

Chapter 1

INTRODUCTION

1.1. Storing Energy from the Sun

An international effort is needed to stabilize the increase in global mean temperatures caused by human-derived carbon dioxide (CO₂) emissions.¹ In order to reach the target of net-zero emissions by mid-century proposed by the IPCC, massive emissions reductions are required. Such reductions rest crucially society's ability to eliminate emissions from the electricity sector.²⁻³ First and foremost we need alternatives to obtaining energy from the combustion of underground carbon to CO₂. Sunlight is a nearly inexhaustible energy resource that emits no CO₂ and is available across the Earth's surface and can therefore address this need.⁴ Photovoltaic devices allow humans to harness energy from the sun as electrical power, but early applications were restricted to photodetectors and space power due to low power conversion efficiencies and high material costs.⁵ Substantial improvements in efficiency, coupled with falling materials costs from improved manufacturing of high-purity crystalline silicon, have led to a > 15-fold reduction in the cost of power purchase agreements for installed photovoltaics.⁶ Today, solar power is often the cheapest form of electricity generation, with 635 GW of photovoltaic systems have been installed worldwide and >95% of present-day production driven by modules prepared from inexpensive, crystalline-Si light absorbers.⁷⁻⁸

Existing electricity grids balance seasonal shifts in the supply and demand of electricity via the ramping up and down of fuel-burning power plants. Increasing penetration of intermittent energy resources, such as solar and wind, into large, net-zero emission electricity grids will require new technologies for storing electricity.⁹⁻¹⁰ Extended

periods (hundreds of days) of 100% renewable electricity generation, demonstrated in countries such as Costa Rica, have been limited to regions that obtain a large fraction of their electricity from hydropower.¹¹ Prodigious expansions to the capacity and deployment of hydropower have been invoked in plans for future 100% renewable grids for the United States, but such expansions may exceed the physical capacity of the country's rivers and reservoirs.¹² Reliable zero-carbon energy systems in regions without preexisting hydroelectric resources will require methods for storing renewable energy. Mechanical methods for energy storage, such as pumped hydro and compressed air storage, could be inexpensive but afford lower energy densities than (electro)chemical energy storage in fuels and batteries.⁹

The capital cost of building electricity storage can be determined by the cost of energy or the cost of power. Power determines what we can do with electricity (e.g. turn on a cell phone or drive a car), whereas energy determines how long your electricity will last. Present-day demand for electricity storage emphasizes the cost of power and round-trip efficiency, allowing lightweight lithium-ion cells to power our phones and electric vehicles. Reductions in the cost of energy stored, however, are needed to smooth the seasonal variations in the availability of wind and solar power.^{10, 13} The average price of lithium-ion batteries has fallen rapidly, along with improving lifetimes, but the cost per kilowatt-hour (energy) would need to fall by an additional two-orders of magnitude in order to address a need for energy storage lasting more than 10 hours.¹³ A closed-process that converted electricity into fuels for long term storage would be better poised to replace existing natural gas power processes.

Nature provides inspiration for our societal need for globally-available, inexpensive energy storage. All plants use water and sunlight to capture and convert CO₂ into molecules that store energy, in a process known as photosynthesis. Using energy from the sun to form fuels has been coined Artificial Photosynthesis. Pure water is an abundant and non-toxic natural resource that can serve as the substrate for a fuel-forming reaction in such a system. The water-splitting reaction leads to the formation of oxygen and hydrogen, a fuel that stores the energy required for the reaction within its chemical bonds.¹⁴ This energy can be liberated using hydrogen fuel cells or via combustion with oxygen to produce pure water.¹⁵ In comparison to an electrolyzer powered by a photovoltaic panel, devices for artificial photosynthesis have the potential to lead to lower systems costs if they reduce the total number of components required for the balance of systems without substantive reductions in device efficiency or stability.¹⁶ Integrated devices that simultaneously capture solar energy and use it to drive electrochemical reactions will be referred to as solar fuels devices throughout this manuscript.¹⁷

