ni\textsubscript{2}P nanoparticles, with the simulated pattern of Ni\textsubscript{2}P shown for comparison. D) Polarization data for three individual Ni\textsubscript{2}P electrodes in 0.5 M H\textsubscript{2}SO\textsubscript{4}, along with glassy carbon, Ti foil, and Pt in 0.5 M H\textsubscript{2}SO\textsubscript{4}, for comparison. Adapted with permission from ref.\textsuperscript{50} Copyright 2013 American Chemical Society.

Many other groups have described similar activities and stabilities for a wide portfolio of Ni\textsubscript{2}P materials, including various nanostructures, films, and bulk powders (Figure 7). For example, Sun and coworkers reported Ni\textsubscript{2}P nanoparticle films prepared via the low-temperature phosphidation of electrodeposited nickel hydroxide
precursors\textsuperscript{107}. The resulting Ni\textsubscript{2}P films displayed a HER performance comparable to those reported previously and made by other methods, requiring an overpotential of approximately \( \eta_{-10\text{mA/cm}^2} = -130\text{mV} \) in 0.50 M H\textsubscript{2}SO\textsubscript{4} and exhibiting stable hydrogen production for at least 15 h. Likewise, Liu and coworkers observed similar activities (\( \eta_{-10\text{mA/cm}^2} \approx -124\text{mV} \)) in samples of Ni\textsubscript{2}P nanoparticles decorated on multiwalled carbon nanotubes (Ni\textsubscript{2}P/CNT)\textsuperscript{108}. The Ni\textsubscript{2}P/CNT material was synthesized in a one-pot reaction by the in-situ thermal decomposition of nickel acetylacetonate and TOP in an oleylamine solution of acid-treated CNTs, followed by deposition onto glassy carbon electrodes.

Figure K.7: A) SEM image of Ni\textsubscript{2}P particles on a Ti plate and B) corresponding linear sweep voltammograms in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Adapted with permission from ref.\textsuperscript{107}. Copyright 2014 Royal Society of Chemistry. C) TEM image of Ni\textsubscript{2}P particles decorating multiwalled carbon nanotubes and D) corresponding linear sweep voltammograms in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Adapted with permission from ref.\textsuperscript{108}. Copyright 2015 Royal Society of Chemistry. E) TEM image of bulk Ni\textsubscript{2}P nanopowders and F) corresponding linear sweep voltammograms in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Adapted with permission from ref.\textsuperscript{104}. Copyright 2014 Royal Society of Chemistry.

Recently, our group also presented a general and scalable strategy for the synthesis of metal phosphide electrodes, including Ni\textsubscript{2}P, based on the phosphidation of commercially available metal foils through the vapor-phase decomposition of
various organophosphine reagents (tributylphosphine and trioctylphosphine).\textsuperscript{58} The resulting films exhibited excellent activities, with the Ni\textsubscript{2}P electrodes requiring overpotentials for the HER of approximately $\eta_{-10\text{mA/cm}^2} = -128\text{ mV}$ in 0.50 M H\textsubscript{2}SO\textsubscript{4} and $\eta_{-10\text{mA/cm}^2} = -183\text{ mV}$ in 1 M KOH. Additionally, we demonstrated that the same phosphidation strategy could be applied to evaporated metal thin films to form conformal metal phosphide coatings on a variety of substrates, including relevant photocathode materials such as highly-doped Si. Despite the low loadings and low surface areas of the samples, the Ni\textsubscript{2}P thin-films on Si exhibited moderate activities for the HER, requiring an overpotential of $\eta_{-10\text{mA/cm}^2} = -240\text{ mV}$ in 0.50 M H\textsubscript{2}SO\textsubscript{4}.

Significant enhancements to the HER activity of Ni\textsubscript{2}P have been reported through the use of various phosphide-carbon composites and 3D electrode geometries. For instance, Wang and coworkers presented carbon-encapsulated Ni\textsubscript{2}P nanoparticles (Ni\textsubscript{2}P/C) prepared by the reduction of glucose-coated NiNH\textsubscript{4}PO\textsubscript{4} \cdot H\textsubscript{2}O nanorods with H\textsubscript{2} at 700 °C.\textsuperscript{109} These Ni\textsubscript{2}P/C nanocomposites showed enhanced HER performance, requiring only $\eta_{-10\text{mA/cm}^2} = -87\text{ mV}$ in 0.50 M H\textsubscript{2}SO\textsubscript{4}. The improved electrocatalytic activity of the Ni\textsubscript{2}P/C composite was attributed to enriched nanoporosity and a more efficient use of the available active sites. Similarly, Du and coworkers reported a three-dimensional few-layer graphene/nickel foam (G@NF) electrode coated with nanostructured Ni\textsubscript{2}P that displayed exceptional HER activity, requiring an overpotential of $\eta_{-10\text{mA/cm}^2} = -55\text{ mV}$ in 0.50 M H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{110} Such high catalytic performance was attributed to the presence of more catalytically active sites provided by the larger surface area of the porous electrode, and to enhanced ion and electron transfer. However, the activity of the 3D Ni\textsubscript{2}P–G@NF electrode was normalized to a flat geometric surface area despite being highly porous. Despite the wide diversity of synthetic preparations, sizes, morphologies, and supports that have been reported for Ni\textsubscript{2}P-based HER catalysts, most results are in agreement, with an average reported overpotential for Ni\textsubscript{2}P of $\eta_{-10\text{mA/cm}^2} = -125\text{ mV}$ in 0.50 M H\textsubscript{2}SO\textsubscript{4}.

Other nickel phosphide phases with different compositions and structures have also been explored as HER electrocatalysts (Figure 8). Dismukes and coworkers reported micron-sized Ni\textsubscript{3}P\textsubscript{4} particles prepared by the decomposition of nickel acetylacetonate, trioctylphosphine and trioctylphosphine oxide at $\approx 330^\circ$C.\textsuperscript{111} Electrodes of the material were fabricated by pressing 50 mg of dried Ni\textsubscript{3}P\textsubscript{4} powders into 6 mm diameter pellets, and sealing all but one side with epoxy. The reported overpotential
required by the Ni$_5$P$_4$ electrodes in 0.50 M H$_2$SO$_4$ was an exceptionally small value of $\eta_{-10\text{mA/cm}^2} = -23$ mV, which is almost identical to that of Pt. It is unclear why this Ni$_5$P$_4$ catalyst has such low overpotentials relative to all other reported metal phosphide HER catalysts. Ni$_5$P$_4$ nanoparticles prepared through similar methods and of comparable surface areas were reported by Liu and coworkers under similar testing conditions to require $\eta_{-10\text{mA/cm}^2} = -118$ mV.\textsuperscript{114} Likewise, Shalom and coworkers reported the growth of Ni$_5$P$_4$ nanoarchitectures directly on Ni foils by heating the metal with red phosphorus at 550 °C for 1 h under an inert atmosphere.\textsuperscript{115} In this case, the reported overpotential for the Ni$_5$P$_4$ nanoarchitectures was $\eta_{-10\text{mA/cm}^2} = -140$ mV, in close agreement with other reports.
Crystal structures of various nickel phosphides spanning a range of Ni:P ratios. The $(P_2)^{2-}$ dimer, which appears in the NiP$_2$ and NiP$_3$ polyphosphides, is also shown.

The Ni$_{12}$P$_5$ phase has also been identified as an active HER electrocatalyst (Figure 8). Ni$_{12}$P$_5$ nanoparticles on a titanium substrate$^{112}$ and Ni$_{12}$P$_5$/CNT nanohybrids$^{116}$ were reported to require overpotentials of approximately $\eta_{10\text{mA/cm}^2} = -105$ and
$\eta_{-10\text{mA/cm}^2} = -129\text{ mV}$ in acid, respectively. In addition, the HER activity of NiP$_2$ nanosheet arrays supported on carbon cloth (NiP$_2$ NS/CC) has also been reported by Sun and coworkers.$^{113}$ The NiP$_2$ NS/CC material was obtained through a two-step synthetic strategy. First, Ni(OH)$_2$ nanosheets were grown on carbon cloth through hydrothermal methods, followed by phosphidation with NaH$_2$PO$_2$ at $300^\circ$C for $2\text{ h}$ in an inert atmosphere. The NiP$_2$ NS/CC composites were highly active for the HER in acidic solutions and required an overpotential of $\eta_{-10\text{mA/cm}^2} = -75\text{ mV}$. The NiP$_2$ NS/CC electrodes also maintained their catalytic activity for at least $57\text{ h}$. However, it is worth noting again that 3D electrode geometries and other porous architectures can produce artificially enhanced performance if the reported activity is not normalized for exposed and/or active surface areas.

