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INVESTIGATION OF LIGHT MANAGEMENT STRATEGIES AND PHOTOCHEMISTRY OF Si/TiO₂ TANDEM MICROWIRE SLURRIES FOR SOLAR HYDROGEN GENERATION

By
Saumya Gulati
B.Tech., Harcourt Butler Technological Institute, 2015
M.S., Columbia University, 2017

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Submitted to the Faculty of the
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in Chemical Engineering

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University of Louisville
Louisville, Kentucky

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A Dissertation Approved on

January 11, 2023

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ii
“Tough times never last, tough people do”

Robert H. Schuller

This dissertation is dedicated to my parents

Dr. Mohita Gulati

and

Dr. Shashi Kumar Gulati

and my grandparents who have given me invaluable educational opportunities and unconditional love and support.
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The intermittent nature of the Sun makes it difficult to use it as a primary source of electricity and often needs to be supplemented by electricity from the grid which comes from fossil fuels. This motivates the need for solar energy storage.

Photoelectrochemical (PEC) water-splitting has been explored as a means to convert solar energy into hydrogen (and oxygen), which can be stored as fuel. The current method of coupling PV and electrolyzer units has been widely commercialized, however, the cost of H₂ generated is far from the target of $1/kg set by the DOE under the Energy EarthShot initiative.

One of the approaches to reducing the cost associated with electrical connections and panel installation (as in the case of coupled PV + Electrolyzer) is using a semiconductor-based anode and cathode in direct contact with the electrolyte along with catalysts to aid the water-splitting reaction. The initial part of this dissertation explores a relatively low-cost and abundant Ni-based molecular catalyst (NiATSM) for H₂ production reaction on a p-Si photocathode.
However, various techno-economic analyses suggest that semiconductor particulate slurry reactors are a potential route for reducing the cost of $H_2$ even further. This dissertation also explores the fabrication and characterization of a novel tandem semiconductor particle slurry that has the potential to produce cost-effective hydrogen by achieving high solar-to-hydrogen (STH) efficiencies. In this work, a tandem-junction microwire array was fabricated by coating p+n-Si radial homojunction microwire arrays sequentially with fluorine-doped tin oxide (FTO) and titanium dioxide ($TiO_2$). These tandem microwires were cleaved from the growth substrate to form a Si/$TiO_2$ tandem particulate slurry. Ni hydrogen evolution catalyst (HEC) was selectively photodeposited at the exposed Si microwire core to serve as the cathode site as well as a handle for magnetic orientation. Since the Ni bulb at one end of the microwire would be highly opaque and lead to poor performance for a tandem microwire in an upside-down arrangement, a magnetic field was used to control the orientation of the particle. The ferromagnetic Ni HEC bulb was magnetized and used as a handle for the alignment of tandem microwires under active dispersion of the particles with uplifting bubbles. The photoactivity of the tandem slurry was also tested via photodegradation of methylene blue indicator dye. Light management strategies, to improve the degradation rate and light absorptance in the slurry, were also explored. Optical properties of the slurry were measured under varying reactor conditions such as particle concentration, uplifting bubble flowrate, etc. The results indicate that particle suspension reactors may provide the lowest-cost option for solar hydrogen generation.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER 1</td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Climate Change and Energy Storage</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Fundamentals of photoelectrochemical (PEC) water-splitting</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Particle based approach for H₂ production: A technoeconomic outlook</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Photoactive Slurry: State-of-the-art and Challenges in Scaling Up</td>
<td>12</td>
</tr>
<tr>
<td>1.5 Key Questions and Proposed Solutions</td>
<td>15</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td>19</td>
</tr>
<tr>
<td>PHOTOCATALYTIC HYDROGEN EVOLUTION ON Si PHOTOCATHODES MODIFIED WITH</td>
<td>19</td>
</tr>
<tr>
<td>BIS(THIOSEMICARBAZONATO)NICKEL(II)/NAFION</td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Results and Discussion</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Experimental Section</td>
<td>35</td>
</tr>
<tr>
<td>2.4 Conclusion</td>
<td>40</td>
</tr>
<tr>
<td>CHAPTER 3</td>
<td>41</td>
</tr>
<tr>
<td>IN-SITU MAGNETIC ALIGNMENT OF A SLURRY OF TANDEM SEMICONDUCTOR</td>
<td>41</td>
</tr>
<tr>
<td>MICROWIRE SLURRIES USING A Ni CATALYST</td>
<td></td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>41</td>
</tr>
<tr>
<td>3.2 Results and Discussion</td>
<td>45</td>
</tr>
<tr>
<td>3.3 Experimental Section</td>
<td>60</td>
</tr>
<tr>
<td>3.4 Conclusion</td>
<td>65</td>
</tr>
<tr>
<td>CHAPTER 4</td>
<td>69</td>
</tr>
<tr>
<td>OPTICAL PROPERTIES AND PHOTOCATALYTIC PERFORMANCE OF Si/TiO₂ TANDEM</td>
<td>69</td>
</tr>
<tr>
<td>SEMICONDUCTOR MICROWIRE SLURRIES</td>
<td></td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>69</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1 - US greenhouse gas emissions by gas..................................................1
Figure 2 - US energy consumption by source and sector.................................2
Figure 3 Comparison of levelized cost of electricity from solar PV......................3
Figure 4- Valence and conduction band edge positioning for an ideal semiconductor w.r.t electrochemical potential energy for both H⁺/H₂ and O₂/H₂O redox couple….6
Figure 5- The band energetics of a semiconductor/liquid contact in quasi-static equilibrium under steady state illumination..........................................................7
Figure 6- Standard solar spectra...........................................................................8
Figure 7- TEA of various hydrogen production technologies.................................10
Figure 8- Effect of efficiency, particle or panel cost, and component lifetime on the cost of hydrogen from Type 1 reactor.................................................................11
Figure 9- Cost comparison of panel and slurry reactors.........................................11
Figure 10- NMR characterization of NiATSM.......................................................21
Figure 11- Comparing JE behavior of NiATSM in dark and under AM1.5 illumination..............................................................................................................22
Figure 12- Stability measurement of NiATSM in 1M H₂SO₄...................................24
Figure 13- Comparison of different HEC on p-Si under AM1.5 illumination.......26
Figure 14- JV curves before and after CA to test the effect of Nafion on stability…27
Figure 15- Comparing the effects of Nafion on PEC performance......................29
Figure 16- Elemental mapping of NiATSM

Figure 17- XPS spectra for the Ni 2p region for various p-Si substrates

Figure 18-.XPS spectra for (a) the S 2p region (b) the Si 2p region for various p-Si substrates

Figure 19- JE behavior of electrodeposited Ni/p-Si electrodes as a function of Ni catalyst loading

Figure 20- JE behavior of bare n+p-Si, and n+p-Si/NiATSM/Nafion

Figure 21- FT-IR and UV-Vis spectra of H₂ATSM and NiATSM

Figure 22- Conceptual schematic of the vertical alignment of tandem semiconductor microwires

Figure 23- Schematic of the tandem Ni/n⁺p-Si/FTO/TiO₂ microwire fabrication process

Figure 24- SEM images of microwires during the tandem fabrication process

Figure 25- Tandem structure and water-splitting performance

Figure 26- SEM images and elemental maps for Si, Ti, Sn, and Ni of the cross-sectional base of a tandem microwire

Figure 27- SEM images of the cross-sectional base of tandem microwires after detachment from the n-Si substrate and photodeposition of the Ni catalyst

Figure 28- Calibration curve for the magnetic field strength

Figure 29- SEM images of an electrodeposited Ni-coated n-Si microwire array cross-section

Figure 30- Frequency distribution of Ni-coated n-Si microwires as a function of the Ni loading
Figure 31- Optical high-speed camera images for a microwire slurry suspended with and without bubbling.................................................................55

Figure 32- Optical high-speed camera images with superimposed color-coded orientation angle.................................................................56

Figure 33- Frequency distribution of Ni-coated n-Si and tandem microwires dispersed without bubbling.............................................................57

Figure 34- Frequency distribution of Ni-coated n-Si and tandem microwires dispersed with bubbling.................................................................59

Figure 35- Schematic of tandem Ni/np⁺-Si/FTO/TiO₂ microstructure driving photodegradation of methylene blue and image of an integrating sphere.........73

Figure 36- Transmittance, Reflectance and Absorptance as a function of different particle concentration and N₂ bubble flowrate............................75

Figure 37- Transmittance, Reflectance and Absorptance as a function of different particle concentration at 35 sccm N₂ bubble flowrate......................77

Figure 38- UV-Vis spectroscopy absorbance spectrum for unused aqueous 40 µM methylene blue and Normalized absorbance of MB showing effect of dissolved O₂.................................................................79

Figure 39- PEC behavior of planar tandem under AM1.5 in KOH and 40 µM methylene blue.................................................................80

Figure 40- Normalized absorbance of MB vs. time to test the effect of planar vs. microwire slurry form factor.............................................................81
Figure 41- SEM images of tandem microwires (a) before and (b) after a 1-hour MB photodegradation

Figure 42- Normalized absorbance of MB vs. time to test the effect of particle concentration

Figure 43- Normalized absorbance of MB vs. time to test the effect of carrier gas dispersive bubble flowrate

Figure 44- Normalized absorbance of MB vs. time to test the effect of spectral mismatch

Figure 45- Normalized absorbance of MB vs. time to test the effect of UV light bias

Figure 46- Normalized absorbance of MB vs. time to test the effect of scattering particles and back reflection

Figure 47- Transmittance, Reflectance and Absorptance for different Al$_2$O$_3$ scattering particle concentrations
CHAPTER 1

INTRODUCTION

1.1 Climate Change and Energy Storage

Since the large-scale industrialization began in the mid-1800s there has been a substantial increase in the production of greenhouse gases. These gases trap heat in the atmosphere and warm the planet. Examples include, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and water-vapour (H₂O). One of the major sources of CO₂ production is burning of fossil fuels. According to the EIA, in 2019, of the total greenhouse gases produced, fossil fuel combustion produced roughly 75% CO₂.¹ (Figure 1)

![Figure 1- US greenhouse gas emissions by gas, 2019.¹](image_url)
The working group II of the Intergovernmental Panel on Climate Change (IPCC) recently released a report analysing the level of impact of global surface temperature changes on humans and on the ecosystem.\(^2\)

The report suggests that the rise of temperature change beyond 1.5 °C will lead to extreme weather events, loss of terrestrial, marine, and coastal biodiversity, changes in agricultural productivity and access, increased risk of water and energy security, and reduced economic output, to name a few. Hence, to limit the global warming, we need to limit the amount of CO\(_2\) emissions and subsequently reduce our dependence on fossil fuels. To achieve this, enormous efforts have already been made to incorporate renewable sources of energy like solar, wind, geothermal, biomass and hydropower into the mix.

![Figure 2- US energy consumption by source and sector, 2021.\(^3\)](image)
Figure 2 shows that renewable energy constitutes ~12% of the total energy consumed in 2021. Of that fraction wind energy consumption was the highest at 27% followed by hydroelectric and solar at 19% and 12%, respectively. In the last decade, solar power has become more affordable and prevalent in the US. Its capacity increased from 0.34 GW in 2008 to 97.2 GW in 2021 and the average cost of a solar panel dropped by ~70% since 2014. Furthermore, the cost of electricity also dropped from $0.28 (2010) to $0.06 (2020) per kWh for utility-scale solar PV power and similar trends were seen for both residential and commercial scale solar power. (Figure 3a)

![Figure 3](https://example.com/figure3.png)

**Figure 3 (a)** Comparison of levelized cost of electricity from solar PV (b) Comparison of curtailment of utility-scale solar in the CAISO region between 2020 and 2021.

While the cost reduction and policy targets for decarbonization have increased the installed solar capacity and output, it has made it more challenging for grid operators to balance electricity demand and supply. Often, this leads to curtailment of renewable solar energy during times of low demand which is generally in early afternoon; the time when solar output is relatively high. In 2020, the California Independent System Operator (CAISO) region curtailed about 1.5 million MWh of utility-scale solar (~5% of utility-scale solar production). Figure 3b This is not only
an economic loss but an environmental one as well. Many novel solutions are being tested to overcome this problem, such as, using ‘grid-friendly’ controls on a solar PV plant or utilizing machine-learning technology to better predict solar energy production.\textsuperscript{7,8} However, as the penetration of solar PV increases, advanced solutions will be needed to circumvent this issue. Of the many potential solutions, coupling of solar energy with storage technologies will likely be the key to its continued expansion. Although Li ion batteries is one of the most widely used energy storage devices, a net energy analysis has shown that (for the same manufacturing energy input) a renewable hydrogen-fed fuel cell can provide more energy than a lithium-ion battery over the lifetime of the facility.\textsuperscript{9}

Hydrogen is one of the most lucrative options for energy storage since it has the highest gravimetric energy density (120MJ/kg) and is a clean fuel, in that when consumed it produces energy and harmless water-vapour. Hydrogen can be produced by solar-driven electrochemical process thus achieving a net-zero-carbon pathway. Solar water splitting is a promising route for H\textsubscript{2} production which can readily be achieved by combining two commercial technologies photovoltaics (PV) and electrolysis. This has been tested widely from lab scale investigation to solar hydrogen pilot plan demonstration.\textsuperscript{10,11} Unfortunately, PV-electrolysis is too expensive for large scale solar-hydrogen production.\textsuperscript{12,13}

This motivates the research on photoelectrochemical (PEC) water-splitting wherein both the light harvesting, and electrolysis functions are merged into a single unit. The configuration comprises of single or multijunction PV electrodes which provides the necessary photovoltage to perform the reaction. These are often
decorated with hydrogen and oxygen evolution catalyst to construct an integrated
device called the “artificial leaf”.

1.2 Fundamentals of photoelectrochemical (PEC) water-splitting

At the heart of this process lies the fundamental concept of photoelectric effect.
Discovered in 1839 by Edmond Becquerel, he explained this effect as the emission
of free electron from a material when hit by an electromagnetic radiation i.e., light.
This is closely related to the photovoltaic effect wherein the external light stimulus
doesn’t lead to a free electron but excitation of an electron from a lower energy state
(valence band) to a higher energy state (conduction band) in a semiconductor
material leaving behind an electron vacancy or hole.

As shown in Figure 4, a single semiconductor can drive hydrogen evolution
reaction (HER) and oxygen evolution reaction (OER) using the electrons and holes
generated under solar illumination if it has a bandgap ($E_g$) large enough to overcome
the thermodynamic minimum required for the reaction, and its conduction band
(CB) and valence band (VB) edge energy straddle the standard electrochemical
potential $E^\circ(H^+/H_2)$ and $E^\circ(O_2/H_2O)$.

In acidic conditions the reactions are:

HER: $2H^+ + 2e^- \rightarrow H_2 (g) \quad E^\circ(H^+/H_2) = 0V$

OER: $H_2O \rightarrow (1/2) O_2 + 2H^+ + 2 e^- \quad E^\circ(O_2/H_2O) = 1.23V$

The CB should be more negative than the standard reduction potentials of $H^+/H_2$
redox couple and the VB should be more positive than the standard reduction
potentials of $O_2/H_2O$ redox couple. Typically, electrolysis requires application of
energy >1.23 eV (per mole of H\textsubscript{2}) due to the kinetic barriers that need to be overcome while performing this multistep and multielectron transfer reaction.

Formation of H\textsubscript{2} in acidic medium requires a combination of two protons with two electrons. On most bare semiconductor surfaces formation or desorption of reaction intermediates present a large energy barrier to H\textsubscript{2} production. The extra energy that needs to be supplied, over the thermodynamic minimum, for the reaction to proceed at a reasonable rate is called the overpotential. This overpotential is a current-dependent deviation from equilibrium potential with values ranging from ~50mV for HER and 300mV for OER (at 10mA cm\textsuperscript{-2}) This raises the practical photovoltage requirement from the semiconductor to ~1.6- 1.7 V. It can be calculated using the current-overpotential equation:

\[
I = I_0 \left[ \frac{C_O}{C_O^*} \exp \left( -\frac{\alpha nF}{RT} \eta \right) - \frac{C_R}{C_R^*} \exp \left( \frac{(1 - \alpha) nF}{RT} \eta \right) \right]
\]
Where,

- \( I \) = operating current
- \( I_0 \) = exchange current density
- \( C_O \) = concentration of oxidant in the bulk
- \( C_O^* \) = concentration of oxidant at the electrode surface
- \( C_R \) = concentration of reductant in the bulk
- \( C_R^* \) = concentration of reductant at the electrode surface
- \( \eta \) = overpotential
- \( \alpha \) = transfer coefficient

\( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)), \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( n \) is the number of electrons participating in the reaction, and \( T \) is operating temperature (K).

In a PEC cell, a semiconductor is in direct contact with the electrolyte. Under solar illumination it undergoes fermi level splitting developing quasi-Fermi levels within the bandgap. Figure 5 This free energy difference between the majority carriers and photoexcited minority carriers determines the photoelectrochemical reaction that can be driven by that semiconductor. The excited holes must reach one surface to drive OER while the electrons are consumed on a surface for HER.

![Figure 5](image_url)

**Figure 5.** The band energetics of a semiconductor/liquid contact in quasi-static equilibrium under steady state illumination. \( E_{F,e} \) is the electron quasi-Fermi level and \( E_{F,h} \) is the hole quasi-Fermi level. The voltage generated by the junction under illumination is given by the difference between \( E_{F,e} \) and \(-qE(A/A^-)\). \( E(A/A^-) \) is the electrochemical redox potential for a generic \( A/A^- \) redox pair.\(^{15}\)
The degree between the electron and hole fermi-level splitting under no net current flow is referred to as the open-circuit voltage ($V_{oc}$). The analytical expression for $V_{oc}$ can be generated by solving the ideal diode equation under equilibrium conditions:

$$V_{oc} = \frac{n k T}{q} \ln \frac{I_{ph}}{I_0}$$

Where,

$I_{ph}$ = photocurrent
$I_0$ = saturation current

Here, $n$ is the diode quality factor, $k$ is the Boltzmann’s constant, $T$ is the temperature, $q$ is the charge on an electron.

For a single semiconductor to perform water-splitting, a minimum of 1.6 V of photovoltage will be needed. This requires the bandgap to be at least ~2.2 eV. This is because the $V_{oc}$ can never be equal to the bandgap since it is limited by radiative recombination. This means that a large portion of the solar spectrum above 560 nm will not be absorbed (shaded portion in Figure 6) leading to extremely low current

Figure 6- Standard solar spectra.  

16
output. One of the ways to circumvent this problem is by using multiple semiconductors in tandem with each other.\textsuperscript{17} In such setup the top cell absorbs the higher energy photons, and the bottom cell absorbs the low energy photons. This allows absorption of larger portion of the solar spectrum thus increasing the efficiency of the device.

