CONTROLLING INTERFACIAL TRANSFER PROCESSES FOR IMPROVED PHOTOELECTROCHEMICAL PERFORMANCE

A Dissertation

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by

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Abstract

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As the Earth's population continues to grow exponentially and become more technologically advanced, fossil fuel prices rise concurrently, a reflection of the diminishing resources available at a reasonable price and with reasonable effort. A significant part of the solution to this energy problem is to utilize renewable energy resources—wind, hydroelectric, geothermal, and solar, among others. The amount of solar energy reaching the surface of the Earth each day is orders of magnitude more than the energy needs of all the people of the world combined. An important question, however, immediately arises: how can excess energy be stored to power homes when the sun goes down? Hydrogen is an excellent candidate as a storage medium. It can be used in current internal combustion engines, and it can be stored in pressurized tanks or metal hydrides for ease of access and transportation. Currently, the vast majority (approximately 95%) of hydrogen is produced at a net energy loss from steam-methane reforming. To be useful as an energy carrier, hydrogen must be produced using a "free" energy input like sunlight. Following Fujishima and Honda's demonstration of photolysis
of water on TiO$_2$ using simulated sunlight in 1972, the field of water photolysis and hydrogen generation has grown quickly.

In this dissertation, improvement of photoelectrochemical performance by intercalation of Li$^+$ to passivate Ti$^{4+}$ trap states have been demonstrated. This passivation increases both the photovoltage and photocurrent generated by increasing the rate of collection of photogenerated electrons. Pulsed laser deposition was used to synthesize metal oxide heterostructures while retaining an excellent electron conducting substrate has also been demonstrated, and this SrTiO$_3$-TiO$_2$ heterostructure was observed to enhance photoelectrochemical performance due to an increase in charge separation. IrO$_2$, a widely studied water oxidation catalyst that has the lowest overpotential for the oxygen evolution reaction, was shown to catalyze an undesirable side reaction on TiO$_2$. The scavenging of trapped holes by reduced oxygen radicals was enabled only in the presence of IrO$_2$, and this scavenging occurred on a timescale approximately 1000 times faster than that of water oxidation, which means that it represents a serious obstacle to developing a water photolysis system that does not rely on external power input. Continuous hydrogen generation in a reverse fuel cell has been demonstrated using CdS on TiO$_2$, and the quantum efficiency of the reaction has been determined using chemical actinometry, demonstrating that calculation of efficiency based on current-voltage characteristics is insufficient. Based on the research presented in this dissertation, future directions to pursue are also discussed.
Dedicated to my beautiful wife Maggie and my wonderful family.
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CHAPTER 1:
INTRODUCTION

1.1 Global Energy Demands and The Roles of Solar Energy and Hydrogen

The need to develop renewable energy resources has come to the forefront of discussion as increased demand from developing countries like China and India, coupled with plateauing and decreasing supply, have led to huge leaps in fossil fuel prices. Power demand projections have the world needing nearly 35 TW by the year 2050. The 2011 US International Energy Outlook prepared by the Energy Information Administration estimates a worldwide power demand of approximately 26 TW by 2035, a more recent estimation that includes the reduction in power consumption caused by the ongoing global recession. Even with this slowdown, China and India are expected to contribute significantly in the coming years to the increase in power demand as the two countries expand the use of advanced technology in their growing industrial and residential sectors. Figure 1.1 shows how energy demands are projected to increase until the year 2035 and how much China, the US, and India will contribute individually.

As of 2011, 83.7% of the world energy consumption was from fossil fuel based sources (coal, natural gas, liquid petroleum) while just 10.9% comes from renewable sources. Wind power accounted for just 0.03 TW of power production in the US in 2010, and hydroelectric, a resource considered to be largely tapped, accounted for 0.08 TW of
Figure 1.1: Projected energy demand growth for the entire world (left) and for China, the US, and India (right) through 2035.¹

power in 2010. Coal is abundant in the United States, but it is non-renewable, and the pollution associated with the burning of coal, even with "clean coal" technology, is a steep price to pay. Unfortunately, energy produced from consumption of coal is still approximately twice as much as that from all renewables combined in the US as of 2010, and this trend looks to continue in the near future. Nuclear power is relatively non-polluting, but it is also non-renewable, and the rate at which new plants would need to be built to keep up with the rising power demand of the world is not feasible. Solar/PV energy production accounted for just 0.003 TW of all US power produced in 2010, although that number has been rising and will continue to do so. In fact, energy generation from renewables is projected to increase at a rate of about 2.8% per year. Increases in power efficiencies and decreases in cost realized from utilizing cheaper materials and processing techniques for solar panels should help the rate increase more rapidly.
Solar cell technology has gone through several iterations. The first generation of solar cells were composed of single crystal silicon (see Figure 1.2). Although they are still the most efficient commercially available solar cells, the manufacturing process required is labor-, cost-, and energy-intensive. They are also relatively limited in where they can be used due to the rigidity and fragile nature of the silicon single crystals. Single crystal silicon solar panels were first developed at Bell Labs in 1954 by Daryl Chapin, Calvin Fuller, and Gerald Pearson after nearly two years of experimentation\textsuperscript{5}. Chapin, Fuller, and Pearson achieved high efficiency by forming a near-surface p-n junction with boron and arsenic or phosphorus dopants (for p- and n-doping, respectively) in single-crystal silicon cells. This doping is necessary to increase the conductivity of the silicon, thus improving the mobility of the charge carriers that are generated under illumination. By creating the p-n junction near the surface of the silicon cell, they maximized the conversion of photons to electron-hole pairs at the junction,
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The second generation of solar cells sought to reduce the cost of the silicon single-crystal cells and shift to other, more abundant semiconductor materials. Solar cells from this generation include amorphous silicon, cadmium telluride (CdTe), and copper-indium-gallium-selenide (CIGS). The major benefits of second generation solar cells are the decrease in cost and the ability to construct more flexible cells. These cells comprise the majority of commercial thin-film solar cells currently sold.

Amorphous Si (a-Si) cells are typically deposited by chemical vapor deposition of silane and hydrogen. While the power efficiency of an a-Si cell is much less than of a monocrystalline Si cell, the manufacturing process is much simpler, requiring relatively low temperatures and has the ability to produce the panels quickly. In addition, because the amorphous Si absorbs light well (~90% with just 1 micron thickness), it uses much less silicon than the monocrystalline wafers. This decrease in cost is somewhat offset by the need to deposit multiple layers to achieve a reasonable efficiency. Even so, the result is a net decrease in price that makes a-Si solar cells an attractive prospect for low power applications. One downside to a-Si cells is the tendency of the completed panels to lose
about 15-30% of their efficiency in the first 6 months of operation. This effect is known as the Staebler-Wronski Effect, named after the researchers who first reported the loss of efficiency under intense illumination. The cause of the effect is not fully known, but the favored explanation is that the intense illumination causes defects by breaking weak Si-Si bonds during non-radiative recombination. Upon annealing at approximately 150 °C, the a-Si cell can be regenerated, though it will undergo the same loss of efficiency under illumination.

Cadmium telluride thin-film cells are a second product of this generation. CdTe has a bandgap of 1.5 eV, allowing it to absorb light across the entire visible spectrum while achieving high efficiencies, much like silicon. Research on CdTe for solar applications dates to the 1950s, but the commercial technology hit its stride in the 1970s and 1980s when the p-type CdTe was paired with n-type CdS to form an effective heterojunction. Ting Chu, a researcher at Southern Methodist University and the University of Florida, is credited with pushing efficiency of the CdS/CdTe cell higher by optimizing the CdS layer, thus allowing more light to pass through to the CdTe. This resulted in NREL-certified solar cell efficiencies nearing 15%. On the industrial side, many companies have attempted to make headway in the solar cell market with CdTe panels, including Kodak, BP, and GE. One of the current leaders in the CdTe market is First Solar, which has recently posted new certified efficiency records of 17.3%. They were also the first company to produce solar cells at less than $1 per watt, considered an important threshold for the viability of solar power, and they have since achieved a price point of just $0.74 per watt. The main concern for CdTe cells is the toxicity of the
cadmium used when the life of the cell is finished, although recycling of scrap cells has been demonstrated.

CIGS solar panels are another of the thin-film technologies developed in the second generation. CIGS-based cells have gained popularity for their low band gap and relative ease of manufacturing. The band gap of a CIGS cell can range from 1.0 – 1.7 eV, depending on the ratio of indium and gallium. Most commercial cells will be around 1.1 – 1.2 eV\(^{12}\), as the highest performing ratio has the Ga/(In+Ga) ratio at approximately 0.3. In addition to this small band gap, CIGS has a strong absorption coefficient (~10,000/cm\(^{13}\)), allowing the active layers to be very thin and reducing both the amount of materials needed and the costs associated with them. Given cadmium's toxicity, this is a significant benefit. CIGS cells are generally formed by sputtering of the precursor materials, followed by selenization of the as-deposited metals. The use of H\(_2\)Se as selenization agent, however, is a hazard due to its toxicity. Some companies use a slightly different method that involves the printing of metal or metal oxides in an aqueous solution. This solution is printed onto an appropriate substrate, dehydrated, reduced (if using metal oxides) in a hydrogen/nitrogen atmosphere, sintered, and finally selenized. Although this method has more steps, it could potentially allow production of larger modules courtesy of the initial printing step. Efficiencies of CIGS solar modules vary depending on the method of production used. Commercial efficiencies range from about 9% to 14% while lab efficiencies have gone as high as 20\(^{14}\).

The third generation of solar cells is focused on both efficiency gains and cost reduction. The third generation includes dye-sensitized cells, thin-film polymer cells, and
quantum dot solar cells. Currently, dye-sensitized cells are the champions of this generation in terms of efficiency at just over 12%, but organic and quantum dot solar cells are cheaper to make and can potentially reach efficiencies rivaling and surpassing dye-sensitized solar cells.

Interest in dye-sensitized solar cells (DSSCs) increased greatly following the publication of work from O'Regan and Gratzel in 1991. In their manuscript, they demonstrated a simple method for constructing a solar cell that gave a power conversion efficiency of 11% using a TiO$_2$ nanoparticle film, a ruthenium dye, and an iodide/tri-iodide redox couple. Since that publication, a flurry of activity has led to the synthesis of many new dyes, with some capable of high conversion efficiencies across the entire visible light spectrum, new non-corrosive redox couples, and even new counter electrodes designed to replace the traditional, but expensive, platinum while maintaining and improving on the power conversion efficiency. In spite of all of this research, however, DSSC efficiencies have only risen to 12.3%. DSSCs are limited by relatively low extinction coefficients (~$10^4$ M$^{-1}$ cm$^{-1}$), especially when compared to other absorbers like quantum dots ($2 \times 10^4 - 10^5$ M$^{-1}$ cm$^{-1}$), and low open circuit voltages. The low extinction coefficients limit the amount of light that can be absorbed by the thin layer of dye that is adsorbed onto the TiO$_2$ substrate. This has been combated in part by the use of highly porous nanoparticle films that maximize the amount of dye that can be loaded. The open circuit voltage limitation is due to the overpotential required to form the oxidized species of the redox couple, I$_3^-$.

The redox reaction steps are ($D$ is the dye that has been photoexcited):
\[ I^- + D^+ \rightarrow I^+ + D \quad \text{Equation 1.1} \]
\[ I^+ + I^- \rightarrow I_2^- \quad \text{Equation 1.2} \]
\[ 2I_2^- \rightarrow I^- + I_3^- \quad \text{Equation 1.3} \]

The use of Co\textsuperscript{II}/Co\textsuperscript{III} redox couples has already been shown to increase the open circuit voltage. If photocurrent output can be increased to match that of the iodide/tri-iodide couple, DSSC efficiencies should be able to increase significantly. In addition, the development of solid-state DSSCs will eliminate the issue of evaporating electrolyte. The final step before large-scale commercial production becomes truly viable will be to move away from Ru-based dyes due to the scarcity of ruthenium metal.

Polymer solar cells rely on an acceptor-donor system for producing electricity. In many cases, both the donor and acceptor are photoactive, although the systems are designed such that one will be the primary absorber. The field of polymer solar cells took off with the publication describing the synthesis of a cell composed of two organic components, copper phthaloacyanine and tetracarboxylic perylene, by Ching Tang while he was working at Eastman Kodak Laboratories.\textsuperscript{26} Tang's organic photovoltaic (OPV) cell attained a demonstrated efficiency of approximately 1%. A second seminal work by Sariciftci and co-workers\textsuperscript{27} in 1992 demonstrated electron transfer from a polymer to C60. The most attractive aspect of polymer solar cells is the potential for low-cost, flexible efficient modules that can be solution-processed. They have high extinction coefficients, so thin layers of materials can be used in modules, and the polymers absorb in the visible region, taking advantage of a large piece of the solar spectrum. The use of these thin layers helps ameliorate one of the major issues holding power conversion
efficiencies for polymer solar cells down—the cells suffer from high rates of recombination due to the strong attraction of the generated electron-hole pairs. By creating bulk heterojunctions in the thin films, the distance an electron-hole pair must travel before separating is greatly reduced, thus lowering the rate of recombination. Common polymers used to construct this type of solar cell include (6,6)-phenyl-C61-butyric acid methyl ester (PCBM), poly(3-hexylthiophene) (P3HT), and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). The PCBM acts as an electron acceptor, the P3HT acts as an electron donor, and the PEDOT:PSS is used a blocking layer to ensure the proper funneling of electrons and holes. Commercial organic polymer cells have reached efficiencies as high as 8.3%. Current research is focused on further reducing recombination and development of new photoactive polymers and organic materials that are air-stable.

Quantum dot solar cells (QDSCs) represent one of the most promising technologies currently being developed. Quantum dots (QDs) are three-dimensionally confined particles that can absorb throughout the visible and infrared regions. This absorbance can be easily controlled by manipulating the size of the quantum dot during and after synthesis. QDSCs are typically comprised of a conducting nanoparticle substrate upon which the dots are deposited by chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), or adsorption of pre-synthesized quantum dots. As mentioned previously, quantum dots have high extinction coefficients, which means that relatively low loading of QDs will absorb most of the incident wavelengths of light that are greater than their band gaps. Beyond this
absorbance, however, is the demonstration of multiple exciton generation in QDs. Multiple exciton generation (MEG) is the generation of more than one electron-hole pair from a single incident photon. The significance of this effect is that it could move the Schokley-Quiesser efficiency limit much higher. While MEG has been demonstrated in multiple types of QDs\textsuperscript{40-42}, only recently has an incident-photon-to-charge-carrier efficiency (IPCE) of greater than 100\% been demonstrated experimentally\textsuperscript{43}. Between this phenomenon and the possibility of hot electron injection—the transfer of an electron that has not yet thermally relaxed to the conduction band of the quantum dot—QDSCs offer plenty of opportunity for greatly increased power efficiencies. Current liquid junction cell efficiencies have topped 5\%\textsuperscript{44} while solid state cells have reached about 6\%.\textsuperscript{45}

For solar power to be viable, however, a major question remains: how will power be provided at night or when cloudy days reduce illumination intensity?