![Figure K.10: TEM images of Ni$_{12}$P$_5$, Ni$_2$P, and Ni$_5$P$_4$ nanoparticles and their respective linear sweep voltammograms in 0.5 M H$_2$SO$_4$. Adapted with permission from ref.$^{114}$ Copyright 2015 Royal Society of Chemistry.](image)

Comparisons among the different nickel phosphides are particularly interesting and instructive (Figure 9). In face-centered cubic (fcc) Ni, each Ni atom is surrounded by and coordinated to 12 other Ni atoms. However, as phosphorus is incorporated and the P:Ni ratio in metal phosphides increases, the number of direct Ni–Ni interactions progressively decreases while the Ni–P coordination increases. In the case of pyrite-type NiP$_2$, no direct Ni–Ni interactions remain and phosphorus-phosphorus bonding
(P–P dimers, as mentioned previously) is observed. Additionally, the introduction of P into the structure significantly changes the geometry and arrangement of the Ni sites and leads to a gradual increase in the Ni–Ni bond distance from around 2.49 Å on the Ni(111) surface to 3.85 Å on the NiP2 (001) surface (Figure 9). These differences in crystal structure and bonding may have a direct impact on the catalytic properties of the various metal phosphides. Liu and coworkers prepared different nanostructured nickel phosphide phases (Ni12P5, Ni2P, Ni5P4) and compared their activities for the HER under similar conditions (Figure K.10).\textsuperscript{114} The Ni5P4 phase exhibited superior electrocatalytic performance relative to Ni12P5 and Ni2P, with the behavior attributed to a higher positive charge on the Ni and a stronger ensemble effect from P in Ni5P4. However, as can be seen in Figure K.10, variations in the particle sizes, morphologies, and surface areas of the samples could account for some of the observed differences in HER activity. Along with similar studies by Kucernak and Sundaram comparing Ni12P5 and Ni2P\textsuperscript{117} and by Dismukes and coworkers comparing Ni5P4 and Ni2P,\textsuperscript{111} these results suggest that the metal-to-phosphorus ratio in metal phosphides might play an important role in affecting the HER performance, with more phosphorus-rich phases tending to exhibit higher HER activities. While comparing the intrinsic activities of HER catalysts tested using different electrode fabrication methods and loadings poses significant challenges, reports on the HER activity of NiP2 nanosheets ($\eta_{\text{10 mA/cm}^2} = -75$ mV) also seems to support these conclusions.\textsuperscript{113} The observed trends are consistent with the putative mechanism for the HER on Ni2P(001), which invokes an ensemble effect involving cooperativity of the P and Ni atoms that implies a dependence on the P: Ni ratio.
Table K.1: Compilation of HER performance metrics for various nickel phosphide catalysts synthesized under different conditions and evaluated in 0.5 M H₂SO₄

<table>
<thead>
<tr>
<th>Material</th>
<th>η_{10 mA/cm²}</th>
<th>η_{20 mA/cm²}</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Exchange Current Density (A/cm²)</th>
<th>Loading density (mg/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃P Ni/P/Ti</td>
<td>≈116</td>
<td>-130</td>
<td>46</td>
<td>3.3 × 10⁻⁴</td>
<td>1</td>
<td></td>
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<tr>
<td>Ni₃P/PNi</td>
<td>-128</td>
<td>-153</td>
<td>66</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni₃P NS/NI foam</td>
<td>≈115</td>
<td>≈140</td>
<td>68</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Polydisperse Ni₃P/GCE</td>
<td>≈125</td>
<td>≈140</td>
<td>≈87</td>
<td>-</td>
<td>0.38</td>
<td>134</td>
</tr>
<tr>
<td>Nanoparticle films Ni₃P/Ti</td>
<td>≈130</td>
<td>-138</td>
<td>60</td>
<td>-</td>
<td>2</td>
<td>133</td>
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<tr>
<td>Ni₃P/CNT</td>
<td>-124</td>
<td>-33</td>
<td>35</td>
<td>5.37 × 10⁻⁵</td>
<td>-</td>
<td>136</td>
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<tr>
<td>Peapod-like Ni₃P/C</td>
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<td>-115</td>
<td>54</td>
<td>-</td>
<td>0.36</td>
<td>136</td>
</tr>
<tr>
<td>Ni₃P-G/NF</td>
<td>≈150</td>
<td>≈80</td>
<td>≈30</td>
<td>-</td>
<td>-</td>
<td>136</td>
</tr>
<tr>
<td>Ni₃P MP pellet</td>
<td>23</td>
<td>33</td>
<td>177</td>
<td>-</td>
<td>177</td>
<td>136</td>
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<tr>
<td>Ni₃P MP pellet</td>
<td>-42</td>
<td>-38</td>
<td>-177</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni₃P₂/P/Ti</td>
<td>-107</td>
<td>-141</td>
<td>63</td>
<td>-</td>
<td>3</td>
<td>132</td>
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<tr>
<td>Ni₃P₂ NS/C/C</td>
<td>-75</td>
<td>-51</td>
<td>2.60 × 10⁻⁴</td>
<td>4.3</td>
<td>-</td>
<td>133</td>
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<tr>
<td>Ni₃P NPs</td>
<td>-137</td>
<td>-49</td>
<td>1.99</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P₂ NPs</td>
<td>-118</td>
<td>-42</td>
<td>-1.99</td>
<td>-</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P₂/Ps</td>
<td>-208</td>
<td>-75</td>
<td>-1.99</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P₂/Ps/Ni</td>
<td>-140</td>
<td>-40</td>
<td>-1.99</td>
<td>-</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P₂/Ps/CNT</td>
<td>-129</td>
<td>-56</td>
<td>7.10 × 10⁻⁴</td>
<td>0.75</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P/CNT</td>
<td>-84</td>
<td>2.90 × 10⁻⁴</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P/GCE</td>
<td>-108</td>
<td>3.70 × 10⁻⁴</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>134</td>
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<tr>
<td>MOF-derived Ni₃P</td>
<td>≈200</td>
<td>-62</td>
<td>7.10 × 10⁻⁴</td>
<td>0.35</td>
<td>-</td>
<td>134</td>
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<tr>
<td>MOF-derived Ni₃P₂</td>
<td>≈650</td>
<td>4.50 × 10⁻⁴</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P/CNSS</td>
<td>-92</td>
<td>-108</td>
<td>4.90 × 10⁻⁴</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P/Ps/NI foam</td>
<td>-136</td>
<td>-209</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P films</td>
<td>-93</td>
<td>33 and 98</td>
<td>-134</td>
<td>0.35</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P-Pd/NI</td>
<td>-131</td>
<td>-163</td>
<td>106.1</td>
<td>8.62 × 10⁻⁵</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P₂</td>
<td>-62</td>
<td>46.1</td>
<td>2.75 × 10⁻⁴</td>
<td>0.15</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P</td>
<td>-228</td>
<td>83.3</td>
<td>2.10 × 10⁻⁴</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>Ni₃P/PNRGO</td>
<td>-102</td>
<td>-122</td>
<td>59</td>
<td>4.90 × 10⁻⁴</td>
<td>-</td>
<td>134</td>
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<tr>
<td>Ni₃P/P/G/NF</td>
<td>-75</td>
<td>-51</td>
<td>-134</td>
<td>-</td>
<td>-</td>
<td>134</td>
</tr>
<tr>
<td>(Ni₃P/P)@graphitized carbon</td>
<td>-45</td>
<td>-46</td>
<td>-134</td>
<td>0.38</td>
<td>-</td>
<td>134</td>
</tr>
</tbody>
</table>

Cobalt Phosphides

Following the initial studies of Ni₃P as an Earth-abundant HER catalyst, cobalt phosphide (CoP) was also identified as an active and acid-stable HER catalyst. Like Ni₃P, CoP is a structurally and compositionally distinct but active HDS catalyst. CoP nanoparticles, which were prepared by reacting Co nanoparticles with TOP at about 320 °C, were quasi-spherical, multi-faceted, highly uniform, and hollow, with an average diameter of 13 ± 2 nm (Figure K.11), similar to those of Ni₃P mentioned previously. Electrodes comprised of CoP nanoparticles on a Ti support outperformed Ni₃P and other nickel-containing phosphides in both activity and stability in 0.50 M H₂SO₄, requiring an overpotential of η_{10 mA/cm²} = -75 mV and remaining stable for over 24 h while exhibiting 100 % Faradaic efficiency.