1.3 Particle based approach for H\textsubscript{2} production: A technoeconomic outlook

Cost is likely the strongest market driver for any applied technology. Similarly, for renewable H\textsubscript{2} production, all the technologies must compete against the steam reforming process of relatively low-cost fossil fuels which generates H\textsubscript{2} at a cost of $1.39 \text{kg}\textsuperscript{-1} or $0.042 \text{kWh}\textsuperscript{-1}. Multiple technoeconomic analyses have shown cost comparison of H\textsubscript{2} from different solar-driven systems.\textsuperscript{18,19-21} The systems are generally based on the following 2 reactor configurations:

1) Coupled PV+ electrolyzer (with/without solar concentration)
2) PEC reactors (with/without solar concentration)

The PEC reactors can be further classified into four different reactor types, namely Type1, Type 2, Type 3, and Type 4. Type 1 and 2 are enclosed aqueous reactor beds of suspended photoactive particles while Type 3 and 4 are single or multi absorber planar arrays immersed in an electrolyte.

Figure 7 compares the cost of H\textsubscript{2} from different solar-driven production technologies.\textsuperscript{21} The coupled PV/Electrolyser are projected to generated H\textsubscript{2} at a levelized cost ranging from $4.7 to $13.1 whereas the cost from integrated PEC reactors ranges from $2.1 to $12.3. The latter might have a slight economic
advantage over the former since it does not require an electrical interface between the PV and electrolytic components. Of the different PEC reactors explored in this work Type 1 and Type 2 systems show the most promise of achieving the levelized cost of H₂ (LCH) close to that obtained from the steam methane reforming.

![Table Image]

Figure 7. TEA of various hydrogen production technologies.\(^{21}\)
However, that is an optimistic outlook. In such studies, the assumed base-case STH efficiency for a Type 1 system is ~10% which do not match the current state of the art of 1-2% (See section 1.4). Pinaud et. al conducted a sensitivity analysis to identify the most impactful parameters that affect the final cost of H₂ (per kg) from Type 1 systems.  

Figure 8 shows that even though the cost differentials are minute, efficiency has the highest impact.

There are 2 large scale Type 1 reactor design currently being used, (i) panel and (ii) slurry-based system. These two systems have also been assessed from an economic and technical standpoint with the aim to improve future design. Even

![Figure 8](image-url)

Figure 8. Effect of efficiency, particle or panel cost, and component lifetime on the cost of hydrogen from Type 1 reactor

![Figure 9](image-url)

Figure 9. Contribution of CAPEX and OPEX to the overall cost of panel and slurry reactors. “Panel−1%” and “Slurry −1%” represent the base-case scenario with 1% photon conversion efficiency, while “Panel −5%” and “Slurry −5%” represent panel and slurry systems with 5% photon conversion efficiency, respectively.
though the current state-of-the-art high throughput system is panel based (Section 1.4), there are many advantages of a large-scale slurry reactor such as simple design, better light penetration, mass transfer, higher catalyst surface area etc.\textsuperscript{24}

Figure 9 shows that in the case where the photocatalyst photon conversion efficiency is 1%, the cost of the slurry reactor is 88\% that of the panel array. However, if the efficiency of the photocatalyst were to increase to 5\%, this difference would be very minimal. This motivates further investigation into upscaling of slurry reactors using currently available photocatalysts while working towards improving the photocatalyst photon conversion efficiency.

1.4 Photoactive Slurry: State-of-the-art and Challenges in Scaling Up

Some of the most efficient systems for H\textsubscript{2} production using solar energy have been PV+electrolyser systems (30\% STH efficiency) or PEC systems with solar concentrators using III-V absorbers (~14-18\% STH).\textsuperscript{10, 25, 26} However, various TEA suggests that photoactive particulate systems are simpler, and more amenable to scale-up for cost-effective H\textsubscript{2} production\textsuperscript{19, 22} Such systems have attracted attention in the last 40 years.\textsuperscript{27, 28} A variety of particulate photocatalysts for scalable solar H\textsubscript{2} generation have been explored. SrTiO\textsubscript{3} systems, in particular, have been explored intensively.\textsuperscript{29-35} Z-scheme reactors made of SrTiO\textsubscript{3} and BiVO\textsubscript{4} were shown to achieve STH efficiency of 1.1\%. Al-doped SrTiO\textsubscript{3} loaded with RhCrO\textsubscript{x} cocatalyst demonstrated >1000 hours of water splitting activity under constant illumination however the STH efficiency was only ~0.3\%. Similarly, other photocatalysts materials like BaTaO\textsubscript{2}N, Ta\textsubscript{3}N\textsubscript{5} etc. have been studied.\textsuperscript{36, 37} Metal free photocatalysts
such as C₃N₄ loaded with carbon nano dots have shown STH efficiency of 2% and stable performance over 200 days for overall water splitting.³⁸ Systems generating H₂ using a Z-scheme approach have been able to reach ~1% under ambient conditions. There have also been particulate systems that use moisture from air as the source of water to split into H₂ and O₂, but the process is still in an exploratory phase.³⁴,³⁹,⁴⁰ Evidently, none of them have come close to achieving the set target of 10% STH efficiency for an economical H₂ production.

In contrast to the PV+Electrolyzer systems which have been commercialized and installed over large areas, there have only been a few instances of scaled up photocatalytic reactors. The first pilot plant for photocatalytic water-splitting was demonstrated back in 2009. In the presence of sacrificial species, Pt/CdS particles were used in a glass tubular reactor coupled to a compound parabolic collector with an illuminated area of 0.6m². The STH efficiency however was just ~0.07%.⁴¹ However, with further optimization they were able to achieve an STH efficiency of 0.47%. Similar design was later adopted to showcase the largest pilot with an illuminated area of 103.7 m² using 720 L of NiS/CdₓZn₁₋ₓS slurry.⁴² However, in both these instances the reverse reaction was made insignificant by the use of Na₂SO₃/Na₂S (sacrificial hole scavengers) and significantly reduced chemically stored energy in the overall reaction compared to overall water splitting.

Goto et. al demonstrated the first pilot-scale system for pure water splitting. RhCrOₓ/SrTiO₃·Al particles were used to fill up a panel-reactor of area 1m². This relatively large system was able to generate H₂ at a STH efficiency of ~0.4% efficiency under natural solar irradiation. This is significant considering since
SrTiO$_3$:Al absorbs only the UV portion, which is only 5%, of the incident solar irradiation. The same group later worked on scaling up their system to demonstrate safe operation of a 100-m$^2$ array of a panel-type reactor using Al-doped SrTiO$_3$ photocatalyst. This is by far been the largest photocatalytic solar hydrogen production known and it reached a maximum STH efficiency of 0.76% over a period of several months.

The primary challenges with such PEC devices are developing materials with sufficient photovoltage to electrolyze water, minimizing internal resistance losses, having high corrosion-resistance, maximizing photon utilization efficiencies, and reducing plant capital cost. But these kinds of slurry reactors have so far yielded low efficiencies and lifetime due to the following drawbacks: (1) Co-evolution of H$_2$ and O$_2$ in the same space for a Type 1 reactor, leading to a safety concern and a need to keep the hydrogen concentration below the flammability limit (4% in a H$_2$/O$_2$ mixture). Production of both gases in the same space also leads to extra energy input to separate the products. (2) A single-bandgap particle system requires a bandgap $>2.2$ eV to achieve the minimum photovoltage to split water, which limits the theoretical max STH efficiency to $\sim$12% or lower. (3) Uniform nanoparticles immersed in electrolyte generally do not have a built-in electric field to provide directionality to charge-carrier transport and instead rely on diffusion to drive charges to sites of lower charge concentration, which leads to a less efficient photochemistry. (4) Undesired back reactions reduce the coulombic efficiency, which is especially problematic for a Type 2 system in which the fast, one-electron redox couple is kinetically easy to reduce or oxidize. [Type 2 systems include two
different particles for HER and OER, separated by a membrane, with a redox couple to shuttle charges between the two particles] (5) For such systems, significant ohmic overpotential losses can result from transporting charge across macroscopic distances through a membrane and between particle types via diffusion of the redox couple. (6) Type 2 system efficiency can benefit from complementary tandem bandgaps (i.e., ~1.7 + 1.1 eV) like a multijunction device, but this requires sequential light absorption in the higher bandgap particles before the narrow bandgap particles and can suffer from parasitic light absorption in the membrane and concentrated redox couple.

1.5 Key Questions and Proposed Solutions

Although the technology readiness level of the PEC slurry systems are pretty low efforts are being made to increase the efficiency of such systems to make it cost-competitive with fossil-based fuels. In this work we propose a novel single particle design which utilizes two semiconductors in tandem with each other which addresses the limitation associated with a single bandgap material (Section 1.4).

Ideally, a combination of 1.7eV (for top subcell) and 1.1eV (for bottom subcell) can help reach a STH efficiency of ~25%. Silicon is an ideal candidate for the bottom subcell material as it has a bandgap of 1.1eV and can be readily fabricated with p-n buried junction to make high efficiency photocathodes. Chapter 2 explores the effect of different HER catalysts, like platinum, as well as cost-effective and abundant Ni based molecular catalyst (NiATSM), on a p-Si photocathodes under simulated 1 Sun. With the ideal band edge positioning for HER and a highly commercialized
growth process, silicon is frequently studied as a photocathode material either by itself or in tandem with other semiconductors as has been done in this work.

On the other hand, candidates for top subcell materials are less well developed. Ternary III-V alloys have tunable bandgap and strong optical properties that have been used to make some very efficient photoanodes, but they are unstable in oxidative environment. In the meantime, for this work we chose a more readily available photoanode substitute, TiO$_2$, which in tandem with Si has shown to perform unassisted water-splitting and can be easily fabricated with solution-based methods. This allowed us to understand the fabrication challenges and gather preliminary data on the optical and photoelectrochemical properties of a tandem particle slurry reactor.

Si is chosen to have a cylindrical morphology (or a microwire structure) which, relative to a planar semiconductor junction, will orthogonalize the direction of light absorption and charge carrier collection. TiO$_2$ is grown on the surface of the Si microwire essentially coating the entire surface area except on the base. The base of Si is coated with layer of Ni metal which acts as a HER catalyst.

In a slurry reactor of tandem microwires, random particle orientation is predicted to impair the H$_2$ production by non-optimal light absorption between the current-matched subcell. This work proposes the innovative solution of aligning tandem particles in a slurry by balancing the forces of uplifting fluidizing bubbles and a downward magnetic force on the Ni at the bottom of the wire.

With the fabrication procedure of Si/TiO$_2$ tandem microwire in place there were 3 key questions that needed to be addressed:
1. How does the mode of particle dispersion and the magnetic field strength affect the angle of alignment of the microwires?

Chapter 3 introduces a particulate photocatalyst design that utilizes TiO$_2$/p$^+$n-Si in tandem with each other leading to an increased absorption of the AM 1.5 solar spectrum. Ni metal is incorporated into the design (TiO$_2$/p$^+$n-Si/Ni) via photodeposition. Upon solar illumination the photogenerated holes are directed towards the TiO$_2$ for the oxidation reaction and the electrons are directed towards the n-Si/Ni interface for the reduction reaction. Magnetic fields are used to leverage the ferromagnetic properties of Ni to control the orientation of photoactive microparticle which is hypothesized to have a significant effect on the STH efficiency of the slurry reactor. High-speed camera videos are analysed to plot a frequency distribution of these wires w.r.t the angle from the horizontal to assess the in situ magnetic alignment capability.

2. How does varying the particle concentration and dispersing bubble flowrate affect the light absorption properties of the slurry?

Chapter 4 presents an investigation of optical performance of the tandem microwire slurry under varying reactor conditions. Transmittance, reflectance and absorptance of the system were measured via UV-Vis spectroscopy with an integrating sphere as a function of wavelength, slurry particle concentration, and dispersion flowrates.

3. Is the Si/TiO$_2$ microparticle slurry photoactive under solar illumination? If yes, what light management strategies can be used to improve the activity?

Chapter 4 also discusses the photochemical performance of the Ni/np$^+$-Si/FTO/TiO$_2$ microwire slurry, characterized via organic methylene blue (MB) dye degradation
under visible and UV illumination. The photodegradation of the MB dye enabled direct in-situ monitoring of the performance of the slurry to test the effect of particle concentration, bubble flowrate, spectral mismatch, intermixed light scattering particles, and a back reflector.

Chapter 5 summarizes the work done and provides recommendations to improve the current tandem particle and reactor design for energy storage applications.

The objective of this dissertation was to design a semiconductor particulate system that can generate cost-effective H₂ via PEC water-splitting at high STH efficiency. The work presented herein elaborates the experimental progression towards achieving that goal.
CHAPTER 2

PHOTOCATALYTIC HYDROGEN EVOLUTION ON Si PHOTOCATHODES MODIFIED WITH BIS(THIOSEMICARBAZONATO)NICKEL(II)/NAFION

2.1 Introduction

Cost-effective, scalable hydrogen production from water-splitting is a grand challenge in the field of clean energy. By coupling the electrolysis to light absorption via artificial photosynthesis, the intermittent energy of sunlight can be captured as H₂ fuel. While platinum remains the state-of-the-art catalyst for the hydrogen evolution reaction (HER) at the cathode, numerous other catalysts have been studied. Molecular catalysts for HER have certain advantages, including low loadings of non-platinum group metal elements, and thus relatively low cost and high abundance. Moreover, the ligand structures can be tailored to tune the active site energetics for activity and selectivity without the constraints imposed by an extended solid lattice in heterogeneous catalysts. Molecular HER catalysts based on cobalt, iron, molybdenum, and nickel have been the most common. Molecular Ni complexes are among the most active, such as the well-known DuBois’ nickel-bis(diphosphine) catalysts. More recently, we and others
have explored a novel monomeric Ni(II) complex of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato), or NiATSM, for its role as a ligand-assisted, metal-centered HER electrocatalyst (Figure 10). The structures of bis(thiosemicarbazones) (BTSCs) are easily modified and usually synthesized in high yields from inexpensive organic reagents, making them attractive platforms for the design of new HER electrocatalysts. In addition, BTSC ligands are redox non-innocent and can function as a reservoir for charge with hydrogen evolution at either the metal or the ligand.

There have been a number of studies to leverage molecular HER catalysts for solar H₂ generation by incorporating these structures onto the surface of semiconductor photocathodes. In many cases, the catalyst was immobilized on the semiconductor surface via covalent linking strategies for direct charge transfer between the electrode and catalyst. Covalent attachment is often necessary to prevent catalyst delamination or dissolution in aqueous media but adds processing complexity as well as charge-transfer resistance at the interface. Ideally then, a molecular catalyst could be durably coupled to a photoelectrode with low overpotential in aqueous solution at low or high pH where electrolysis efficiency is maximized. NiATSM co-catalyst with CdS nanorods was recently reported for light-driven hydrogen evolution using monochromatic illumination with a sacrificial species at moderate pH values. Herein we report the characterization of the NiATSM catalyst under conditions for practical solar hydrogen generation. Simple catalyst attachment methods were used with p-Si photocathodes in pH 0 aqueous
electrolyte to yield robust photoelectrochemical energy-conversion behavior that clearly outperforms an equivalent loading of Ni metal catalyst.

2.2 Results and Discussion

2.2.1 Photoelectrochemical characterization

NiATSM was synthesized following previously reported methods\textsuperscript{70, 71} and the complex was characterized by NMR (Figure 10a), elemental analysis, FT-IR (Figure 21a), and UV/vis spectroscopy (Figure 21b). NiATSM is known to be a robust HER homogeneous catalyst in organic solutions, and insoluble in 1 M H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{64, 72} NiATSM was loaded to \textapprox 60 nmol cm\textsuperscript{-2} onto Si photoelectrodes as described in the experimental section.

![Figure 10. (a) \textsuperscript{1}H NMR of NiATSM (500 MHz, d\textsubscript{6}-DMSO): 7.69 (1H, br. s), 2.75 (3H), 1.94 (3H, s) (b) Representation of ligand-assisted, metal-centered HER electrocatalysis by NiATSM on p-Si (Nafion not shown).]
Figure 11 shows the photoelectrochemical energy-conversion behavior of NiATSM-coated p-Si photocathodes in 1 M H₂SO₄. Degenerate n⁺-Si electrodes were measured as well to test the behavior of the electrodes in the absence of the photoelectrochemical diode, which instead yields ohmic behavior and permits the measurement of dark electrocatalytic Butler-Volmer HER kinetics on the Si substrate. The onset potential and the potential for each electrode at a standard 10 mA cm⁻² is reported in Table 1. The resulting HER overpotential for the bare n⁺-Si was 860 mV, while 1 Sun-illuminated bare p-Si had a potential of -0.220 V vs. RHE, indicating a typical photovoltage from these electrodes of ~640 mV. With the inclusion of the molecular catalyst layer, the n⁺-Si/NiATSM overpotential decreased to 712 mV, a decrease of 148 mV relative to the bare n⁺-Si. Under illumination, the p-Si/NiATSM potential at 10 mA cm⁻² was -0.080 V vs. RHE. This represents a shift of 140 mV from the illuminated bare p-Si and is consistent with the observed catalytic shift on photo-inactive substrates. Durability of the drop-cast NiATSM
catalyst layer was investigated with extended potentiostatic operation under illumination at -0.2 V vs. RHE, a potential with a notable initial difference in current density between p-Si/NiATSM and bare p-Si. The p-Si/NiATSM current density vs. potential ($J-E$) behavior declined after this extended potentiostatic measurement back to the approximate behavior of bare p-Si (Figure 14a). This response indicates that the molecular catalyst, which is not covalently attached to the Si surface, may be dislodged under extended operation and generation of $H_2$ bubbles at the surface. However, by casting the NiATSM layer in a dilute Nafion solution (see Section 2.3) as a cation-exchanging binder, the extended current density vs. time performance became steady at ~22 mA cm$^{-2}$ at -0.2 V vs. RHE over the measured period (Figure 12a), with consistent $J-E$ behavior (Figure 14b). Other than promoting adhesion, the Nafion binder had little effect on the initial energy-conversion behavior of the photocathodes (Figure 11, Table 1, and Figure 15). Furthermore, characterization of the $H_2$ faradaic efficiency by gas chromatography displayed almost total direction of the charge to HER (Figure 12b). SEM images of the as-deposited NiATSM/Nafion layer on p-Si show that the catalyst formed 1 – 5 µm crystalline particles in the Nafion film (Figure 12c). After extended potentiostatic operation,

Table 1. Photoelectrochemical energy-conversion parameters.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Onset Potential (V vs. RHE)</th>
<th>Potential at 10 mA cm$^{-2}$ (V vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n$^+$-Si</td>
<td>-0.670</td>
<td>-0.860</td>
</tr>
<tr>
<td>n$^+$-Si/NiATSM</td>
<td>-0.630</td>
<td>-0.712</td>
</tr>
<tr>
<td>p-Si</td>
<td>-0.060</td>
<td>-0.220</td>
</tr>
<tr>
<td>p-Si/NiATSM</td>
<td>-0.020</td>
<td>-0.080</td>
</tr>
<tr>
<td>p-Si/NiATSM/Nafion</td>
<td>0.006</td>
<td>-0.080</td>
</tr>
<tr>
<td>p-Si/Ni$^+$</td>
<td>-0.024</td>
<td>-0.180</td>
</tr>
<tr>
<td>p-Si/Pt$^b$</td>
<td>0.124</td>
<td>-0.012</td>
</tr>
<tr>
<td>n$^+$-p-Si/NiATSM</td>
<td>0.170</td>
<td>0.025</td>
</tr>
</tbody>
</table>

[a] Electrodeposited Ni at 60 nmol cm$^{-2}$ to match the loading of NiATSM.