Hydrogen gas is an energy carrier that can fill this role. Hydrogen can be readily transported and utilized in homes and vehicles with some modifications to existing infrastructure. The use of hydrogen as a fuel has an extensive history. The discovery of hydrogen is credited to Henry Cavendish in 1766, although the generation of hydrogen was described (though not recognized as a new substance) nearly 105 years prior by Robert Boyle\textsuperscript{46-47}. Francois Issac de Rivaz is generally credited with being the first to develop a hydrogen internal combustion engine in 1806.\textsuperscript{48} The car he designed based on the hydrogen internal combustion engine (HICE) was a commercial failure, but de Rivaz was able to demonstrate the proof-of-concept. Car manufacturers like Mazda\textsuperscript{49} and
BMW\textsuperscript{50} have both developed full engines and limited production model vehicles based on the use of hydrogen in the internal combustion engine. Other companies have poured their resources into development of hydrogen fuel cell vehicles. The Chevy Equinox FCV\textsuperscript{51} and Honda FCX Clarity\textsuperscript{52} are two limited production models that have been manufactured in recent years. Hyundai\textsuperscript{53} and Toyota\textsuperscript{54} have announced plans to bring hydrogen fueled cars to market in the near future as well.

Setting aside the potential and realized issues with fuel cells and the expected difficulty of practical implementation of a standardized refueling system for hydrogen vehicles, whether direct combustion or fuel cell based, the issue of how exactly to generate all the hydrogen necessary for powering all of these homes, vehicles, and industrial buildings must be addressed. Currently, about 95% of all hydrogen is produced by natural gas reforming as shown in Equations 1.4 and 1.5.\textsuperscript{55}

\begin{align*}
\text{Equation 1.4} \\
CH_4 + H_2O & \rightarrow CO + 3H_2 \\
\text{Equation 1.5} \\
CO + H_2O & \rightarrow CO_2 + H_2
\end{align*}

The process is performed at a net energy loss—in other words, by simply burning the natural gas, one would get more energy than can be obtained by burning the generated hydrogen when the additional energy needed to perform the steam-methane reforming reactions are considered. Clearly this process is not an option for sustainable worldwide operation. To be a realistic solution to the problem of excess energy storage, this generation process must make use of a "free" energy source.

Given the orders-of-magnitude excess energy from sunlight available to us, the sun (itself a major user of hydrogen!) is an excellent resource that can be harnessed to
generate hydrogen from water, which also exists in a large enough quantity to be a viable feedstock. The fact that hydrogen, when burned, produces only water means that a sustainable generation-consumption cycle is feasible. Photogeneration of hydrogen represents one method for storing energy to be used in the absence of sunlight. It also enables the use of solar energy for transportation in the form of compressed hydrogen in tanks or through the use of metal hydrides. Achieving solar fuel conversion efficiencies approaching those of commercial solar cells, however, is a daunting task.

1.2 Semiconductor Materials Used to Perform Photoelectrolysis of Water

Fujishima and Honda are generally credited with beginning the boom of research into semiconductor water photolysis with their seminal paper demonstrating generation of oxygen and hydrogen using TiO$_2$ as a working electrode and platinum as their counter electrode. Even before their work, however, there was interest in replicating the process of photosynthesis to generate hydrogen and oxygen on demand. Experiments on the evolution of oxygen using chlorophyll and chloroplasts were explored and demonstrated at least twenty years prior to Fujishima and Honda's work.

Unassisted direct overall water splitting has been demonstrated on TiO$_2$,$^{56}$ SrTiO$_3$,$^{59}$ GaN,$^{60-62}$ La:NaTaO$_3$,$^{63}$ BiYWO$_6$,$^{64}$ Ta$_2$O$_5$,$^{65}$ and a multitude of other metal oxides.$^{65-69}$ While using just a single semiconductor for overall water splitting is ideal from the standpoint of simplicity, the overall efficiencies demonstrated are generally low (0.1-1%), and spectral response is often limited to the ultraviolet region. The ultraviolet region only accounts for about five percent of sunlight hitting the surface of the Earth.
To be an effective and viable method for generating hydrogen, any photoelectrolysis device must utilize the visible region of the solar spectrum, which accounts for approximately forty-five percent of the light reaching the Earth. Many visible region absorbers, however, suffer from problems that limit or effectively prohibit their use. A number of materials, like CdS\textsuperscript{70-72}, Si\textsuperscript{73-76}, and Cu\textsubscript{2}O\textsuperscript{77-79}, suffer from photocorrosion caused by a side reaction that occurs on a timescale competitive with oxidation of water:

\[
\text{CdS} + 2h^+ \rightleftharpoons \text{Cd}^{2+} + S \tag{1.6}
\]

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4e^- \tag{1.7}
\]

\[
\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e^- \rightleftharpoons 2\text{Cu} + 2\text{OH}^- \tag{1.8}
\]

Some materials, though they have a bandgap greater than 1.23 eV, have band alignments that preclude unassisted water splitting or have such high recombination that they require an applied bias to function efficiently. Materials with these characteristics include BiVO\textsubscript{4}\textsuperscript{80-81}, WO\textsubscript{3}\textsuperscript{82}, Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{83-86}, Ta\textsubscript{3}N\textsubscript{5}\textsuperscript{87-88}, CdSe\textsuperscript{89-90}, and CuGaSe\textsubscript{2}\textsuperscript{91}, among others. Much of the recent published research in the field of photoelectrolysis has focused on the development of new photoactive materials for water splitting. New families of oxynitride materials\textsuperscript{92-99} and mixed metal oxides\textsuperscript{66, 100-109} are designed to utilize more of the visible region of the light spectrum by narrowing the band gap of the starting metal oxides.

Semiconductors that can only perform one of the two half-reactions can be paired together in what is known as a Z-scheme. In the Z-scheme system\textsuperscript{96, 110-113}, an electron relay is used to connect two semiconductors that each perform one of the evolution reactions. Figure 1.3 is a general scheme depicting this system. Examples of Z-schemes
include Rh: SrTiO$_3$/WO$_3$\textsuperscript{110}, TaON/WO$_3$\textsuperscript{111}, and Rh: SrTiO$_3$/BiVO$_4$\textsuperscript{112}. There has even been a demonstration of using the same material, TaON, with different co-catalysts to form a Z-scheme system\textsuperscript{113}. One downside of a Z-scheme system, however, is the possibility of recombination with the electron relay.

Combinations of semiconductors—typically a p-type photocathode and n-type photoanode—have also been utilized to perform photoelectrolysis. This strategy represents an enticing solution to counter the lack of utilization of the visible region of the solar spectrum, especially as it presents the option of utilizing the ultraviolet, visible, and near infrared regions efficiently by matching the p- and n-type semiconductor to different regions based on their respective band gaps. Monolithic structures based on this p-n junction method have given solar-to-hydrogen conversion efficiencies of 8.2%\textsuperscript{114},
12.4%\textsuperscript{115}, and 18.3%\textsuperscript{116}, though they did rely on relatively exotic materials and processing steps.

1.3 Oxygen Evolution Catalysts

The formation of oxygen from water requires four holes to proceed\textsuperscript{117}, making this reaction the rate-determining step for the overall water splitting reaction. Transient spectroscopy experiments using $\alpha$-Fe$_2$O$_3$ and TiO$_2$\textsuperscript{117-118} have shown that the oxidation step occurs on the order of milliseconds to seconds without applied bias. It is clear that to achieve practical efficiencies for solar water splitting, this slow reaction step must be improved upon by speeding up the hole transfer and oxidation steps. The slow reaction is reflected in the relatively large electrochemical overpotentials measured in all water oxidation experiments. The current champion electrocatalyst is IrO$_2$, with an overpotential of $\sim$150 mV\textsuperscript{119}. More commonly, the overpotentials on IrO$_2$\textsuperscript{120-122} are on the order of 150 to 300 mV, the overpotentials for RuO$_2$\textsuperscript{70, 123-127} are on the order of 250 to 350 mV, and overpotentials for Co$_3$O$_4$\textsuperscript{118, 128-136} are between 250 and 400 mV. Co-based catalysts in particular have recently garnered significant interest courtesy of a manuscript from Kanan and Nocera\textsuperscript{137}. Their demonstration of the deposition of a cost-effective, robust, and reasonably efficient water oxidation catalyst by a simple method tackled a significant step in the process of making large scale water splitting a reality. It is interesting to note that the idea of electrodepositing a cobalt oxide catalyst from a solution of Co$^{2+}$ is not a new one. As far back as 1950, this process had been demonstrated using CoSO$_4$\textsuperscript{138}. The researchers even noted that using a phosphate buffer
(similar to the buffer used by Kanan and Nocera) prevented the dissolution of the deposited Co into solution. In that work, however, the authors did not perform water oxidation experiments. Later work did report\textsuperscript{139-142} that these electrodeposited Co-oxide films are active for the water oxidation reaction, and the reported overpotentials are similar to that reported by Kanan and Nocera (\(\eta \sim 300-400\) mV).

IrO\textsubscript{2} has curried favor for both its low overpotential, which makes it ideal for commercial electrolyzers, and its stability in corrosive, extreme pH solutions. Previous research investigated IrO\textsubscript{2} films deposited anodically\textsuperscript{143-145} or by thermal decomposition of an iridium salt,\textsuperscript{143} which gave overpotentials that were closer to 300 mV during cyclic voltammetry experiments. More recent work has focused on deposition of IrO\textsubscript{2} colloids from solution in a method similar to the Co\textsuperscript{2+} deposition, albeit without the need for a phosphate buffer.\textsuperscript{119, 121-122, 146} These colloidal solutions are formed through hydrolysis of the hexachloride salt (IrCl\textsubscript{6}\textsuperscript{2-}) by adjusting the pH to 13. The hydroxide ions are sufficient to stabilize \(\sim2\) nm nanoparticles for up to a few months.\textsuperscript{121, 146} Direct evolution of oxygen in the presence of an electron acceptor like AgNO\textsubscript{3} has also been observed.\textsuperscript{147}

One major drawback for IrO\textsubscript{2}, however, is the scarcity and cost of iridium metal. The price of iridium metal, as of February 2nd, 2012, is approximately $1080 per ounce, and the price has risen by a factor of nearly two and a half times in the last two years from about $420 to its current $1080.\textsuperscript{148} Cobalt, to compare, is currently at \(\sim$20 per ounce.\textsuperscript{149} A second drawback of IrO\textsubscript{2} is that, despite its incredible activity as an electrolysis catalyst, it showed no activity as a co-catalyst in combination with a W:BiVO\textsubscript{4} photocatalyst in a study of combinatorial measurements from Ye and Bard.\textsuperscript{150}
Others, though, have observed IrO$_2$ taking part in the photochemical oxidation of water, although an external bias is usually applied.$^{99, 120, 151-152}$ Furthermore, as will be discussed in Chapter 4, IrO$_2$ catalyzes the scavenging of trapped holes formed on TiO$_2$ during band gap excitation.

1.4 Water Splitting Requirements and Mechanisms

To perform photolysis of water using sunlight under ideal conditions, three conditions must be met: (1) the bandgap of the semiconductor must be at least 1.23 eV, (2) the conduction band of the semiconductor must be more negative than the reduction potential of water and the valence band must be more positive than the oxidation potential of water, and (3) the rate of charge recombination within the semiconductor must be slow enough to allow separation of photogenerated charges. Figure 1.4 shows a general scheme for photocatalytic water splitting as well as the band positions of several semiconductors relative to the potentials for hydrogen and oxygen evolution (at pH 0).

The splitting of water can be described as an overall reaction:

$$H_2O \rightarrow \frac{1}{2}H_2 + O_2$$

Equation 1.9
Figure 1.4 A general depiction of the necessary conditions for overall water splitting. It is important to emphasize that reaction overpotentials, due primarily to the four-hole oxygen evolution reaction, increase the required band gap to 1.7 eV. The bottom of the figure shows where the conduction and valence bands of several semiconductors lie relative to the hydrogen and oxygen evolution reactions at pH 0.

This apparently simple reaction is comprised of two half-reactions. The hydrogen evolution reaction (HER) is the more facile of the two, requiring just two electrons to proceed:

\[ 2H^+ + 2e^- \rightarrow H_2 \]  

Equation 1.10

The overpotential for the evolution of hydrogen on Pt, the best HER catalyst, is on the order of 10 to 30 mV.\textsuperscript{153} Because platinum is a fairly expensive and scarce material, some work has focused on using as little Pt as possible by coating cheaper materials with a monolayer or few monolayers of Pt. Non-noble metal catalysts have also been
synthesized that show high activity for the HER. NiMoZn,\textsuperscript{154} CuW alloys,\textsuperscript{155} MoS\textsubscript{2},\textsuperscript{156} Cu-Cr mixed oxides,\textsuperscript{157} WS\textsubscript{2},\textsuperscript{156,158} and NiS\textsuperscript{159} are all co-catalysts that have demonstrated high activity toward the HER. Accordingly, this half-reaction is not considered a limiting step in the overall water splitting reaction.

The oxygen evolution reaction, on the other hand, is a four-hole process\textsuperscript{117} and, thus, the rate limiting step:

\[
4\text{OH}^- \rightarrow 2\text{O}_2 + 4\text{H}^+ + 4e^-
\]

Equation 1.11

The steps that comprise the oxygen evolution reaction have been the subject of much speculation and investigation. The pH of the electrolyte solution has been observed to affect the mechanistic pathways available for oxygen evolution. One proposed mechanism\textsuperscript{127} for acidic environments was determined using RuO\textsubscript{2}, both as a single crystal and in a compact film (\(S\) represents a catalytically active site):

\[
S + \text{H}_2\text{O} \rightarrow S - \text{OH} + \text{H}^+ + e^-
\]

Equation 1.12

\[
S - \text{OH} \rightarrow S - \text{O} + \text{H}^+ + e^-
\]

Equation 1.13

\[
S - \text{OH} + S - \text{OH} \rightarrow S - \text{O} + S + \text{H}_2\text{O}
\]

Equation 1.14

\[
S - \text{O} + S - \text{O} \rightarrow \text{O}_2 + 2S
\]

Equation 1.15

In basic solutions, the proposed mechanism is altered slightly in the first step due to the predominance of hydroxide ions:

\[
S + \text{OH}^- \rightarrow S - \text{OH} + e^-
\]

Equation 1.16

Once the hydroxide has bound to the active site, there are two proposed general pathways which result in oxygen formation. The first involves the formation of hydrogen peroxide, according to Equation 1.17, which then decomposes to oxygen and hydrogen:
\[ S - OH + OH^- \rightarrow S + H_2O_2 + e^- \quad \text{Equation 1.17} \]

\[ H_2O_2 \rightarrow O_2 + H_2 \quad \text{Equation 1.18} \]

The second pathway involves further deprotonation of the hydroxyl group and subsequent reaction with a second oxygen atom on an adjacent active site to form oxygen gas:

\[ S - OH + OH^- \rightarrow S - O^- + H_2O \quad \text{Equation 1.19} \]

\[ S - O^- \rightarrow S - O + e^- \quad \text{Equation 1.20} \]

\[ 2(S - O) \rightarrow 2S + O_2 \quad \text{Equation 1.21} \]

More recent work that takes advantage of more precise experimental techniques has allowed for elucidation of some reaction intermediates. A comprehensive study on cobalt oxide water oxidation catalysts by Gerken and co-workers\textsuperscript{130} gave rise to two separate reaction mechanisms depending on the pH of the solution. In acidic conditions (pH = 0 to 3.5), the water oxidation pathway culminated in the formation of a hydrogen peroxide molecule, which could later decompose to oxygen. Also of note is that the Co\textsuperscript{2+} ions that are electrochemically deposited during the water oxidation reaction are not stable and dissolve back into solution as part of the mechanism in the absence of the phosphate buffer. In solutions from pH 3.5 to 14, however, the Co\textsuperscript{2+} deposits and forms a stable oxide layer, which drives the catalytic mechanism toward the electrochemical formation of oxygen.