Several groups have since corroborated these results for a wide variety of CoP morphologies and supports (Figure K.12). For example, Sun and coworkers have reported similar HER activities in 0.50 M H₂SO₄ for a number of different CoP-based electrodes obtained via the low-temperature phosphidation of various cobalt...
precursors with NaH$_2$PO$_2$. These reports include carbon nanotubes decorated with CoP nanocrystals ($\eta_{-10 \, \text{mA/cm}^2} = -122 \, \text{mV}$),\textsuperscript{129} CoP nanosheet arrays supported on Ti plates ($\eta_{-10 \, \text{mA/cm}^2} = -90 \, \text{mV}$),\textsuperscript{128} self-supported nanoporous cobalt phosphide nanowire arrays on carbon cloth ($\eta_{-10 \, \text{mA/cm}^2} = -67 \, \text{mV}$),\textsuperscript{127} CoP nanotubes ($\eta_{-10 \, \text{mA/cm}^2} = -72 \, \text{mV}$),\textsuperscript{128} three-dimensional interconnected networks of porous CoP nanowires ($\eta_{-10 \, \text{mA/cm}^2} = -100 \, \text{mV}$),\textsuperscript{130} and CoP nanoparticle films on carbon cloth ($\eta_{-10 \, \text{mA/cm}^2} = -48 \, \text{mV}$).\textsuperscript{131} It is worth noting that the increased activity observed in a few of these instances could be attributed to the use of highly porous 3D electrodes without normalization to exposed or active surface areas. Many other reports, too numerous to include as an exhaustive list, describe related iterations and comparable HER activities for various CoP materials.

Interestingly, Lewis, Soriaga, and coworkers have demonstrated that electrode-deposited amorphous Co–P films exhibit HER activities comparable to those of crys-
talline CoP phases (Figure K.13).\textsuperscript{81} The Co–P films were synthesized by cathodic deposition from a boric acid solution of Co$^{2+}$ and H$_2$PO$_2^-$ on Cu foils, followed by operando purification to produce an electrocatalyst with a Co:P atomic ratio of 1:1. The electrodeposited CoP catalysts showed high activities with an overpotential of $\eta_{-10\text{mA/cm}^2} = -85\text{ mV}$ needed in highly acidic solutions (0.50 M H$_2$SO$_4$). In agreement with this report, Sun and coworkers later observed comparable activities using electrodeposited amorphous Co–P films prepared under similar experimental conditions ($\eta_{-10\text{mA/cm}^2} = -98\text{ mV}$).

As in the case of Ni$_2$P, despite the wide diversity of synthetic preparations, sizes, morphologies, and supports that have been reported, most results are in agreement, reporting an average overpotential for CoP of $\eta_{-10\text{mA/cm}^2} = -80\text{ mV}$ in 0.50 M
H$_2$SO$_4$. Table K.6 summarizes the performance of various cobalt phosphide HER catalysts synthesized under various conditions and evaluated in 0.5 M H$_2$SO$_4$.

Figure K.13: (A) Low-magnification and (B) high-magnification SEM images of electrodeposited amorphous Co-P films. (C) XPS spectrum of Co-P films before and after voltammetry. (D) Linear sweep voltammograms in 0.5 M H$_2$SO$_4$, along with Pt, Co, and Cu controls. Adapted with permission from ref. 81. Copyright 2014 American Chemical Society.

Comparisons among electrocatalysts with different structures, but identical constituent elements and morphologies, are important for identifying key structural characteristics that could lead to higher HER activities. With this in mind, we recently studied nanostructures of Co$_2$P, a cobalt phosphide phase that is compositionally and structurally distinct from CoP, by synthesizing by morphologically equivalent Co$_2$P and CoP nanoparticles and evaluating their catalytic activity for the HER in 0.50 M H$_2$SO$_4$ (Figure K.14). The Co$_2$P phase displayed slightly higher overpotentials ($\eta_{-10 \text{ mA/cm}^2} = -95 \text{ mV}$) than CoP ($\eta_{-10 \text{ mA/cm}^2} = -75 \text{ mV}$). This behavior correlates with the different Co/P ratio of the phases, and suggests that the increased Co–P character of CoP may provide a higher density of proximal cobalt and phosphorus surface atoms, which are hypothesized to be active sites for the HER. Liu and coworkers further explored the influence of phase, structure, and support effects on the HER activity by synthesizing a series of cobalt phosphide-based electrocatalysts, including Co$_2$P, CoP, Co$_2$P/CNTs, CoP/CNTs, Co$_2$P/nitrogen-doped carbon nanotubes (NCNTs) and CoP/NCNTs, through the solution-based decomposition of various organophosphine reagents. Their results indicated that catalytic activity
Table K.2: Compilation of HER performance metrics for various cobalt phosphide catalysts synthesized under different conditions and evaluated in 0.5 M H₂SO₄