[b] Pt deposited by electroless deposition (see ESI).
however, these particles were observed to agglomerate into larger rod-like particles, some as long as ~ 100 µm (Figure 12d). We have previously reported the structural rearrangement and stacking interactions of NiATSM under cathodic cycling, and the observed agglomeration here is attributed to similar structural behavior after the passing of significantly more charge. EDS mapping showed that the Ni and S of the initial catalyst was confined to this larger agglomerate particle, with Nafion along the rod edges (Figure 16).

A common challenge for molecular catalysis researchers is to ensure that the observed electrocatalytic activity is attributable to the molecular structure of the ligand-modified metal center rather than direct heterogeneous catalysis of the metal atoms left behind after decomposition of the organic framework. Our previously

![Figure 12. (a) Current density vs. time at -0.2 V vs. RHE under 1 Sun AM1.5 illumination in 1 M H2SO4. (b) Calculated vs. measured H2 produced by illuminated p-Si/NiATSM/Nafion at -0.2 V vs. RHE in N2-bubbled 1 M H2SO4. SEM images of the p-Si/NiATSM/Nafion electrode (c) before and (d) after the stability measurement in (a). Scale bars correspond to 40 µm and 2 µm for the inset.](image)

reported X-ray photoelectron spectroscopy (XPS) data on the Ni 2p and S 2p orbitals of the NiATSM catalyst before and after cathodic current cycling in strongly acidic
aqueous electrolyte indicates that the molecular structure does not significantly decompose.\textsuperscript{72} XPS measurements for the NiATSM on p-Si show similar behavior. Though complicated by the presence of the thin Nafion layer, the XPS data indicated that there was no shift in the Ni oxidation state of the catalyst after the 1 h stability measurement (Figure 17). For NiATSM, this conclusion was further tested by measuring p-Si photocathodes with Ni\textsuperscript{0} metal electrodeposited at various loadings. With relatively thick Ni loading (430 nmol cm\textsuperscript{-2}, corresponding to a 35% decrease in the light-limited photocurrent due to parasitic absorption), the illuminated p-Si/Ni potential at 10 mA cm\textsuperscript{-2} was -0.080 V vs. RHE (Figure 19). The Ni-metal-catalyzed potential gradually decreased to -0.180 V vs. RHE for a loading of 60 nmol cm\textsuperscript{-2}, which is the matching loading of Ni atoms calculated to be present in the NiATSM catalyst layer. The photoelectrochemical behavior of p-Si photocathodes for equivalent molar loadings of metallic Ni and NiATSM is shown in Figure 13 with a 100 mV improvement in overpotential at 10 mA cm\textsuperscript{-2} for the molecular catalyst relative to the pure metal. The enhanced activity of NiATSM relative to Ni nanoparticles may be attributed to metal-ligand cooperativity during catalysis.\textsuperscript{73} In addition to the beneficial contribution of the BTSC ligands to promoting the HER mechanism, the enhancement of the molecular catalyst could be partially attributed to greater access of the electrolyte to each Ni site in the NiATSM molecule compared to the metal Ni deposits.

The behavior of electrolessly deposited Pt on a p-Si photocathode is also included Figure 13 for a comparison of the NiATSM to the state-of-the-art HER catalyst. As expected, the Pt-catalyzed electrode displayed the more efficient energy-conversion
behavior, but it only reduced the overpotential by 68 mV at 10 mA cm\(^2\) relative to NiATSM (Table 1). Notably, the Pt loading is difficult to control by galvanic displacement and the reduced light-limited current density of the p-Si/Pt curve indicates a significantly heavier catalyst loading in this case as well. Furthermore, forming an n\(^+\)p-Si buried homojunction before NiATSM deposition led to even better performance. In this case, a solid-state diode was produced by heavily doping a thin (~ 300 nm) n-type emitter layer at the surface before attachment of the NiATSM for aqueous HER (see experimental section). The 105 mV increase for the buried junction at 10 mA cm\(^2\) relative to the p-Si/NiATSM/Nafion semiconductor/liquid junction case can be attributed to improved interfacial energetics, increased band bending, and reduced recombination in the p-Si depletion region for a buried junction, as has been demonstrated before for Si photocathodes.\(^{74}\) The enhanced HER activity thus comes from the improved photovoltage of the Si

![Figure 13. Current density vs. potential (J-E) behavior for electrodes in H\(_2\)-saturated 1 M H\(_2\)SO\(_4\). Illuminated 1 Sun AM1.5 photoelectrochemical behavior for p-Si photocathodes with no co-catalyst (black), electrodeposited Ni (blue), NiATSM (red), and Pt (green), as well as a buried junction n\(^+\)p-Si with NiATSM (magenta).]
how Si/NiATSM photocathodes could be improved. The photoelectrochemical energy-conversion behavior for bare n+p-Si is shown in Figure 20a and the time-dependent photocurrent at -0.2 V vs. RHE of n+p-Si/NiATSM/Nafion is shown in Figure 20b.

2.2.2 Nafion Binding Effect on $J$-$E$ Behavior Stability

Although the $J$-$E$ behavior of drop-cast NiATSM on p-Si initially showed a significant positive shift in the potential relative to bare p-Si, this enhancement was not stable under extended operation (Figure 14a). After 1 hour of potentiostatic operation at -0.2 V vs. RHE, the photoelectrode $J$-$E$ behavior became indistinguishable from that of bare p-Si. This performance decline was attributed to gradual detachment of the NiATSM catalyst from interfacial agitation during H₂ bubble formation. Thus, a Nafion solution was added to the NiATSM solution to

![Figure 14](image_url)

Figure 14. Current density vs. potential ($J$-$E$) behavior of (a) p-Si/NiATSM without Nafion in 1 M H₂SO₄ under 1 Sun AM1.5 illumination. The Before data is the initial, as-deposited performance and the After data is the performance after 1 h at -0.2 V vs. RHE (b) p-Si/NiATSM with Nafion in 1 M H₂SO₄ under 1 Sun AM1.5 illumination. The Before data is the initial, as-deposited performance and the After data is the performance after 1 h at -0.2 V vs. RHE.
provide an acid-compatible binding layer during drop-casting. The resulting current density vs. potential photoelectrochemical behavior for p-Si/NiATSM/Nafion photoelectrodes became much more stable (Figure 12, Figure 14b). The photocurrent response slightly increased after the 1 hour potentiostatic measurement, which may be partially attributable to the beneficial effect of NiATSM molecular catalyst morphology stacking and restructuring as reported in our previous work.\textsuperscript{72}

2.2.3 Effect of Nafion on the p-Si performance

The NiATSM was cast from a dilute solution of Nafion (see Experimental Section), with the cation-exchange selective ionomer used to enhance the binding of the molecular compound to the semiconductor surface while permitting stable performance in acidic media. As shown in Figure 15, an equivalent thickness of Nafion film on p-Si in the absence of NiATSM had only a minor effect on the illuminated current density vs. potential behavior. There was a slight positive shift in potential for a Nafion film relative to a bare p-Si photoelectrode. This minor effect could speculatively be attributed to the charged groups in the Nafion sulfonic acid side chains creating a slight dipole at the interface, which contributes to band bending and has been experimentally demonstrated to affect the photoelectrochemical photovoltage.\textsuperscript{75} However, initial $J$-$E$ performance curves for p-Si/NiATSM with and without Nafion binder were indistinguishable between multiple electrodes within experimental error (Figure 11).
Following extended potentiostatic operation of the p-Si/NiATSM/Nafion photocathodes, the catalyst particles were observed to agglomerate into larger rodlike particle structures (Figure 12). Energy dispersive x-ray spectroscopy (EDS) analysis was performed to map the distribution of the key elements before and after this restructuring. As seen in Figure 16 below, Ni and S, which are primarily present in the NiATSM (S is a minor component in Nafion), are mostly confined to the observed particles even after the agglomeration. Fluorine, F, which is introduced in the polytetrafluoroethylene backbone of the Nafion binder, is initially observed to be uniformly distributed. However, after particle agglomeration, it was observed to be more concentrated along the edges of the rodlike NiATSM particle. Si, as the underlying substrate, displayed a strong signal everywhere, which was only weakened in the locations of the catalyst particle.
Although XPS data for NiATSM after cathodic cycling on glassy carbon substrates in aqueous acidic electrolyte has already shown a steady Ni oxidation state in our previous work, it was measured and reported again here on p-Si photoelectrodes and in the presence of the Nafion binder. For an as-deposited p-Si/NiATSM without Nafion, a p-Si/Nafion without NiATSM, and p-Si/NiATSM/Nafion before and after 1 h under 1 Sun at -0.2 V vs. RHE in 1 M H$_2$SO$_4$, the measured binding energies for the Ni 2p, S 2p, and Si 2p regions are shown in Figure 17 and Figure 18a,b, respectively.

Without Nafion, the as-deposited p-Si/NiATSM shows the same Ni 2p character as previously reported for NiATSM. When the NiATSM is co-deposited with Nafion binder, the Ni 2p signal was significantly reduced in intensity, which is consistent with a thin surface coating of polymer reducing the signal (Figure 17). The Ni 2p peak intensity was further reduced after operation, consistent with the dispersed catalyst particles concentrating into larger particles (Figure 12) and leaving less area.

Figure 16. SEM images (far left) and EDS corresponding elemental maps for Ni (purple), S (red), F (green) and Si (yellow) for p-Si/NiATSM/Nafion before (top panels) and after (bottom panels) 1 h at -0.2 V vs. RHE in 1 M H$_2$SO$_4$ under 1 Sun AM1.5 illumination. The scale bar is 20 µm.
of exposed Ni to measure. However, the main Ni 2p peak position at ~856 eV remained unchanged before and after operation, indicating no shift in the oxidation state. For sulfur, the XPS spectra is more complicated by the presence of the Nafion layer. Nafion polymer owes its cation-selective permeability to the negatively charged groups arising from the clustering of sulfonic acid side chains. Thus, there are S atoms present throughout the Nafion film, as evidenced by the broad S 2p peak observed for p-Si/Nafion without NiATSM catalyst (Figure 18a). For p-Si/NiATSM without Nafion, a sharper S 2p was observed at ~168 eV, which would be attributed to the Ni-adjacent S atoms in NiATSM (Figure 10). When NiATSM is co-deposited with Nafion, the resulting S 2p spectra appears to be a convolution of the broad Nafion S peak and the underlying NiATSM S signal. Interestingly, after the p-
Si/NiATSM/Nafion stability measurement, the sharper NiATSM S 2p peak increased in intensity relative to the spectra before photocathodic hydrogen evolution. The nature of this shift is not entirely clear, but we speculate that the NiATSM agglomeration to large rodlike particles during operation leaves more of the NiATSM directly exposed to the x-ray signal, as opposed to the smaller as-deposited NiATSM clusters which have a surface coating of Nafion to interfere with the measurement.

The effect on the underlying Si substrate was also probed with the Si 2p XPS binding energy spectra (Figure 18b). After the 1 h stability measurement, the Si peak at 99.6 eV and the SiO₂ peak at 103.4 eV both became more intense relative to the as-deposited substrates. As observed in our SEM measurements after extended
potentiostatic operation, the initial smaller microparticles of NiASTM left behind gaps in the Nafion thin film when they migrated and agglomerated into larger particles. We thus attribute the increased Si peak (and Si oxidation) to the underlying Si in these gaps being directly exposed to the x-ray.

2.2.6 Behavior of Electrodeposited Ni on p-Si
Metallic Ni was deposited photoelectrochemically on p-Si (see experimental section) for comparison to the performance of photocathodes catalyzed with molecular NiATSM. By controlling the charge passed per electrode area during electrodeposition, well-controlled Ni loadings were achieved.

![Figure 19. Current density vs. potential (J-E) behavior of electrodeposited Ni/p-Si electrodes in 1 M H₂SO₄ under 1 Sun AM1.5 illumination as a function of Ni catalyst loading.](image)

With a single Ni site per NiATSM molecule, a molar loading of Ni of ~60 nmol cm⁻² was present as NiATSM catalyst during photoelectrochemical measurements. Thus, 60 nmol cm⁻² of electrodeposited Ni catalyst was used to directly compare the activity of an equivalent amount of metallic Ni. As shown in Figure 19, this low
loading of Ni as HER catalyst produced little improvement in the $J$-$E$ behavior of a p-Si photocathode. Progressively higher loadings of Ni managed to reduce the overpotential, with a loading of 430 nmol cm$^{-2}$ reaching 10 mA cm$^{-2}$ at -0.080 V vs. RHE. This potential is comparable to that achieved for p-Si/NiATSM/Nafion photoelectrodes (Table 1), however, it required 7.2x as much Ni. Moreover, parasitic light absorption in the catalyst layer become more significant at this loading, leading to a 35% decrease in the light-limiting current density.

2.2.7 Behavior of NiATSM in Buried Junction n$^+$p-Si
Buried junction photocathodes were fabricated by producing a solid-state diode with an n$^+$ emitter layer. This approach can lead to better junction performance, and was shown in Figure 13 to highlight the increased HER performance possible for Si/NiATSM photocathodes with this additional processing step. The $J$-$E$ performance for a bare n$^+$p-Si photocathode is shown in Figure 20a for comparison to the NiATSM-catalyzed behavior. At 10 mA cm$^{-2}$, the bare n$^+$p-Si had a potential of -0.110 V vs. RHE. Thus, the n$^+$p-Si/NiATSM/Nafion potential was shifted 135 mV positive relative to the uncatalyzed electrode, which was consistent with the behavior for p-Si electrodes without a buried junction (Table 1). The NiATSM with Nafion binder was also observed to be stable on buried junction n+p-Si photoelectrodes under the same operating conditions tested in Figure 12. At -0.2 V vs. RHE for 1 h, the current density stabilized at ~ 27 mA cm$^{-2}$ (Figure 20b), consistent with the corresponding observed value during cyclic voltammetry.
2.3 Experimental Section

2.3.1 NiATSM Catalyst Synthesis and Characterization

All reagents were obtained from commercially available sources and used as received unless otherwise noted. Commercial solvents were additionally dried and purified using an MBraun solvent purification system unless otherwise noted. All reactions were performed open to air and under ambient conditions unless otherwise indicated. The diacetyl-bis(N-4-methyl-3-thiosemicarbazone) (H₂ATSM) ligand and the diacetyl-bis(N-4-methyl-3-thiosemicarazonato)nickel(II) (NiATSM) complex were prepared following previously reported methods.⁷⁰, ⁷¹ The prepared NiATSM complex was characterized by NMR (Figure 10), elemental analysis, FT-IR (Figure 21a), and UV/vis spectroscopy (Figure 21b). The ¹H NMR data were collected on a Varian Inova 500 MHz NMR Spectrometer in commercial deuterated solvents (Aldrich or Cambridge Isotopes). The ¹H NMR of NiATSM displays

![Figure 20. (a) Current density vs. potential (J-E) behavior in 1 M H₂SO₄ under 1 Sun AM1.5 illumination for bare n⁺p-Si, and n⁺p-Si/NiATSM/Nafion (b) Current density vs. time at -0.2 V vs. RHE under 1 Sun AM1.5 illumination in 1 M H₂SO₄ for n⁺p-Si/NiATSM/Nafion.](image-url)
characteristic peaks at 1.94 ppm for the backbone methyl protons, at 2.75 ppm for the pendant methyl protons, and at 7.69 ppm for the pendant NH protons (Figure 10). Elemental analyses were performed by Midwest Microlab, (Indianapolis, IN, USA). The purity of NiATSM complex was confirmed by elemental analysis: Anal. Calc. for C$_8$H$_{14}$N$_6$NiS$_2$: C, 30.31; H, 4.45; N, 26.51. Found: C, 30.55; H, 4.35; N, 26.42. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer equipped with an ATR attachment (4 cm$^{-1}$ resolution). The infrared spectrum of the H$_2$ATSM ligand displays two N–H stretches at 3238 and 3357 cm$^{-1}$. Upon complexation of H$_2$ATSM with Ni(II) the characteristic hydrazino N–H stretch at

![Figure 21. (a) FT-IR spectra of H$_2$ATSM (black) and NiATSM (red) (b) UV-vis spectra of H$_2$ATSM (blue) and NiATSM (red) recorded in a mixture of acetonitrile/methanol solution (1:1). (Inset) The d-d charge-transfer region](image-url)
3238 cm\(^{-1}\) disappears in the NiATSM spectrum (Figure 21a). Electronic UV/vis absorption spectra were recorded with an Agilent 8453 diode array spectrometer with a 1 cm path length quartz cell. The electronic spectrum of H\(_2\)ATSM displays a strong band at 328 nm that upon complexation with Ni(II) is significantly decreased with the appearance of a ligand-to-metal charge-transfer band near 398 nm and a more intense ligand-to-ligand charge-transfer band near 257 nm in the NiATSM spectrum (Figure 21b).