Sivasankar and co-workers\textsuperscript{151} have used rapid-scan FTIR spectroscopy in a study of photochemical water oxidation on IrO\textsubscript{2} to identify an intermediate species that lasts only a few hundred milliseconds. The FTIR scans revealed an oxygen-oxygen bond
stretching that was confirmed by isotope labeling to occur only during the process of water oxidation following a laser excitation pulse. This, along with identification of an oxygen-hydrogen bending mode from the isotope labeling, allowed them to determine that an Ir$^{III}$OOH species was formed as an intermediate. Their proposed mechanism had the iridium metal site changing valence from +4 to +5, followed by a reduction to +3 and subsequent reoxidation to +4. This stands in some contrast to the reaction mechanism proposed by Nakagawa and co-workers$^{121}$ based on electrochemical experiments that showed oxidation and reduction peaks assigned to Ir$^{III}$/Ir$^{IV}$ and Ir$^{IV}$/Ir$^{V}$ redox couples. The assumption made was that the Ir$^{V}$/Ir$^{VI}$ transition was masked by the current from the water oxidation, with the only indication of a Ir$^{V}$/Ir$^{VI}$ redox being a small, broad reduction peak during the reverse sweep.

In a similar vein to Sivasankar, McAlpin and co-workers$^{160}$ used electron paramagnetic resonance (EPR) to prove that the cobalt oxide catalyst also changes valence from a +2/+3 state to +4 in the course of the water oxidation process before returning to a +2/+3 valence. It is clear from these experiments that the transfer of holes at the photocatalyst/co-catalyst/liquid interface is of great importance.

1.5 Interfacial Charge Transfer Processes and the Motivation For This Work

Interfacial transfer processes ultimately govern how efficiently solar cells and photoelectrolysis devices operate. Effective separation of electrons and holes is vital to any photoelectrochemical process and is affected by the electrolyte$^{31, 161}$, the counter
Because oxygen evolution is a kinetically slow process, special attention must be paid to eliminating side reactions that occur on similar or faster timescales as oxygen evolution. The addition of co-catalysts to photocatalysts to assist this reaction has a demonstrable effect by increasing the lifetime of holes by a few orders of magnitude and thus the probability of the completing the water oxidation reaction.\textsuperscript{117-118, 131, 150, 164} This research, which focuses on understanding the function of the co-catalyst rather than simply how well it performs, is key to figuring how to design more efficient catalysts. The rapid transfer of the hole from the semiconductor to the co-catalyst is integral in the development of an efficient water splitting device.

The focus of the work presented in this dissertation is to elucidate how interfacial transfer processes governs efficiency and how interfacial charge transfer processes can be manipulated to improve those efficiencies. Chapter 2 discusses control of trap sites on TiO\textsubscript{2} and how this control affects the improvement in photovoltaic performance that is observed. Chapter 3 describes the synthesis of a SrTiO\textsubscript{3}/TiO\textsubscript{2} heterostructure that shows improved photovoltaic performance due to increased charge separation. Chapter 4 discusses the role of IrO\textsubscript{2} in shuttling photogenerated holes away from TiO\textsubscript{2} and an unexpected side reaction that directly competes with water oxidation. Chapter 5 focuses on hydrogen generation from a CdS/TiO\textsubscript{2} electrode in a continuous flow "reverse fuel cell" system. Also discussed is the calculation of the quantum efficiency of the formation of hydrogen in the system and how that correlates with the predicted efficiency based on
the current-voltage measurements. Finally, Chapter 6 summarizes the research as a whole and proposes at future directions for research in this area. If large scale sustainable hydrogen production is to become a reality, recombination must be minimized and the rate of formation of oxygen maximized. To accomplish this goal, thorough understanding of the fundamental processes is paramount.
As discussed in Chapter 1, it is important to better understand how manipulation of the working electrode interface can improve photoelectrochemical performance. There are a number of ways in which this can be achieved. In this chapter, the intercalation of Li\(^+\) and H\(^+\) ions is discussed, with a focus on the effect these cations have on the surface trap sites of TiO\(_2\). Through a combination of electrochemistry and diffuse reflectance ultraviolet-visible spectroscopy, the formation and stability of these trap states were tracked. Improvements in the photoelectrochemical characteristics of the liquid junction solar cell are discussed with respect to the role of the intercalated cations.

2.1 Formation of TiO\(_2\) Nanotube Arrays by Anodization

The use of TiO\(_2\) as a substrate is well-documented in the literature.\(^{15-16, 21, 32, 34, 36-37, 39, 152, 163, 165-167}\) The well-known Gratzel cell uses a TiO\(_2\) nanoparticle film as the substrate onto which the ruthenium-based dye is adsorbed. The primary advantages of TiO\(_2\) are its resistance to corrosion, commonality, and ease of use. Commercial TiO\(_2\) pastes are readily available. TiO\(_2\) nanoparticle films have also found extensive use in quantum dot-based solar cells (QDSCs), both liquid junction and solid state.\(^{35, 43-45, 162}\)
One drawback of the TiO$_2$ nanoparticle films is that each junction between two particles represents a point of potential recombination as a photogenerated electron moves to the back contact. As each electron diffuses and hops along a wandering path (depicted in Figure 2.1) through the nanoparticulate film toward the back contact, there is a high chance for recombination with either photogenerated holes or the electrolyte. It is desirable to have an electron "highway" that will quickly and efficiently shuttle photogenerated electrons away from holes while also efficiently bringing holes to the electrode/electrolyte interface. Nanotube arrays, a 1-D structure, meet these criteria and have been shown to increase the lifetime of photogenerated electrons by an order of magnitude.$^{168}$ This increased carrier length allows the use of a thicker substrate, which in turn allows higher loading of sensitizers like dyes or quantum dots. Because the nanotubes are synthesized by a corrosive etching process, they have an intimate connection with the back contact.

**Figure 2.1:** The random walk of a photogenerated electron in a TiO$_2$ nanoparticle film (left) and the directed collection of a photogenerated electron in a 1-D TiO$_2$ nanotube array (right). Each particle hop in the nanoparticle film represents a chance for recombination.
In the most general case, the nanotubes are formed by electrochemical anodization of titanium metal in a fluoride solution that has a small volume percentage of water. A DC voltage is applied, and a series of reactions takes place (depicted in Figure 2.2):

$$Ti + H_2O \rightarrow TiO_2 + 2H^+ + 2e^- \quad \text{Equation 2.1}$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad \text{Equation 2.2}$$

Oxidation of water at the Ti foil surface generates a TiO$_2$ layer. Fluoride ions in solution are driven to the positively biased Ti/TiO$_2$ electrode and react with the TiO$_2$ layer, forming pits on the surface. Within these pits, the electric field is slightly concentrated, and the fluoride ions are preferentially driven to them, causing the pits to become deeper and the field to concentrate more. These competing reactions will continue, if allowed, until there is no titanium metal left to oxidize, at which point the TiO$_2$ will simply be corroded away as TiF$_6^{2-}$ until the submerged section of the electrode disintegrates. Accordingly, the reaction is stopped by shutting off the applied voltage and washing the electrode clean of any remaining solvent.
**Figure 2.2:** Diagram of the steps in the TiO$_2$ anodization process that form nanotubular structures. Ti foil (A) is oxidized by the decomposed water, forming a TiO$_2$ layer on the Ti foil (B). Fluoride ions corrode the TiO$_2$ as TiF$_6$$^{2-}$, forming pits in the TiO$_2$ layer. The TiO$_2$ formation and corrosion continues, and the applied electric field, which is slightly stronger in the pitted areas, drive F$^-$ ions into the pits, digging them deeper (D). As the process continues, uniform tubes are formed in the TiO$_2$ layer with a small buffer layer (~200-300 nm) between the pits and the remaining Ti metal (E).

The length, diameter, and wall thickness of the nanotubes are determined by the electrolyte solvent, the concentration of fluoride ions, the applied voltage, the temperature of the solution, anodization time, and the amount of water present in the electrolyte. A high concentration of fluoride ions causes the corrosion reaction (Equation 2.3) to proceed much more quickly and form nanotubes with thin walls that are prone to cracking and breaking. Past a critical F$^-$ concentration, a porous TiO$_2$ layer will form rather than nanotubes due to the rapid dissolution of TiO$_2$ from the entire Ti electrode as opposed to within the pores. Increasing the applied voltage causes both the formation and dissolution of the oxide layer (Equations 2.1 and 2.2) to proceed more quickly, resulting in long, but thin-walled tubes. Purposeful modulation of the voltage during the anodization process has been used to alter the morphology of the nanotubes.$^{169}$
anodization duration determines the length of the nanotubes, and it is possible to grow nanotubes up to about one millimeter in length, provided the titanium metal foil is thick enough.

The solvent affects the growth rate of the nanotubes based on its dielectric constant—the higher the dielectric constant of the solvent, the weaker the effect of the electric field on the fluoride ions and, consequently, the more slowly the ions move to the TiO₂ layer to react. As a comparative example, formamide has a dielectric constant of about 109 while ethylene glycol has a dielectric constant of just 37. All other conditions ([F⁻] = 0.27M, 2 vol% water, 60V applied) being equal, generating 5 µm long nanotube arrays takes approximately 12 hours in formamide and just 1 hour in ethylene glycol. Experiments detailing how each variable affects nanotube growth can found in review articles.¹⁷⁰-¹⁷³

As synthesized, the TiO₂ nanotubes are amorphous, although at least one published report claims that it is possible to form crystalline TiO₂ nanotubes during anodization.¹⁷⁴ Another manuscript describes the spontaneous formation of the anatase phase by soaking freshly prepared amorphous TiO₂ nanotubes in water.¹⁷⁵ More commonly, however, the nanotubes are converted to the anatase or rutile phase by annealing at high temperature (350-580 °C for anatase, >580 °C for rutile)¹⁷² in air or pure oxygen.¹⁷³, ¹⁷⁶-¹⁷⁹ These polycrystalline nanotubes are then used as substrates for everything from QDSCs³⁴, ³⁹ to dye-sensitized solar cells¹⁸⁰ to hydrogen detection.¹⁸¹ TiO₂ nanotube arrays can suffer from a high number of trap states that capture
photogenerated electrons. Accordingly, maximizing photovoltaic performance of the TiO₂ nanotube array substrate requires minimizing the influence of these trap sites.

2.2 Using Spectroscopy to Observe Ti⁴⁺ Trapping Sites

Photocurrent is a result of the difference between the rate of charge separation and collection and the rate of charge recombination. If the rate of separation and collection is faster than that of recombination, a photocurrent will be measured. If the rate of separation and collection is not faster than that of recombination, or if the source of photoexcitation is removed, then the measured photocurrent will decrease to zero. When TiO₂ is excited by incident light, an electron moves to the conduction band and travels toward the back contact. During the process of diffusing to the back contact, however, some electrons may be trapped at oxygen vacancies. Once trapped, these electrons may be re-excited to the conduction band, or they may recombine with photogenerated holes. These trap sites are known to be Ti⁴⁺, which can be readily reduced to Ti³⁺ by the photogenerated electrons.¹⁸²-¹⁸⁵

Under nitrogen atmosphere, Ti³⁺ sites are stable, as evidenced by the deep blue color that is formed upon band-gap illumination of TiO₂ in an ethanol solution.¹⁸⁶ As the deep blue color suggests, UV-visible absorption measurements show a wide band of absorption for the colloidal TiO₂ solution across the visible region of the light spectrum attributed to the Ti³⁺ sites. In the presence of oxygen, no blue color is observed as the oxygen will readily scavenge the trapped electrons.¹⁸²-¹⁸³
While absorption of TiO$_2$ colloidal solutions is easily measured with standard absorption spectroscopy methods, absorption of TiO$_2$ nanoparticle films and nanotube arrays is more difficult. In the case of the TiO$_2$ nanotube arrays, the Ti metal foil precludes standard spectroscopy because light is unable to pass through the sample. Instead, diffuse reflectance ultraviolet-visible spectroscopy (DR UV-VIS) must be used. Diffuse reflectance is a measurement of diffusely (as opposed to specularly) reflected light from the sample compared to a reference sample. The measured reflectance of a sample can be converted to a form of absorbance using the Kubelka-Munk Theory$^{187}$ as shown in Figure 2.3. The absorbance is plotted as a function of the reflectance, F(R), according to Equation 2.3, where $R$ is the measured change in reflectance relative to a reference sample:

$$F(R) = \frac{(1-R)^2}{2R} \quad \text{Equation 2.3}$$

This theory was originally developed to check absorbance of dyes on paper during production processes and paint films. Kubelka-Munk Theory relies on three assumptions: 1) that the grains of the samples are smaller than the thickness of the sample, 2) that at least 50% of the incident light is reflected, and 3) that no more than 20% of the incident light is absorbed or transmitted. DR UV-VIS spectroscopy allows for the determination of band gaps of solid materials as well direction observation of changes in their absorption properties.
Figure 2.3: Diffuse reflectance (converted to Kubelka-Munk values) of a TiO$_2$ nanotube array after each potential shown was applied for 3 seconds. As the potential applied becomes more negative, a greater number of Ti$^{4+}$ sites are reduced to Ti$^{3+}$ and the broad absorption feature in the visible and infrared grows.

The reference sample used in diffuse reflectance measurements is chosen to match closely with background scattering and reflection. For instance, if a TiO$_2$ nanotube array sample is the working sample under observation, it is advisable to use another TiO$_2$ nanotube array as a reference. A mirror switches the illumination beam path between the reference and working samples repeatedly while the diffusely reflected light is collected in a photomultiplier in the top of the chamber. Absorbance can be measured as a steady state value for all wavelengths (from 300 to 800 nm here), or it can be measured at a single wavelength over time as a kinetic trace. The kinetic trace provides information about how quickly the trap sites are reduced and how stable the reduced trap sites are. An increase in measured absorbance at 700 nm indicates the formation of Ti$^{3+}$.\textsuperscript{182, 186}
2.3 \( \text{Li}^+ \) and \( \text{H}^+ \) Intercalation by Short Application of Negative Potential

At negative applied potentials, electrons are injected into the TiO\(_2\) nanotube array working electrode. In this study, a significant amount of Ti\(^{4+}\) sites were reduced at potentials more negative than -1.0V vs. Ag/AgCl. This reduction was evident from the change in the color of the electrode (a blue color on the electrode that is visible to the naked eye). In the presence of a cation like \( \text{Li}^+ \) or \( \text{H}^+ \), the reduction of Ti\(^{4+}\) to Ti\(^{3+}\) was accompanied by intercalation of the cation as depicted in Figure 2.4.
For the intercalation of both Li$^+$ and H$^+$ ions, a negative potential was applied for 3 seconds, during which time a significant cathodic current was observed. There was a threshold for stable reduction of Ti$^{4+}$ sites—this could be seen from a lack of sustained current during the 3 seconds of applied potential. When the sites were unstable, the measured current would increase initially and then drop quickly (within the 3 second voltage application) to nearly zero. SEM images of TiO$_2$ nanotube arrays before and after intercalation of Li$^+$ ions can be seen in Figure 2.5. It is clear from these images that no structural changes are caused by the brief application of the negative potential. Figure 2.6 shows the formation and stability of Ti$^{3+}$ sites as a function of the negative potential.

**Figure 2.5:** Scanning electron micrographs showing TiO$_2$ nanotube arrays before (A, C) and after (B, D) Li$^+$ ion intercalation. A and B are profile images while C and D are a bird's-eye view. Both the profile and top-down shots show no major structural changes upon intercalation of Li$^+$ ions.

It can be seen that at -0.9V vs. Ag/AgCl essentially no stable Ti$^{3+}$ sites are
formed. Once the threshold voltage is met, DR UV-VIS measurements reveal the stable formation of Ti$^{3+}$ sites, as indicated by the wide absorption band through the visible and near-infrared regions. As more negative potential is applied and more trap sites are reduced, the absorption corresponding to Ti$^{3+}$ sites increases in intensity, as shown in Figure 2.6. Diffuse reflectance measurements also reveal that there is a maximum number of trap states that are able to be reduced electrochemically, as evidenced by the plateau in absorption seen in Figure 2.6.