<table>
<thead>
<tr>
<th>Material</th>
<th>η_{-10mA/cm²}</th>
<th>η_{-20mA/cm²}</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Exchange Current Density (A/cm²)</th>
<th>Loading density (mg/cm²)</th>
<th>Reference</th>
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<tr>
<td>Co₃P/Co</td>
<td>-0.174</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Co₃P/CC</td>
<td>-0.49</td>
<td>-0.59</td>
<td>30.1</td>
<td>-</td>
<td>13.6</td>
<td>[8]</td>
</tr>
<tr>
<td>CoP films</td>
<td>-0.53</td>
<td>-</td>
<td>50</td>
<td>2.00 × 10⁻⁴</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NPs/Ti</td>
<td>-0.75</td>
<td>-0.85</td>
<td>50</td>
<td>1.40 × 10⁻⁴</td>
<td>2</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP/CC</td>
<td>-0.67</td>
<td>-0.100</td>
<td>51</td>
<td>2.88 × 10⁻⁴</td>
<td>0.92</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NPs</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NPs/CC</td>
<td>-</td>
<td>-0.297</td>
<td>82</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
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<td>CoP NWs/Ti</td>
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<td>-0.95</td>
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<td>-</td>
<td>0.8</td>
<td>[9]</td>
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<tr>
<td>CoP NWs/CC</td>
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<td>-</td>
<td>70</td>
<td>4</td>
<td>4</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP/NWs</td>
<td>-0.37</td>
<td>-</td>
<td>54</td>
<td>1.30 × 10⁻⁴</td>
<td>0.28</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP/Ti</td>
<td>-0.90</td>
<td>-</td>
<td>43</td>
<td>-</td>
<td>2</td>
<td>[9]</td>
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<tr>
<td>CoP NPs/Ti</td>
<td>-0.95</td>
<td>-0.109</td>
<td>45</td>
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<td>CoP</td>
<td>-0.406</td>
<td>101</td>
<td>3.20 × 10⁻³</td>
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<td>-</td>
<td>[9]</td>
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<td>CoP/PCNTs</td>
<td>-0.195</td>
<td>-0.219</td>
<td>74</td>
<td>3.90 × 10⁻⁴</td>
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<td>[9]</td>
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<td>CoP/PCNTs/CC</td>
<td>-0.165</td>
<td>-0.198</td>
<td>68</td>
<td>6.80 × 10⁻⁴</td>
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<td>CoP/NCNTs</td>
<td>-</td>
<td>-0.171</td>
<td>62</td>
<td>1.02 × 10⁻⁴</td>
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<td>Branched CoP</td>
<td>-</td>
<td>-0.117</td>
<td>48</td>
<td>-</td>
<td>1</td>
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<td>CoP NWs</td>
<td>-0.110</td>
<td>-0.142</td>
<td>54</td>
<td>1.60 × 10⁻⁴</td>
<td>0.35</td>
<td>[9]</td>
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<td>CoP NPs</td>
<td>-0.221</td>
<td>-</td>
<td>61</td>
<td>3.40 × 10⁻³</td>
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<td>[9]</td>
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<td>CoP NPs</td>
<td>-0.164</td>
<td>-</td>
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<td>3.20 × 10⁻³</td>
<td>0.35</td>
<td>[9]</td>
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<td>CoP NPs/Ti</td>
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<td>-0.167</td>
<td>51.7</td>
<td>-</td>
<td>1</td>
<td>[9]</td>
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<td>CoP films</td>
<td>-0.94</td>
<td>-0.42</td>
<td>-</td>
<td>2.6</td>
<td>-</td>
<td>[9]</td>
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<td>CoP/RGO</td>
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<td>4.00 × 10⁻³</td>
<td>0.29</td>
<td>-</td>
<td>[9]</td>
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<td>CoP/C</td>
<td>-0.130</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>[9]</td>
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<td>Urchin-like CoP NCs</td>
<td>+0.100</td>
<td>-0.46</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>[9]</td>
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<td>CoP NPs/Ti</td>
<td>-0.203</td>
<td>-0.40</td>
<td>-</td>
<td>1.96</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NWs/CC</td>
<td>-0.170</td>
<td>-0.61</td>
<td>-</td>
<td>0.35</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NW</td>
<td>+0.100</td>
<td>-0.45</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NW/NCNTs</td>
<td>-0.100</td>
<td>-0.41</td>
<td>-</td>
<td>2.0</td>
<td>2</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NPs/CC</td>
<td>+0.88</td>
<td>-0.106</td>
<td>50</td>
<td>-</td>
<td>0.28</td>
<td>[9]</td>
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<tr>
<td>CoP hollow polyhedron</td>
<td>-0.159</td>
<td>-0.59</td>
<td>59</td>
<td>3.70 × 10⁻²</td>
<td>0.10</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP particles</td>
<td>-0.355</td>
<td>-0.77</td>
<td>77</td>
<td>5.00 × 10⁻³</td>
<td>0.10</td>
<td>[9]</td>
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<tr>
<td>CoP NPs</td>
<td>-0.393</td>
<td>-0.105</td>
<td>105</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>CoP NPs</td>
<td>-0.181</td>
<td>-0.69</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
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<tr>
<td>CoP@P/GCE</td>
<td>-0.160</td>
<td>53</td>
<td>2.10 × 10⁻⁴</td>
<td>-</td>
<td>-</td>
<td>[9]</td>
</tr>
</tbody>
</table>

followed the order CoP/NCNTs > Co₂P/NCNTs > CoP/PCNTs > Co₂P/CNTs > CoP > Co₂P, with the more phosphorus-rich CoP phase outperforming the corresponding Co₂P counterparts in each case. The highest activity of the series was obtained by the CoP/NCNTs catalysts, which required η_{-10mA/cm²} = -85 mV. While preliminary, these reports are in agreement with observations on the nickel phosphide system, indicating that more phosphorus-rich phases exhibit higher HER activities. Furthermore, direct comparisons by our group of multifaceted CoP nanoparticles with highly branched CoP nanostructures that exposed a high density of (111) facets suggested that the high HER activity of CoP is intrinsic to the system, and that shape control may not play a significant role in defining the magnitude of the overpotentials required to produce operationally relevant cathodic current densities. 136
Iron Phosphides

As the cheapest and most terrestrially abundant transition metal, iron is a particularly interesting target for incorporation into metal phosphide HER catalysts. Iron-containing clusters have been found in the active sites of various enzymes including [FeFe] and [Fe]-only hydrogenases, which have been demonstrated to be highly active and efficient HER catalysts in biological systems. Interestingly, iron phosphides such as FeP and Fe₂P are also known hydrodesulfurization catalysts, yet with significantly lower activities than other transition metal phosphides.
such as Ni$_2$P.\textsuperscript{48,49,135,151} Both our group and the Sun group independently identified MnP-type FeP as an exceptionally active HER electrocatalyst in acidic, basic and neutral-pH conditions (Figure K.15),\textsuperscript{152,153} that outperforms other comparable metal phosphide systems including CoP and Ni$_2$P. Table 3 summarizes the performance of various iron phosphide HER catalysts synthesized under various conditions and evaluated in 0.5 M H$_2$SO$_4$.

Similar to our CoP system, we synthesized colloidal FeP nanoparticles by reacting premade Fe nanocrystals with TOP at elevated temperatures.\textsuperscript{152} The resulting FeP nanoparticles were spherical and hollow, with an average diameter of 13 ± 2 nm (Figure K.15), and were morphologically comparable to the Ni$_2$P and CoP nanoparticles that had been synthesized previously. Working electrodes (FePNP/Ti) with FeP nanoparticles were prepared by drop-casting appropriate amounts to obtain mass loadings of 1 mg/cm$^2$ of an FeP nanoparticle suspension onto Ti substrates, followed by treatment at 450°C in a reducing atmosphere to remove any remaining surface ligands. Linear sweep voltammetry measurements for the FeP NP/Ti
electrodes in acidic solutions (0.5 M H$_2$SO$_4$) demonstrated exceptionally high HER activities, with overpotentials of only $\eta_{-10 \text{mA/cm}^2} = -50 \text{ mV}$ required. Sun and coworkers studied FeP nanowire arrays supported on conductive Ti plates (FeP-NA/Ti) (Figure K.15). These arrays were synthesized chemically by converting FeOOH nanowire arrays, which were hydrothermally grown directly onto Ti plates, into FePNA/Ti by a low-temperature phosphidation reaction with NaH$_2$PO$_2$. The resulting FePNA/Ti system required an overpotential of $\eta_{-10 \text{mA/cm}^2} = -55 \text{ mV}$ in 0.5 M H$_2$SO$_4$, comparable to the behavior of the FePNP/Ti system. While both FeP electrodes exhibited HER activities that were significantly higher than comparable electrodes of Ni$_2$P and CoP, long-term stability measurements indicated decreases in activity of the Fe-based systems after more than 15 h of sustained hydrogen production. In the case of the FePNP/Ti sample, the required overpotential increased by approximately 52 mV, compared to an increase of 11 mV for comparable CoP nanoparticles after 24 h of sustained operation at $-20 \text{ mA/cm}^2$. While activity is an important metric for HER performance, a practical catalyst clearly requires a balance between activity and long-term stability. As such, CoP might be a more robust candidate for further development and testing efforts, such as integration with light absorbers and use in solar-driven water-splitting devices.