2.3.2 Electrode Preparation

Two different types of Si substrate were used in this work. Degenerately doped n\(^{+}\)-Si(100) (doped with As to a resistivity of 0.001 – 0.005 Ω cm, University Wafer) substrates were used to measure the dark electrocatalytic behavior of the Si semiconductor surface as well as the Si-supported NiATSM electrocatalyst behavior. Photoactive substrates for illuminated hydrogen evolution consisted of p-Si(100) (doped with B to 1 – 10 Ω cm, University Wafer). Before attaching the NiATSM co-catalyst, the Si native oxide layer was removed with a > 10 s dip in 10% HF. To load the catalyst on the electrodes, a 2.0 mM solution of NiATSM in acetonitrile was dropcast on the Si surface to a consistent loading of ~60 nmol cm\(^{-2}\), followed by 1 min in a vacuum oven at 70 °C. For Nafion-bound NiATSM, each 20 mL of 2 mM solution also contained 25 µL of 5% aqueous Nafion solution (Beantown Chemical) and was further heated in air at 60 °C for 1 min. In the case of electrodeposited Ni metal catalyst on p-Si for comparison, the Si working electrode was placed in nickel electroplating solution (nickel sulfamate and boric acid, Sigma Aldrich) with a Ag/AgCl reference and a fritted Pt counter electrode.
and held at -0.5 V vs. RHE under illumination to pass various amounts of charge corresponding to different Ni loadings. To match the molar loading of Ni atoms on the NiATSM/p-Si electrodes with 60 nmol NiATSM cm$^{-2}$, a charge of 0.012 C cm$^{-2}$ was passed. An ohmic back contact to Si substrates was made using Ga/In eutectic (Alfa Aesar), with the back contact sealed in epoxy. Pt deposition on p-Si was accomplished via a galvanic displacement reaction whereby Si is oxidized (and then etched by HF) and Pt is reduced onto the electrode surface.$^{76}$ The Si wafer was immersed for 2 minutes in an aqueous solution of 0.5 M HF and 2 mM K$_2$PtCl$_6$. The n$^+$ p junction was formed on the Si by thermal P diffusion using solid-source CeP$_5$O$_{14}$ wafers (Saint-Gobain, PH-900 PDS) at 950 °C for 30 min under N$_2$ ambient, to yield an n$^+$ emitter layer. The room temperature n$^+$p-Si was then etched in 10% HF for > 2 min to remove the dopant glass layer, followed by physical abrasion of the wafer edges to eliminate shunting.

2.3.3 Photoelectrochemical Measurements

Current density vs. potential ($J$-$E$) photoelectrochemical energy-conversion behavior for all electrodes was measured in hydrogen-saturated 1 M H$_2$SO$_4$ (pH 0, made with 18 MΩ cm H$_2$O) under vigorous stirring with active bubbling of H$_2$ (99.99%, Specialty Gases) at room temperature. The Si electrode was the working electrode in each case, with a Ag/AgCl (saturated KCl) reference electrode (CH instruments, Inc.) along with a Pt gauze counter electrode separated by a glass frit, all in a glass cell with a flat quartz window for illumination. Before each measurement with a Si electrode, the native oxide was removed with a > 10 s dip in 10% HF. A Bio-Logic SP-200 potentiostat was used for all measurements. The
results are reported versus the reversible hydrogen electrode (RHE) scale according to \( V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059*\text{pH} \). Simulated sunlight at an intensity of 100 mW cm\(^{-2}\) at normal incidence to the working electrode was generated with a 300 W Xe lamp (Newport 6258) coupled with an AM1.5 global filter (Newport 81094) and calibrated in the electrolyte with a Si photodiode (Thorlabs FDS100-CAL). Cyclic voltammetry measurements of \( J-E \) behavior were measured at a scan rate of 20 mV s\(^{-1}\). Reported 1 h stability data was measured potentiostatically at -0.2 V vs. RHE. Hydrogen quantification and faradaic efficiency determination were measured under potentiostatic conditions at -0.2 V vs. RHE using gas chromatography (GC, SRI 8610). For this measurement, \( \text{H}_2 \) was not bubbled but instead nitrogen (99.99%, Specialty Gases) was used as the carrier gas to enable accurate hydrogen quantification. The gas outlet from the catholyte was connected to the GC, which used an automatic valve injection (1 mL sample) and a thermal conductivity detector (TCD). Faradaic efficiency was calculated by determining the charge required to produce the measured \( \text{H}_2 \) concentration and dividing by the total charge passed in the electrolysis during the gas collection period.

2.3.4 Materials Characterization

The electrode surfaces were characterized with scanning electron microscopy (SEM) using a NOVA FEI microscope at an accelerating voltage of \( \sim 15 – 18 \) kV. Energy dispersive X-ray spectroscopy (EDS) mapping measurements were conducted using an FEI Tecnai F20 microscope with an accelerating voltage of 20 kV. Surface elemental analysis was performed using X-ray photoelectron spectroscopy (XPS) with a VG Scientific Multilab 3000 custom-built ultra-high
vacuum system with Mg-Kα radiation. XPSPEAK 4.1 software was used for peak deconvolution and the XPS data analysis.

2.4 Conclusion

Molecular NiATSM complex was used as a co-catalyst with planar p-Si for photocathodic hydrogen evolution without covalent surface attachment. The addition of Nafion binder during drop-casting was shown to promote catalyst adhesion and steady potentiostatic operation without degradation of the electrochemical energy-conversion performance. The p-Si/NiATSM/Nafion photocathodes produced H₂ with near unity faradaic efficiency. Moreover, the photoelectrode with Ni molecular catalyst displayed a potential 100 mV more positive than an electrode with an equivalent molar loading of Ni metal, demonstrating the benefit of the BTSC ligands for promoting HER by the ligand-assisted, metal-centered mechanism previously described for NiATSM.⁶⁴
CHAPTER 3

IN-SITU MAGNETIC ALIGNMENT OF A SLURRY OF TANDEM SEMICONDUCTOR MICROWIRES USING A Ni CATALYST

3.1 Introduction

Photoelectrolysis of water, first reported by Fujishima and Honda in 1972, is a promising technology for the storage of intermittent solar energy as clean, carbon-free hydrogen fuel. Many advancements have been made for solar fuels over decades of research, including a demonstration of over 30% solar-to-hydrogen (STH) efficiency for state-of-the-art photovoltaics (PV) coupled to electrolyzers. Despite promising efficiencies, widespread commercialization of solar hydrogen has remained elusive due to prohibitive costs for a PV+electrolyzer system approach. Instead, technoeconomic analyses have found that integrated semiconductor photoelectrolysis reactor designs, in particular photoactive particle suspensions, have the greatest potential to yield cost-effective solar hydrogen by reducing balance-of-plant costs and eliminating many of the components that contribute to capital expense. These analyses assumed a base case for single particle-type slurry reactors of 10% STH efficiency in order to produce solar hydrogen at a price competitive with H₂ produced from steam methane reforming.
To date, however, practical demonstrations of water-splitting semiconductor particulate reactors have resulted in fairly low STH efficiency.\textsuperscript{83} The Domen group has made significant advancements studying particulate photocatalysts, such as SrTiO\textsubscript{3}, both as a single particle and as part of a tandem Z-scheme design.\textsuperscript{84-89} A particulate reactor with Al-doped SrTiO\textsubscript{3} over a relatively large area of 1 m\textsuperscript{2} achieved an STH efficiency of 0.4\% under natural sunlight,\textsuperscript{84} while Z-scheme SrTiO\textsubscript{3} and BiVO\textsubscript{4} were shown to achieve 1.1\% STH efficiency.\textsuperscript{88} Numerous other semiconductor photocatalyst particles have been studied for water-splitting, including BaTaO\textsubscript{2}N, Ta\textsubscript{3}N\textsubscript{5}, and CoO, among others.\textsuperscript{90-92} Although such systems have shown continued improvement, none of them have gotten close to achieving the 10\% STH efficiency target assumed in the technoeconomic models for cost-effective solar H\textsubscript{2} in particulate slurry reactors. Besides having non-ideal semiconductor materials, there are several limitations to the particle approach that have contributed to low efficiencies. In the case of a single-bandgap particle, a minimum bandgap $>$ 2.2 eV is required to achieve the necessary photovoltage to split water, which strongly limits the theoretical maximum STH efficiency.\textsuperscript{93} Also, uniform nanoparticles immersed in electrolyte lack a built-in electric field to provide migration-directed charge-carrier transport and instead have to rely on diffusion to drive charges to sites of lower charge concentration, which leads to less efficient photochemistry.

A high STH efficiency system will likely require a tandem approach with complementary bandgaps to efficiently utilize the energy of a wider range of the solar spectrum. Modeling of an integrated tandem system has shown that an ideal
combination of 1.6-1.8 + 0.9-1.1 eV bandgaps is capable of splitting water at > 25% STH efficiency.$^{94}$ Monolithic multijunction semiconductor systems benefit from additive photovoltage between the subcells due to having the photoactive regions in electrical series; however, as a consequence the current must be matched between junctions as well. Thus, tandem devices are designed for an optimal illumination condition which balances the photogenerated current between subcells. If a change in light absorption leads to subcell regions with different or mismatched current, the region of lesser current will limit the entire device, which has significant detrimental consequences for the overall efficiency.

In pursuit of a high efficiency water-splitting tandem, Si is a logical choice for the narrow gap bottom subcell with a near-ideal bandgap ($E_G = 1.12$ eV), cost-effective fabrication, and highly developed photoactive properties. However, Si has an indirect gap and requires ~100 µm or more to absorb most of the above-bandgap light. Making Si particles with a minority-carrier diffusion length > 100 µm is cost-prohibitive, but extensive research has shown that high-aspect-ratio microwires permit sufficient light absorption in the axial dimension while enabling effective charge-carrier collection in the much shorter radial direction, which makes it feasible to use cost-effective low minority-carrier diffusion length material.$^{95-97}$ Furthermore, dense Si microwire arrays of controlled dimensions and high fidelity can be grown from the bottom up via the vapor-liquid-solid mechanism and fabricated cost-effectively by reuse of the growth substrate.$^{98,99}$ Tandem structures for solar water-splitting have been demonstrated using p-n junction Si microwire arrays on a planar substrate in combination with materials such as TiO$_2$,$^{100}$ WO$_3$,$^{101}$
and BiVO$_4$. Efforts have also been made to embed these microwire arrays without the growth substrate in a polymer or membrane for unassisted water-splitting, but fabrication challenges have made this approach difficult. However, when these tandem microwires are dispersed in a slurry, random orientation of the high-aspect-ratio particles can lead to non-ideal light absorption and resultant unequal current distribution between the subcell layers of the microwire, which would decrease the individual particle STH efficiency.

Therefore, to make use of monolithic tandem microstructures with a buried junction built-in electric field to achieve high STH efficiency particle suspensions, it may be beneficial to have a strategy for light management within the tandem structure. Maintaining vertical alignment of the microwires towards the illumination is one way to prevent current mismatch within the subcell layers. Ni coatings have previously been demonstrated to allow magnetic orientation of Si particles on a surface, but to date the principle has not been leveraged to control the orientation of practical water-splitting photocatalyst particles under realistic operating conditions. Herein, we characterize a tandem microwire structure for unassisted water-splitting and demonstrate a method for their in-situ alignment using a magnetic field to orient the particles via a Ni hydrogen evolution catalyst (HEC) at the bottom of the microwire.
3.2 Results and Discussion

3.2.1 Tandem Structure and Performance
To further motivate the possible benefit of vertically aligning water-splitting tandem microwires, the detrimental effect of non-ideal orientation of the microwire relative to the illumination can be highlighted by a simple calculation assuming a tandem with a complementary top subcell layer bandgap of 1.7 eV, which has been previously modeled to lead to peak tandem efficiency with a 1.12 eV bandgap Si bottom subcell. Si microwires were chosen to be 100 µm tall to allow effective light absorption and 9 µm in diameter to accommodate a shorter diffusion length. Assuming unity internal quantum efficiency and neglecting reflection, the Beer-Lambert law indicates that a vertically oriented Si wire would lead to a photocurrent density of 15.6 mA cm\(^{-2}\) from photons between 1.12 – 1.7 eV absorbed along the 100 µm thick wire axis. In a horizontal orientation, however, with a 9 µm diameter Si core perpendicular to the illumination, the Beer-Lambert law yields a photocurrent density of 6.4 mA cm\(^{-2}\) from photons between 1.12 – 1.7 eV absorbed in a 9 µm thick layer, which drops to roughly 5.4 mA cm\(^{-2}\) when considering the curvature-dependent thickness of a cylinder cross-section. Thus, in this idealized case assuming the Si core as the limiting layer, a horizontally aligned wire would be predicted to have only 35% of the STH efficiency of a vertically aligned wire.

An ideal 1.7 eV bandgap tandem match to Si which enables stable photoelectrolysis is not readily available, however, and is still the subject of intense research. For this work, a reliable semiconductor of non-ideal bandgap was selected just to establish a proof-of-concept unassisted water-splitting tandem microwire
with which to develop an in-situ alignment method. TiO$_2$ was chosen as the top subcell semiconductor because it is highly stable, it can generate the requisite photovoltage for electrolysis in combination with Si, and it is straightforward to fabricate on microwires by solution-based methods. With the photoanode TiO$_2$ surface performing water oxidation, the exposed Si core is the cathodic site for hydrogen evolution. Ni was chosen as the hydrogen evolution reaction (HER) catalyst because it is stable and highly active in alkaline media,\textsuperscript{47} it can be selectively photodeposited on the exposed Si, and it is ferromagnetic.

![Figure 22](image.png)

**Figure 22.** Conceptual schematic of the vertical alignment of tandem semiconductor microwires in a slurry performing unassisted solar water-splitting, in which an increasing magnetic field strength, $B$, acting on a Ni hydrogen evolution catalyst (HEC) leads to increasing alignment (left to right). The microwire cross-section at the far right depicts the proof-of-concept tandem Ni/p$^+$-Si/FTO/TiO$_2$ structure used in this work.

Figure 22 illustrates the concept of a tandem microwire slurry performing unassisted water-splitting under the influence of varying magnetic fields. In the absence of a magnetic field, the suspended microwires are expected to have random orientation, but under an increasingly strong magnetic field originating from the base of the slurry, magnetic forces on the Ni HEC bulb at the bottom of the wire act to
progressively align the microwires vertically with respect to their long axis. The cross-sectional schematic at the right of Figure 22 shows the tandem structure used to establish a proof-of-concept unassisted water-splitting system with in-situ alignment capability.

![Cross-sectional schematic of tandem microwire structure](image)

Figure 23. Schematic of the tandem Ni/np⁺-Si/FTO/TiO₂ microwire fabrication process. (A) An n-Si(100) wafer was photolithographically patterned and (B) DRIE etched to create an array of microwires, then (C) diffusion doped with B to make a radial p⁺-emitter layer. (D) A ~500 nm thick FTO layer was spray deposited on the microwire array, followed by (E) hydrothermal deposition of a ~2 µm thick layer of TiO₂ nanorods. To turn a microwire array into detached integrated tandem microwires, (F) the array was infilled with a nail polish polymer and (G) mechanically detached from the substrate. (H) The polymer layer was selectively dissolved and the microwires filtered and collected. (I) Finally, Ni was photodeposited at the bottom of the tandem at the exposed n-Si core and subsequently magnetized with a rare-earth magnet.

Figure 23 illustrates the tandem microwire fabrication process. Si microwire cores were fabricated via deep reactive ion etching (DRIE) of an n-Si substrate for rapid, reproducible fabrication of dense wire arrays. A radial emitter layer was then formed via diffusion doping from a B source. The presence of a high-quality np⁺-Si homojunction is predicted to improve performance by providing migration-induced directionality to photogenerated charge-transport and by maintaining a high built-in
voltage at the junction, as has been previously reported for Si microwire array photocathodes.\textsuperscript{74} Emitter layer formation was followed by sequential spray deposition of a conformal fluorine-doped tin oxide (FTO) layer. The transparent, conductive FTO minimizes interfacial recombination between the semiconductors and establishes ohmic contact. A hydrothermal solution-based method was then used to deposit a \( \sim 2 \, \mu m \) thick layer of a dense nanorod rutile TiO\(_2\) film to complete an np\(^+\)-Si/FTO/TiO\(_2\) tandem electrode (see Experimental Section). Figure 24 shows select SEM images of the microwire array during the fabrication process.

![Figure 24. SEM images of microwires during the tandem fabrication process, including (a) DRIE etched microwires from an n-Si substrate, (b) spray-deposited FTO at the top of an n-Si microwire, and (c) the bottom of a freshly cleaved array of np\(^+\)-Si/FTO/TiO\(_2\) tandem microwires embedded in nail polish. The scale bar is 50 \( \mu \)m in (a), 1 \( \mu \)m in (b), and 20 \( \mu \)m in (c).](image)

The np\(^+\)-Si/FTO/TiO\(_2\) tandem combination produced sufficient photovoltage under 1 Sun AM1.5 illumination to generate current at 0 V vs. RHE in a 1 M KOH electrolyte.\textsuperscript{100} Both planar and substrate-attached microwire array electrodes were tested as photoanodes in 3-electrode measurements. Figure 25 shows cross-sectional SEM images as well as the photoelectrochemical energy-conversion behavior of the tandem photoelectrodes. Planar TiO\(_2\) deposited on a photo-inactive degenerate p\(^+\)-Si wafer had an onset potential at \( \sim 0.35 \, V \) vs. RHE, while the np\(^+\)-Si/FTO/TiO\(_2\) tandem had an onset potential of -0.3 V vs. RHE. The buried-junction Si thus added
a photovoltage of ~650 mV to the TiO$_2$ photoelectrochemical junction, which gave the electrode enough potential to produce current at 0 V vs. RHE without additional electrical bias. Although it was still able to produce ~0.3 mA cm$^{-2}$ at 0 V vs. RHE, the tandem microwire array performance decreased modestly relative to the planar electrode, as has been seen previously in microwire array electrodes and attributed to enhanced recombination from the increased surface area per light-absorbing projected area.$^{96}$

Figure 25. Tandem structure and water-splitting performance. Cross-sectional SEM images of the (a) planar and (b-c) microwire array np$^+$-Si/FTO/TiO$_2$ structure. Scale bar is 3 µm in (a), 50 µm in (b), and 10 µm in (c). (d) Photoelectrochemical energy-conversion behavior for electrodes under 1 Sun AM1.5 illumination in aqueous 1 M KOH. Tandem np$^+$-Si/FTO/TiO$_2$ electrodes in a planar (red curve) and microwire array (black curve) structure are shown. In addition, an analogous planar single-junction p$^+$-Si/FTO/TiO$_2$ (green curve) is included to highlight the contribution from the TiO$_2$ layer, with the additional photovoltage in the red curve coming from the np$^+$-Si homojunction. (e) Tandem electrode photoelectrochemical behavior in a two-electrode measurement with a Ni foil counter electrode. (f) Tandem electrode current density vs. time behavior (red curve) at 0 V vs. the Ni counter electrode without a separator, and corresponding H$_2$ faradaic efficiency measurements (black curve).
To demonstrate the capability of the tandem structure for full unassisted solar water-splitting, the electrode was measured in a two-electrode arrangement with a Ni foil HEC counter electrode of the same projected area (Figure 25e). At 0 V applied bias, the tandem electrode produced 0.25 – 0.30 mA cm$^{-2}$ over a 2 h measurement, with current oscillations corresponding to bubble formation and release (Figure 25f). Hydrogen faradaic efficiency was measured at 80 – 90%, with losses attributed to back reactions since there was no separator employed between the anode and cathode.