While the Ti$^{3+}$ sites were observed to be stable after application of negative potential and intercalation of Li$^+$ or H$^+$, it is also important to determine how resistant

**Figure 2.6:** (Left) Kinetic traces of the formation of Ti$^{3+}$ by monitoring 700 nm before, during, and after the 3 second application of negative potentials of (a) -0.9V, (b) -1.2V, and (c) -1.5V vs. Ag/AgCl. Stable Ti$^{3+}$ sites are only observed once the threshold potential of -1.1V is reached. (Right) Normalized steady state absorbance versus the potential applied for three seconds. The absorbance was allowed to equilibrate for 20 minutes. A clear difference in the onset of formation of Ti$^{3+}$ sites can be seen, attributable to both pH and ionic radius differences. Also of note is that there is a maximum amount of Ti$^{4+}$ sites that can be electrochemically reduced in the three second potential window.
they are to de-intercalation after the fact. In TiO$_2$ nanoparticulate films, Li$^+$ ions could be easily intercalated$^{188-190}$ but they were also found to be easily de-intercalated, requiring only a minimal amount of potential. The Li$^+$ ions intercalated into the TiO$_2$ nanotube array, on the other hand, show remarkable resistance to de-intercalation upon reversal of the applied potential. Even at +1.0V vs. Ag/AgCl, spectroscopic measurements show that about 75% of the Ti$^{3+}$ sites remain.

It was also observed that the pH of the electrolyte led to a shift in the voltage required to initiate stable formation of Ti$^{3+}$. In 1M HClO$_4$ (pH 0), the formation of stable Ti$^{3+}$ sites begins with an applied potential of -0.5V vs. Ag/AgCl. The number of reduced trap sites grows until approximately -0.9V vs. Ag/AgCl where a plateau is reached. This plateau indicates that all of the Ti$^{4+}$ sites available to be reduced have been reduced and stabilized by H$^+$ intercalation. In 1M LiClO$_4$ solution (pH 7), the formation of stable Ti$^{3+}$ sites does not begin until the applied potential is at least -1.1V vs. Ag/AgCl. The Nernstian shift of the conduction and valence bands of TiO$_2$ is well known$^{191}$ so this shift in onset potential is expected. The pH shift accounts for approximately 480 mV of the negative shift (~60 mV per pH unit). The remaining difference in required potential is likely attributable to the larger size of the Li$^+$ ion compared to the H$^+$ ion. The size effect of the cations was confirmed by the fact that larger tetrabutylammonium ions could not be intercalated into the TiO$_2$ lattice at all.
2.4 Effect of the Cations on the Photoelectrochemical Behavior of the TiO₂ Nanotube Array Substrates

Photoelectrochemical measurements provide insight into the effect of reduction of the electron trap states of TiO₂. For all the experiments, the electrolyte used was 1M KOH, the counter electrode was a platinum mesh, and the reference electrode was Ag/AgCl (saturated KCl). Illumination of the electrode was carried out using a 300 W Xe lamp with a CuSO₄ water filter. The CuSO₄ water filter cuts off both low UV (< 300 nm) and infrared (> 800 nm) wavelengths. All photovoltaic measurements were performed after bubbling nitrogen through the electrolyte for at least 30 minutes, and the nitrogen atmosphere was maintained by flowing nitrogen over the electrolyte for the duration of the measurement.

Photocurrent is a measure of how effectively photogenerated charges are collected and sent through an external circuit. Figure 2.7 shows the photocurrent response of TiO₂ nanotube arrays before and after the intercalation of Li⁺ and H⁺ ions. In both cases, the response to UV illumination was prompt and reproducible. Both of the TiO₂ nanotube arrays subjected to a short application of negative potential (3 seconds, -1.5V vs. Ag/AgCl) exhibited higher photocurrent generation when compared to the pristine samples. The intercalation of Li⁺ results in nearly four times as much measured photocurrent while intercalation of H⁺ results in approximately three times as much photocurrent. TiO₂ nanotube arrays have shown some degree of irreversibility while TiO₂ nanoparticles have shown nearly complete reversibility. The applied potential used in this work (-1.5V vs. Ag/AgCl) is more negative than potentials applied in other
Figure 2.7: (Left) Photocurrent time profile for TiO$_2$ nanotube arrays (a, b) before and (c, d) after (a, c) H$^+$ and (b, d) Li$^+$ ion intercalation. Photocurrent response is immediate and reaches a steady state in the illumination windows (30-60 sec, 90-120 sec, 150-180 sec). (Right) Current-voltage curves for TiO$_2$ nanotube arrays (a, b) before and (c, d) after intercalation of (a, c) H$^+$ and (b, d) Li$^+$ ions.

studies. This more negative potential should facilitate reduction of deep trap sites in the TiO$_2$ nanotubes. The stability of the measured photocurrent through multiple on-off cycles of band gap illumination confirms that the Li$^+$ ions intercalated during the three seconds of applied potential are stable and prevent the Ti$^{3+}$ trap sites from being re-oxidized. The photocurrent was also observed to remain stable for 15 minutes at 0V vs. Ag/AgCl under illumination.

Current-voltage (I-V) characteristics were also measured. The traces in Figure 2.7 confirm that the intercalation of Li$^+$ and H$^+$ increase the photocurrent output of the TiO$_2$ nanotube arrays approximately four-fold for Li$^+$ and two-fold for H$^+$. A slight shift of the flat-band potential—the point of zero current—to more negative potentials is also observed. Both the Li$^+$ and H$^+$ intercalated TiO$_2$ nanotube arrays show a 20 to 50 mV negative shift compared to the pristine arrays. This shift suggests that intercalation of
cations can cause Fermi level unpinning in TiO$_2$, allowing the Fermi level to shift closer to the conduction band.$^{192}$

Figure 2.8 shows how the measured photocurrent changes with the applied potential used for intercalation of Li$^+$ ions. This is contrasted with the measured change in absorbance at 700 nm, which indicates the formation of Ti$^{3+}$. The absorbance was measured before, during, and after the three second application of voltage until a steady state absorbance was reached. Following the application of potential, the electrode was washed, dried, and allowed to rest overnight before any photoelectrochemical measurements were recorded. It can be clearly seen that the photocurrent rises sharply as the potential is increased from -1.0V to -1.2V vs. Ag/AgCl before reaching a plateau from -1.25V to -1.7V vs. Ag/AgCl. The plateau suggests that although more negative potentials reduce more—and presumably, deeper—Ti$^{4+}$ trap sites, these deeper trap sites do not have a significant effect on the collection of photogenerated charges. The sharp initial rise, on the other hand, suggests that the more easily-reduced shallow traps do have a significant effect, and their reduction prevents them from trapping electrons. Based on these results, it can be concluded that the intercalation of Li$^+$ ions in conjunction with reduction of Ti$^{4+}$ sites suppresses electron trapping and increases electron collection.
Figure 2.8: This is a figure showing the photocurrent measured versus the negative potential applied to intercalate Li\(^+\) ions (red line, left axis) and the measured steady-state absorbance at 700 nm corresponding to reduced Ti\(^{4+}\) sites. A plateau is seen at relatively low concentrations of Ti\(^{3+}\) sites, indicating that deep traps do not play a significant role in photocurrent generation.

To show that the increase in photocurrent is due to an increase in collected charges, photocurrent action spectra were recorded using the Li\(^+\) and H\(^+\) intercalated nanotube arrays. Incident Photon to Charge carrier Efficiency (IPCE) is a measure of how efficiently incident photons are converted to collected electrons. IPCE is calculated according to Equation 2.4, where \(i_{SC}\) refers to the measured short circuit current in mA/cm\(^2\), \(\lambda\) is the wavelength of the incident light, and \(I_{inc}\) is the power of the incident light in mW/cm\(^2\):

\[
IPCE(\%) = \frac{1240i_{SC}}{\lambda I_{inc}} \times 100\% 
\]

Equation 2.4

It is expected that no photocurrent will be measured for wavelengths with energy less than the band gap of the active material. It is also important to emphasize here that
IPCE measurements should be made using a two-electrode system and should be performed in the absence of any external bias. While it is fashionable to apply bias during IPCE measurements to achieve higher efficiencies, the application of bias greatly increases electron-hole separation, which artificially inflates measured efficiencies, and the electrons pushed into the system by the potentiostat to provide the bias are not reliably accounted for. By the same token, IPCE measurements should never use a reference electrode. With a reference electrode, the potentiostat will again be pushing electrons into the photoelectrochemical system to ensure that a potential is held.

As can be seen in Figure 2.9, the onset of photocurrent occurs at 380 nm (3.2 eV) for all samples before and after the intercalation of Li\(^+\) or H\(^+\). The maximum efficiency increases by approximately 3.5 times from 12% to 42% for the Li\(^+\) ion intercalated nanotube array. The maximum efficiency of the H\(^+\) intercalated array can be seen to increase by just over two times compared to the pristine sample (15% to 34%). It can be concluded that intercalation of Li\(^+\) does not alter the band gap of TiO\(_2\) and the increase in photocurrent is due to the stabilization of Ti\(^{3+}\) sites.
Figure 2.9: IPCE measurements (a) before and (b) after Li$^+$ and H$^+$ intercalation (left and right, respectively). These measurements demonstrate that the ion intercalation does not alter the band gap of the TiO$_2$ nanotube arrays and does increase charge collection.

To better elucidate the mechanism by which the intercalation of cations led to an increase in photocurrent, the open circuit potential steady state and decay characteristics were monitored. First, the open circuit potential was allowed to equilibrate under band gap excitation. Once equilibrium was achieved, the light was turned off, and the open circuit potential was allowed to decay. The rate of decay of the open circuit potential from its illuminated steady state value provides insight into how quickly recombination occurs at the working electrode. The rate of decay is a measure of the recombination of electrons on the working electrode with both the electrolyte and adsorbed species like oxygen. Figure 2.10 shows the open circuit potential of pristine and Li$^+$ ion intercalated TiO$_2$ nanotube arrays in the presence and absence of oxygen versus time under band gap illumination and decaying away in the dark. It is clear from the traces that the intercalation of Li$^+$ ions increases the open circuit potential and significantly decreases the rate of recombination as evidenced by the much slower decay. The open circuit
Figure 2.10: Open circuit potential time profile for TiO$_2$ nanotube arrays before (a, b) and after (c, d) intercalation of Li$^+$ ions in (a, c) air-saturated and N$_2$-saturated 1M KOH electrolyte. Li$^+$ ion intercalation results in a slightly more negative OCP and much longer electron lifetime under N$_2$. In air, the Li$^+$ ion intercalated TiO$_2$ nanotubes show much faster recombination, evidence that electrons are in the conduction band of TiO$_2$, not trap sites.

Potential measurements in the presence of oxygen also reveal how readily oxygen scavenges electrons from TiO$_2$, with or without intercalation of cations. The fact that the open circuit potential shifts more positive in air after the intercalation of Li$^+$ ions suggests that electrons are being scavenged from the conduction band of TiO$_2$, where the reaction occurs much readily, rather than the Ti$^{4+}$ trap sites, where electrons are known to have very long lifetimes. The slower decay with Li$^+$ intercalation under a nitrogen atmosphere suggests that the intercalation of Li$^+$ ions slows recombination with both the electrolyte and with trapped holes on TiO$_2$.

Bisquert and co-workers$^{193}$ derived a simple expression, written in Equation 2.5, to describe the recombination of conduction band, shallow trap, and deep trap electrons...
Figure 2.11: Electron lifetimes calculated (See Equation 2.6) at each open circuit potential decay point before (a, b) and after (c, d) Li⁺ ion intercalation in (a, c) air equilibrated and (b, d) N₂-purged 1M KOH electrolyte. Note that both the calculated lifetime and the potential at which that lifetime exists are both important parameters. Longer lifetime at a more negative potential is the best result.

with adsorbed species like O₂ or the electrolyte, where $k_B$ is Boltzmann's constant, $T$ is the temperature in degrees Kelvin, $e$ is the elementary charge of an electron, and $V_{OC}$ is the open circuit potential at a given time $t$:

$$
\tau = \frac{k_B T}{e} \left( \frac{dV_{OC}}{dt} \right)^{-1}
$$

Equation 2.5

This slowed recombination rate is clear in Figure 2.11, which shows the calculated electron lifetime versus the measured open circuit potential. Two observations can be made from the electron lifetime plots in Figure 2.11. First, the electron lifetime is significantly shorter when oxygen is present for both pristine and Li⁺ ion intercalated TiO₂ nanotube arrays. Second, Li⁺ ion intercalation increases the electron lifetime by an
order of magnitude for a TiO$_2$ nanotube array under nitrogen. This indicates that the stabilization of the Ti$^{3+}$ sites decreases recombination in the TiO$_2$ nanotube array.

2.5 Conclusions

The work discussed in this chapter describes how manipulation of surface trap sites in TiO$_2$ can have a significant impact on its photoelectrochemical performance. The number of trap states in a TiO$_2$ nanotube array was reduced by application of a negative potential (-1.5V vs. Ag/AgCl) in the presence of a suitably small cation like H$^+$ or Li$^+$. The intercalation of these ions stabilized the Ti$^{3+}$ sites. IPCE experiments demonstrated that this intercalation of Li$^+$ and H$^+$ was not a doping effect as the wavelength of the onset photocurrent remained the same. Photocurrent measurements showed an increase in photocurrent generation, and open circuit potential decay measurements revealed that this increase in photocurrent was attributable to a decrease in the rate of recombination of photogenerated electrons on TiO$_2$. A small shift in the Fermi level as determined from both open circuit potential and current-voltage measurements confirmed that the intercalation of the Li$^+$ and H$^+$ slows recombination in the TiO$_2$ nanotube array electrode.

Chapter 3 discusses a different method of manipulating interfaces to increase photoelectrochemical performance. Instead of altering the properties of the TiO$_2$ nanotube array, a second wide band gap semiconductor with more negative valence and conduction bands is deposited in such a way that an intimate connection is made between the two semiconductors. The effects of such an interface are described in detail with respect to photovoltaics and hydrogen generation.
CHAPTER 3:

IMPROVED PHOTOVOLTAIC PERFORMANCE AND HYDROGEN GENERATION WITH SRTIO$_3$-TIO$_2$ HETEROSTRUCTURES

Separation of photogenerated electron-hole pairs is vital to achieving high conversion efficiencies in solar cells. In the previous chapter, this was accomplished by reducing the number of potential trap sites with the application of a strong, short negative potential, which decreased the number of electrons that were trapped and subsequently recombined with the electrolyte, oxygen, or trapped holes. In the work presented in this Chapter, the efficient separation of photogenerated electrons and holes was accomplished by using a second wide band gap metal oxide semiconductor, SrTiO$_3$, deposited using pulsed laser deposition (PLD). The synthesis of the heterojunction and its effect on photoelectrochemical performance and hydrogen generation is discussed.

3.1 Introduction

It is well-known that band gap offset can be utilized to drive electron injection from one semiconductor to another semiconductor. Typically, a visible-region absorbing semiconductor is deposited on a wide band gap semiconductor.$^{15, 21, 30-31, 33, 36-37}$ In this Chapter, however, SrTiO$_3$ was deposited on TiO$_2$ nanotubes to improve the photoelectrochemical performance, as demonstrated by improved photovoltaic
characteristics and increased hydrogen generation. SrTiO3 is a wide band gap (3.2 eV) semiconductor that has been used in a variety of applications, including water splitting, as a dielectric material in capacitors, and as a substrate for solar cells. Its conduction band lies at approximately -0.3V vs. NHE, 100 mV more negative than the conduction band of TiO2. It has been demonstrated that a SrTiO3-TiO2 nanotube array composite generates a larger photovoltage than TiO2 nanotubes alone. This increase in photovoltage was attributed to the more negative conduction band of SrTiO3. The hydrothermal synthesis method used in that research, however, caused a decrease in measured photocurrent as the underlying TiO2 backbone was consumed in the hydrothermal reaction. To counter this consumption of the TiO2 nanotube array, a new method to deposit SrTiO3 was developed that creates a heterojunction of the two wide band gap semiconductors without causing the deterioration of the underlying substrate.