Other phases in the iron phosphide system have also been studied as HER catalysts. For example, Yang and coworkers reported phosphorus-rich FeP$_2$/C nanohybrids prepared by the pyrolysis of ferrocene and red phosphorus in an evacuated and sealed quartz tube at 500 °C. The resulting material was investigated for the HER in 0.50 M H$_2$SO$_4$ and showed very low HER activities, requiring an overpotential of $-500 \text{ mV}$ to achieve a current density of $-5 \text{ mA/cm}^2$. In addition, Fe$_2$P nanoparticles encapsulated in a sandwichlike graphited carbon envelope were reported by Wang and coworkers, with an observed overpotential for the HER of $\eta_{-10 \text{mA/cm}^2} = -88 \text{ mV}$. While still preliminary, the lower HER activity of Fe$_2$P relative to FeP is in agreement with previously established general trends that phosphide phases having a higher phosphorus content show improved activities for the HER. However, it is possible that this activity trend may not extend to phosphorus-rich phases, such as FeP$_2$, because their different structures and bonding (e.g. P–P bonds) may impact their relative activities and stabilities. While still preliminary, the lower HER activity of Fe$_2$P relative to FeP is in agreement with previously established general trends that phosphide phases having a higher phosphorus content show improved activities for the HER. However, it is possible that this activity trend may not extend to phosphorus-rich phases, such as FeP$_2$, because their different
Material & \eta_{-10mA/cm^2} & \eta_{-20mA/cm^2} & \text{Tafel slope (mV dec}^{-1}) & \text{Exchange Current Density (A/cm}^2) & \text{Loading density (mg/cm}^2) & \text{Reference} \\
Fe_{2}P/Fe & -191 & - & 55 & - & - & 98 \\
FeP NPs/Ti & -50 & - & 37 & 4.30 \times 10^{-4} & 1 & 52 \\
FeP NA/Ti & -55 & -72 & 38 & 4.20 \times 10^{-4} & 0.28 & 53 \\
FeP2C & - & - & 66 & 1.73 \times 10^{-8} & 0.42 & 52 \\
FeP/CC & 100 & - & 49 & - & 0.36 & 55 \\
FeP/C & - & -43 & 29.2 & 6.80 \times 10^{-4} & 4.9 & 56 \\
HMFeP@C & -115 & - & 56 & 1.91 \times 10^{-4} & - & 57 \\
FeP NWs & -96 & - & 39 & 1.70 \times 10^{-4} & - & 58 \\
FeP2 NWs & -61 & - & 37 & 5.50 \times 10^{-4} & - & 58 \\
Fe/P/CC & -123 & - & 50 & 1.20 \times 10^{-4} & 0.28 & 57 \\
FeP NAs/CC & -58 & - & 45 & 5.00 \times 10^{-4} & 1.5 & 59 \\
FeP NAs/Ti & -85 & - & 60 & - & - & 50 \\
FeP NAs & -240 & - & 67 & - & - & 52 \\
FeP-CS & -112 & - & 58 & 2.20 \times 10^{-4} & 0.28 & 55 \\

Table K.3: Compilation of HER performance metrics for various iron phosphide catalysts synthesized under different conditions and evaluated in 0.5M H2SO4.

Material & \eta_{-10mA/cm^2} & \eta_{-20mA/cm^2} & \text{Tafel slope (mV dec}^{-1}) & \text{Exchange Current Density (A/cm}^2) & \text{Loading density (mg/cm}^2) & \text{Reference} \\
MoP & \approx -130 & - & 54 & 3.40 \times 10^{-3} & - & 55 \\
Mo3P & \approx -500 & - & 147 & - & - & 55 \\
WP/Ti & -120 & -140 & 54 & 4.50 \times 10^{-3} & 1 & 55 \\
WP NAs/CC & -130 & - & 69 & 2.90 \times 10^{-4} & 2 & 55 \\
WP2 SMPs & -161 & - & 65 & 1.70 \times 10^{-3} & 0.5 & 55 \\
MoP NPs & -125 & - & 54 & 8.60 \times 10^{-3} & 0.36 & 56 \\
MoP/GCE & -246 & - & 60 & 4.15 \times 10^{-6} & 7.1 \times 10^{-4} & 57 \\
MoP/CF & -200 & - & 36.4 & - & 0.36 & 57 \\
MoP MPs & -150 & - & 50 & 1 \times 10^{-3} & 0.1 & 72 \\
MoP flakes & - & -155 & 71.77 & - & 1.425 & 73 \\
MoP2 NPs/Mo & -143 & - & 57 & 6.00 \times 10^{-3} & - & 74 \\
WP2 nanorods & -148 & - & 52 & 1.30 \times 10^{-3} & - & 74 \\

Table K.4: Compilation of HER performance metrics for various molybdenum and tungsten phosphide catalysts synthesized under different conditions and evaluated in 0.5M H2SO4.

structures and bonding (e.g. P–P bonds) may impact their relative activities and stabilities.

**Molybdenum and Tungsten Phosphides**

Molybdenum and tungsten phosphides are among some of the most active HDS catalysts reported to date, making them attractive targets as catalysts for the HER.48,49 Table 4 summarizes the performance of various molybdenum phosphide and tungsten phosphide HER catalysts synthesized and evaluated under various conditions. Wang and coworkers reported the HER activity of crystalline Mo3P and MoP prepared through bulk solid-state approaches.165 The metal-rich Mo3P phase dis-
played low HER activity, requiring an overpotential of $\eta_{-10 \text{mA/cm}^2} = -500 \text{mV}$ in 0.50 M H$_2$SO$_4$. However, the stoichiometric MoP phase exhibited much improved performance even in bulk form, exhibiting an overpotential of approximately $\eta_{-10 \text{mA/cm}^2} = -125 \text{mV}$ under the same conditions (Figure K.16). Our group reported on the synthesis and HER performance of amorphous molybdenum phosphide (MoP) nanoparticles having diameters of $\approx 3 \text{nm}$ prepared through the decomposition of Mo(CO)$_6$ and TOP in squalane at 320 °C (Figure K.16).$^{176}$ The MoP nanoparticles remained amorphous even after annealing to 450 °C to remove the organic surface ligands. Working electrodes of the MoP nanoparticles on Ti foil (MoP/Ti) exhibited overpotentials of $\eta_{-10 \text{mA/cm}^2} = -90 \text{mV}$ in 0.50 M H$_2$SO$_4$. These potentials remained constant after 18 h of galvanostatic testing and after over 500 cyclic voltammetric sweeps, indicating substantial stability under operating conditions. Amorphous tungsten phosphide (WP) nanoparticles of comparable morphology and size were also obtained using similar synthetic methods (Figure K.17).$^{166}$ When tested for the HER, WP/Ti electrodes displayed slightly lower ac-
tivities than MoP, producing a current density of $-10 \text{ mA/cm}^2$ at an overpotential of $-120 \text{ mV}$ in 0.50 M H$_2$SO$_4$. Crystalline WP nanorod arrays on carbon cloth (WP NAs/CC) reported by Sun and coworkers displayed similar activity, requiring an overpotential of $\eta_{-10 \text{ mA/cm}^2} = -130 \text{ mV}$ in 0.50 M H$_2$SO$_4$ (Figure K.17). Under the same conditions, crystalline, submicron WP$_2$ particles reported by the same group required a slightly higher overpotential of $\eta_{-10 \text{ mA/cm}^2} = -161 \text{ mV}$.}

Figure K.17: (A) TEM image of amorphous WP nanoparticles and (B) corresponding polarization data in 0.5 M H$_2$SO$_4$, along with a Pt control. Adapted with permission from ref. Copyright 2014 Royal Society of Chemistry. (C) TEM image of crystalline WP$_2$ nanoparticles and (D) corresponding polarization data in in 0.5 M H$_2$SO$_4$, along with a Pt control. Adapted with permission from ref. Copyright 2015 American Chemical Society.

**Copper Phosphides**

Compared to the phosphides of the iron group elements (Fe, Co, Ni), copper phosphides have attracted significantly less attention as HER electrocatalysts, and only a few studies on Cu$_3$P have been reported to date. An initial study by Sun and coworkers on self-supported Cu$_3$P nanowire arrays grown on commercial porous copper foams (Cu$_3$P NW/CF) reported catalytic current densities at an overpotential of $\eta_{-10 \text{ mA/cm}^2} = -143 \text{ mV}$, with only minor degradation after continuous hydrogen production for 25 h (Figure K.18). Likewise, Kong and coworkers described the phosphidation of Cu(OH)$_2$ precursors to form Cu$_3$P nanocubes, which exhibited moderate activities for the HER ($\eta_{-10 \text{ mA/cm}^2} = -320 \text{ mV}$) when tested on glassy carbon electrodes (GCE) (Figure K.18). Recently, our group reported the synthesis of phase-pure Cu$_3$P films grown directly onto Cu foils through the
vapor-phase phosphidation of commercially available metal foils with organophosphine reagents.\textsuperscript{58} The Cu\textsubscript{3} P films appeared to be very unstable under the operating conditions, perhaps due to rapid degradation at the Cu\textsubscript{3} P/Cu interface. The previous report on Cu\textsubscript{3} P nanowire arrays presumably was performed on a more robust catalyst/substrate interface. Cu\textsubscript{3} P therefore shows some evidence of moderate HER activity, but overall is not as stable at this point as the Fe, Co, and Ni phosphide systems.