To produce microparticles for full water-splitting in a slurry, a method was required to selectively deposit the Ni HEC to the cathodic site of disconnected tandem microwires. Microwire arrays were encased in a nail polish polymer layer, mechanically peeled from the growth substrate, and then freed from the polymer in acetone. This approach helped to transfer the microparticles from the substrate to a liquid media with minimal losses. Once filtered, the wires were suspended in a Ni electrodeposition solution with 0.056 M Na$_2$SO$_3$ and irradiated with AM1.5 light with an additional UV illumination source. The extra UV light bias was added to boost the limiting photocurrent in the TiO$_2$ layer for faster Ni deposition (see Experimental Section). The photogenerated holes oxidized the sulfite ion, SO$_3^{2-}$, at the TiO$_2$ surface while photogenerated electrons reduced Ni$^{2+}$ to Ni$^{0}$ metal at the exposed surface of the n-Si core at the base of the microwire. The sodium sulfite acts as a hole scavenger to enable oxidation at the anode with a lower energetic demand than water oxidation. Similar approaches have been used previously to deposit Ni on photocatalyst particles.$^{107}$
Energy dispersive x-ray spectroscopy (EDS) elemental maps of individual detached microwires show the success of the selective Ni photodeposition at the base of the wire (Figure 26), which indicates that detached tandem microwires retained their photoelectrochemical activity. For a microparticle not subjected to the Ni deposition process, the cleavage point at the base of the wire appeared relatively smooth with easily resolvable components for the Si core, the Ti shell, and even a Sn ring in the middle where the FTO layer was deposited. Following the photodeposition process, a bulb of Ni metal was observed confined to the exposed Si face. The uniformity of the Ni deposition between tandem microwires varied, with some microwires displaying more Ni than others and variations in the number and size of bulbous Ni deposits on each Si core.

Some representative examples of Ni deposits are shown in SEM images in Figure 27. Possible reasons for an uneven Ni loading between microwires include variability in photocurrent due to the shadowing effect of other microwires as well as Ni ion mass transport limitations to areas of higher microwire concentration.

Figure 26. SEM images (leftmost panels) and EDS elemental maps for Si (orange), Ti (blue), Sn (green), and Ni (red) of the cross-sectional base of a tandem microwire (a, top row) after detachment from the n-Si substrate and (b, bottom row) after photodeposition of the Ni catalyst. The scale bar in each of the two SEM images is 4 μm.
Erratic morphology for each Ni bulb could be attributable to variations in the surface defects and exposed crystal planes after microwire detachment, as well as the onset of Si oxide layer formation leading to irregular patterns for Ni deposition nucleation sites.

![Image of Ni bulb morphology](image1)

Figure 27. SEM images of the cross-sectional base of tandem microwires after detachment from the n-Si substrate and photodeposition of the Ni catalyst. The scale bar in each image is 5 μm.

3.2.2 Orientation of Suspended Microwires in a Magnetic Field

The in-situ orientation of suspended microwires in a slurry was studied using high-speed videography with optical magnification (see Experimental Section). The camera was focused on a cuvette containing microwires suspended in water with a tunable electromagnet or rare-earth magnet at the base. A gaussmeter probe was

![Graph of magnetic field strength vs. distance](image2)

Figure 28. Calibration curve for the magnetic field strength in gauss (G) as a function of the distance from the outside bottom of the cuvette cell used for microwire slurry suspensions. Magnetic field strengths for an electromagnet and a rare-earth magnet were measured. The percentage of full power applied to the electromagnet is reported in the legend for each curve.
used to calibrate the electric field strength at various conditions as a function of the distance from the bottom of the cuvette (Figure 28). By measuring the angle from horizontal for many microwires across numerous disparate frames of the video, frequency distributions of the orientation angle at different magnetic field strengths were generated. Furthermore, in addition to tandem Ni/np\textsuperscript{+}-Si/FTO/TiO\textsubscript{2} microwire slurries, suspensions of electrodeposited Ni-coated n-Si microwires were tested as well for comparison as a best-case scenario for magnetic alignment. Previous work for the alignment of Ni-coated microstructures on a surface showed that increasing the length of the Ni deposit led to a greater degree of alignment.\textsuperscript{106} Thus, for these best-case test microwires, a \(~0.7\, \mu\text{m}\) thick Ni layer was coated along the entire length of an n-Si microwire (Figure 29). Orientation of the suspended microwires in a magnetic field was also tested as a function of the electrodeposited Ni loading (Figure 30).

Figure 29. SEM images of an electrodeposited Ni-coated n-Si microwire array cross-section. The scale bar is 30 \(\mu\text{m}\) in (a) and 5 \(\mu\text{m}\) in (b).

Particles in the 100 \(\mu\text{m}\) size regime such as the microwires studied herein will quickly settle out of suspension in the absence of an uplifting force. Two approaches were used to maintain a microwire dispersion: fluidization by uplifting bubbles
rising from a microporous frit installed at the base of the cuvette and agitation via sonication or fluid injection. Figure 31 shows selected optical images of microwire dispersions with and without bubbling in the presence and absence of a magnetic field. Without bubbling, sonication was very effective at maintaining a dispersion but was found to cause damage and delamination of the TiO$_2$ layer in tandem microwires. Fluid injection from a micropipette was a gentler means to create a dispersion and was used for tandem microwire orientation studies without bubbling. Dispersion by bubbling was investigated as well because it may be a more practical way to maintain a microwire suspension in a real solar water-splitting reactor.

![Figure 30](image_url)

Figure 30. In-situ microwire alignment for electrodeposited Ni-coated n-Si microwires as a function of the Ni loading in terms of charge passed during the deposition. Measured microwire angle from horizontal vs. the percentage of wires in 10° increments for a suspended slurry under a magnetic field strength of (a) 140 G and (b) 300 G.
The carrier gas composition and flow rates could also be tuned to affect the output \( \text{H}_2/\text{O}_2 \) concentration for safety purposes. Individual bubbles were observed to have a strong disruptive effect on the orientation of microwires in their local vicinity as they rose through the focus area of the video. As seen in Figure 31, microwires were dispersed with fairly random orientation without a magnetic field but showed a high degree of alignment in the presence of a sufficiently powerful magnetic field. Quantification of the in-situ alignment with a magnetic field was achieved with a frequency distribution of the microwire orientation angle from the horizontal. Figure 32 shows a color-coded visualization of the orientation angle counting process. Figure 33 shows the average percentage of microwires with a given orientation angle in increments of 10° for microparticle suspensions without bubbling. With 0 G applied magnetic field, both the electrodeposited Ni/n-Si and Ni/np\(^{+}\)-Si/FTO/TiO\(_2\)
microwires show a fairly flat frequency distribution with percentages from ~5-15%, indicative of a random distribution. As the power was increased to the electromagnet to increase the magnetic field strength, the electrodeposited Ni-coated/n-Si microwires quickly responded, with low angles becoming less frequent. The majority of the wires had an orientation > 70° to horizontal at 140 G, the lowest field strength tested. At 300 G these microwires were highly aligned despite active dispersion, with 64% of the wires having an orientation angle > 80°, and 84% having an angle > 70°.

Relative to the tandem microwires, the test case electrodeposited Ni-coated/n-Si microwires had the advantages of a heavier Ni loading distributed along the full axial dimension of the microwire. For a given magnetic field, more ferromagnetic Ni will result in a greater force applied to each microparticle. Moreover, strong alignment in this case was also attributed to the induced north/south poles in the Ni deposit.
applying leverage to the high-aspect-ratio particle which causes it to align with the magnetic field lines. However, to prevent significant parasitic light absorption in the microwire slurries that were less sensitive to the magnetic field strength. In fact, initial experiments for as-deposited Ni bulbs showed only a weak alignment effect for the tandem Ni/np⁺-Si/FTO/TiO₂ microwires. Stronger alignment was achieved by magnetization of the Ni bulb. During the photodeposition step, the fully fabricated tandem microwires were magnetized by periodically sweeping a rare-earth magnet underneath the suspension. After magnetization of the Ni deposit, tandem microwire slurries were observed to be significantly more responsive to the applied magnetic field and displayed in-situ vertical alignment tendencies similar to

![In-situ microwire alignment without bubbling as a function of magnetic field strength in gauss (G). Measured microwire angle from horizontal vs. the percentage of wires in 10° increments for a suspended slurry of (a) electrodeposited Ni-coated n-Si microwires and (b) tandem Ni/np⁺-Si/FTO/TiO₂ microwires.](image-url)
the electrodeposited Ni-coated test microwires. At 300 G the suspension had 53% of the tandem microwires oriented to > 70° from horizontal. The vertical alignment increased to 75% of tandem microwires at > 70° upon application of the rare-earth magnet (1100 G).

As a ferromagnetic material, Ni has different magnetic domains in which groups of atomic magnets are formed via exchange coupling. In the absence of an aligning magnetic field, the magnetic moments of the atoms are aligned randomly between the domains. The nearby presence of the rare-earth magnet during the Ni photodeposition process helps to align the magnetic domains and magnetize the Ni bulb. This sensitization step was observed to be critical to making the tandem microwires sufficiently responsive to the magnetic field to induce alignment despite the limited amount of Ni confined to one end of the microwire. Besides the magnetic poles of the Ni bulb shape providing less leverage than the high-aspect-ratio electrodeposited Ni coating, another reason for reduced alignment of the tandem microwires relative to the electrodeposited test microwires is the greater variability in the photodeposited Ni loading. Tandem microwires with less Ni will require a stronger magnetic field to achieve the necessary force to sufficiently overcome ongoing dispersive forces and induce vertical alignment.

Micron-scale bubbling was also tested as an alternative method for maintaining a dispersion of tandem semiconductor microwires. In a real solar water-splitting slurry, carrier gas bubbling would be a more effective and efficient method for large-area particle dispersion than sonication or locally induced convection.
In addition, microbubbles could encourage mass transfer of the generated H\(_2\) and O\(_2\) products to the gas output to minimize back reactions, while the carrier gas flow rate could be tuned to affect the product H\(_2\) concentration to optimize the balance between safety and the efficiency of downstream purification processes. As shown in Figure 34, the magnetic field was able to achieve a high degree of vertical alignment in the microwire suspension despite strong local disturbances in the vicinity of a passing bubble. For electrodeposited Ni-coated/n-Si test microwires, a magnetic field of only 190 G was enough to orient 84% of them to > 70°. As

![Figure 34](image)

Figure 34. In-situ microwire alignment under active bubbling as a function of magnetic field strength in gauss (G). Measured microwire angle from horizontal vs. the percentage of wires in 10° increments for a suspended slurry of (a) electrodeposited Ni-coated n-Si microwires and (b) tandem Ni/n\(^{+}\)-Si/FTO/TiO\(_2\) microwires.

expected, stronger magnetic field strength was required to align the tandem microwires, but alignment was still achievable with 65% of the microwires orienting to > 70° from horizontal at 700 G. The magnetic field strengths in Figure 34 are lower than those in Figure 33 for the same rare-earth magnet or electromagnet power.
due to the added distance from the magnet required to accommodate the bubbling unit.

3.3 Experimental Section

3.3.1 Tandem Structure Fabrication

Si(100) wafers (375 µm thick, n-type doped with P to a resistivity of 1 – 10 Ω cm, single side polished, Cz-grown, University Wafers) were used for both planar and microwire samples. n-Si microwire arrays were fabricated from the wafer using deep reactive ion etching (DRIE) (University of Michigan, Lurie Nanofabrication Facility). The Si substrate was patterned with hexagonally packed dots (9 µm diameter and 15 µm center-to-center pitch) using standard photolithography (Microposit 1827 photoresist). This pattern was then etched into the n-Si wafer by DRIE (SF6 and C4F8, STS Pegasus, SPTS Technologies) to a depth of ~ 100 µm. The microwire array was subsequently cleaned by reactive ion etching with oxygen to remove the residual photoresist.

A B-doped p⁺ radial emitter layer was formed on the n-Si planar or microwire array (2 cm x 1 cm wafer) using diffusion from solid-source BN dopant wafers (Saint Gobain-BN-975). The silicon wafers were placed between the dopant wafers in a ceramic boat at 950 °C for 4 min under N2 flow (200 sccm in a 1-inch diameter tube). The boat was slowly removed from the furnace over > 1 min while the temperature ramped down to 750 °C. After cooling, each Si sample was etched in buffered HF for 30 s to remove any unreacted dopant glass and then loaded again at 750 °C under O2 flow (100 sccm) for 30 min to grow a low temperature oxide (LTO).
The cooled wafers were then etched in 10% HF for 1 min to remove any residual Si-B layer oxidized during the LTO step.

A ~500 nm thick fluorine-doped tin oxide (FTO), SnO$_2$:F, layer was deposited on the Si as an ohmic contact layer between the tandem Si and TiO$_2$ subcell layers. The np$^+$-Si planar and/or microwire arrays were again etched with 10% HF for 30 s immediately prior to placing them on a hotplate at 400 °C. FTO was deposited by spraying a fine mist of a precursor solution, which was made by mixing 97% by volume of 0.50 M butyltin trichloride in pure ethanol and 3% by volume of 0.50 M ammonium fluoride in DI water.$^{100,112}$ The FTO layer required 30 cycles of spraying with 3 sprays per cycle with 45 s between cycles to allow the equilibration of the Si sample temperature. The Si samples were rotated after 15 cycles to ensure conformal coverage of the FTO.

A contiguous layer of rutile TiO$_2$ nanorods was grown on the planar or microwire array np$^+$-Si/FTO using a hydrothermal method.$^{112}$ The Si/FTO samples were placed in 60 mL of an aqueous solution of 0.05 M titanium n-butoxide and 6 M HCl in a Teflon cell at an angle supported by the cell wall. The cell was then put in a hydrothermal autoclave reactor and placed in a muffle furnace at 200 °C for 4 h. The autoclave reactor was then cooled under running water for 15 min. The np$^+$-Si/FTO/TiO$_2$ planar and/or microwire array samples were then removed from the Teflon cell, rinsed with DI water, and annealed at 450 °C for 30 min in air.

3.3.2 Photoelectrochemical Measurements

To make electrodes for current density vs. potential (J-E) measurements, the tandem semiconductor wafers were first cleaved at the edges and the back surface of the n-
Si was scratched thoroughly with a diamond scribe to eliminate shunting via the p⁺-Si layer. The back side was coated with Ga-In eutectic (99.99%, Alfa-Aesar) to make ohmic contact and then attached to a Cu-Sn wire with Ag paint (SPI-05001-AB) and sealed with epoxy (Loctite Hysol 9640). Three-electrode photoelectrochemical measurements were performed in a glass cell with a flat quartz window using a BioLogic SP-200 potentiostat. The np⁺-Si/FTO/TiO₂ planar and/or microwire arrays were the working electrode, a fritted platinum mesh was the counter electrode, and a Ag/AgCl (sat. KCl) (CH Instruments, Inc.) was the reference electrode. Two-electrode photoelectrochemical measurements were performed with the reference shorted to a Ni foil counter electrode immediately adjacent to the semiconductor working electrode without a separator. Measurements were performed in aqueous 1 M KOH under 1 Sun illumination of 100 mW cm⁻² generated with a 300 W Xenon lamp (Newport 6258) and an AM1.5 global filter (Newport 81094). The J-E behavior was measured at a scan rate of 50 mV s⁻¹, and all current density values were calculated relative to the geometric projected area of the photoelectrode. The hydrogen faradaic efficiency was determined by quantifying H₂ in the headspace via gas chromatography (GC, SRI 8610) with a thermal conductivity detector (TCD). Faradaic efficiency was calculated for chronoamperometric measurements by determining the charge required to produce the measured H₂ and dividing by the total charge passed at the time of sampling.

3.3.3 Electrodeposited Ni on Si Microwires
To make electrodeposited Ni/Si microwires, an n-Si microwire array electrode was prepared as described above but sealed with a removable nail polish polymer in
place of epoxy. Ni electroplating solution (aqueous nickel sulfamate with boric acid, Sigma-Aldrich) was used as the electrolyte. The potential was held at -1.5 V vs. Ag/AgCl until the set charge per electrode area in C cm$^{-2}$ was passed through the n-Si working electrode. The nail polish polymer was then dissolved in acetone to recover the sample for detachment of the Ni-coated n-Si microwires from the substrate.

3.3.4 Detached Microwire Particles
To detach either electrodeposited Ni/n-Si or tandem np$^+$-Si/FTO/TiO$_2$ microwires from the n-Si substrate, the back of the wafer was secured to a glass slide with mounting wax, the microwire array was mechanically coated with nail polish polymer, and a razor blade was used to scrape off the microwires embedded in the polymer film.$^{113}$ The sacrificial polymer was then dissolved in acetone for > 1 h and the microwires filtered from the solution using a porous alumina membrane (Sterlitech Corporation) of 0.2 µm diameter pore size. The wires were subsequently transferred to a vial of DI water.

A photodeposition process was used to selectively deposit Ni catalyst at the exposed n-Si base of the np$^+$-Si/FTO/TiO$_2$ microwires. Ni electroplating solution was added to the DI water containing the detached microwires in a 1:2 volume ratio, and then sodium sulfite (Na$_2$SO$_3$, Sigma Aldrich) was dissolved to a concentration of 0.056 M to serve as a hole scavenger. The tandem microwires in the Ni deposition bath were illuminated with the AM1.5 light at 1.6 Suns for 3.5 h with added illumination from a UV lamp (3 mW cm$^{-2}$, AT1000Ex, Advanced Technologies International) to accelerate the photodeposition of Ni. During illumination, an N52-
neodymium rare-earth magnet (CMS Magnetics) was passed back and forth under the particles for 30 s every half hour until the end of the photodeposition to magnetically sensitize the Ni bulb. The microwires were then filtered from the Ni deposition bath using the porous alumina membrane.