Pulsed laser deposition is a technique that allows deposition of solid material onto a chosen substrate by vaporizing the target material in a controlled atmosphere chamber. The rate of deposition is determined by the parameters chosen for deposition, including laser power, laser repetition rate, the target material, the pressure of the deposition chamber, and the gas used for backfilling. The backfilling gas can be used to perform reactive deposition by controlling both the type of gas and back pressure used. When the target is struck by the laser, the solid material is instantly vaporized and rises through the near-vacuum to the substrate, which is suspended a few centimeters above the target. Both the target material and substrate can be rotated during deposition to
ensure the formation of an even film. The substrate can also be heated during deposition to increase crystallinity of the material being deposited. 201, 205

For the experiments described in this chapter, SrTiO$_3$ was deposited using a KrF laser (248 nm) with a laser fluence of 120 J operating at a repetition rate of 20 Hz in oxygen backfilled to a pressure of 75 mTorr. The deposition rate was empirically determined to be 31 nm per second by SEM cross-sectional measurements.

TiO$_2$ nanotubes were synthesized by a common electrochemical anodization method. 173 In brief, a piece of Ti metal foil (5 cm by 0.8 cm) was immersed in 0.27M NH$_4$F in 2/98 vol% water/ethylene glycol. 60 V were applied for 1 hour, resulting in nanotubes about 5 microns in length. After anodization, the TiO$_2$ nanotube array samples were sonicated for 5 seconds in ethanol and dried. The nanotube arrays were then annealed at 450 ºC for 3 hours to convert the amorphous TiO$_2$ to the anatase phase.

Photoelectrochemical measurements were performed in 1M KOH unless otherwise noted. Platinum mesh was used as a counter electrode with Ag/AgCl (sat. KCl) as the reference. All electrolyte solutions were bubbled for at least 30 minutes before measurements began, and a nitrogen blanket was maintained at all times by flowing nitrogen just over the top of the electrolyte. Samples were illuminated with a 300W Xe lamp with an AM 1.5 filter, and the samples were placed such that the measured incident power was 100 mW/cm$^2$.
3.2 SrTiO₃ Layer Thickness and Its Effect on Photovoltaic Performance

In a previous study, increasing the amount of SrTiO₃ on the photoanode was found to increase the measured photovoltage. The nominal thickness of the SrTiO₃ layer deposited on the TiO₂ nanotube array samples was controlled by the time of deposition. SrTiO₃ was deposited in a continuous fashion for 1, 2, 5, 10, and 15 minutes. This corresponds to nominal film thicknesses of 31, 62, 155, 310, and 465 nm. After deposition of the SrTiO₃, the samples were annealed at 450 °C for 3 hours. It is important to note that this step was required to observe any increase in photocurrent or photovoltage. Samples that were submerged in the 1M KOH electrolyte used for photoelectrochemical measurements and subsequently annealed showed no improvement over the baseline TiO₂ nanotube array. The reason for the lack of improvement is unclear, but the presence of K⁺ from the electrolyte, even after washing with DI water, may have played a role in disrupting the crystalline structure of the SrTiO₃ film during the annealing step. Figure 3.1 shows scanning electron microscopy (SEM) images of the SrTiO₃ layer deposited on a TiO₂ nanotube array using the PLD technique. These images reveal that the SrTiO₃ layer is not formed as a continuous layer but rather as a series of discontinuous islands. As the deposition time increases, the islands grow larger and finally connect. The images also show that the SrTiO₃ layer is made up of small crystalline particles. It can also be seen from Figure 3.2 that the SrTiO₃ layer does deposit inside of the nanotubes, although the depth of deposition appears to be shallow.
**Figure 3.1:** SEM pictures showing TiO$_2$ nanotube arrays with A) 0 nm, B) 31 nm, C) 62 nm, D) 155 nm, E) 310 nm, and F) 465 nm of SrTiO$_3$ deposited. It is clear from these images that the SrTiO$_3$ is discontinuous at lower nominal thicknesses and becomes a more continuous layer only at greater thicknesses.

**Figure 3.2:** SEM profile images of TiO$_2$ nanotube arrays A) without and B) with SrTiO$_3$ deposited. It is clear from B that the SrTiO$_3$ is capable of penetrating approximately 500 nm into the nanotubes.
Figure 3.3A shows how measured photocurrent changed with increasing SrTiO$_3$ layer thickness. A sharp increase is seen as the layer grows to 155 nm, with a small decline observed as the SrTiO$_3$ layer thickness increases to 465 nm. This suggests that a relatively thin SrTiO$_3$ layer will enhance charge separation while a thicker layer will absorb too much of the incident light, leading to high recombination rates within the SrTiO$_3$ layer. Given that the layer grew largely on top of the TiO$_2$ nanotube array (though some deposition inside the tubes is observed), this improvement in photocurrent also suggests that if the SrTiO$_3$ film could be grown in such a way that it covers the entire nanotube array, rather than just the top of the nanotubes, higher photocurrents are feasible. Open circuit potential measurements, shown in Figure 3.3B, also show improvement in the SrTiO$_3$-TiO$_2$ nanotube array heterostructure compared to TiO$_2$ nanotubes alone. Nearly 300 mV of additional open circuit potential is observed for the SrTiO$_3$-TiO$_2$ heterostructure under UV illumination. The photovoltage reaches a maximum at a SrTiO$_3$ layer thickness of 155 nm, the same thickness that corresponded to the best photocurrent generation.

To elucidate how the SrTiO$_3$ layer contributed to the increase in photocurrent, open circuit potential decay measurements were performed. The open circuit potential was first allowed to reach an equilibrium under AM1.5 illumination. Then, the illumination was stopped, and the decay of the open circuit potential was recorded. The electron lifetime could then be calculated as described in Chapter 2 using Equation 2.6. Calculated electron lifetimes are plotted in Figure 3.4 and show that the presence of the SrTiO$_3$ layer increases the electron lifetime—or, put another way, decreases the
Figure 3.3: A) Current density (at 0 V vs. Ag/AgCl) of SrTiO$_3$-TiO$_2$ nanotube array heterostructures with increasing SrTiO$_3$ film thickness. A maximum is observed at a film thickness of 155 nm. For SrTiO$_3$ layers thicker than 155 nm, a smaller increase in photocurrent is seen. B) Maximum open circuit potential for increasing SrTiO$_3$ film thickness. A sharp increase is seen for film thickness of 31 and 62 nm, with a plateau reached beginning at 155 nm thickness.

recombination rate—by at least an order of magnitude at all potentials. The greatest improvement in electron lifetime is observed at 155 nm. This improvement in electron lifetime confirms that the increase in photocurrent is attributable to improved charge separation in the SrTiO$_3$-TiO$_2$ nanotube array heterostructure. It is important to note that the SrTiO$_3$ layer alone, deposited under identical conditions onto a clean Ti foil and annealed at the same temperature as the layers deposited onto TiO$_2$ nanotube arrays, gave negligible photocurrent and photovoltage. Accordingly, the increase in photocurrent is not an additive result of the individual components of the heterostructure, and the increase in photovoltage is a result of the SrTiO$_3$ being able to inject electrons into the TiO$_2$ nanotube array.
Incident photon to charge carrier efficiency (IPCE) measurements were performed with a Xe lamp passed through a monochromator, with wavelengths stepped from 300 nm to 800 nm. Cutoff filters were used to prevent error from wavelength doubling. A Si cell with known current to power characteristics was used as a reference to account for differences in power at each wavelength. The IPCE experiments confirm that the increase in photocurrent is due to an increase in charge separation, not doping. Photocurrent onset occurs at 380 nm, corresponding to a band gap of about 3.2 eV. Figure 3.5 shows that the maximum IPCE increases about 50% when a 155 nm layer of SrTiO₃ is deposited as compared to the baseline measurement. The fact that the photocurrent onset occurs at the same wavelength also confirms that there is no doping effect from the pulsed laser deposition. The increase in photocurrent observed is due to an increase in charge separation as electrons migrate to the TiO₂ nanotube array and holes migrate to the SrTiO₃ layer.
Figure 3.5: A representative plot showing calculated (see Equation 2.6) electron lifetime for a) TiO₂ nanotube array alone and b) with 155 nm SrTiO₃ deposited. It is clear that not only is a more negative open circuit potential observed, but the electron lifetime is approximately an order of magnitude longer in the SrTiO₃/TiO₂ heterostructure at all potentials. A similar trend of longer electron lifetime in the SrTiO₃/TiO₂ heterostructure was observed for all SrTiO₃ layer thickness with 155 nm resulting in the greatest increase.

In addition to depositing SrTiO₃ on TiO₂ nanotube arrays, TiO₂ nanoparticle films
were also utilized as substrates. TiO$_2$ is widely used as a solar cell substrate, but the increase in photovoltage that SrTiO$_3$ can provide would increase the efficiency of those cells.

A QDSC was constructed using the SrTiO$_3$-TiO$_2$ nanotube heterostructure to elucidate the ability of the heterostructure as a solar cell substrate. CdS nanoparticles were deposited by the Successive Ionic Layer Adsorption and Reaction (SILAR) method directly onto the SrTiO$_3$-TiO$_2$ nanotube heterostructure. The Cd$^{2+}$ precursor solution was an aqueous 0.1M CdSO$_4$ solution. The S$^{2-}$ precursor solution was 0.1M Na$_2$S in 50/50 vol% methanol/water. CdS was deposited by a dipping method where each cycle consisted of the following: 1 minute in the Cd$^{2+}$ solution, a wash with water, 1 minute in the S$^{2-}$ solution, and a final wash with water. A greater number of cycles resulted in greater CdS particle growth—from quantized particles to near-bulk particles. To compare the effect of the SrTiO$_3$ layer on the QDSC performance, 6 cycles of CdS were deposited onto both a pristine TiO$_2$ nanotube array and a SrTiO$_3$-TiO$_2$ nanotube heterostructure, and the photovoltaic characteristics of each QDSC were measured after each cycle of CdS deposition. Photoelectrochemical measurements were carried out using 0.1M Na$_2$S electrolyte with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference.

Figure 3.6A summarizes this photovoltaic performance for each cycle from 0 to 6 cycles. From the 3rd cycle on, a significant increase is seen for the CdS-SrTiO$_3$-TiO$_2$ electrode as compared to the CdS-TiO$_2$ nanotube electrode. This suggests that the cascading conduction bands of the three semiconductors enables efficient shuttling of
electrons to the back contact while holes are shuttled to the electrolyte. Figure 3.6B shows calculated electron lifetimes for CdS-SrTiO₃-TiO₂ and CdS-TiO₂ electrodes. The electron lifetime is an order of magnitude greater for the CdS-SrTiO₃-TiO₂, which demonstrates that the SrTiO₃-TiO₂ nanotube heterostructure slows recombination, mirroring the observed slower decay in the SrTiO₃-TiO₂ heterostructure by itself.

![Figure 3.6: A) Photocurrent density for increasing number of CdS SILAR cycles (a) without SrTiO₃ and (b) with 155 nm SrTiO₃. As the amount of CdS increases, approximately 50% greater photocurrent is observed for the CdS/SrTiO₃/TiO₂ heterostructure. B) Calculated electron lifetimes for 1 cycle of CdS (a) on a TiO₂ nanotube array and (b) on a SrTiO₃-TiO₂ nanotube array heterostructure. The calculated lifetime is an order of magnitude greater in the SrTiO₃-TiO₂ heterostructure.](image)

3.3 Hydrogen Generation

A more negative open circuit potential means that more energetic electrons are being produced at the working electrode. It is expected that this increased reduction capability should lead to the formation of more hydrogen gas in a photoelectrolysis system. Along the same lines, an increase in photocurrent means that more
photogenerated electrons are being captured and passed through the external circuit, which should in turn also result in more formation of hydrogen. These assumptions were tested by performing photoelectrolysis of 1M KOH solution in a two-electrode configuration.

A custom-made glass H-cell was used for these experiments. Figure 3.7 shows a diagram of the cell. The fittings were all airtight, and the gas was collected in a bulb above the counter electrode. A platinum mesh was used as the counter electrode, and the entire cell was purged with argon for a minimum of an hour to remove other gases from the system. 10 µL gas samples were collected using a gas-tight 50 µL syringe and measured using a Thermo Fisher Trace GC Ultra with a 30 meter, 0.32 mm ID MS-5A column. The oven/column temperature was 50 °C, the inlet temperature was 200 °C, and the TCD block and transfer temperatures were 200 and 190 °C, respectively. Argon was the carrier, make-up, and reference gas. Column flow was set at 3 mL/min, reference flow was set at 30 mL/min, and make-up flow was set at 27 mL/min. The TCD signal (1x gain) was adjusted to 1000, per operating instructions, before each run to ensure reproducible results. A calibration curve was generated using the average of four samples each of 10, 20, and 30 µL of a 5/95 vol% H₂/N₂ gas mix. The peak corresponding to hydrogen was observed at approximately 2.3 minutes after starting the measurement. Accordingly, the amount of hydrogen in each sample was determined by integrating the area under this peak and fitting them on the calibration curve.
Figure 3.7: Schematic of the H-cell used for the hydrogen generation experiments. All fittings were air-tight, and argon was bubbled through and above the electrolyte (1M KOH) for at least one hour before any experiments were carried out. Hydrogen gas was evolved at the platinum mesh counter electrode and measured by gas chromatography.

Hydrogen generation experiments were recorded with a positive bias of 0.5V. The total charge that was passed through the external circuit can be calculated by integrating the area under the transient photocurrent measured, according to Equation 3.1:

\[ Q = \int I \, dt \]  

Equation 3.1

where \( Q \) is the total charge passed, \( I \) is the photocurrent measured, and \( t \) is the time. From the calculated total charge, it is then possible to calculate the amount of hydrogen that should be produced, assuming 100% Faradaic efficiency:

\[ mols \, H_2 = \frac{Q}{nF} \]  

Equation 3.2
where $F$ is Faraday's constant (96485 C/mol e$^-$) and $n$ is the number of electrons needed to form one molecule of hydrogen ($n = 2$). The transient photocurrent under irradiation by a Xe lamp with an infrared water filter (10 cm) and AM1.5G filter is shown in Figure 3.8A. The active area of both the SrTiO$_3$-TiO$_2$ nanotube heterostructure and TiO$_2$ nanotube array was 2 cm$^2$ (2.5 cm by 0.8 cm). It is clear that the SrTiO$_3$-TiO$_2$ heterostructure produced more photocurrent. For both the SrTiO$_3$-TiO$_2$ heterostructure and the TiO$_2$ nanotubes alone, bubbles could be clearly seen to evolve from the platinum counter electrode upon irradiation. The amount of hydrogen actually evolved, as measured by gas chromatography, is shown in Figure 3.8B along with the predicted amount based on the photocurrent measured. The Faradaic efficiency for both samples is low—approximately 20% for the SrTiO$_3$-TiO$_2$ heterostructure and 9% for the TiO$_2$ nanotube array alone. One possible reason for the low Faradaic efficiency is that some of the evolved hydrogen remained in the solution. The solubility of hydrogen in a 1M KOH aqueous solution is approximately 0.542 µmol per mL.$^{206}$ 30 mL of electrolyte was used, so the maximum amount of hydrogen that could have remained in solution is approximately 16.25 µmol. Based on the photocurrent that was measured, approximately 45 µmol of evolved hydrogen was expected for the SrTiO$_3$-TiO$_2$, and 35 µmol of evolved hydrogen was expected for the TiO$_2$ nanotube array. If in fact 16.25 µmol of hydrogen was in the electrolyte, the Faradaic efficiencies of both the SrTiO$_3$-TiO$_2$ heterostructure and TiO$_2$ nanotube array increase to approximately 58% and 55%, respectively.
Figure 3.8: A) Measured photocurrent during photoelectrolysis of 1M KOH using (a) TiO2 nanotube array and (b) 155 nm SrTiO3 on TiO2 nanotube array. The applied bias was 0.5V in a two electrode system, and the area of both electrodes was 2 cm². B) Hydrogen evolution measured by gas chromatography from (a) TiO2 nanotube array and (b) SrTiO3-TiO2 nanotube heterostructure. The solid lines represent the expected hydrogen evolution based on the photocurrent measured for (a') the TiO2 nanotube array and (b') the SrTiO3-TiO2 nanotube heterostructure.