Figure K.18: (A) SEM image of Cu\textsubscript{3}P nanocubes and (B) corresponding polarization data in 0.5 M H\textsubscript{2}SO\textsubscript{4}, along with a Pt control. Adapted with permission from ref.\textsuperscript{177}. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) SEM image of self-supported Cu\textsubscript{3}P nanowires on carbon cloth and (D) corresponding polarization data in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Adapted with permission from ref.\textsuperscript{178}. Copyright 2016 Royal Society of Chemistry.

Cation and Anion Substituted Metal Phosphides

Mixed-metal transition metal phosphides have recently been explored as electrocatalysts for the HER through a combined experimental and theoretical approach. Jaramillo and coworkers utilized density functional theory calculations to predict the hydrogen adsorption free energies, $\Delta G_H$, for a series of mixed-metal transition metal phosphides, and compared these results to experimentally determined HER activities to identify optimized metal phosphide catalysts for the HER (Figure K.19).\textsuperscript{149} Applying this methodology, a Fe\textsubscript{0.5}Co\textsubscript{0.5}P alloy was found to be the most active of all the studied systems, with a near-zero theoretical $\Delta G_H$ of 0.004 eV and an experimental TOF\textsubscript{avg} of $0.19 \pm 0.01$ H\textsubscript{2} s\textsuperscript{−1}. Nevertheless, the study also indicated that monometallic CoP exhibits a comparable HER activity, with a theoretical $\Delta G_H = -0.09$ eV and an experimental TOF\textsubscript{avg} of $\approx 0.18$ H\textsubscript{2} s\textsuperscript{−1}, suggesting that
strategies based exclusively on cation solid solutions might not lead to significant improvements in HER activity. A different study by Wang and coworkers also explored the use of mixed-metal phosphides for the HER, in particular Fe-substituted Ni$_2$P sandwich nanocomposites. These (Fe, Ni)$_2$P nanocomposites were prepared by soaking NiNH$_4$PO$_4$·H$_2$O nanosheets synthesized by a hydrothermal approach in an aqueous FeCl$_2$ solution, followed by a second hydrothermal process to carbon-coat the nanostructures, followed by reduction in a H$_2$ atmosphere at 680 °C. The polarization data for the Fe-substituted Ni$_2$P composites and Ni$_2$P controls indicated enhanced activity for (Fe, Ni)$_2$P system, which required an overpotential of approximately $\eta_{-10 \text{ mA/cm}^2} = -75 \text{ mV}$ compared to the $\eta_{-10 \text{ mA/cm}^2} = -150 \text{ mV}$ required by Ni$_2$P to reach the same current density. However, iron phosphide controls were not included for comparison.

Figure K.19: (A) Polarization data for several transition metal phosphides in 0.5 M H$_2$SO$_4$, along with a Pt control. (B) Volcano plot showing the TOF of several transition metal phosphides as a function of hydrogen adsorption free energies. The color-coded key for both panels is shown in (B). Adapted with permission from ref. Copyright 2015 Royal Society of Chemistry.

Anion substitution has also been explored as an approach for improving the HER activity of metal phosphides. Based on the mechanistic commonalities shared
by many HER and HDS catalysts, Jaramillo and coworkers hypothesized that the introduction of sulfur onto metal phosphides might lead to enhancements in their catalytic activity and stability for the HER, as surface phosphosulfides are considered to be the sites of enhanced activity during HDS catalysis by both Ni$_2$P and MoP.$^{180}$

To explore this possibility, sulfur was introduced into the surface region of MoP films by post-sulfidation in a quartz tube furnace at 400 °C under a mixture of 10 % H$_2$S in H$_2$. The introduction of sulfur led to significant improvements in the electrocatalytic HER activity of the MoP films, with the MoP|S catalyst requiring an overpotential of only $\eta_{-10\ mA/cm^2} = -64 \text{ mV}$ compared to the required $\eta_{-10\ mA/cm^2} = -117 \text{ mV}$ of the unmodified MoP films (Figure K.20). Similarly, Jin and coworkers developed a nanostructured pyrite-type cobalt phosphosulfide (CoPS) catalyst for the HER (Figure K.21).$^{181}$ The CoPS electrodes were prepared by reacting a series of cobalt-based precursors at 500 °C with sulfur and phosphorus vapors produced by the evaporation of the elemental powders in an inert atmosphere. High-surface-area CoPS nanoplates grown on carbon paper displayed the highest HER performance of the studied samples, achieving a geometric current density of $-10\ mA/cm^2$ at an overpotential of only $\eta_{-10\ mA/cm^2} = -48 \text{ mV}$ in 0.50 M H$_2$SO$_4$. This activity places CoPS among the best Earth-abundant HER electrocatalysts reported to date, and perhaps more importantly demonstrates that tuning the electronic structure and reactivity of catalysts by substituting non-metallic atoms can serve as a powerful strategy to enhance the activity of transition metal compounds.
Figure K.20: (A) Low-magnification and (B) high-magnification SEM images of MoP|S. (C) Polarization data for MoP and MoP|S in 0.5 M H₂SO₄, along with a Pt control. Adapted with permission from ref.¹⁸⁰. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure K.21: (A) SEM images of cobalt hydroxide carbonate hydrate precursor. (B) SEM images of CoPS nanoplate product after reaction in a thiophosphate atmosphere. (C) Crystal structure of CoPS. (D) EDS spectra for CoPS films, CoPS nanowires on graphite, and CoPS nanoplates on carbon fiber paper. (E) Polarization data in 0.5 M H₂SO₄ for CoPS films, nanowires and nanoplates, along with a Pt control. Adapted with permission from ref.¹⁸¹. Copyright 2015 Macmillan Publishers Limited.
Mechanistic and Surface Studies of Metal Phosphides

Despite great interest in the use of metal phosphides as catalysts for the HER, to date only a few mechanistic and surface studies have been reported. The surface structure of the catalysts under operating conditions, the identity of the catalytically active sites, and key details of the HER mechanism on metal phosphide surfaces remain largely unknown. The existing studies have focused mainly on density functional theory (DFT) calculations of the hydrogen absorption energies on various metal phosphide surfaces. Based on such calculations, Liu and Rodriguez associated the HER behavior of Ni$_2$P to an ensemble effect, in which the presence of P atoms dilutes the number of highly active Ni sites on the surface, potentially leading to more moderate binding of the products and intermediates (Figure K.22).$^{45}$ Importantly, they also identified the P sites as active, suggesting that the presence of both proton-acceptor and hydride-acceptor centers on the surface could be playing a role in facilitating the HER. Based on DFT calculations, Hu and coworkers suggested that phosphorus-stabilized Ni-bridge sites on Ni$_2$P could also serve as active sites and provide moderate binding to hydrogen atoms.$^{182}$ Further studies by Jaramillo$^{27}$ and Wang$^{165}$ indicated that several metal phosphide surfaces have hydrogen absorption energies that are close to thermo-neutral, but specific structural or mechanistic characteristics that could lead to better catalyst design have not been explicitly identified. Additionally, several experimental surface studies by Asakura and coworkers on nickel phosphide crystals, including low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and photoemission electron microscopy (PEEM), indicate the presence of reconstructed surface structures, implying that the bulk terminated structures of metal phosphides may not be stable.$^{183,184}$ However, these and similar experiments are carried out in environments that are very different from those used during actual HER operating conditions. In situ and ex situ characterization studies of transition metal phosphide materials under HER conditions could thus provide insights into the origin of the high catalytic activity, and ultimately the mechanism by which the HER occurs.
Figure K.22: Optimized structures for the (001) surface of Ni$_2$P, during different steps in hydrogen evolution reaction. Hydrogen atoms shown in white, nickel in blue, and phosphorus in purple. Reproduced with permission from ref. 45. Copyright 2005 American Chemical Society.