3.3.5 Magnetic Orientation Measurements
Microwires from ~0.2 cm² of Si substrate were dispersed in 0.5 mL of DI water in a cuvette with a magnet placed outside at the base. A 24 V DC solenoid electromagnet (Uxcell) generated variable magnetic field strengths with a variable power supply. The N52 neodymium rare-earth magnet was also used to produce a higher magnetic field strength. Magnetic field strength was measured with a handheld digital high precision gaussmeter probe (Dyrabrest TD8620). In the case of slurry testing without bubbling, Ni/n-Si microwires were suspended with a VirTis VirSonic 100 probe sonicator, and for the separate tandem Ni/np⁺-Si/FTO/TiO₂ measurements microwires were dispersed throughout the fluid by injecting DI water at the base of the cuvette with a micropipette. In the case of slurry testing with bubbling, both microwire types were suspended by incorporating a microporous glass disk frit at the bottom of the cuvette and flowing N₂ gas at 70 sccm through the frit. The added microporous frit in the case of bubbling raised the focal point for orientation analysis to 8.5 mm above the magnet, as compared to 5.0 mm above the magnet for a cuvette without bubbling. Suspended microwire particles were monitored via high-speed video microscopy using a HiSpec2 camera (FASTEC). The camera had a resolution of 1280 x 1024 and a pixel size of 14 µm x 14 µm. Nikon 4X and 10X objective lenses were used to focus on the particles. In-situ particle orientation distributions
were determined by using ImageJ software to analyze > 7 separate still frames from each video spaced over > 0.5 s to determine the angle from horizontal of at minimum 100 microwires for each experimental condition. To approximate error bars, the data was compiled into three equal-size subsets for three smaller histograms and the standard deviation was taken of the percentage of microwires at each interval of angles.

3.4 Conclusion

Integrated tandem semiconductor microparticles are a promising strategy for achieving sufficiently high STH efficiency in a solar water-splitting slurry to enable low-cost solar hydrogen generation. However, asymmetric micron-scale tandem particles are likely to face issues of photogenerated current mismatch between the subcell layers and an accompanying decrease in efficiency under conditions of non-ideal orientation to the illumination that cause an imbalance in photon absorption between the photoactive semiconductors. This effect would be greatest for an ideal set of complementary bandgaps which are already current matched under top-down illumination conditions. While the pursuit of a stable ideally matched tandem remains the subject of active research, a proof-of-concept system for the in-situ magnetic alignment of tandem microwires capable of unassisted water-splitting was demonstrated using a Si/TiO$_2$ combination. Although the wide bandgap TiO$_2$ shell prevents current matching with the Si microwire core under AM1.5 light, an added UV illumination bias could be used to raise the TiO$_2$ photocurrent to match Si so
that the orientation-dependent performance of tandem microwire slurries can be studied in future experiments.

For the proof-of-concept case, a Ni/np⁺-Si/FTO/TiO₂ system was fabricated and shown to be capable of unassisted solar hydrogen generation. The tandem structure was incorporated into microwire particles, using a selective photodeposition scheme to put a Ni bulb on the cathodic site of the Si core cross-section. Notably, the relatively thick Ni HEC bulb at one end of the microwire would be highly opaque and lead to poor performance for a tandem microwire in an upside-down arrangement, further indicating the importance of controlling the orientation. The ferromagnetic Ni hydrogen evolution catalyst bulb was magnetized and used as a handle for the alignment of tandem microwires within a magnetic field under active dispersion of the particles with or without uplifting bubbles. A best-case test system of electrodeposited Ni-coated n-Si microwires showed high levels of vertically aligned particles at relatively low magnetic field strength. Tandem microwires, with only the Ni bulb at one end, were able to achieve a similar frequency distribution of orientation angles but required stronger magnetic fields to do so. In all cases, the frequency distribution showed that the percentage of vertically aligned microwires (> 70° from horizontal) increased with increasing magnetic field strength. The applied magnetic field can thus be used as an ongoing self-correction strategy to maintain a particular orientation of high-aspect-ratio integrated photoelectrochemical particles relative to the illumination despite persistent disturbances within an active slurry.
The demonstrated in-situ magnetic alignment of microwire particles in this work could be broadly extended to other materials systems in a similar form factor. The Ni is a highly active and abundant HER catalyst which protects the Si layer from oxidation in addition to its ferromagnetic properties which enable the coordinated mass alignment of particles in a solution. The TiO$_2$ layer, on the other hand, could readily be replaced with a narrower bandgap semiconductor for better current matching to the Si without inhibiting the principle of alignment. It is also possible that a magnetic oxygen evolution catalyst along the length of the tandem microwire could further encourage alignment, which could benefit the system provided this catalyst layer did not absorb too much light.$^{114}$ There are a few other possible benefits to the presence of a magnetic field in a photoelectrochemical system that have been observed in other systems but would require further examination in these tandem microparticles: magnetic field-generated Lorentz force-assisted charge-carrier separation to suppress recombination$^{115, 116}$ and magnetic field-affected spin polarization for improved photocatalytic activity in metal oxides.$^{117}$

Although the results herein demonstrate the feasibility of aligning unassisted water-splitting tandem microwires under realistic operating conditions, experimental exploration of the orientation effect is the subject of future work. An individual vertically aligned microwire might maintain higher STH efficiency than a horizontal wire, but the projected area for light absorption is minimized in the vertical orientation. Thus, the effect on the entire slurry will likely depend on the microwire density as well as the orientation. It is also unclear at present what effect light scattering within a slurry would have on microwire orientation-dependent light
absorption. Nevertheless, the ability to maintain a general orientation of photoactive particles within a slurry provides researchers with an additional tool for optimizing performance.
CHAPTER 4

OPTICAL PROPERTIES AND PHOTOCATALYTIC PERFORMANCE OF Si/TiO$_2$ TANDEM SEMICONDUCTOR MICROWIRE SLURRIES

4.1 Introduction

Hydrogen has the potential to be a clean alternative to fossil fuels, and H$_2$ synthesis from water electrolysis is an ideal, highly scalable, and energy-dense way to store the energy from intermittent power generation sources. The present predominant industrial method of H$_2$ production via steam methane reforming (SMR) from natural gas produces large amounts of greenhouse gas CO$_2$ emissions. With the urgent need to shift society from fossil fuels to a cleaner alternative, extensive research has been directed towards renewably produced, or green, hydrogen. In the most straightforward route, efficiently coupled photovoltaic (PV) + electrolyzer technologies have yielded solar hydrogen from water splitting at high solar-to-hydrogen (STH) efficiencies.$^{118-120}$ However, this approach has been far from cost-competitive with hydrogen produced by SMR.$^{13, 121}$ An alternative solar water-splitting reactor design may be needed to commercialize economically viable green hydrogen.

Rigorous solar water-splitting technoeconomic analyses have concluded that photoactive particle-based reactors have the potential to generate H$_2$ at a lower cost
than either a PV + electrolyzer or flat-panel photoelectrochemical (PEC) system.\textsuperscript{13, 82, 122} Numerous particulate photocatalyst systems have been investigated, though few have been capable of unassisted solar water-splitting, and photoconversion efficiencies have generally been quite low.\textsuperscript{83, 84, 88-92} Semiconductor particle-based reactors face several critical issues which have inhibited their energy-conversion efficiencies and prevented practical commercial deployment.\textsuperscript{83, 123} Key challenges include achieving material stability of the photoactive semiconductor, high recombination and/or poor charge separation of the photogenerated carriers, and the need for wide bandgaps to produce the requisite photovoltage which leads to poor utilization of the solar spectrum.

One approach to achieve high efficiency unassisted solar water-splitting is to use tandem complementary bandgap semiconductors in series to build photovoltage while utilizing more of the solar spectrum. Modeling such tandems has found that an ideal combination of 1.6 – 1.8 eV and 0.9 – 1.1 eV bandgaps is capable of > 25\% STH efficiency.\textsuperscript{94, 124} Si, with a bandgap of 1.1 eV, is a prime candidate for the lower subcell of the tandem since it is abundant with an established low-cost production process. Extensive work has shown that Si microwires can be produced cost-effectively with optimal dimensions to match the material quality.\textsuperscript{98, 99, 113} With an axial dimension longer than the optical penetration depth (> 100 µm) and a radius commensurate with the minority-carrier diffusion length (typically 3 – 10 µm), such microwires can decouple the directions of light absorption and charge-carrier collection and permit the use of cheaper quality Si.\textsuperscript{125} Si microwire arrays have been utilized in promising photovoltaic and photoelectrochemical applications.\textsuperscript{74, 105, 126}
Si microwires are thus a promising platform for a tandem microparticle structure that could enable high efficiency photochemical reactions.

Several wider bandgap top subcell candidates have been explored in tandem with Si, as both photoanodes and photocathodes. Demonstrated tandem core-shell microstructure combinations include Si/TiO$_2$,\textsuperscript{100} Si/BiVO$_4$,\textsuperscript{127} Si/Ga$_{1-x}$In$_x$P,\textsuperscript{128} Si/WO$_3$,\textsuperscript{101} Si/Ta$_3$N$_5$,\textsuperscript{129} and Si/CuO$_2$.\textsuperscript{130} The microscale dimension of the Si wires in these tandems allows the incorporation of a buried pn-homojunction, which aids charge separation via migration with a built-in electric field. A transparent conductive oxide such as fluorine-doped tin oxide (FTO) is frequently employed as an ohmic contact between the subcell layers.\textsuperscript{100, 101} While materials scientists continue to pursue improved semiconductors to be a top subcell of ideal bandgap which is stable with the necessary photovoltage, the properties of tandem-particle-based photocatalytic reactors can be explored with established materials. In particular, TiO$_2$, though far from an ideal bandgap top subcell, is a stable photoanode material that provides sufficient photovoltage in combination with Si for unassisted solar water-splitting.\textsuperscript{100, 131}

In the previous chapter, a proof-of-concept np$^+$-Si/FTO/TiO$_2$ microwire structure capable of unassisted solar hydrogen generation was grown on a Si substrate.\textsuperscript{131} Detached, free-floating tandem Ni/np$^+$-Si/FTO/TiO$_2$ microparticles were fabricated with a photodeposition process to selectively attach a Ni bulb on the cathodic site of the n-Si core at the wire base. The Ni bulb served as a hydrogen evolution co-catalyst and was demonstrated to enable in-situ magnetic alignment of the suspended tandem microwire slurry.\textsuperscript{131}
An understanding of the parameters which influence the optical properties of a tandem microwire slurry is necessary to improve the corresponding photocatalytic behavior and optimize the efficacy of individual photoactive particles. A high light absorptance with a relatively low volume fraction of photoactive material is an important strategy to improve the cost-effectiveness of the slurry by minimizing particle fabrication expense. Remarkably, a previous study of aligned, substrate-bound Si microwire arrays found that up to 96% light absorption was possible with only 5% areal coverage of Si wires using light management techniques including scattering particles and a back reflector. Microwire particles in solution will rapidly settle if unperturbed but can be suspended with uplifting carrier gas bubble flow. Unlike nanoscale particle suspensions in which the fluid has fairly homogeneous properties, the microscale dimensions and concentration of the wires and bubbles can lead to complex mesoscale optical phenomena that influence the photochemical performance.

Herein, the conditions to optimize photoactive microparticle utilization while maintaining an overall high light absorption in the slurry were investigated. The optical properties of the tandem microwires dispersed in aqueous media were characterized to improve the understanding of light propagation through the class of photochemical microparticle slurry reactors. Transmittance and reflectance of the system as a function of wavelength, slurry particle concentration, and dispersion flowrates were measured via UV-Vis spectroscopy with an integrating sphere. Corresponding photochemical performance of the Ni/np⁺-Si/FTO/TiO₂ microwire slurry was characterized via organic methylene blue (MB) dye degradation under
visible and UV illumination (Figure 35). The photodegradation of the MB dye enabled direct in-situ monitoring of the performance under different reactor conditions.

Figure 35. (a) Schematic of a tandem microwire slurry dispersed by uplifting N₂ carrier gas bubbles (left) and the tandem Ni/np⁻⁺-Si/FTO/TiO₂ microstructure driving photodegradation of methylene blue (right). (b) 3D image of the integrating sphere and (c) 2D cross-sectional images of the modes of operation for measuring transmittance and reflectance with an actively bubbled cuvette reactor.
4.2 Results and Discussion

4.2.1 Tandem Microwires Slurry Optical Properties

Because of the tendency of microparticles and bubbles in the slurry to scatter light, an accurate measurement of the optical properties required the use of an integrating sphere to account for the diffuse light (Figure 35). Transmittance and reflectance were measured separately in different operating modes and used to calculate the absorptance in the slurry. UV-Vis spectroscopy employed a broad wavelength range of 200 – 1100 nm to cover photon energies greater than the bandgaps of either the Si or TiO$_2$ subcell layers. The $T$, $R$, and $a$ values of the slurry were measured for variable dispersive N$_2$ bubble flowrates (25 – 35 sccm) and different concentrations of tandem microwires (12.4 – 37.1 g L$^{-1}$, corresponding to a photoactive volumetric percentage of 0.34 – 1.01%, see Appendix for the calculation). Lower N$_2$ flowrates were observed to lead to inactive areas of the bubbling frit and eventual settling of microwires in the solution dead space.

Figure 36 shows the optical properties of the slurry as a function of bubble flowrate for three microwire concentrations as well as in the absence of photoactive particles. Without tandem microwires, the bubbling DI water exhibited fairly high specular transmittance of $\sim$60 – 70%, and a corresponding reflectance of $\sim$20 – 30% (Figure 36 a-b). Increased flowrate led to a slight increase in reflectance and decrease in transmittance due to scattering off the bubbles, but the difference was minimal. Ideally, the absorptance of N$_2$ bubbles in DI water should be negligible (except for the water absorbance peak at 970 nm), but a consistent value of $\sim$10%
was measured in the visible region and primarily attributed to the portion of light that was reflected and then absorbed by the microporous frit and sealing epoxy at the bottom of the cuvette (Figure 36c).

Figure 36. Measured (a, d, g, j) transmittance, (b, e, h, k) reflectance, and (c, f, i, l) absorptance vs. wavelength for different carrier gas N$_2$ bubble flowrates for different tandem microwire concentrations of (a-c) 0.0, (d-f) 12.4, (g-i) 24.7, and (j-l) 37.1 g L$^{-1}$. 
Upon the addition of tandem microwires to the DI water, the flowrate dependence of the optical properties became more pronounced. At the lowest particle concentration tested, 12.4 g L\(^{-1}\), transmittance at visible wavelengths was \(~60\%\) at 25 sccm, only slightly lower than the case without particles (Figure 36 d). However, increasing the N\(_2\) flow to 35 sccm decreased \(T\) to \(~25\%\), which demonstrates the importance of a robust bubble flow to keep the microwires well dispersed and thus highly absorbing as a slurry. Although the effect on reflectance was less notable, the bubble flowrate was a significant factor in minimizing the transmittance for all three tandem microwire concentrations tested. Consequently, the absorptance increased with bubble flowrate as well.

The tandem particles were uniformly dispersed under vigorous bubbling at 35 sccm, and thus this condition was selected as the default flowrate for future experiments. Figure 37 shows the optical properties of slurries as a function of tandem microwire concentration and corresponding photoactive volume percentage. The visible region transmittance decreased from a value of \(~60\%\) without microwires to \(~25\%\) with 12.4 g L\(^{-1}\) to as low as \(~5\%\) with 37.1 g L\(^{-1}\) of tandem particles. Notably, this dramatic drop in \(T\) was accomplished with only 1\% of the slurry volume filled with photoactive particles. Although there was a slight increase in \(R\) at wavelengths > 400 nm in the presence of tandem microwires, most of the decreased transmittance was attributable to an increase in the slurry absorptance at higher particle concentrations, reaching as high as 87\% at 300 nm (Figure 37c). This particle concentration of 37.1 g L\(^{-1}\), from harvesting the tandem microwires from a
1.5 cm² array, was used as the default condition for subsequent photochemical experiments.

The shape of the absorptance curves is indicative of the tandem microstructure in DI water. The spectra showed a sharply increasing absorptance at wavelengths < 400 nm. This transition marks the onset of photon energies capable of exciting electrons across the TiO₂ bandgap. Any photons at this energy not absorbed in the TiO₂ layer can still be absorbed in the underlying Si microwire core, and thus absorptance in this region is higher than the wavelengths that can only be absorbed by Si. Between 400 – 900 nm, light absorption was primarily due to the Si and peaked at ~70% at 600 nm for 37.1 g L⁻¹ (Figure 37c). Decreasing absorptance at longer wavelengths is consistent with the indirect bandgap of Si and corresponding drop in the absorption coefficient for photon energies closer to the 1.1 eV bandgap. This effect would be exacerbated for light incident on horizontally oriented microwires, resulting in absorption through the much shorter radial dimension as opposed to the longer axial dimension. The absorptance peak at 970 nm was due to water absorption.
in the infrared (Figure 36c), and the uneven shift at 850 – 900 nm was attributed to signal noise during an automated UV-Vis detector switch.

4.2.2 Photocatalytic Performance via Methylene Blue degradation

Because of the in-situ photocatalytic characterization advantages of using an indicator dye and the difficulty of accurately quantifying H₂/O₂ in the presence of the slurry carrier gas flow, methylene blue degradation was the primary method utilized to characterize slurry photochemical performance. MB, an organic dye, is a model compound for testing the performance of the tandem particles because it provides a simple and standard way of measuring photocatalytic activity in liquid-phase reactions. The MB photodegradation behavior with time was examined under variable conditions of tandem Ni/np⁺-Si/FTO/TiO₂ microparticle concentration, dispersive N₂ bubble flowrate, illumination spectral conditions and UV intensity, and light management techniques including highly-reflective alumina particles or a back reflector.

The general mechanistic pathway for the degradation of the MB dye is understood to proceed through free radical species. Photogenerated charge-carriers lead to the formation of •O₂⁻ and •OH radicals which subsequently attack the aromatic rings of the MB molecule to break it down into intermediates and eventually into CO₂ and H₂O. The MB degradation is readily monitored by tracking the decay in the main absorbance peak via UV-Vis spectroscopy (Figure 38 a). The •O₂⁻ radical, however, is formed from photoexcited electrons reducing O₂. Under N₂ carrier gas bubble flow, the MB solution herein is highly depleted of dissolved O₂, inhibiting this radical pathway. The MB solution was thoroughly deaerated with N₂ for an hour
prior to measurements for consistency. MB degradation thus proceeded primarily through the oxidative formation of •OH radicals only, which leads to slower rates of absorbance decay than can be observed in the presence of dissolved oxygen (Figure 38 b). Some MB dye can also adsorb onto surfaces, leading to a drop in absorbance that is not attributable to photocatalytic activity. To minimize adsorption effects during experiments, photoactive samples were pre-soaked in the MB solution during the 1-hour deaeration to allow adsorption to equilibrate on the frit and tandem samples prior to illumination.