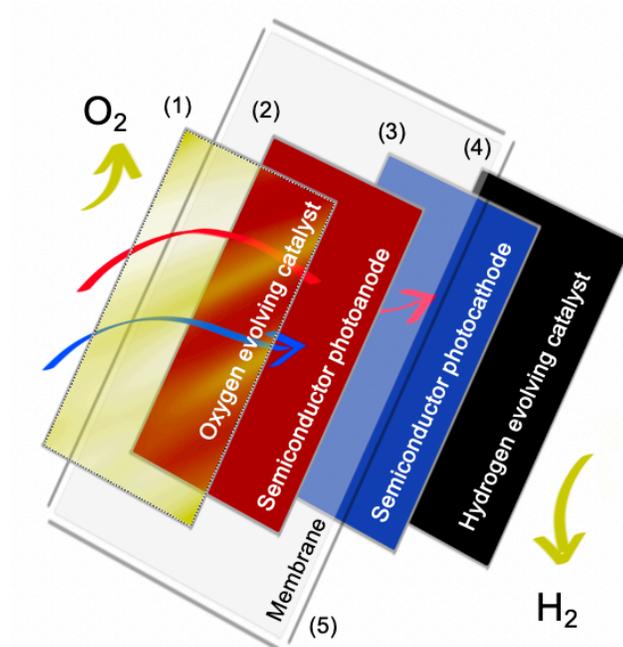
1.2 Materials for Producing Solar Fuels

Over the last 10 years, a global research effort been made towards bringing solar fuels devices from research-scale demonstrations to a commercially viable technology.¹⁸ To be considered for implementation within an energy system, devices must be safe, stable, and scalable.¹⁹ A general sketch of the components required for a practical solar fuels device meeting these requirements is provided as **Scheme 1.1**. Two catalyst layers serve to lower the energetic barriers for charge transfer when converting protons and/or hydroxide ions to oxygen and hydrogen. Two semiconductors, a photoanode and a photocathode, produce a voltage sufficient to drive the water-splitting reaction when combined in series.

Strongly acidic (pH \sim 0) or strongly basic (pH \sim 14) electrolytes are required during water-splitting to prevent the accumulation of concentration gradients within the cell, which impose stringent stability requirements on catalysts and light absorbers.²⁰ Membranes are necessary to separate explosive fuels from coevolved oxygen gas. Early reports of unassisted solar-driven water splitting under concentrated sunlight demonstrated stable operation for 20 hours.²¹ A more recent report of fully-integrated solar fuels device using Si light absorbers and rare-earth metal catalysts demonstrated 33 days of intermittent day/night cycling in 1 M H₂SO₄(aq).²² A two-order-of-magnitude increase in stability is needed in order for device lifetimes to be comparable to commercial photovoltaic modules.

Materials discovery efforts have yielded a number of light-absorbers and catalysts capable of sustained operation in strongly acidic and/or strongly basic electrolytes,²³⁻²⁴ facilitated by the development of transparent conducting oxides for use as protection layers for semiconductors that form passivating oxides.²⁵ Earth-abundant, acid-stable catalysts for the hydrogen-evolution reaction could serve as alternatives to rare earth metals such as Pt,^{24, 26} but significantly greater mass loadings are required for these catalysts to operate at acceptable overpotentials. Much of this dissertation involves cobalt phosphide, CoP, which is among the fastest catalysts that could serve as a Pt replacement. Careful investigations of metal dissolution rates under potential control suggest earth-abundant catalysts including CoP, are likely to corrode during dark, open-circuit conditions.²⁷ Increased catalyst loadings and/or new strategies for protecting catalysts against dissolution must be demonstrated in order for these materials to be considered as alternatives to thermodynamically stable Pt.²⁸ Si has been used as a model light-absorbing semiconductor throughout. Si is stable in acidic solutions and can be protected from dissolution in basic

solutions via thin layers of metal oxides.²⁵ Si can be readily cleaned and processed to form photoactive, charge-separating junctions, making it well suited for the study of electrocatalyst integration. Silicon microwires are a potentially scalable alternative to crystalline Si wafers and can be grown directly from SiCl_4 gas using copper catalysts as “seeds”.²⁹