K.7 Integration with Light Absorbers

Integration of kinetically competent catalysts with light absorbers remains challenging because of the delicate interplay between light absorption, carrier collection, charge transfer at interfaces, and catalysis. For the HER, most studies involving the integration of catalysts with light-absorbing materials have focused on Pt and MoS$_2$, but recently have expanded to metal phosphide systems. In this section we discuss key metrics, experimental conditions, specific challenges, and recent highlights involving the coupling of metal phosphide electrocatalysts to photocathodes.

Background, Considerations, and Metrics

Solar-powered hydrogen production depends critically on the judicious choice of materials to maximize the overall system solar-to-hydrogen efficiency, $\eta_{\text{STH}}$. This quantity represents the ratio of useful power out (H$_2$ and O$_2$) to the total power of sunlight illuminating the system. A single light absorber can potentially reach a maximum efficiency of 11% while a stacked configuration consisting of two light absorbers may yield in excess of 22% (Figure K.23). As such, on the path toward economic viability, considerable efforts have been invested in achieving high efficiencies by developing photoelectrosynthetic cells driven by tandem photoabsorbers, with the highest achieved $\eta_{\text{STH}}$ of 18% reported by Licht and coworkers in 2000 using Pt black and RuO$_2$ as electrocatalysts for the hydrogen- and oxygen-evolution reactions, respectively. While $\eta_{\text{STH}}$ remains the key figure of merit for an entire...
cell, optimization occurs by understanding the behavior of the individual components comprising the whole system. An important metric for a single component is the ideal regenerative cell efficiency, $\eta_{IRC}$, which represents the ratio of the total electrical power output relative to the input solar power for each half reaction.$^{187}$ This differs from $\eta_{STH}$ because only electrical power is generated while measuring instead of a net chemical reaction only driven by solar energy for $\eta_{STH}$. Ideally, the photoelectrode performance should be determined without a coupled catalyst, with an electrochemically reversible one-electron redox couple such as methyl viologen (MV$^{2+/+}$), to establish the maximum performance obtainable from the absorber. This measurement aids in distinguishing issues intrinsic to the semiconductor from those due to the coupling of a catalyst with the electrode surface.

![Figure K.23](image.png)

Figure K.23: Solar-to-hydrogen efficiency for (A) single and (B) double light-absorber water splitting systems. Adapted with permission from ref.$^{185}$. Copyright 2013 Royal Society of Chemistry.

Fundamental electrode characteristics can be determined using three-electrode measurements to probe the current density as a function of applied potential on each photoelectrode. Additionally, experiments should not be limited by mass trans-
port (i.e. should be performed with rapid stirring of the solution), uncompensated resistance overpotentials (by correcting for the $iR$ drop whenever possible), cell geometry, the nature of the counter electrode (by avoiding precious metals which could contaminate the cell) or the reference electrode (by using a well-defined Nernstian potential with a known pH and maintaining 1 atm of H$_2$), or the nature of the illumination source (by using an artificial light that matches well with the solar spectrum). For example, for metal working electrodes, the solution resistance can be electronically compensated using a current-interrupt method. In contrast, for a photoelectrode the uncompensated resistance of the setup should be determined with a glassy carbon electrode in place of the semiconductor. Instead of electronic compensation, a Luggin capillary reference electrode can be used to minimize solution resistance for either metal or semiconducting electrodes. Pt contamination is a common pitfall in the evaluation of HER catalysts, because even sub-monolayer deposits of Pt can result in high HER activities and therefore produce apparent enhancements in activity and/or stability.\textsuperscript{188,189} When possible, it is best to avoid the use of Pt counter electrodes, by using high-purity carbon rods or other Pt-free electrodes instead. The catalyst and synthesis preparation should additionally be performed with precautions taken to minimize the possibility of noble metal contamination, e.g. all glassware should be carefully cleaned using aqua regia. The possibility of trace surface contamination underscores the importance of utilizing XPS to check for trace metal impurities. Together the open-circuit voltage ($V_{oc}$), short-circuit photocurrent density ($J_{sc}$), and fill factor (ff) form the basis set of metrics for evaluating the characteristics of a given photoelectrode. The open-circuit potential is the potential measured at zero current with a high-quality multimeter. The magnitude of the photovoltage is governed by the band gap of the material, practically reaching approximately two-thirds of the band gap in well-engineered systems. Photovoltages are lower in practice due to recombination.

In contrast to the short-circuit current density, which is the current measured with a high-resistivity multimeter at zero voltage and generally depends linearly on the photon flux reaching the semiconductor, the open-circuit voltage depends logarithmically on the illumination intensity. The actual photocurrent depends on the rate at which the current approaches the limiting photocurrent, with the potential dependence of the current called the fill factor, reflecting the “squareness” of the $J$–$V$ characteristic of the photoelectrode. Hence $J$–$V$ measurements obtained with a potentiostat yield information about the light absorption and photocarrier collection. The Faradaic yield for H$_2$ production should also be determined. The ultimate test
is to measure all of these parameters after prolonged operation, which ultimately must be stable on the order of 10 years for a commercially viable electrode with $\eta_{\text{STH}} > 10\%$, but more tractably on the bench by measuring $\eta_{\text{IRC}}$ after accelerated degradation with an appropriate benchmarking protocol.$^{190}$

**Structuring of Photoelectrodes**

![Figure K.24](image-url)  

Figure K.24: (A) SEM image of CoP nanoparticles on n$^+$p-Si microwire (MW) arrays. (B) Effect of catalyst loading on the current density vs potential behavior of n$^+$p-Si planar photocathodes in contact with H$_2$(g)-saturated 0.50 M H$_2$SO$_4$(aq) and under 100 mW/cm$^2$ of AM1.5G simulated solar illumination. Adapted with permission from ref.$^{191}$. Copyright 2015 American Chemical Society.

One guiding principle to produce high $\eta_{\text{IRC}}$ for a photocathode relies on maximizing simultaneously the photovoltage and short-circuit current density, while accommodating thick catalyst overlayers. In a semiconducting device, both the voltage and current intimately depend on the generation rate of electron-hole pairs. This rate, in turn, depends on the flux of photons with energies greater than the bandgap. Illumination can occur on either the backside or front side of a solar cell, so the absorbance and reflectivity of a catalyst are important properties. For frontside exposure to the sun, it is critical for the catalyst film to have low light absorption, but for backside illumination, light absorption by the catalyst is not crucial.$^{192}$ Micro- and nano-structured photoelectrodes may offer an alternative approach for decoupling light absorption of a catalyst film from the light absorption necessary to produce photogenerated carriers within the semiconductor. High-aspect-ratio microwire or nanowire devices, for example, can utilize catalysts with lower TOFs by enabling higher mass loadings of the catalytic materials without compromising necessary light absorption by the semiconductor. For example, when CoP nanoparticle HER catalysts were coupled with n$^+$p-Si microwires, high catalyst mass loadings were easily accommodated on the microwires (Figure K.24). The resulting performance (of 2\%) was limited by parasitic resistance, presumably due to poor contact,$^{191}$ rather than by light absorption, as would have occurred with a planar geometry. Likewise,
Jin and coworkers used a structured photoelectrode with a catalytically active metal phosphide film that had intimate contact between the catalyst and the light absorber. Integration of CoPS with micropyramid n⁺-p silicon substrates was achieved first by electron-beam deposition of cobalt, followed by heating in a furnace in the presence of 1:1 sulphur: phosphorous powder. Using this approach, $\eta_{IRC}$ was nearly 5% (Figure K.25).\textsuperscript{181}

Figure K.25: (A) SEM images of micropyramid-structured silicon photocathodes coated with 10 nm CoPS showing top and cross-section views. (B) $J$–$V$ curves in 0.5 M H$_2$SO$_4$ and under one sun illumination of microstructured n⁺-p-Si electrodes coated with 3, 5, 7.5, 10, and 15 nm of CoPS and 5 nm of Pt. A planar CoPS/p-Si electrode is shown for comparison. Adapted with permission from ref.\textsuperscript{181}. Copyright 2015 Macmillan Publishers Limited.