4.2.2.1 Effect of planar vs. microwire slurry form factor

The first MB photodegradation experiments compared the performance of a tandem microwire slurry to that achievable with a planar tandem device. Planar tandem samples can be electrically connected to make an np+−Si/FTO/TiO2 photoanode to directly measure the current density vs. potential (J−E) energy-conversion performance. Two-electrode J−E curves under 1 Sun AM1.5 of a planar tandem vs. Ni in 1 M KOH and in the MB solution are shown in Figure 39. The structure is
capable of unassisted solar water-splitting, but the $J$-$E$ curve fill factor and onset potential was worse in the MB solution due to the low concentrations and relatively high ohmic resistance. Figure 40 shows the normalized absorbance, $A/A_0$, of MB over the course of an hour under illumination for a planar tandem compared to a tandem microwire slurry. A blank MB solution did exhibit a slight drop in absorbance when illuminated, indicating that a slow direct photoexcited deactivation of the dye occurs as well. In all cases throughout the study, however, the presence of photoactive samples accelerated the rate of decreasing absorbance, consistent with photocatalysis of the MB degradation.

While the planar tandem showed increased decay of the absorbance relative to the blank, the tandem microwire slurry exhibited faster MB photodegradation. Better performance from the microwire slurry compared to the planar form factor was somewhat surprising considering that planar electrodes routinely outperform microwire array electrodes in photoelectrochemical studies.\textsuperscript{74, 97, 100, 131}
Lower planar performance could be partially attributed to a smaller sample area (necessary to fit it in the cuvette reactor) compared to the wafer area used to harvest the microwires, but the volumetric photoactive tandem component was comparable. We speculate that ohmic overpotential, which is significant in the MB solution (Figure 39), inhibits the planar sample to a greater degree than the microwires.\textsuperscript{141}

Ion conduction between the anodic TiO$_2$ and cathodic Ni sites must follow a much longer pathway on a macroscopic planar sample compared to the corresponding microscopic distance on a microwire.

Tandem microwires were also analyzed for morphological and chemical changes from photochemical operation as a slurry. Figure 41 show SEM images of individual microwires before and after a MB photodegradation measurement. For the large majority of observed microwires, there was no indication of dissolution or breakdown of the TiO$_2$ or Si components. In a few cases, regions of the TiO$_2$ nanowire coating shell appeared physically damaged, presumably from aggressive

![Figure 40](image)  

Figure 40. Normalized absorbance of MB vs. time for the blank solution and tandem Ni/n$^{+}$-Si/FTO/TiO$_2$ planar and microwire slurry samples under 1 Sun AM1.5 illumination at a dispersive bubble flowrate of 35 sccm.
collisions during vigorous dispersal. After operation, some microwires had lost their Ni bulb (Figure 41b), indicating that co-catalyst adhesion may need improvement for increased photochemical durability. Otherwise, EDS analysis indicated no other notable changes in the elemental composition of the structure (Figure 41 c,d).

Figure 41. SEM images of tandem microwires (a) before and (b) after a 1-hour MB photodegradation experiment. Scale bar is 10 µm for both images. EDS elemental maps of tandem microwires (c) before and (d) after a 1-hour MB photodegradation experiment. (c) and (d) each include a composite image (top) and individual element maps (bottom) for Si, Ti, Ni, and Sn. Scale bar is 20 µm for composite images.

4.2.2.2 Effect of tandem particle concentration
The effect of the tandem microwire concentration on the slurry photochemical activity was investigated with concentrations of 12.4, 24.7, and 37.1 g L⁻¹, corresponding to photoactive volume percentages of 0.34, 0.68, and 1.01 % v/v, derived from harvesting the microwires from 0.5, 1.0, and 1.5 cm² growth substrates, respectively. Figure 42 shows the resulting MB degradation with time at a dispersive bubble flowrate of 35 sccm. In the dark, the absorbance remained relatively steady even for the highest concentration of tandem microwires, indicating that dye adsorption was not a significant source of absorbance loss after the initial pre-experiment equilibration period. Again, in the absence of photoactive particles, a blank MB solution still displayed some non-negligible absorbance decay under 1
Sun AM1.5 illumination. Methylene blue absorbs light most strongly in the 500 – 700 nm region (Figure 38a) and undergoes self-decomposition via electronic transition and intersystem crossing.\textsuperscript{140} The kinetics of MB degradation are complex, with several intermediate reactions and peroxide formation possible.\textsuperscript{139} Quantitatively correlating the measured absorptance values (Figure 37c) to the rate of MB absorbance decay is therefore difficult. However, a higher absorptance leads to an increased rate of charge-carrier photogeneration, a concomitant increase in radical species formation and subsequent dye degradation, and thus a faster decrease in the MB solution absorbance. This qualitative trend held for the photoactive slurries, with higher tandem microwire concentrations leading to greater absorbance decay (Figure 42).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure42.png}
\caption{Normalized absorbance of MB vs. time for the blank solution and tandem microwire slurries of varying particle concentration in the dark or under 1 Sun AM1.5 illumination at a dispersive bubble flowrate of 35 sccm.}
\end{figure}
4.2.2.3 Effect of carrier gas dispersive bubble flowrate

MB photodegradation was characterized vs. N$_2$ flowrate (25 – 35 sccm) for the 37.1 g L$^{-1}$ particle concentration which had yielded peak absorptance (Figure 37c). The resulting normalized MB absorbance vs. time with varying flowrate is shown in Figure 43. Although increased bubble flowrate did lead to greater MB degradation, the difference from 25 to 35 sccm was minor (at most 5.4% lower for 35 sccm at 20 min). Notably, a slurry of this microwire concentration also did not vary greatly in its optical properties within this range of flowrates (Figure 36j-l). The reflectance showed almost no change with flowrate, while the absorptance displayed less variation than at lower particle concentrations (Figure 36k-l). The limited dependence of MB photodegradation on flowrate within the 25 – 35 sccm range was thus consistent with the light management within the slurry as measured with the integrating sphere.

Figure 43. Normalized absorbance of MB vs. time for tandem microwire slurry samples of 37.1 g L$^{-1}$ particle concentration in the dark or under 1 Sun AM1.5 illumination at varying dispersive bubble flowrates.
The main role of the bubbles was to uniformly suspend the microwires, and at 25 sccm and above for this particle concentration there was no significant change from bubble light scattering. However, as previously mentioned, below 25 sccm bubbling from the frit became uneven and dead spots in the microwire fluidization were observed. A MB photodegradation experiment at 20 sccm was performed to highlight the consequences of non-uniform particle dispersion. As the flowrate dropped below the critical threshold for producing bubbles evenly across the frit, the tandem microwires were poorly suspended in these regions which resulted in locally decreased particle concentration. Consequently, the MB absorbance remained appreciably higher at 20 sccm than the other measured flowrates, in accordance with the microwire-concentration-dependent slurry photochemical behavior (Figure 42).

4.2.2.4 Effect of spectral mismatch

The TiO$_2$ and Si tandem combination is capable of generating sufficient photovoltage for unassisted solar water-splitting by connecting the subcell layers in electrical series. However, like all series-connected tandems, the current flowing through each subcell unit of the circuit must be matched. If one semiconductor layer underperforms the other in photocurrent, the partner subcell current will be limited, thus more strongly decreasing the efficiency of the overall tandem device. Spectral mismatch is one way in which tandem devices are detrimentally affected by their current-matching requirement, in which the spectral distribution of the illumination deviates from the standard AM1.5 and changes the relative above-bandgap photon flux to each subcell layer. Although the Ni/np$^+$-Si/FTO/TiO$_2$ tandem structure is not an ideal bandgap combination for balanced photocurrents at AM1.5, it is still
illustrative to investigate the slurry photochemical performance as the photon flux to each photoactive semiconductor layer is varied.

Figure 44. Normalized absorbance of MB vs. time for tandem microwire slurries under different light conditions. AM1.5 illumination was 1 Sun. Filtered AM1.5 used a longpass filter to cut off wavelengths less than 800 nm. UV excitation was 60 mW cm\(^{-2}\) at 365 nm. Except for the blank solution, all slurries had a particle concentration of 37.1 g L\(^{-1}\). The N\(_2\) flowrate was 35 sccm.

Illumination sources targeting the narrow bandgap Si and wider bandgap TiO\(_2\) were provided with longpass-filtered AM1.5 and a UV LED, respectively. Using a filter to eliminate the AM1.5 wavelengths below 800 nm (i.e., the UV and parts of the visible spectrum), the activity of the tandem microwire slurry for MB photodegradation was dramatically decreased compared to the full unfiltered 1 Sun AM1.5 (Figure 44). TiO\(_2\) is the current-limiting subcell layer under unfiltered AM1.5 (Figure 39), but after applying the longpass filter there are almost no photons capable of exciting electrons across its bandgap. Consequently, the TiO\(_2\) photocurrent plummeted under longpass-filtered light, series-limiting the tandem microwires and causing the MB photodegradation activity to drop sharply.
other hand, the addition of an extra UV optical bias to the AM1.5 illumination led to significantly higher MB photodegradation. As the outer shell of the core-shell tandem microwire structure, the TiO$_2$ gets the first opportunity to absorb the above-bandgap monochromatic light produced by the UV LED at 365 nm. Because the wide bandgap of TiO$_2$ is current-limiting to the Si subcell under AM1.5, moderate increases to the TiO$_2$ photocurrent can be sustained by the full tandem, leading to proportionately enhanced photochemical activity.

When illuminating with just the UV source, one might naively predict decreased performance for the tandem microwire slurry comparable to the performance under longpass-filtered AM1.5. A rutile TiO$_2$ layer of comparable thickness to the microwire shell (~1.5 µm) can be calculated by the Beer-Lambert law to transmit much less than 1% of the photons at 365 nm, thus leading to a condition severely current-limited by the inadequate availability of light for the underlying Si subcell. However, the tandem microwire slurry under the UV source alone displayed comparable MB photodegradation activity to the AM1.5 + UV condition (Figure 44). In this case, the morphology of the TiO$_2$ shell layer may partially explain the lack of a spectral mismatch current-limited response in the tandem microwire. Rather than a compact, contiguous layer, the hydrothermal rutile TiO$_2$ synthesis produces a coating of TiO$_2$ nanorods (Figure 41a) that may enable a portion of the incident illumination to pass between nanorods and across the FTO layer to excite the Si core. Thus, the UV source could excite both subcell layers to enable the tandem microwire to have high MB photodegradation activity despite the spectral mismatch. Photoelectrochemical $J$-$E$ behavior of a planar tandem under only the UV
excitation showed that the photocurrent was decreased but not as severely as would be expected if the Si subcell had little to no photogeneration (Figure 39). We speculate the strong tandem performance under only UV may also be attributable to highly excited UV-generated holes in the TiO$_2$ valence band leading to radical species formation faster than tandem current-limitations can force recombination.

4.2.2.5 Effect of UV light bias

As mentioned, the wide bandgap of TiO$_2$ is not an ideal match to Si for a current-matched tandem under AM1.5 illumination. Consequently, the TiO$_2$ photocurrent was limiting for the Ni/np+-Si/FTO/TiO$_2$ tandem device. TiO$_2$ was used in the present system for its large photovoltage and photoanodic durability for water-splitting. An ideal replacement top subcell layer would generate a higher photocurrent from a narrower bandgap while still providing the requisite photovoltage for water-splitting in combination with Si. Improved performance for a tandem not as limited by the top subcell photocurrent can be simulated by adding an optical light bias of a wavelength sufficient to excite the wider bandgap. Improved tandem microwire slurry photochemical performance was demonstrated with a UV optical bias at several intensities (Figure 45). As expected, higher intensity optical bias led to greater MB photodegradation. A significant enhancement in the rate of MB absorbance decay was observed upon adding UV bias, but further increases of x2 and x3 in the UV intensity led to only modestly faster MB photodegradation.
4.2.6 Effect of scattering particles and back reflection

Light management techniques are a potentially useful strategy to increase the photochemical conversion efficiency of the slurry without unnecessarily driving up costs with excessively high photoactive tandem microwire concentrations. Previously, vertically aligned Si microwire arrays constituting only 5% of the projected area were modified to enable 96% light absorptance independent of the angle of incidence. In that study, light was redirected and concentrated in the Si by introducing Al₂O₃ particles within the microwire array to scatter photons passing between microwires, and a back-reflector layer behind the microwire array redirected light for a second opportunity at absorption. Similar light management strategies were investigated in this work to concentrate light in the photoactive microwires.
Alumina particles of ~5 μm diameter were mixed at two different concentrations with the tandem Ni/np⁺-Si/FTO/TiO₂ microwire slurry. Figure 46 shows the resulting MB photodegradation behavior in comparison to the microwire slurry without scattering particles. Unlike the case of alumina scattering particles within a vertically aligned microwire array, scattering particles mixed within a three-dimensionally dispersed microwire slurry proved to be detrimental to the photoactive performance. At only 3.0 g L⁻¹, Al₂O₃ particles slightly decreased the MB photodegradation, while an increase of the concentration to 6.0 g L⁻¹ led to a severe decline in the absorbance decay. Notably, in the case of the reported aligned microwire array, the alumina scattering particles were confined to a region between Si microwires so that any light scattered by the alumina had a high likelihood of being reflected into the photoactive material.¹³²

Figure 46. Normalized absorbance of MB vs. time for tandem microwire slurry samples with added Al₂O₃ light scattering particles at a concentration of 0.0, 3.0, or 6.0 g L⁻¹ and one case with a BaSO₄ back reflector. All slurries had a tandem microwire particle concentration of 37.1 g L⁻¹. The N₂ flowrate was 35 sccm. Illumination was 1 Sun AM1.5.
In the slurry medium, however, the photoactive microwires and alumina particles were intermixed and free to disperse within the solution volume. As such, light entering the cuvette from one side can encounter alumina particles which scatter light back out of the reactor before it has the opportunity to be absorbed by photoactive microwires deeper in the slurry. A higher concentration of alumina particles thus had the effect of reflecting more light out of the cuvette, as shown in example integrating sphere measurements in Figure 47. An increasing concentration of alumina particles thus decreased the absorptance of the slurry, making intermixed reflective scattering particles an ineffective light management technique for photoactive particle suspension reactors.

![Graphs showing transmittance, reflectance, and absorptance vs. wavelength for different Al₂O₃ scattering particle concentrations](image)

Figure 47. Measured (a) transmittance, (b) reflectance, and (c) absorptance vs. wavelength for different Al₂O₃ scattering particle concentrations for slurries at a bubble flowrate of 35 sccm and a tandem microwire concentration of 24.7 g L⁻¹.

On the other hand, the inclusion of a BaSO₄ reflective layer at the back and sides of the cuvette reactor led to a notable improvement in the MB photodegradation activity of a tandem microwire slurry (Figure 46). Barium sulfate has high diffuse reflectance and is the same material used to coat the interior of the integrating sphere. Thus, BaSO₄ made an ideal Lambertian back reflector to redirect transmitted light back into the slurry for another chance to be absorbed. After 1 hour of
illumination with a back reflector, the tandem microwire slurry decreased the MB normalized absorbance another 10% beyond what it achieved in the absence of back reflection. Thus, back reflectors could be a critical tool for optimizing performance and mitigating costs in microparticle suspension reactors.

4.3 Experimental

4.3.1 Tandem Semiconductor Fabrication

The Ni/np⁺-Si/FTO/TiO₂ tandem microwire particles were prepared as described in our previous work.¹³¹ Briefly, n-Si microwire arrays (9 µm diameter, 15 µm center-to-center pitch hexagonally close packed) were fabricated using deep reactive ion etching (DRIE) (Washington Nanofabrication Facility). A B-doped p⁺ radial emitter layer was formed on the n-Si microwire array using diffusion from solid-source BN dopant wafers (Saint Gobain-BN-975) at 950 °C for 4 min under N₂ flow. A ~500 nm thick FTO, SnO₂:F, layer was spray-deposited on the Si as an ohmic contact layer between the tandem Si and TiO₂ subcell layers. A layer of rutile TiO₂ nanorods was subsequently grown on the np⁺-Si/FTO microwire array using a hydrothermal method.¹¹² To detach the tandem np⁺-Si/FTO/TiO₂ microwires from the n-Si substrate (projected areas of 0.5 – 1.5 cm²), the back of the wafer was secured to a glass slide with mounting wax, the microwire array was mechanically coated with nail polish polymer, and a razor blade was used to scrape off the microwires embedded in the polymer film.¹¹³ The sacrificial polymer was then dissolved in acetone for > 1 h and the microwires filtered from the solution using a sintered fine glass frit (Chemglass Life Sciences LLC). A photodeposition process was then used
to selectively deposit Ni catalyst at the exposed n-Si base of the tandem microwire. A bath of Ni electroplating solution and 0.112 M Na$_2$SO$_3$ as hole scavenger was used for the photodeposition. The wires were then dispersed in 1 mL deionized (DI) water or MB solution for the optical and photocatalytic dye degradation measurements, respectively. The photomask pattern spacing was used to calculate the wafer-area-dependent concentration of particles. A 1 cm$^2$ microwire array wafer area had $\sim$5.13x10$^5$ wires.

4.3.2 Optical Characterization
The reflectance, $R$, and transmittance, $T$, of the microwire slurry under various conditions of bubble flowrate and particle concentration were measured using UV-Vis spectroscopy with an integrating sphere (Perkin Elmer Lambda 950). A quartz cuvette of 1 cm width x 1 cm depth cross-section had the base cut off, leaving a 1 cm height, and a microporous glass frit (Chemglass CG-201-09) was sealed to the cuvette using Hysol 9460 epoxy. A cannula tubing inlet was then introduced below the frit and sealed in with the closed bottom base of the quartz cuvette. Custom 3D-printed holders were fabricated for the modified cuvette reactor to fit it to the integrating sphere for reflectance and transmittance mode measurements. The cuvette was filled with 1 mL of particle slurry in DI water and placed on the 3D-printed holder. During operation, N2 gas was passed through the cannula tubing which pressurized the chamber below the frit and led to microbubble generation which flowed upward and dispersed the microwires in solution. For the transmittance measurement, the cuvette was placed at the integrating sphere entrance port and the exit port was closed by a Spectralon reflectance standard. An
air baseline was measured without the cuvette but with the holder on the entrance port. For the reflectance measurement, the cuvette was placed at the integrating sphere exit port such that it was just inside the sphere, while a gap in the holder allowed transmitted light to exit the sphere through the back face of the cuvette. The fraction of light absorbed in the system, the absorptance \( a \), was calculated as \( a = 1 - R - T \) for measured reflectance and transmittance values as a function of wavelength.