3.4 Conclusions

In this chapter, the synthesis by pulsed laser deposition of a SrTiO3-TiO2 nanotube array heterostructure that produced both higher photocurrent and higher photovoltage was described. Maximum photoelectrochemical performance was observed at a SrTiO3 film thickness of 155 nm, and open circuit photovoltage decay and IPCE experiments confirmed that the increase in photovoltage and photocurrent was attributable to an increase in charge separation (and thus a decrease in recombination rate) and not a doping effect. The SrTiO3-TiO2 heterostructure synthesized by pulsed laser deposition has better performance compared to the hydrothermal synthesis because the TiO2 nanotube backbone is preserved. The SrTiO3-TiO2 nanotube heterostructure
also exhibited better photoelectrochemical performance when used in a SILAR-deposited QDSC and in a photoelectrolysis device. In the QDSC, an increase in photocurrent was observed for the SrTiO$_3$-TiO$_2$ heterostructure as compared with a pristine TiO$_2$ nanotube array. In the photoelectrolysis device, the increase in both photocurrent and photovoltage observed with the SrTiO$_3$-TiO$_2$ heterostructure resulted in a higher rate of hydrogen generation from a 1M KOH solution.

While Chapters 2 and 3 focused on the photocatalyst and how it can be altered to improve performance, high-efficiency photoelectrolysis will only become a reality with suitable co-catalysts that reduce the overpotentials of each half-reaction, especially the oxygen evolution reaction. Chapter 4 details work that focused on the interaction of a well-known OER catalyst, IrO$_2$, and a well-known photocatalyst, TiO$_2$. The interfacial relationship was studied through absorption spectroscopy and pulse laser photolysis, and a surprising side-reaction was observed that had not been previously reported.
CHAPTER 4:
THE ROLE OF IRIDIUM DIOXIDE IN MEDIATING HOLE TRANSFER FROM
TITANIUM DIOXIDE DURING WATER PHOTOLYSIS

Chapters 2 and 3 focused on the photocatalysts used in solar cell and hydrogen generation applications. The research presented in those chapters dealt with the manipulation of the photocatalysts and elucidating the source of the photovoltaic improvements observed in both cases. Photocatalytic water splitting, however, relies on the use of co-catalysts to enhance the hydrogen and oxygen evolution reaction rates. This chapter discusses the interaction of a common and well-understood photocatalyst, TiO₂, and a heavily-studied oxygen evolution catalyst, IrO₂, in a photocatalytic system. While IrO₂ is fairly well understood in an electrochemical setting, its role in a photocatalytic system is not as well-defined. The results detailed here elucidate the role of IrO₂ as a hole transfer mediator and also reveal an unexpected side reaction that has important implications on the use of IrO₂ in a photoelectrolysis device.

4.1 Introduction

Most work on photocatalytic water splitting has focused the development of new semiconductors or sensitization schemes to utilize the visible region of the solar spectrum. Little work, however, has focused on the co-catalysts used to improve the rate
of the oxygen evolution reaction. As discussed in Chapter 1, for photoelectrolysis to proceed at any kind of reasonable rate, the oxygen evolution rate must be maximized. The use of co-catalysts with photocatalysts is the primary method by which this can be accomplished. IrO$_2$ is the best oxygen evolution catalyst with an overpotential for oxygen evolution of just 150 mV as well as stability across a wide range of pHs.\textsuperscript{119, 121-122, 143, 207} In purely photocatalytic applications, however, the efficacy of IrO$_2$ as a co-catalyst is questionable. Ye and co-workers\textsuperscript{150} used a combinatorial approach to test multiple co-catalysts and observed that IrO$_2$ did not improve photocurrent generation. In other studies where IrO$_2$ is used as a co-catalyst with a photocatalyst, an external bias is applied in addition to the photogenerated bias. The external bias makes it difficult to determine how effective IrO$_2$ is as a co-catalyst in a photo-driven system. Accordingly, the work presented in this Chapter sought to elucidate the role of IrO$_2$ in a purely photocatalytic system.

4.2 Spectroscopic Characterization of Trapped Holes on TiO$_2$ Colloidal Particles

Trapped holes on TiO$_2$ exhibit a characteristic absorbance peak at 360 nm.\textsuperscript{182} By tracking the formation and disappearance of this absorbance, it is possible to follow the transfer of the trapped holes from TiO$_2$. TiO$_2$ colloids typically only exhibit trapping of electrons in ethanol solutions under UV illumination as Ti$^{4+}$ is photoreduced to Ti$^{3+}$ and the photogenerated holes are scavenged by the ethanol.\textsuperscript{186} By synthesizing the TiO$_2$ colloids in the presence of a small amount of acetic acid, however, trapping of holes can also be achieved. These trapped holes are oxygen anion radicals bound covalently to Ti$^{4+}$.
ions as Ti$^{IV}$-O-Ti$^{IV}$-O. 208-209 Electron paramagnetic resonance (EPR) studies have shown that the trapped holes exist as an association with alcoholic groups. 210-211 The EPR studies revealed a quintet signal that was attributed to the formation of Ti-O-Ti-OCHCH$_3$ on the TiO$_2$ surface. The formation and trapping of electrons and holes proceeds according to Reactions 4.1-4.4:

\begin{align*}
TiO_2 & \rightarrow TiO_2(e - h) \quad \text{Reaction 4.1} \\
TiO_2(e - h) & \rightarrow TiO_2(e) + TiO_2(h) \quad \text{Reaction 4.2} \\
TiO_2(e) & \rightarrow TiO_2(e_t) \quad \text{Reaction 4.3} \\
TiO_2(h) & \rightarrow TiO_2(h_t) \quad \text{Reaction 4.4}
\end{align*}

Under band gap excitation in air atmosphere, TiO$_2$ colloids synthesized in the 5/95 vol% acetic acid/ethanol solution exhibit a yellow color. This yellow color is persistent in air over the course of several hours. Band gap UV illumination under nitrogen atmosphere produces a green color in the TiO$_2$ colloidal solution. Figure 4.1 shows absorbance spectra corresponding to trapped holes, trapped electrons, and both trapped holes and electrons on the TiO$_2$ colloids formed after UV illumination. Spectrum $a$ shows an absorption feature at around 360 nm, which is attributed to trapped holes due to its stability in air, and a second broad absorption feature through the visible and near-infrared regions corresponding to trapped electrons. The broad absorption in the visible and near-infrared regions disappears upon exposure to air, confirming that it is attributable to trapped electrons, and only the 360 nm absorbance feature is left behind (Spectrum $b$). Spectrum $c$ shows the broad visible region absorption from electrons that are trapped on TiO$_2$ colloids synthesized in a pure ethanol solution, providing further
evidence that the 360 nm absorbance is due to the trapped holes. It is also important to note that the stability of the trapped holes in the ethanol solution means that the trapped holes have less oxidizing power than valence band holes.

**Figure 4.1**: Absorbance spectra of 16 mM TiO₂ colloids (a) in deaerated 5/95% acetic acid/ethanol solution following UV illumination, (b) after allowing the solution from trace a to equilibrate with air, and (c) in deaerated ethanol solution after UV illumination. TiO₂ colloids synthesized in the presence of acetic acid will trap holes that are stable in air and give the yellow color seen. The green color of (a) is the combination of the yellow from the trapped holes and the characteristic blue color corresponding to trapped electrons.

Trapped electrons on TiO₂ are well studied, and it is known that several electrons can be stored on a single TiO₂ colloid. An extinction coefficient of 760 M⁻¹cm⁻¹ has been calculated for the trapped electrons.⁸⁶ Although the trapped holes are not as strong an oxidant as the holes in the valence band, they are an important piece of the overall oxidation scheme, and previous work has shown that trapped holes are formed on TiO₂ during water photolysis.¹¹² As such, their role in water splitting must be considered, and the ability to track the trapped holes via absorption spectroscopy can help elucidate the role that IrO₂ plays as an oxygen evolution catalyst.
IrO₂ colloids were synthesized by hydrolysis of IrCl₆²⁻ using a method refined by Mallouk and co-workers.²¹³ An aqueous solution of K₂IrCl₆ was heated to 90 °C and adjusted to pH 13 with KOH while stirring the solution. After heating the solution for 30 minutes, a blue color was observed, signaling the formation of IrO₂. The solution was cooled to room temperature and placed in an ice bath. After further cooling in the ice bath, nitric acid was added while stirring to quickly bring the pH of the solution to 1. It should be noted that the ice bath is required to prevent precipitation of the IrO₂ colloids due to aggregation as the pH changes from 13 to 1. As can be seen in Figure 4.2, this synthesis produces IrO₂ colloidal particles that are approximately 2 nm in diameter.

Figure 4.2: (Left) Transmission electron microscopy (TEM) image of a grouping of 2 to 3 nm diameter IrO₂ nanoparticles. (Right) TEM image of a representative IrO₂ nanoparticle showing the diameter of the as-synthesized particles to be about 2 nm.

4.3 Characterization of Hole Transfer from TiO₂ to IrO₂

Quantitative information was gathered by utilizing the iodide oxidation reaction. The iodide ions were able to titrate the trapped holes on TiO₂ and form tri-iodide. The
oxidation of I- by semiconductors\textsuperscript{214} as well as by sonolysis\textsuperscript{215} is documented and occurs by the pathways shown in Reactions 4.5 and 4.6:

\[
\begin{align*}
I^- + h_t & \rightarrow I^- (\text{I}^-) \rightarrow I_2^- \quad \text{Reaction 4.5} \\
2I_2^- & \rightarrow I_3^- + I^- \quad \text{Reaction 4.6}
\end{align*}
\]

The iodide radical formed by scavenging the trapped holes quickly reacts with another iodide anion to form I$_2^-$ radical. Two of these radicals can then react to form a tri-iodide anion. More detailed information on the formation and breaking of the I-I bond can be found elsewhere.\textsuperscript{216} Based on Reactions 4.5 and 4.6, the formation of each I$_3^-$ species corresponds to the consumption of two trapped holes on TiO$_2$.

Figure 4.3A shows the absorbance spectra before and after band gap excitation of the TiO$_2$ colloids in 5/95 vol\% acetic acid/ethanol solution. As the TiO$_2$ is photoexcited by the UV illumination, holes are trapped and the peak at 360 nm appears (spectrum b). After the appearance of the 360 nm peak, a known quantity of KI solution (170 µL, 60 mM) was added to the TiO$_2$ colloidal solution, bringing the total volume of the solution to 3.17 mL. Spectrum b' shows the appearance of a peak corresponding to the formation of I$_3^-$. Although this new absorbance feature is spectrally similar to the peak attributed to the trapped holes, the peaks are separated by approximately 15 nm. The position of the I$_3^-$ peak was also confirmed by chemical oxidation of I$^-$ with H$_2$O$_2$. The formation of I$_3^-$ when KI is added to the TiO$_2$ solution with trapped holes proves that the hole trap sites are oxidative.
Figure 4.3: A) Absorbance spectra of TiO$_2$ colloids (a) before and (b) after UV illumination. Spectra a' and b' show the absorbance after the addition of I$^-$ to the TiO$_2$ colloidal solutions from spectra a and b. The peak of spectrum b', though similar to the peak of spectrum b, is due to the formation of I$_3^-$.

B) A plot of the absorbance due to the trapped holes at 360 nm versus the calculated hole concentration (based on Reactions 4.5 and 4.6). The extinction coefficient is calculated from the linear fit of this plot according to Equation 4.1.

The ability of the trapped holes to oxidize I$^-$ also allows for the quantitative determination of the concentration of trapped holes that are stored on the TiO$_2$ colloids upon UV illumination. To calculate the concentration of trapped holes, TiO$_2$ colloidal solution were illuminated for times ranging from 0 to 7 minutes in 1 minute intervals. After excitation, the absorbance of the TiO$_2$ colloidal solution was measured. A known amount of KI (170 µL, 60 mM) was then added, and the solution was allowed to equilibrate for 1 minute to ensure that all holes were reacted with I$^-$.

The absorbance was then measured again. Figure 4.3B shows the relationship between the trapped hole absorbance and the concentration of trapped holes as calculated from the concentration of I$_3^-$ (see Reactions 4.5 and 4.6). A clear linear trend is observed, and from the slope of the
plot, the extinction coefficient of the trapped holes can be determined using Beer's Law, where $A$ is the measured absorbance, $l$ is the path length of the cell, $C$ is the concentration of the species absorbing the light, and $\varepsilon$ is the extinction coefficient:

$$A = \varepsilon Cl$$  \hspace{1cm} \text{Equation 4.1}

Based on the slope, the extinction coefficient of the trapped holes was found to be 11,220 M$^{-1}$cm$^{-1}$. Previous work has estimated the size of the TiO$_2$ colloids to be approximately 3 to 5 nm in diameter. Based on this diameter, it is possible to calculate the number of trapped holes per TiO$_2$ colloid as follows:

$$\frac{\text{#TiO}_2 \text{molecules}}{\text{TiO}_2 \text{ NP}} = \frac{4}{3} \pi r^3 \frac{\rho N_A}{M_W}$$  \hspace{1cm} \text{Equation 4.2}

$$MW_{anatase} = 79.88 \frac{g}{mol}$$  \hspace{1cm} \text{Equation 4.3}

$$\rho_{anatase} = 3.79 \frac{g}{cm^3}$$  \hspace{1cm} \text{Equation 4.4}

$$\#TiO_2 \text{ NPs} = \frac{[TiO_2] \times N_A}{\#TiO_2 \text{ molecules}}$$  \hspace{1cm} \text{Equation 4.5}

$$\frac{\# \text{holes}}{\text{TiO}_2 \text{ NP}} = \frac{[h^+] \times V_{initial} \times N_A}{\#TiO_2 \text{ NPs}}, V_{initial} = 3 mL$$  \hspace{1cm} \text{Equation 4.6}

Given the range of diameters expected for the TiO$_2$ colloidal nanoparticles and using Equations 4.2-4.6, the number of trapped holes on each TiO$_2$ particle is calculated to be between 1 and 3 during 7 minutes of UV illumination.