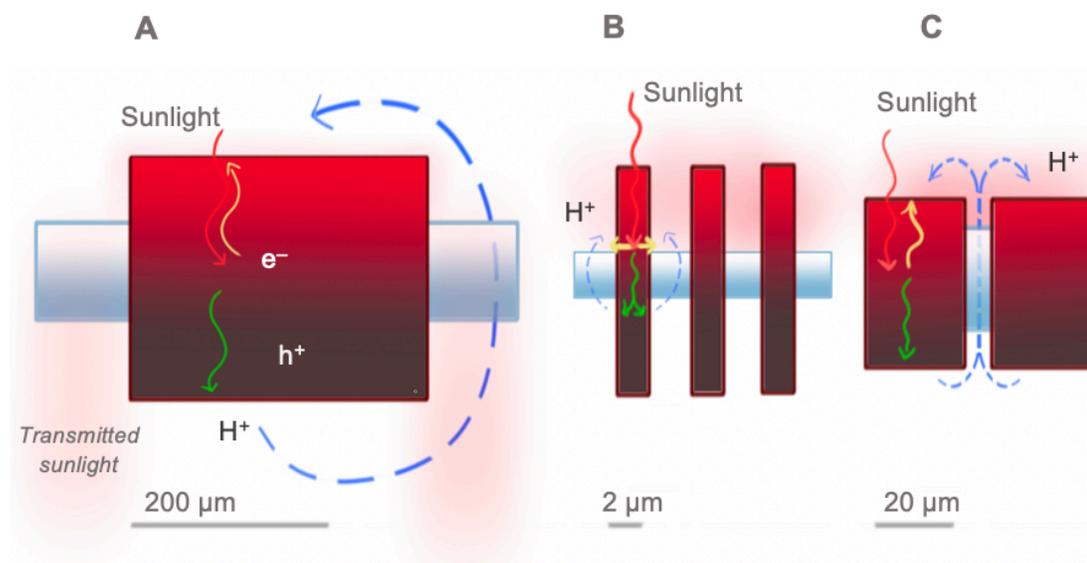


Scheme 1.1: Layered representation of the components required for a solar fuels device. In this orientation, light passes through the (1) oxygen evolution catalyst, with the blue half of the solar spectrum absorbed by a (2) semiconducting photoanode and the remaining, red photons absorbed by a (3) semiconducting photocathode. (4) A hydrogen-evolving catalyst on the bottom side of the device produces fuel for energy storage. (5) A membrane allows ions to transfer from reactions occurring at (1) and (4) while keeping the combustible products separate.

1.3 Integration of Semiconductors and Electrocatalysts

1.3.1 Thesis statement

Designing a solar fuels device that is safe, stable, and scalable requires engineers to navigate trade-offs in performance of individual components. Macroscale integration of components often leads to devices that perform equal to or worse than the sum of their parts, whereas micro- and nanoscale integration strategies can lead to complementary effects. Consider the example of a water-splitting solar fuels device in which a membrane must be incorporated to allow the transfer of ions between the anode and cathode while keeping combustible hydrogen and oxygen gases separate (**Scheme 1.2**). A macroscopic light absorber surrounded by an ion conducting membrane will absorb less light than a continuous solar panel while increasing the ohmic drop in comparison to catalysts integrated adjacent to a membrane (**Scheme 1.2A**). However, *micro- or nanoscale* light absorbing elements embedded within a polymer membrane could exhibit an absorptivity equivalent to a continuous panel while simultaneously reducing the distances required for charge carrier collection and without increasing the distance required for ion transfer (**Scheme 1.2B**).³⁰⁻³¹ Comparable results might be possible at microscale, ion-conducting channels within a monolithic solar fuels device, when illuminated at non-normal incidence or using light-scattering elements within the channel (**Scheme 1.2C**).



Scheme 1.2: Representative solar fuels device designs. **(A)** Macroscale integration of a light absorber (red) surrounded by an ion-conducting membrane (blue). The optical penetration depth and the minority carrier collection length are mutually similar. The maximum distance traveled by protons (H^+) via diffusion is set by the thickness and width of the absorber. The projected area of the light absorber is directly proportional to the quantity of light absorbed. **(B)** Microscale integration of light absorbers within an ion conducting membrane. The minority carrier collection length is much smaller than the optical penetration depth. The maximum distance traveled by ions is set by the length of the absorbing elements. The projected area of the light absorber is not necessarily proportional to the quantity of light absorbed. **(C)** Alternate microscale integration of a membrane within a light absorber.