**Maintaining Charge Separation**

Various strategies have been developed for enhancing the separation of charge carriers, including judicious selection of materials with optimal properties and careful
engineering of the junction between the catalyst and light absorber. Considering the coupling of metal phosphide HER catalysts to light-absorbing semiconductors, a large barrier height and a correspondingly high photovoltage – in an ideal Schottky contact – could be obtainable with a low work function catalyst contacting the p-type semiconductor. The work functions of metal phosphide HER catalysts have not yet been determined. However, Liu and coworkers reported that a heterostructure of CoSe and p-type Si exhibited $\eta_{IRC}$ of 0.6 \%.\textsuperscript{193} Zhang and coworkers anchored Ni$_{12}$P$_5$ nanoparticles onto p-type silicon nanowires and illuminated for 2.8 h with $\approx 3$ \%.\textsuperscript{112} Liu observed an initial $\eta_{IRC}$ of 2\% upon coupling CoP nanoparticles with p-type silicon nanowire-array photocathodes.\textsuperscript{194} This system was fabricated by first electrodepositing Co and then using phosphidation at 500 °C to produce crystalline CoP particles. Significant enhancement of catalytic activity (compared with a bare surface) was observed over the course of an hour. However, a loss in activity occurred shortly thereafter, and this decline in performance was attributed to passivation by silicon oxide. Zang obtained $\eta_{IRC} \approx 3\%$ without using a p-n junction by dipping p-type silicon nanowires into a solution of iron nitrate and then heating in the presence of NaH$_2$PO$_2$, to yield FeP. The photoelectrode remained active for over 1 h of operation.\textsuperscript{195}

Another approach for enhancing the separation of charge carriers relies on forming a metallurgical junction created by diffusing dopants that create an appropriate built-in electric field necessary for photocarrier collection. The built-in potential in this strategy does not depend on the work function of the catalyst; however, the formation of well-behaved buried junctions remains an unsolved challenge for many semiconductor systems. Both approaches potentially face challenges associated with colloidal synthesized nanoparticle catalysts capped by organic ligands, which require high temperatures to expose the catalytically active sites. Interstitial defects introduced by diffusion of a foreign material into the bulk of the semiconductor can lead to trap-assisted recombination, thereby lowering the performance of the photoelectrode. Low-temperature processing is therefore desirable for integrating materials with many photocathodes. For example, preliminarily results suggest that extension of an electrodeposition procedure\textsuperscript{81} for growing amorphous CoP onto planar p-WSe$_2$ or n$^+$ p-Si appears tenable.

**Charge Transfer Between Catalyst and Light Absorber**

The charge transfer of electrons from the absorber to the catalyst depends on the electrical and mechanical contact. Poor contact could result in parasitic series re-
sistances, thereby detrimentally affecting the device performance. Charge transfer within the bulk of the catalyst could also result in a parasitic resistance. As such, a thin layer or low-resistivity catalyst film is desirable. The resistivities of metal phosphides have not yet been reported. Ensuring intimate electrical and mechanical contact between nanoparticles and substrates remains an open challenge. Appropriate binding agents could result in improved adhesion and electron transport. An alternative strategy is to deposit the materials directly by vacuum deposition, potentially resulting in thin, conformal, highly active electrodes. Jaramillo and coworkers demonstrated that Co metal deposited by electron-beam evaporation onto n$^+$p-Si, followed by phosphidation, yielded highly active CoP on planar silicon (Figure K.26).\textsuperscript{196} The TOF values were nearly ten times those reported previously, allowing for thinner films and suggesting a more intrinsically active material than the nanoparticles, and/or better interfacial contact between the substrate and catalyst film. The resulting photocathode exhibited $\eta_{IRC} = 5\%$ while showing stability for 24 h of operation.

![Figure K.26: Linear sweep voltammograms of a CoP thin film on n$^+$p-Si photocathodes under one sun illumination before and after 24 hours of operation in 0.5 M H$_2$SO$_4$. Adapted with permission from ref.\textsuperscript{196}. Copyright 2012 Macmillan Publishers Limited.](image)

**Particle-Based Absorbers**

One technoeconomic analysis suggests that H$_2$ generation systems using multi-junction semiconductors have an undesirably high calculated H$_2$ cost ($6 per kg of H$_2$), which is driven primarily by the expected cost of cell packaging. In contrast, water splitting using colloidal systems that function in inexpensive plastic bags could potentially result in a system that has a very low cost of H$_2$ ($1.49 per kg of H$_2$).\textsuperscript{197} Thus, a particle-bed PEC device in bags is an attractive option for an economically
scalable hydrogen generation platform, provided that an intrinsically safe system can be designed such that \( \text{H}_2 \) and \( \text{O}_2 \) are not evolved in the same bag at the same time. Along these lines, FeP nanoparticles anchored onto TiO\(_2\) under UV illumination produced \( \text{H}_2 \) for 16 h at nearly the same rate as Pt.\(^{152}\) Fu and coworkers coupled CoP, Ni\(_2\)P, and Cu\(_3\)P to CdS particles and produced \( \text{H}_2 \) for over 10 h, obtaining a maximum \( \text{H}_2 \) production rate of 251 \( \mu \text{mol h}^{-1} \) with CoP.\(^{198}\)

**Outlook**

Metal phosphides demonstrate promising photocatalytic activity when coupled to light absorbers. Future efforts should also include longer stability windows, which will be important for evaluating commercially viable photocathode systems. The design of an efficient water-splitting system will be aided by reporting the intrinsic resistivities of these catalyst films, and including absorption and reflection spectra of the films. An expanded suite of deposition techniques that ensures intimate contact between the semiconductor and catalyst film, in addition to more complete characterization, will be useful for integrating these materials into devices.

A challenge facing the construction of a functional, inexpensive water-splitting device operating in acidic regimes is the lack of Earth-abundant oxygen-evolving catalysts. As the search continues for compatible families of anode materials, another approach relies on the incorporation of a bipolar membrane situated in between an acidic catholyte and an alkaline anolyte. The membrane simultaneously maintains a steady-state pH difference between each compartment and prevents gaseous product crossover, thereby allowing the use of an optimized acid-compatible photocathode and base-compatible photoanode. Sun demonstrated solar-driven water-splitting with an \( \eta_{\text{STH}} \) of 10 % for > 100 h using a GaAs/InGaP tandem stack immersed in an anolyte compartment (pH 9.3) driving the OER with a NiO\(_x\) coating and a back contact wired to a Ti mesh coated with CoP carrying out the HER in the catholyte compartment.\(^{199}\) In addition to the overpotential losses from catalysis, the bipolar membrane operating at a current density of 10 mA/cm\(^2\) results in an additional 400 mV to 500 mV resistive loss. Luo similarly reported a device using a perovskite light harvester located outside of the solutions wired to a NiFeO\(_x\) electrode in the anolyte (pH 13.9) and a CoP on Ti foil electrode in the catholyte (pH 0.4) giving \( \eta_{\text{STH}} \) of 12 % for nearly 100 h.\(^{200}\) Future work may result in completely wireless devices.
K.8 Conclusions
Transition metal phosphides have emerged as a robust family of Earth-abundant catalysts for the HER. The high catalytic activity and stability displayed by these materials, including in strongly acidic aqueous electrolytes, has motivated extensive efforts in synthesis, characterization, catalytic testing, and device integration. Currently, several phosphides of Ni, Co, Fe, Mo, and W are considered to be highly promising HER catalysts, and anion substitution appears to be a particularly useful approach for further improving their catalytic performance. Despite these discoveries and ongoing improvements as more systems are being interrogated, mechanistic studies remain scarce. In situ studies, coupled with computational investigations, will be especially useful for furthering our understanding of how the HER proceeds on transition metal phosphide surfaces under operational conditions. Such studies will also help to reveal design guidelines for producing catalytic materials that expose the highest possible density of surface active sites. Finally, the integration of metal phosphides with light absorbers is still at an early stage. Nonetheless, the development of methods capable of producing favorable interfaces between catalysts and light absorbers, as well as novel photocathode architectures, may be key steps towards realizing integrated water-splitting systems comprised entirely of inexpensive and Earth-abundant materials.

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K.10 References
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