A TiO$_2$ colloidal solution was first irradiated in air in the absence of IrO$_2$ to build up trapped holes, as can be seen in Figure 4.4, spectrum $a$. Then, a known concentration of IrO$_2$ colloids were added to the TiO$_2$ and the absorbance was measured. Additional IrO$_2$ was added in known quantities until the absorbance at 360 nm reached a steady state. Figure 4.4, spectra $b$-$f$, shows how the absorbance changes with increasing
Figure 4.4: Absorption spectra of trapped holes on TiO$_2$ (obtained by UV irradiation of TiO$_2$ colloids in air) (b-f) after addition of IrO$_2$ to the colloidal solution (a). The concentrations of IrO$_2$ are (b) 0.04 mM, (c) 0.08 mM, (d) 0.12 mM, (e) 0.157 mM, and (f) 0.193 mM. (g) The absorbance spectrum of 0.193 mM IrO$_2$ with 16 mM in acetic acid/ethanol (without UV irradiation).

amounts of IrO$_2$. It can be seen that the peak decreases approximately 20%. This indicates that some holes are transferred to IrO$_2$, but an isoenergetic point is reached where no more holes will freely transfer. Once this steady state point was reached, the sample containing both TiO$_2$ with trapped holes and IrO$_2$ was again irradiated with UV light. The absorbance was checked in 1 minute intervals, and the absorbance was found to decrease continuously (see Figure 4.5B) with increasing times of UV irradiation until it completely disappears after 8 minutes. From these results, it is clear that IrO$_2$ has a significant role in transferring holes from TiO$_2$. It must also be noted that electrons generated during UV illumination are scavenged by oxygen in the system, as indicated by Reaction 4.7. Based on the observed decrease in absorbance in Figure 4.5B, it is suggested that reduced oxygen species are able to scavenge the trapped holes on TiO$_2$ through the mediation of IrO$_2$ as shown in Reaction 4.8.
Figure 4.5: A) Absorbance spectra of trapped holes following UV irradiation for (a) 2, (b) 6, and (c) 10 minutes of an aerated 16 mM TiO$_2$ colloidal solution. B) The decrease in absorbance corresponding to the trapped holes of the previously irradiated TiO$_2$ colloidal solution (Left, spectrum c) in the presence of 0.193 mM IrO$_2$ after UV irradiation for (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 minutes. The decrease is observed to be complete, with the only remaining absorbance attributable to the IrO$_2$ itself (see Figure 4.4, spectrum g).

\[
O_2 + e^- \rightarrow O_2^-
\]

\[
TiO_2(h_t) + O_2 \overset{IrO_2}{\rightarrow} TiO_2 + O_2
\]

The fact that the trapped holes are stable in air in the absence of IrO$_2$ rules out oxygen as a direct scavenger of the trapped holes on its own. It must also be noted that when TiO$_2$ colloids were irradiated in the presence of IrO$_2$ under a nitrogen atmosphere, both the trapped hole and trapped electron feature was observed, further confirming the need for both oxygen and IrO$_2$ to be present for Reactions 4.7 and 4.8 to proceed.

Although the ability of IrO$_2$ to transfer trapped holes from TiO$_2$ was demonstrated by the steady-state absorbance measurements, the rate at which this transfer occurs must also be determined to elucidate its potential role in photocatalytic water oxidation. This
was accomplished using nanosecond flash photolysis. Nanosecond flash photolysis is a pump-probe technique that involves exciting the sample with a laser pulse and tracking the change in absorbance for a period of time immediately after the pulse. Figure 4.6 is a diagram of the flash photolysis setup. In a typical experiment, the white light probe measures the absorbance of the sample in the ground state and is subsequently shuttered. Then, both the laser shuttle and white light probe shutter are opened. The laser pulse excites the sample, and the white light probes the excited state absorbance of the sample. This shuttering cycle constitutes one run. To generate a kinetic curve that was an accurate representation for the sample, an average of at least 5 runs was used in all transient absorption traces shown. Due to the stability of the trapped holes, a homemade system was used to stir the TiO$_2$ colloidal solution very slowly, ensuring that each run was targeting a new batch of colloids rather than building up trapped holes on the same particles. Multiple runs confirmed that this setup gave reproducible results. All transient experiments were conducted under air atmosphere.
Figure 4.6: Schematic of the nanosecond flash photolysis pump-probe system used to determine the timescale of the hole transfer from TiO₂ to IrO₂. The laser and white light probe arrive at the sample perpendicular to each other. The photomultiplier sensitivity is adjusted by controlling the high voltage power supply (HVPS). The signal from the photomultiplier is processed by the digital storage oscilloscope (DSO) before the software builds the representative traces. At least 5 runs are averaged to produce the kinetic traces shown in this Chapter.

Because the trapped holes formed upon UV irradiation of TiO₂ have a known absorbance at 360 nm with a relatively broad tail out to ~400 nm, their formation and decay can be tracked in the nanosecond to microsecond timescale. Figure 4.7A shows the absorption spectra of the TiO₂/IrO₂ system with increasing concentrations of IrO₂ at 2 µs after the laser pulse. The spectral feature attributed to trapped holes is clear at 380 nm (the lower limit of absorbance that could be reliably measured) and a broad absorbance in
the near-infrared due to trapped electrons can be also be seen. As the concentration of IrO₂ is increased, both of the absorption features can be seen to decrease significantly, indicating that the holes are being transferred to the IrO₂ quickly. Figure 4.7B shows the excited state absorbance at 380 nm for TiO₂ alone and with IrO₂. In the absence of IrO₂, the trapped holes show a stable absorbance across the entire 15 µs timescale. When IrO₂ is present, however, the absorbance decays completely within 5 µs. A single exponential fit was used to calculate a lifetime of 1.53 µs. This in turn gives a rate constant for hole transfer from TiO₂ to IrO₂ of 6×10⁵ s⁻¹. This rate constant corresponds to a lower limit for the hole transfer rate because it only depends on the transfer of trapped holes. Valence band holes will be more oxidative than the trapped holes and are expected to transfer more quickly. This hole transfer rate is orders of magnitude faster than measured rates of hole transfer for water oxidation.¹¹⁷⁻¹¹⁸ It is also faster than measured electron transfer from IrO₂ to photoactive species like dyes (~2.2 ms)¹⁵², making this reaction path highly competitive with the desired water oxidation pathway.

4.4 Conclusions and Implications of the Results With Regard to Photocatalytic Water Oxidation

The results of the work presented in this Chapter have important implications regarding the feasibility of constructing a photoelectrolysis device that uses only sunlight to operate. Co-catalysts that assist both the hydrogen and oxygen evolution reactions will absolutely be necessary for the device to run efficiently, but it is vital to understand how the co-catalysts interact with the photocatalyst being used. IrO₂ clearly excels at
Figure 4.7: A) Transient absorption spectra recorded 2 µs after 308 nm excimer laser pulse excitation of 23 mM TiO₂ (in 5% acetic acid / 95% ethanol) containing (a) 0 mM, (b) 0.02 mM, (c) 0.04 mM, and (d) 0.06 mM IrO₂. The spectral feature observed at ~380 nm is due to the trapped holes and the broad absorption in the far visible is from the trapping of electrons. Both features are seen to decrease as the concentration of IrO₂ increases. B) Normalized absorbance kinetic traces recorded at 380 nm following the excitation of a 23 mM TiO₂ colloidal solution (a) without IrO₂ and (b) with 0.06 mM IrO₂.

Discharging holes from the TiO₂ surface, but if those holes are being consumed in a reaction that does not result in oxygen evolution, the system is not performing its task. Water oxidation is known to occur on a timescale that ranges from milliseconds to seconds, which means that this side reaction where oxygen scavenges both electrons and holes, which occurs on a microsecond timescale, presents a significant hindrance. The question that must be answered is how to prevent the scavenging of holes by reduced oxygen species in a photoelectrolysis system. One way to tackle the problem is to separate the two electrodes with a membrane that will allow shuttling of electrons away from the electrode where oxygen is being produced. This separation of the electrodes has the added benefit of separating the oxygen and hydrogen that are produced as well. The results discussed in this Chapter emphasize the need to understand interfacial charge
transfer processes in photocatalytic systems. This is reinforced by a recent manuscript wherein the authors discovered that the anion used in an aqueous electrolyte can alter the overall reaction mechanism—instead of oxygen being produced, anions were being preferentially oxidized by the photocatalyst.²¹⁷
CHAPTER 5:
HYDROGEN GENERATION FROM CADMIUM SULFIDE ON TITANIUM DIOXIDE IN A REVERSE FUEL CELL SYSTEM

5.1 Introduction

The previous chapters have discussed the effects that interfacial transfer processes can have on overall performance. Chapters 2 and 3 detailed the manipulation of photocatalysts to achieve higher photoelectrochemical performance while Chapter 4 focused on the interaction of TiO₂, a photocatalyst, with IrO₂, an oxygen evolution reaction catalyst. The ultimate goal of understanding these transfer processes is to create a photoelectrolysis device. In this Chapter, the generation of hydrogen from a sulfide solution by CdS on TiO₂ is described along with a calculation of quantum efficiency for the conversion of light to hydrogen.

To deal with the energy issues discussed in Chapter 1, it is necessary to store excess energy from sunlight that can be used during periods of low or no solar power. Hydrogen gas formed by photolysis of water is one way to store this energy. For this method to be practical, the production of hydrogen by photolysis should be simple, robust, and allow for easy capture of the gas. Fuel cells traditionally use hydrogen and oxygen as feedstocks, generating electricity and water as products.²¹⁸ A reverse fuel cell can take water as a feedstock and use a photocatalyst to oxidize the water while the
generated protons pass through a proton exchange membrane to the counter electrode. At the counter electrode, these protons are reduced to form hydrogen. The separation of the electrodes has an added benefit of keeping the generated gases completely separate. This electrode separation not only eliminates an additional step in a potential industrial process, but the separated gases are unable to recombine to form water, a common issue in water splitting setups where the gases are evolved together. A proof-of-concept reverse fuel cell has already been demonstrated, using TiO$_2$ as the photocatalyst and methanol as a sacrificial electron donor. This system showed that hydrogen gas can be evolved continuously.

One significant drawback of the system is the fact that TiO$_2$ absorbs only in the ultraviolet region. Many visible light absorbers, like CuGa$_3$S$_5$, CdSe, SrNbO$_2$N, Si, and Cu$_2$O, among others, have shown activity for hydrogen evolution from either water or sacrificial solutions (e.g., methanol or Na$_2$S/Na$_2$SO$_3$). In this Chapter, CdS was used to extend the absorption of the working electrode to the visible region. The increased photocurrent will result in the generation of more hydrogen.

5.2 Photovoltaic Performance of CdS/TiO$_2$ Under Continuous Flow Conditions

The reverse fuel cell (see Figure 5.1) is composed of two conductive graphite blocks with chambers that expose the anode and cathode to pumped solutions. The graphite blocks are sandwiched by metal current collector plates. On the anode side of the reverse fuel cell, holes are cut out, and a quartz window is used to allow light to reach
the anode. A proton conducting membrane separates the two chambers. Peristaltic pumps cycle the solutions being used. An inverted y-shaped glass tube is used to collect the evolved gas bubbles during experiments. The amount of gas evolved is measured by displacement of water. Before and during experiments, nitrogen is bubbled through the solutions.

Figure 5.1: Exploded view of the reverse fuel cell components. Conductive graphite blocks sandwich the teflon spacers used to ensure complete sealing of the membrane electrode assembly (MEA). Not shown are the current collector plates and bolt assemblies used to hold all the pieces together.

Conductive carbon Toray paper was used as the substrate for both working and counter electrodes. The porosity of the carbon paper along with its robustness makes it ideal as the substrate. The counter electrode was constructed by dropcasting an ethanolic solution of platinum black onto the Toray paper, allowing the ethanol to dry, and repeating until the nominal concentration was 1 mg Pt/cm². The Pt Toray electrode was then annealed at 400 °C for one hour. Working electrodes were constructed by
dropcasting a 5 mg/mL P25 methanol solution to a concentration of 5 mg P25/cm² Toray paper. The P25/Toray electrode was then annealed at 400 °C to improve inter-particle contact and adhesion to the Toray paper. Two electrolyte solutions were flowed through the reverse fuel cell. 0.01M Na₂S was flowed past the photoanode while 0.001M H₂SO₄ was flowed past the platinum cathode. A Nafion 115 membrane was used to separate the two electrodes. The Nafion membrane was prepared by boiling for one hour in 1% H₂O₂ and for one hour in 1M H₂SO₄. This process removes any organics that have deposited in the pores of the Nafion and fully protonates the sulfonate groups in the pores, ensuring high proton conductivity during the hydrogen generation experiments. When not in use, the Nafion membrane was stored in water to prevent it from drying out.

Before any photoelectrochemical measurements were made, both sides of the reverse fuel cell were completely filled with their respective solutions, and all gas bubbles were removed by pulsing the peristaltic pumps until no bubbles were observed at the outlet of the anode and cathode chambers. A syringe was used to remove all bubbles in the y-shaped trap. A Xe lamp with either an AM1.5 filter or a 420 nm bandpass filter was used as the illumination source. The incident power with the AM1.5 filter was 100 mW per cm² while the incident power with the 420 nm bandpass filter was 20 mW per cm².

Current-voltage curves (shown in Figure 5.2A and 5.2B) were recorded using a staircase voltammetry technique. This was used to allow sufficient time for the photocurrent to reach an equilibrium under the constant flow conditions. The applied potential was ranged from -1.3V to 0V and stepped 100 mV at a time. Each applied
potential was held for five minutes before the photocurrent was recorded. The current-voltage curves measured under AM1.5 and 420 nm bandpass filtering using staircase voltammetry is shown in Figure 5.2 along with solar fuel conversion efficiencies calculated using Equation 5.1:

\[
Eff(\%) = \frac{I \times (1.23-V_{bias})}{P_{INC}} \times 100\% \tag{Equation 5.1}
\]

where \(I\) is the measured current in mA per cm\(^2\), \(V_{bias}\) is the potential applied, and \(P_{INC}\) is the measured incident power in mW per cm\(^2\). The maximum current density of

\[
\begin{align*}
\text{Figure 5.2:} & \quad \text{Current-voltage curves measured under (A) AM1.5 and (B) 420 nm bandpass filtered illumination showing calculated solar fuel conversion efficiencies based on Equation 5.1. The maximum efficiencies calculated both occur at the short circuit (0V) condition.}
\end{align*}
\]
the CdS-P25 electrode is 1.5 mA per cm² under full AM1.5 light while the 420 nm bandpass has a maximum of 0.5 mA per cm². The calculated solar fuel conversion efficiency maximum for the AM1.5 filtered light is approximately 1.7% at short circuit condition. For the 420 nm bandpass filtered light, the maximum solar fuel conversion efficiency is 3%. The higher efficiency under lower incident power is attributed to higher collection of photogenerated charges.