In this dissertation stems I will address the knowledge gap associated with the design considerations discussed above: *How and why do three-dimensional structures of light-absorbing semiconductors and electrocatalysts allow solar fuels devices to avoid trade-offs during integration?* In particular, high-aspect ratio structures—where the ratio between two length scales defining a feature exceeds 10:1—were found to afford considerable opportunities for improving device performance. High-aspect ratio Si

microwire and microcone arrays allowed for increased loadings of electrocatalysts to be used without substantial absorption or reflection of incident sunlight. Nanostructured metal-phosphide catalyst layers decoupled optical losses from the fractional coverage of the light absorber surface. Downward-facing microwire arrays produced thin films of gas bubbles at high coverages, leading to efficient collection of gaseous products without substantial voltage losses due to catalyst obstruction and ohmic resistance. Planar and microwire-array photoanodes produced gas bubble films that led to minimal optical losses on the sunlight-facing side of a solar fuels device and generated sufficient convection for passive device operation without external convection.

1.3.2 Light-management at high-aspect ratio Si

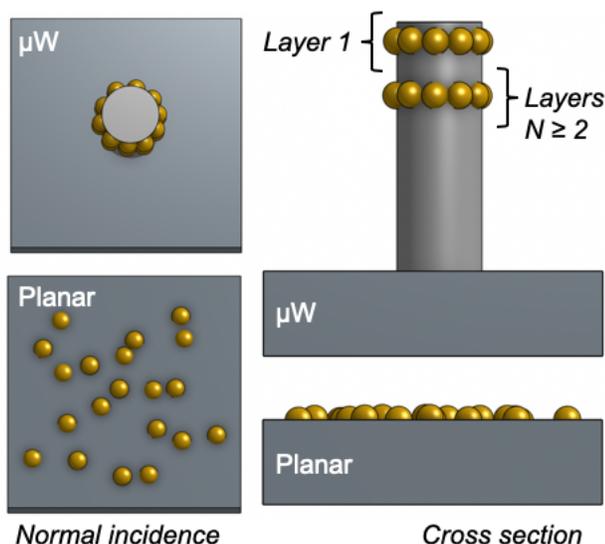
Fully integrated solar fuels devices require that either the oxygen-evolving catalyst and/or the fuel-forming catalyst be placed in the path of incident sunlight.¹⁹ Optical losses due to reflection and parasitic absorption occur when metallic electrocatalysts are placed on the light-facing side of a solar fuels device.^{14, 32} Increasing the density of the catalyst on the surface increases the efficiency of fuel formation by reducing the additional voltage required to drive charge transfer at the electrolyte interface.^{24, 32-33} Conversely, increasing the loading of catalyst on the surface also attenuates the light reaching the semiconductor. The optimal catalyst loading maximizes the charge transfer kinetics while reflecting and absorbing a minimum amount of photons.³⁴ Multi-electron reduction reactions generating products such as methane and ethylene require greater mass loadings of catalyst, which makes such optimization challenging at a planar semiconductor surface. Light management is less challenging for metal oxide catalysts and protection layers

prepared from wide-band gap semiconductors such as nickel-oxide, which exhibit minimal absorptivity towards photons in the visible range of the electromagnetic spectrum.³⁵⁻³⁶

Microstructured photoelectrodes have several advantages in integrated systems for solar fuel production relative to planar electrodes. High-aspect ratio microwires allow for collection of light along the long microwire axis and collection of photogenerated carriers along the narrow microwire radius, which could optimize carrier collection in impure, inexpensive semiconductors grown by scalable methods.³⁷⁻³⁸ Furthermore, the increased area of the semiconductor/electrolyte interface affords an opportunity to support high loadings of electrocatalysts without deleterious absorption of incident photons.³⁹ When the light absorber and electrocatalyst are both on the sunlight-facing surface, strategic placement of the catalyst out of the path has been shown to reduce optical losses due to parasitic light-absorption.⁴⁰

Chapter 2 reports the use of Si photocathodes for sunlight-driven hydrogen evolution using electrodeposited cobalt phosphide, CoP, as a catalyst. CoP is among the most active earth-abundant catalysts for the hydrogen evolution reaction in acid but strongly absorbs and reflects incident sunlight. Integration of a few nm of CoP on planar Si had previously been shown to contribute to a 30% reduction in the photocurrent relative to a polished Si surface.⁴¹ We prepared p-Si microwire-array photocathodes decorated with CoP through a low-temperature and rapid electrodeposition process that led to the selective placement of catalyst along the microwire sidewalls.⁴² At normal incidence, this integration strategy decoupled the projected area of the electrocatalyst from the electrochemically active surface area (**Scheme 1.3**); equivalent loadings, as measured by the charge passed

during electrodeposition, led to 22% reductions in the photocurrent at a p-Si microwire-array electrode whereas the photocurrent at a planar p-Si surface was reduced by 49%.



Scheme 1.3: Identical catalyst loadings on microstructured and planar semiconductors showing the different effects of light blocking at normal incidence. Relative to a planar surface, the shaded area produced by a single hemisphere located on a vertical microwire sidewall is reduced by approximately a factor of two (Layer 1) and additional layers of catalyst particles (Layers $N \geq 2$) do not contribute significantly to shaded areas on the semiconductor.

Chapter 3 extends the strategy of depositing electrocatalysts on vertical sidewalls to the (photo)electrochemical reduction of CO_2 to hydrocarbons. The charge transfer kinetics of CO_2 reduction to methane and ethylene at copper surfaces are many orders of magnitude slower than proton reduction to hydrogen at Pt. Light management at high surface area Cu films used for electrochemical CO_2 reduction has been a bottleneck for the preparation of photocathodes capable of generating hydrocarbon fuels. Photocathodes prepared from nanoparticulate Cu at polished p-Si surfaces exhibited absolute photocurrent

densities $> 20 \text{ mA cm}^{-2}$ but the onset of the production of hydrocarbons was shifted $+0.3 \text{ V}$ —less than the photovoltage provided by the Si. CuAg films on the backside of a Si light absorber—out of the path of incident sunlight—yielded absolute photocurrent densities $> 32 \text{ mA cm}^{-2}$. We deposited high mass loadings of Cu electrocatalyst onto p-Si microwire-arrays doped with a radial-junction n^+ emitter layers leading to efficient photocathodes for the production of CH_4 and C_2H_4 from CO_2 under simulated sunlight. Although the increased junction area at a radially doped n^+ p-Si microwire-array photocathode is expected to lead to a reduced photovoltage in comparison to a planar n^+ p-Si photocathode, a simplified device physics model showed that this reduced photovoltage could be fully offset by increased rates of electrocatalysis for reactions requiring the use of sluggish electrocatalysts.

Chapter 4 investigates the use of an alternate microstructuring strategy: Si microcone, μ -cone, arrays.⁴³ Optical simulation of Si μ W arrays had previously revealed that the planar, top surface of the cylindrical μ Ws contributed significantly to reflections of incident sunlight. Microcones prepared via deep reactive-ion etching with positive tapering exhibited tip radii $\sim 25 \text{ nm}$, and led to surfaces that exhibited 99.5% of the light-trapping limit for wavelengths of light 400–1100 nm. To preserve the optimal light-absorption properties of the Si μ -cone arrays while integrating highly reflective electrocatalysts, we used a templated deposition of Ti/Pt thin films that selectively placed catalyst at the tips of individual μ -cones.⁴⁴ Reflections at the Pt/electrolyte interface were directed towards the internal volume of the μ -cone array such that the otherwise highly reflective catalyst layer did not contribute to reductions in photocurrent relative to a bare μ -cone array. This strategy of leveraging guided reflections from the metal surface is

similar to that used for the preparation effectively transparent contacts (ETCs) for photovoltaics.⁴⁵

1.3.3 *Light-management at high-aspect ratio CoP*

Noble metal catalysts for the hydrogen-evolution reaction in acidic electrolytes lead to efficient devices based on p-type Si and InP photocathodes, because the films can be structured as small islands that are effectively transparent.⁴⁶ In acid, Pt catalyzes the hydrogen evolution reaction at rates that are Nernstian in character—the rate is controlled by mass-transport and not by charge transfer kinetics.⁴⁷ More recently, a transparent Rh film enabled the highest reported solar-to-hydrogen conversion efficiency at a photocathode under 1-Sun.⁴⁸ Integration of earth-abundant catalysts is made more challenging by the higher-mass loadings and decreased stability of such films in corrosive environments.²⁷ Semiconducting transition-metal selenides and transition-metal sulfides, which require absolute overpotentials of 150–183 mV to drive the HER at a current density (J) of -10 mA cm^{-2} , have been integrated with textured, antireflective silicon photocathodes as uniform, amorphous films, approximately 50 nm in thickness.⁴⁹ Such devices have exhibited high photocurrent densities ($|J| > 30 \text{ mA cm}^{-2}$) for 2 h in 0.50 M $\text{H}_2\text{SO}_4(\text{aq})$.⁵⁰⁻⁵² Substantially longer stabilities under reductive bias, and thus increased catalyst loadings or more stable catalyst materials, are required for a practical solar fuels device.