5.3 Hydrogen Generation and Determination of Quantum Efficiency

Quantum efficiency is a measure of how many electrons are collected for every photon that is incident to the photoactive material. This efficiency can be represented as:

\[ QE(\%) = \frac{n}{N} \]  

Equation 5.2

where \( n \) is the number of carriers (electrons, in this case) collected and \( N \) is the number of incident photons. More practically, Equation 5.2 is written:

\[ QE(\%) = \frac{n}{N} = \frac{2 \times \# H_2 \text{ produced}}{\# \text{ of photons}} \]  

Equation 5.3

Thus, with the amount of hydrogen produced measured and the number of incident photons known, quantum efficiency can be directly calculated for a given wavelength. Using quantum efficiency rather than an efficiency derived from a current-voltage curve provides a more accurate description of how well a photocatalyst performs photolysis. The number of incident photons is measured by chemical actinometry. Chemical actinometry relies on the use of a light-reactive substance that has a known quantum yield for a given wavelength. Common among chemical actinometers is
potassium ferrioxalate, which was shown to be a versatile tool for actinometry by Hatchard and Parker in 1956. Potassium ferrioxalate is used due to a relatively wide range of applicable wavelengths (from 222 nm to 550 nm, though a more reliable range is 254 nm to 500 nm) for which quantum yields have been determined. Upon excitation, the ferrioxalate is reduced and forms Fe\(^{2+}\) according to Reactions 5.1 and 5.2:

\[ \text{Fe} \left( C_2O_4 \right)_{3}^{3-} \xrightarrow{\text{hv}} \text{Fe}^{2+} + C_2O_4^- + 2C_2O_4^{2-} \quad \text{Reaction 5.1} \]

\[ \text{Fe} \left( C_2O_4 \right)_{3}^{3-} + C_2O_4^- \xrightarrow{\Delta} \text{Fe}^{2+} + 2\text{CO}_2 + 3C_2O_4^{2-} \quad \text{Reaction 5.2} \]

The dual pathways for the formation of Fe\(^{2+}\) account for the quantum yields greater than 1 that were reported by Hatchard and Parker. The amount of Fe\(^{2+}\) formed can be quantified by complexing the Fe\(^{2+}\) with 1,10-phenanthroline to form Fe(phen)\(_3\)^{2+}, which has an absorption peak at 510 nm with a known extinction coefficient of 11,100 L mol\(^{-1}\) cm\(^{-1}\). By using Beer's Law and adjusting for the change in volume from adding the phenanthroline, the concentration of Fe\(^{2+}\) can be calculated from the Fe(phen)\(_3\)^{2+} absorption at 510 nm:

\[
\text{moles Fe}^{2+} = \frac{V_1 \times V_3 \times \Delta A(510 \text{ nm})}{10^3 \times V_2 \times l \times \varepsilon(510 \text{ nm})}
\]

where \(l\) is the path length of the cell, \(V_1\) is the irradiated volume of ferrioxalate solution, \(V_2\) is the aliquot of irradiated solution taken for spectroscopic measurement (here, \(V_1 = V_2\)), \(V_3\) is the final volume after the addition of phenanthroline, and \(\varepsilon\) is the extinction coefficient of the Fe(phen)\(_3\)^{2+} complex. It is important to note here that both the potassium oxalate and phenanthroline solutions must be kept in the dark as they will each react with exposure to light.
Once the concentration of Fe$^{2+}$ is known, the number of photons absorbed can be calculated based on a known quantum yield at a given wavelength:

$$\frac{\text{moles of photons}}{s} = \frac{\text{moles Fe}^{2+}}{\phi \times t \times F}$$

Equation 5.5

where $F$ is the fraction of light absorbed by the ferrioxalate, $t$ is the length of time the ferrioxalate was irradiated, and $\phi$ is the quantum yield at the irradiation wavelength.

With the number of photons calculated based on the length of irradiation and the number of electrons calculated from the photocurrent measured, the quantum efficiency can be calculated.

The photon flux was determined using 3 mL of 0.012 M ferrioxalate in a horizontally-oriented cylindrical quartz cuvette. A Xe lamp with a 420 nm bandpass filter (40% transmittance at 420 nm) was used as the irradiation source. The ferrioxalate solution was irradiated for 10 seconds, 0.5 mL of a 0.1% phenanthroline (1 g 1,10-phenanthroline with 225 g sodium acetate in 1 L of 0.5 M H$_2$SO$_4$) was added to the ferrioxalate solution to complex the Fe$^{2+}$, and the absorption of the complex solution was immediately measured. The quantum yield at 420 nm for the ferrioxalate solution is 1.12. Figure 5.3 shows the absorption spectrum of the Fe(phen)$_3^{2+}$ complex before and after irradiating the 0.012 M ferrioxalate solution for 10 seconds. From the absorption peak at 510 nm, the photon flux was determined to be $9.68 \times 10^{15}$ photons per second per cm$^2$ at 420 nm. The window of the reverse fuel cell is 4.91 cm$^2$, so the total rate of photon irradiation is $4.75 \times 10^{16}$ photons per second. Assuming 100% conversion of
photons to electrons and 100% Faradaic efficiency, approximately 3.18 mL of hydrogen should be evolved every hour.

**Figure 5.3:** Absorption spectra of (a) 3 mL of the 0.012M \( \text{Fe(C}_2\text{O}_4\text{)}_3^{3-} \) solution before irradiation at 420 nm and (b) after 10 seconds at irradiation from a Xe lamp with a 420 nm bandpass filter and addition of 0.5 mL of the 0.1% 1,10-phenanthroline solution to form \( \text{Fe(phen)}_3^{2+} \). The absorbance of the 0.012M \( \text{Fe(C}_2\text{O}_4\text{)}_3^{3-} \) solution at 416 nm is 1.26, corresponding to light absorption of approximately 94.5% at that wavelength.

Hydrogen evolution was measured by water displacement in a glass y-shaped tube connected to the outlet of the reverse fuel cell. The inner diameter of the tube was 0.7 cm, making the cross-sectional area 0.385 cm\(^2\). Using this area, the height of the displacement could be measured and a volume of evolved hydrogen calculated. As can be seen in Figure 5.4, the initial rate of hydrogen evolution was approximately 5 \( \mu \text{mol} \) (0.11 mL) per hour, but this generation rate slowed to approximately 2 \( \mu \text{mol} \) (0.03 mL) per hour by the end of the 12 hour run. The total measured volume of hydrogen after 12 hours of irradiation with the 420 nm bandpass filter was 0.79 mL. The total number of incident photons over the course of the 12 hours was \( 1.94 \times 10^{21} \), which corresponds to
about 38 mL of H₂. Based on the measured hydrogen and the theoretical maximum hydrogen that could be produced, the quantum efficiency at 420 nm is approximately 2%.

The decrease in the rate of hydrogen generation is likely caused by two things: 1) the crossover of H⁺ ions from the cathode side of the reverse fuel cell and 2) the oxidation of sulfide to polysulfide without an accompanying reduction of polysulfide to sulfide. The crossover of H⁺ ions results in the destruction of the CdS layer as H₂S is formed. This was confirmed by the observation of a yellow color in the Nafion membrane that was separating the anode and cathode chambers of the reverse fuel cell. This yellow color indicated that CdS was dissociating from the carbon paper electrode, the Cd²⁺ was attaching to the SO₃⁻ groups that form the pores of the Nafion, and S²⁻ from

Figure 5.4: Time course of hydrogen evolution at short circuit condition from a 0.01M Na₂S solution by CdS on TiO₂ nanoparticles. The platinum cathode was exposed to a 0.001M H₂SO₄ solution. The illumination source was a Xe lamp equipped with a 420 nm bandpass filter.
the anode sulfide solution was reacting to form CdS in the pores of the Nafion. The formation of polysulfide was indicated by a color change in the 0.01M Na$_2$S solution from clear to a faint yellow. Absorption spectroscopy (see Figure 5.5) confirmed that the color was due to the formation of polysulfide anions.

![Figure 5.5: Absorption spectra of (a) the 0.01M Na$_2$S solution after 12 hours of operation in the reverse fuel cell and (b) a 0.1M Na$_2$S/S solution. Na$_2$S alone shows no absorption features in the wavelength range depicted here, so the peak at 370 nm is attributed to the formation of polysulfide.](image)

5.4 Conclusions, Ongoing Work, and Reporting Solar-to-Fuel Conversion Efficiencies

The goal of photoelectrolysis research is to develop a high efficiency device that can continuously split water into hydrogen and oxygen. As such, the reporting of solar-to-hydrogen efficiencies, much like the reporting of solar power conversion efficiencies, is the capstone of the results of many published articles. Often, however, these efficiencies are calculated from a current-voltage curve, not from actual hydrogen
evolution. When a three-electrode system is used while measuring the current-voltage curve, the potential being applied is measured between the working and reference electrode. In the course of setting a potential between the working and reference electrode, the potential of the counter electrode compared to the working electrode will vary in an unknown way. Thus, calculating a solar-to-hydrogen efficiency using Equation 5.1 will not be accurate. In this Chapter, a CdS-TiO$_2$ photoanode was used to continuously produce hydrogen for 12 hours when coupled with oxidation of sulfide ions in a reverse fuel cell. While the calculated solar fuel conversion efficiency was predicted to be approximately 3% at 420 nm based on the current-voltage curve, the quantum efficiency calculated based on the amount of hydrogen actually produced and the number of incident photons was only 2%. This result confirms that an efficiency calculated without producing hydrogen is likely to overestimate the actual system efficiency.

Although the quantum efficiency measured is relatively low, performance should be improved by limiting hydrogen ion crossover, which causes degradation of the CdS, and limiting build-up of polysulfide ions in the anode solution. One way to prevent polysulfide formation is the addition of sulfite ions, which react with the sulfide radicals that are formed to produce sulfate ions. Although this system is ultimately sacrificial, it should prove beneficial in establishing the highest performance that can be obtained using CdS on TiO$_2$.

Ongoing work for this project is focused on measuring quantum efficiency at different biases to elucidate how the efficiency of the hydrogen evolution reaction is affected by load. This technique can also be extended to forward bias to explore how
efficiently solar-assisted electrolysis proceeds. Hydrogen generation experiments are also being conducted with Nafion membranes that have been loaded with CdS, Pd, and Pt. The advantage of this system is that a direct contact is formed between the photoanode and the cathode through a Pd bridge. This bridge should allow higher charge collection and thus higher rates of formation of hydrogen.

In Chapter 6, the research in this dissertation is summarized and discussed in an overall context. Recommendations for future directions of the research presented in this dissertation are also proposed.
6.1 Summary and Conclusions

The research discussed in this dissertation was the elucidation of the role of interfacial transfer processes in determining overall photovoltaic and solar-to-fuel conversion efficiencies. It has been shown that this understanding enables manipulation of these processes, resulting in improved photovoltaic performance.

Although it has been understood that trap sites on TiO₂ substrates dictate how efficiently photogenerated electrons can be collected, this work was able to specifically track both the formation and stability of these Ti³⁺ trap states by utilizing diffuse reflectance spectroelectrochemistry. These experiments showed that the potential needed for the electrochemical formation of these trap sites is related to the pH of the electrolyte and, to a lesser extent, the size of the cation being intercalated. The work also demonstrated that the trap sites could be stabilized by both H⁺ and Li⁺ ions. The Li⁺ ions are stable enough to resist electrochemical de-intercalation, even at strongly positive potentials (+1.0 V vs. Ag/AgCl). Intercalation of H⁺ ions leads to a doubling of the photocurrent while intercalation of Li⁺ ions resulting in a tripling of the photocurrent.
The increase in photocurrent is explained by a lowered recombination rate that is attributed to the "pre-reduced" trap sites. Because the Ti$^{4+}$ sites are already reduced to Ti$^{3+}$ and charge-balanced by the Li$^+$ ions, they are not available to trap electrons. These trapped electrons can recombine with photogenerated and trapped holes as well as with the electrolyte. By removing some of these traps, more photogenerated electrons can be collected.

This research also demonstrated that SrTiO$_3$ could be layered on a TiO$_2$ nanotube substrate using pulsed laser deposition. This technique created an intimate contact between the two semiconductors that, after annealing, allowed for efficient separation of holes and electrons. This led to an increase in photovoltage, which had been demonstrated previously via a hydrothermal method, as well as an increase in photocurrent, which was not observed with the hydrothermal synthesis. This improved photocurrent was attributed to the preservation of the underlying TiO$_2$ nanotube array, which was partially consumed in the hydrothermal method and resulted in a lesser rate of electron collection. The increase in photocurrent and photovoltage was expected to result in a higher rate of hydrogen generation as well. Greater photocurrent is an indication of greater electron flow through the external circuit, which translates to more hydrogen ions being reduced. More negative photovoltage a greater driving force for the reduction reaction. The rate of hydrogen production on the SrTiO$_3$-TiO$_2$ nanotube array heterostructure was greater than that of the TiO$_2$ nanotubes alone. About 10 $\mu$mol of hydrogen was produced on the SrTiO$_3$-TiO$_2$ heterostructure while about 5 $\mu$mol was produced by the TiO$_2$ nanotubes alone.
In addition to demonstrating that the working electrode can be improved by manipulation of the semiconductor and creating heterostructures with favorable band positions, it was also observed in experiments that IrO$_2$, a popular electrolysis catalyst, will catalyze a side reaction that is competitive with the oxygen evolution reaction. By utilizing a combination of steady-state and transient spectroscopy, it was shown that trapped holes on TiO$_2$ are scavenged by oxygen radicals in the presence of IrO$_2$. Under nitrogen atmosphere or in the absence of IrO$_2$, the trapped holes are stable for hours. The steady-state experiments also allowed for the first time the calculation of an extinction coefficient for the trapped holes. Nanosecond laser flash photolysis experiments revealed that the trapped holes are transferred to the IrO$_2$ particles within approximately 2 µs, which corresponded to a hole transfer rate of about $6 \times 10^5$ s$^{-1}$. Compared to the oxygen evolution reaction that operates on a millisecond to second timescale, this side transfer process is highly competitive and thus detrimental to a photoelectrolysis device.

The ultimate goal of these experiments is to be able to apply the principles elucidated to a working photoelectrolysis system. By using a reverse fuel cell configuration, hydrogen generation from a CdS/TiO$_2$ nanoparticle composite working electrode has been demonstrated under continuous flow conditions. One advantage of this system is that the evolved gases are already separated by the Nafion membrane, which removes a potentially costly step in an industrial process. Hydrogen generation experiments showed that hydrogen could be produced from a sulfide electrolyte over the course of several hours. Actinometric measurements also allowed the calculation of a quantum efficiency of 2% for the CdS/TiO$_2$ system at 420 nm. The solar-to-fuel
conversion efficiency of 3% calculated from the current-voltage curve overestimated the efficiency of hydrogen generation by 50%. This comparison confirmed that the assumption of efficiency based solely on current-voltage characteristics is not accurate, and reporting conversion efficiencies calculated from current-voltage measurements is, at best, an overestimation of activity.

6.2 Recommendations for Future Research

There are many possible avenues that can be explored based on the research presented in this dissertation. This is especially true for the field of photoelectrolysis. While great strides have been made in terms of efficiency at splitting water into hydrogen and oxygen, there is little understanding when it comes to how the reactions proceed. Recent publications have started to tackle this issue, but there is still plenty of research to be performed. Experiments that focus on determining the reaction intermediates are now possible with rapid scan technology, as demonstrated by the observation of an IrOOH intermediate. These experiments can be utilized, along with surface characterization techniques like XANES and EPR, to explicitly delineate the reaction cycle of water photolysis on a given photocatalyst. Where the equipment necessary is not readily available, spectroscopic techniques, like those discussed in Chapter 4, can be used instead. They do not offer as high a time resolution, but it is still possible to demonstrate a lower limit for hole transfer rates and show whether a co-catalyst is capable of operating in a fully catalytic system.
Further work should also focus on expanding the utility of the reverse fuel cell system used in Chapter 5. Thus far, the system has been used more as a proof-of-concept, but it should also be able to act as a functioning system that achieves higher efficiency. With the foundation of proper quantitative measurement of efficiency laid, work can focus on using newer materials like oxynitrides as well as developing p-type/n-type semiconductor systems that operate with light irradiating both the working and counter electrodes to perform photolysis. In this way, the amount of platinum used is reduced greatly, and there is the possibility of using two semiconductors that can each perform one of the half-reactions (hydrogen or oxygen evolution). By using two small band gap materials, more of the solar spectrum is absorbed and utilized, increasing the maximum possible efficiency. The use of concentrated light to boost the efficiency of the cell is also a direction that could be explored.

All in all, the primary underpinning of all future work should be a focus on why and how an observed event occur, not just on how high an efficiency can be achieved. By understanding the fundamental processes that are happening, these processes can be controlled and altered to improve performance.

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