In Chapter 5, we extend the preparation of effectively transparent films, previously demonstrated at noble metals, to transition metal phosphides. Prior integration efforts focused on the three-dimensional structure of the light-absorbing semiconductor to assist in light management; this work showed that the structural control of the electrocatalyst could also allow the catalyst area and optical losses to be decoupled. Continuous films of

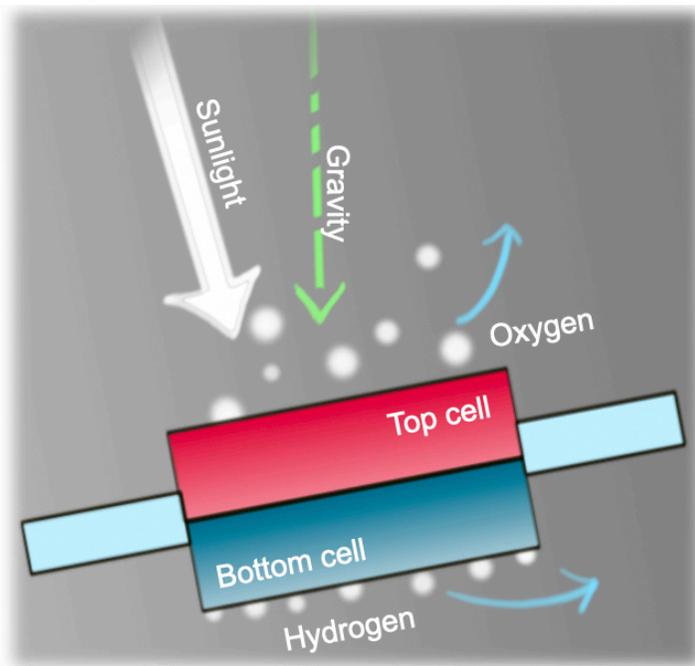
CoP were electrodeposited onto planar n⁺p-Si that had been pre-nucleated for deposition with a thin layer of Co on top of a Ti adhesion layer. Although deposition of this catalyst film led to a > 70% reduction in the photocurrent, operation of the device in 0.50 M H₂SO₄ led to a spontaneous reorganization of the films nanostructure that was accompanied by a > 250% *increase* in the photocurrent. Physical characterization of thin CoP films on polished Si surfaces before and after exposure to H₂SO₄ indicated that the changes to the optical properties of the film were accompanied by the formation of oriented cracks that extended from the substrate to the surface of the film. The optical properties of the film were measured and modeled using spectroscopic ellipsometry, which revealed that the increased transmissivity was due to the film behaving as an effective medium, wherein electromagnetic radiation was forced into the narrow cracks such that the reflection of light was no longer proportional to the fraction of the surface covered by catalyst. Such a strategy for light management is significant in that it does not depend strongly on the optical properties of the metal, and thus can be extended to a variety of other earth abundant catalysts, and could be complementary with other strategies for light-management such as selective placement onto μ W sidewalls.^{42, 53-54} or patterning as catalyst islands.^{32, 55}

1.3.4 Control of H₂ and O₂ bubbles at electrode surfaces

A common feature of water-splitting solar fuels systems is the production of bubbles of H₂ or O₂ on both the light, upward-facing and the dark, downwards-facing sides of the device, once the activity of H₂(aq) or O₂(aq) is sufficient to surpass the free-energy barrier to nucleation.⁴⁻⁶ Bubbles can deleteriously refract light away from the light absorber;⁷ preclude effective contact between the liquid electrolyte and the electrocatalyst;⁸⁻⁹ and affect mass transport of species in the boundary layer as well as in

the internal volume of porous, structured electrodes. In small-scale laboratory demonstration systems, effects of bubbles are often minimized by vigorously stirring the solution and/or by testing the electrodes in a side-facing or upwards-facing geometry.¹ In most device configurations that are contemplated for use in the field, active stirring of the electrolyte over large areas is not practical.³ Management of gas coverage is essential at industrial-scale electrodes, such as downward-facing, CO₂(g)-evolving anodes required for aluminum manufacturing, in which the thickness of bubble fronts moving across the surface can exceed 1 cm.¹⁰

We were motivated to understand the effects of bubbles on solar fuels devices, particularly on devices of a practical size and orientation. Our research efforts considered gas evolution at the illuminated, upward-facing top cell and at the dark, downward-facing bottom cell (**Scheme 1.4**). Our assumption was that most designs would choose to evolve oxygen on the sunlight facing side of the device, such that gas could be vented out into the atmosphere, and hydrogen on the bottom side of the device where it would be collected and stored. Ideally, a solar fuels device could operate passively, with bubbles rising via natural buoyancy, obviating the need for external pumps to stir the electrolyte.



Scheme 1.4: Fully integrated, tandem solar fuels device where the absorber is oriented towards the sun. Such orientation leads to misalignment with the gravitational vector at latitudes off the equator. In the cell represented here, oxygen is evolved from the sunlight facing photoanode whereas hydrogen is evolved from the downward facing photocathode.

In Chapter 6, we considered the effects of hydrogen gas evolution on cathodes oriented against gravity. This allowed us to focus on the electrochemical effects of gas evolution without light as a confounding variable. High-speed videos recorded during testing characterized how the coverage and thickness of the gas layer at a downward-facing electrode impacted the electrochemical performance. The key finding was that capillary forces within Si μ W arrays provided a mechanism for gas bubble removal from a downward-facing electrode surface. Whereas planar surfaces accumulated large, cm-scale gas bubbles that contributed to a significant increase in ohmic resistance, microwire arrays rapidly released small bubbles. Sparsely packed microwire arrays exhibited high gas coverages that led to minimal increases in the ohmic drop and kinetic overpotential but

reduced the concentration overpotential and increased mass-transport in comparison to a bubble-free electrolyte.

The effects of gas bubble evolution on an upward-facing top cell are discussed in Chapter 7. Although crystalline Si would likely serve as the bottom-cell in an integrated device, TiO₂-protected Si photoanodes enabled careful tuning of the electrode microstructure such that its effect on gas bubbles emanating from an upward facing photoanode could be characterized. Very low gas coverages were observed at oxygen-evolving top cells, in stark contrast to coverages previously observed at hydrogen-evolving bottom cells. Ray tracing simulations predicted that higher gas coverages could be tolerated without leading to significant increases in the fraction of light lost, consistent with measurements at photoelectrodes evolving hydrogen and oxygen. Calculated mass-transport velocities indicated that the microconvection generated by the departure of gas bubbles from the surface was sufficient to eliminate the need for external pumping and stirring in solar fuels devices. Microwire surfaces led to smaller and more numerous gas bubbles in comparison to planar surfaces, which could improve the uniformity of bubble-generated microconvection.

1.3.5 Summary and Outlook

In the following chapters, I will share a number of strategies for controlling the three-dimensional structure of semiconductors, electrocatalysts, and the film of gas bubbles evolved on the top and bottom of a solar fuels device. Three-dimensional structures that incorporate high-aspect ratio features can lead to unexpected effects, such as transparent metal films (Chapter 5). New challenges arise when designing microstructured architectures for solar fuels devices, e.g. increased charge-separating junction areas can

lead to unacceptable reductions in photovoltage and may require improved passivation to be viable (Chapter 4). Kinetically-limited, multielectron reductions, such as the reduction of CO₂ to methane and ethylene, require increased mass-loadings of electrocatalysts and thus offset reductions in photovoltage with a greater reduction in overpotential (Chapter 3). Microstructured surfaces can force bubbles away from the surface, even when oriented against gravity, leading to sustained operation in the absence of external convection (Chapters 6 and 7). Although previous advances to the efficiency of solar fuels devices have involved planar, macroscale integration strategies, major breakthroughs in the cost and stability of such systems are required for Artificial Photosynthesis to be deployed. Such breakthroughs may require rethinking the rules of device integration via microstructural design, thus enabling a transition to a cleaner and more sustainable future.