4.3.3 Photocatalytic Dye Degradation

To measure their photocatalytic activity, the Ni/np⁺-Si/FTO/TiO₂ microwires were dispersed in an aqueous solution of 40 µM MB (VWR International) and 0.01 M Na₂SO₄ which was deaerated with N₂ for 60 min prior to any measurement. In addition, tandem semiconductor samples were pre-soaked in the MB solution for 60 min or more before photocatalytic measurements to reach a steady-state level of dye adsorption on the surface. Two-electrode photoelectrochemical current density vs. potential (\( J-E \)) behavior in MB solution was measured under similar conditions using a BioLogic SP-200 potentiostat. The reference, in this case, was shorted to a Ni foil counter electrode immediately adjacent to a planar tandem semiconductor working electrode without a separator. Illuminated experiments were performed under a 1-Sun intensity of 100 mW cm⁻² generated with a 300 W Xenon lamp (Newport 6258) with an AM1.5 global filter (Newport 81094). During spectral mismatch measurements, higher energy photons including the UV were eliminated with a longpass filter (Newport 20CGA-800) with a cutoff for wavelengths less than 800 nm. In some experiments, an external UV-LED lamp (Hamamatsu, L14310-120, light at 365 nm) was used at variable power levels to supply additional UV light.
bias to generate higher photocurrent in the TiO\textsubscript{2}. The optical absorption spectra of the MB solution was measured using a double-beam UV-Vis spectrophotometer (Cary 60 UV-Vis), and MB degradation was monitored by tracking the absorbance value at $\lambda_{\text{max}} = 664$ nm and normalizing to the initial absorbance at the beginning of the measurement.

4.3.4 Materials Characterization

Electron micrographs of the morphology and elemental analysis of the microwires were performed with a Thermo Fisher Apreo C LoVac field emission scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) detector.

4.4 Conclusion

Tandem semiconductor structures provide a pathway to achieving high water-splitting STH efficiency, and particle suspension reactors may be the lowest cost option for solar hydrogen generation. The proof-of-concept Ni/np$^+$-Si/FTO/TiO\textsubscript{2} microwires used herein are capable of unassisted solar water-splitting and were used as a platform to investigate the optical properties of tandem microparticle slurries while methylene blue indicator dye was used for the in-situ monitoring of photochemical activity. The dispersive carrier gas bubbles had little effect on the photoactivity above a threshold flowrate, but below this flowrate, insufficient bubbling led to ineffective and non-uniform particle suspension and decreased absorbance and photoactivity. Higher photoactive particle concentrations enabled
faster MB photodegradation, but notably, a 1% volumetric concentration of tandem microwires was sufficient for 70 – 85% light absorption. Absorptance and corresponding MB photodegradation was even higher when employing a back reflector layer, although photo-inactive light scattering particles actually increased the reflectance loss of the overall slurry. By understanding mesoscale phenomena and light management in a complex medium of bubbles and tandem microwires, operational conditions can be selected to maximize absorbance within each photoactive particle. These optical trends can be extrapolated to other tandem semiconductor particulate systems to lower materials costs and help the field work towards practical, economical solar hydrogen generation.
CHAPTER 5

CONCLUSION AND FUTURE OUTLOOK

This dissertation has outlined the fabrication process for a proof-of-concept Si/TiO$_2$ microwire slurry reactor. There has been some progress in the field of Type 1 reactor for solar H$_2$ production, however, the STH efficiency has been extremely low. Based on the proposed design in this dissertation we believe that there is a large scope for improvement. This work addresses some of the fundamental concerns about low photon conversion efficiency in a single bandgap particle and the problem associated with current-matching in a free-floating tandem semiconductor slurry.

In the introductory chapter we explored the need for solar energy storage. The chapter covered some of the underlying scientific principle that explains the electrons generation process under solar illumination and the principles of electrochemistry that govern the rate of the water-splitting reaction. Different kinds of solar driven H$_2$ producing reactor types are then discussed. Based on the key findings from various techno-economic analyses it is found that particle-based PEC reactors show the highest potential for cost-effective H$_2$ production. This is followed by exploring the state-of-the art Type 1 reactors, their STH efficiencies, and the challenges that such systems face. The last section explains how the proposed particle design in this dissertation, aims at overcoming some of the challenges.
In chapter 2, we explored the catalytic activity of Ni based molecular catalyst (NiATSM) for hydrogen evolution reaction. Among the key findings were that NiATSM on p-Si photocathode showed a lower overpotential for HER at 10 mA cm$^{-2}$ than an equivalent loading of Ni metal. It was also found that the addition of Nafion in the catalyst significantly improved its stability on the p-Si substrate.

Chapter 3 describes the challenges faced by Type 1 particle-based solar-driven H$_2$ producing reactors. We then put forth a particle design that aims at overcoming the said challenges. For the proof-of-concept case, a Ni/np$^+$-Si/FTO/TiO$_2$ system was fabricated and shown to be capable of unassisted solar hydrogen generation. The tandem structure was incorporated into microwire particles, using a selective photodeposition scheme to put a Ni bulb on the cathodic site of the Si core cross section. This chapter also explains our hypothesis of how the alignment of the microwires (w.r.t incident solar irradiance) might affect the STH efficiency. To that end, the ferromagnetic Ni bulb was magnetized and used as a handle for the alignment of tandem microwires within a magnetic field under active dispersion of the particles with or without uplifting bubbles.

In Chapter 4, the optical and photochemical properties of the Ni/np$^+$-Si/FTO/TiO$_2$ slurry was explored. Light absorption within the slurry was studied by measuring reflectance and transmittance using an integrating sphere. It was found that a 1% volumetric concentration of tandem microwires was sufficient for absorbing 70 – 85% of incident illumination. Methylene blue indicator dye was used for the in-situ monitoring of photochemical activity. It was shown that higher photoactive particle concentrations enabled faster photodegradation. The rate of degradation increased
when a back reflector layer was employed, although photo-inactive light scattering particles led to a decreased absorptance and photoactivity due to increased reflectance loss of the overall slurry.

With such design capabilities there are multiple directions that can be explored to improve the current system. Since TiO$_2$ is a high-bandgap semiconductor, the current density under 1 Sun illumination, is very low compared to the series-connected Si. This makes it difficult to discern the effect of orientation without applying addition UV bias for improved TiO$_2$ output. Different top subcell materials such as III-V semiconductors (which have a lower bandgap than TiO$_2$) can be looked at as a replacement. These materials have been a subject of extensive research due to their superior electronic properties. In addition, they also offer the capability of tailoring their bandgap and band edge positions which can be very beneficial for PEC systems.

It is suggested to explore ways of improving Ni coverage on the Si base. Inconsistent Ni deposits expose the underlying Si thus making it prone to oxidation and etching. This can be done by testing different Ni baths, irradiation times and reaction vessel. The reaction vessel can be kept on an orbital shaker stage which leads to slow but continuous movement of the bath thus ensuring equal light absorption opportunity for all wires.

Since the DRIE etched Si wires are very expensive, the dispersive bubble flowrate can be experimented with to reduce aggressive collision and consequent wire loss. The cuvette reactor design can be improved to avoid dead zones (for uniform particle
dispersion) by finding an alternative to epoxy for sealing the microporous frit in the cuvette bottom.

With the reliable and reproducible tandem particle growth, the next logical step would be to perform long term stability measurement under illumination.

There are numerous obstacles to realizing practical solar hydrogen production via slurry reactors. Hopefully, the novel particle design presented herein has provided a prototype for the researchers in this field and will facilitate innovation towards a high efficiency particulate system for a cost-effective solar H₂ generation.
REFERENCES


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95. B. M. Kayes, H. A. Atwater and N. S. Lewis, *J. Appl. Phys.*, 2005, **97**.
APPENDIX

LIST OF PUBLICATIONS

Portions of this thesis have been derived from the following publications:


Gulati, Saumya, Matthew C. Mulvehill, Tyler C. Thompson, and Joshua M. Spurgeon. “Optical properties and photocatalytic performance of Si/TiO$_2$ tandem semiconductor microwire slurries.” (Submitted)
(i) Doping of planar and microwire Si wafer

Si wafers were broken into 1.7 x 0.5 cm pieces to fit into the tube furnace. A Dremel tool was used to make ridges on the boat to support the wafers. The Si wafers were then stacked alternatively between the dopant source wafers in a ceramic boat. The following temperature profile is set to dope n-Si with BN solid-source dopant wafer:

C01- 19 °C (Should be automatically set as the room temperature)
T01- 25 min
C02- 950 °C (Slide the boat with HF etched n-Si wafers along with BN)
T02- 4 min (Flow N2 gas at 200 sccm)
C03- 950 °C (Take boat out, remove the BN wafers)
T03- 13 min (Etch the Si wafers in 10% buffered HF solution for 30 sec)
C04- 750 °C (Place just the Si wafers back in the boat)
T04- 35 min (Turn on O2 gas at 100 sccm)
C05- 750 °C
T05- -121 °C (The program terminates; retrieve the doped Si wafers and etch it again)

To check if the doping process worked as desired, a four-point probe is used to measure the sheet resistance of the Si wafer.

(ii) Spray deposition of fluorinated tin oxide (FTO)

The doped wafers are etched again before the spray deposition of FTO to remove any native oxide layer (SiOx). The wafers are then placed on a ceramic hotplate as
shown in Figure A1. The aluminum foil protects the underlying plate from the ammonium fluoride (highly corrosive) which is in the FTO precursor solution.

The spray bottle is held at a 45° angle and ~10 cm away from the wafers. 30 rounds of spraying leads to a ~430 nm thick layer of FTO (Figure A2). Each round consists of 2 quick consecutive sprays.

(iii) Hydrothermal Synthesis of TiO₂

The FTO/Si wafers are then placed inside a stainless-steel Teflon-lined autoclave chamber with the FTO side facing the wall (Figure A3). The Teflon container is
then slowly filled with a titanium precursor solution. (0.05 M titanium n-butoxide and 6 M HCl)

The container is kept inside a muffle furnace at 220 °C for 4 hours. Thereafter, it is taken out and allowed to cool under running water. It takes ~20 to 25 min for the container to reach room temperature. This can be cross-checked by how easily the Teflon chamber opens. If it is still hot, the chamber will be pressurized, and the cap will not open. This step needs to be done inside a fume hood to avoid inhaling the toxic vapors. These wafers are washed profusely with DI water to remove any trace acid and the transferred into a petri dish for further annealing at 450 °C.

(iv) Photodeposition of Ni on planar Si/TiO₂ tandem and tandem microwires

**Planar Tandem**

Once the tandem wafer is made, the Si face is scratched with a diamond scribe to remove the p-Si layer which grows during the doping process. This ensures that the underlying n-Si is exposed for Ni deposition. The wafer is then transferred into a Ni
precursor solution (in a petri dish) such that the TiO$_2$ layer faces the simulated sun while ensuring that the Si face is slightly raised for proper contact with electrolyte. The solar lamp is then turned on and the intensity if kept as high as possible to speed up the deposition process. Since higher intensity leads to a greater number of photogenerated charge carriers that can perform the Ni$^{2+}$ ion reduction to form a Ni metal layer on the exposed n-Si. Figure A4

![Figure A4. Merged SEM schematic for electroless Ni deposition on a planar tandem](image)

**Tandem Microwires**

After the tandem microwire wafer is made it is then fixed on a glass slide using mounting wax. A glass slide is heated to 150 °C. Solidified wax is then rubbed on the glass slide. The temperature causes the wax to melt, leaving behind a viscous liquid wax on the slide. While it is still in liquid form the tandem microwire wafer is carefully placed on the wax making sure that it is partially dipped in it. The slide is removed from the hotplate and allowed to cool down till the wax solidifies fixing the wafer in place on the slide. The slide is then fixed to a board using a tape. A layer of nail polish polymer is then gently spread onto the wafer and left to dry. This binds the wires in a polymer film which is later scraped off using a one-sided blade (Figure A5a). This film is then later dissolved in acetone thus freeing the tandem microwires.
The wire in acetone slurry is then filtered using an alumina membrane (Figure A5 b). The wire collection cone (Figure A6) is then filled with ~900µL of Ni precursor solution and lowered in a sonication bath such that the cone is partially beneath the meniscus of water in the bath. With the sonication bath on, the filter membrane with the wires is then slowly lowered into the cone using a tweezer. Once the wires are transferred into the solution the sonicator is turned off. The slurry is then pipetted out and transferred into a petri dish which contains ~2-3 mL of the Ni precursor solution.

The petri dish is then kept under solar illumination (similar to the setup used for Ni deposition on the planar tandem) for ~3 hrs. The slurry needs to be mixed, every 30 minutes, by swirling the petri dish to ensure equal opportunity for the wires to receive solar illumination and to magnetize the Ni bulbs that go down on the exposed Si. This is done by swiping a magnet underneath the petri dish for ~30 seconds every 30 minutes.
Figure A 6. Photograph of the wire collection cone.
MATLAB CODE TO ADJUST RAW EC-LAB CURRENT-POTENTIAL DATA FOR ELECTRODE AREA AND ELECTROLYTE pH

prompt2='Number of excel sheets? '; sheets= input(prompt2);
j=2;
st_data=zeros(20);  % stores the values of current and potential
for i=1:1:sheets
    prompt1 = 'What is the area of electrode? '; area = input(prompt1);  % Area sample 1 is 0.32 cm^2
    [A,text,raw]= xlsread('Filename.xlsx',i);
    B = A(1:end,8:9);  % extracts 2 columns from the whole sheet which contains current (8th column) and potential (9th column)
    B(:,1)=B(:,1)+ 0.197+ (0.059 *[enter pH]);  % changing pot to versus RHE
    B(:,2)=B(:,2)./area;  % changing current to current density
    st_header(1,j)=raw(1,1);  % stores the test condition of the sample
    for k=1:1:size(B,1)  % transferring data to another matrix named B
        st_data(k,j-1)=B(k,1);  % stores potential vs RHE
        st_data(k,j)=B(k,2);  % stores current density
    end
    j=j+2;
end
xlswrite('output_CV.xlsx',st_header,1,'A1')
xlswrite('output_CV.xlsx',st_data,1,'A2')
MATLAB CODE TO GENERATE THEORETICAL CURRENT-DENSITY FROM Si AND TiO$_2$ OF VARYING MATERIAL THICKNESS AND AM 1.5 SPECTRUM

Current density from Silicon/TiO$_2$

$q=1.6*10^{-19};$ \hspace{1cm} \text{%charge on 1 electron}
$h=6.63*10^{-34};$ \hspace{1cm} \text{% Plank's constant}
$c=3*10^8;$ \hspace{1cm} \text{% speed of light}
$SunIntensityFactor=1;$
nopz=51; \hspace{1cm} \text{% No. of layers in which thickness of Si or TiO$_2$ is divided into}

spec_irrad= xlsread('newAM1pt5_spectrum2',2); \hspace{1cm} \text{% Portion of spectrum falling on the electrode}
lambda=spec_irrad(:,1); \hspace{1cm} \text{% extracts the wavelengths into the variable lambda}
F_lambda=spec_irrad(:,2).*SunIntensityFactor; \hspace{1cm} \text{% changes the power density depending on the multiplication factor}
alpha= spec_irrad(:,3);
f1= F_lambda.*lambda;
z= linspace(0,100*10^{-6},nopz); \hspace{1cm} \text{% creating an array along z dirxn}
% z=z';
% n=0;
LGC= zeros(numel(z),1);
for k=1:1:nopz
  % whos
  % if(z(k)>CellThickness)|| abs(DFE)>0
  %   IQEf=0;
  % else if (z(k)<=CellThickness) %abs(DFE)<=Le+w) ||
  %   IQEf=1;
  % else if(z(k)<=CellThickness)
  %   IQEf=1;
  % end
  % end

  for j=1:1:length (f1)
    p=-1*alpha(j)*z(k);
    f2=exp(p); \hspace{1cm} \text{% gives transmittance}
    f3=(1-f2); \hspace{1cm} \text{% gives absroptance}
    f4(j)=f3.*f1(j);
  end
  LGC(k)=trapz(lambda,f4);

  % if(LGC(k)<0)
  %   LGC(k)=0;
  % end
  f4=zeros(0,1);
end
LGC;

LGC_net=max(LGC)*10^-10 * q /(h*c)  % gives LGC in mA/cm^2
MATLAB CODE TO GENERATE COLOR PLOTS FOR REFLECTANCE, TRANSMITTANCE AND ABSORPTANCE DATA

x = [10; 15; 20];  % flowrates in sccm
y = [0 0.002 0.004];  % alumina particles densities
z = xlsread('Filename.xlsx', 'D44:F46');

surf(x,y,z,'EdgeColor','None','Facecolor','interp');
view(2);
xlabel('Flowrate (sccm)');
ylabel('Alumina particle weight (g)');
zlabel('Absorptance (%)');
% colorbar
c = colorbar;
c.Label.String = 'Absorptance of Si at 640 nm (%)';
caxis([0 100])
% c.Limits = [15 35]
% lims=clim
% clim([0 100])
colormap jet;
TANDEM MICROWIRE DENSITY AND VOLUME FRACTION CALCULATIONS

Different concentrations of tandem microwires in a slurry were prepared by carefully measuring the area of the wire array growth substrate from which the particles were harvested. Most of the microwires were successfully transferred to the solution, but as some small loss is likely, the following particle concentration calculations represent an upper bound. The photomask pattern spacing (15 µm center-to-center pitch hexagonally close-packed) was used to calculate the wafer-area-dependent concentration of particles. A 1 cm$^2$ microwire array wafer area had $\approx 5.13 \times 10^5$ wires:

$$\frac{\text{Wires}}{\text{Wafer cm}^2} = \frac{(3)(\frac{1}{2})}{\left(\frac{1}{2}(15 \ \mu m)\left(\sqrt{15^2 - (\frac{15}{2})^2} \ \mu m\right)\right)^2} = \frac{0.5}{(\frac{15}{2} \ \mu m)(12.99 \ \mu m)} = 0.5 \ 97.43 \ \mu m^2$$

$$\frac{\text{Wires}}{\text{Wafer cm}^2} = \left(\frac{0.00513}{\mu m^2}\right)\left(\frac{10^4 \ \mu m}{cm}\right)^2 = 5.13 \times 10^5 \ \text{cm}^{-2}$$

Each tandem microwire had an estimated Si core diameter of 9 µm, with an FTO shell 500 nm thick, and a TiO$_2$ outer shell $\sim 1.5 \ \mu m$ thick. The wires were $\sim 100 \ \mu m$ tall. Using these dimensions (but neglecting the TiO$_2$ at the top and the small Ni bulb), the mass of a wire was calculated:

$$m_{\text{Si}} = \pi R_{\text{Si}}^2 L \rho_{\text{Si}} = \pi (4.5 \ \mu m)^2 (100 \ \mu m) \left(\frac{cm}{10^4 \ \mu m}\right)^3 \left(2.33 \ \frac{g}{cm^3}\right) = 1.48 \times 10^{-8} \ g \ \text{wire}^{-1}$$

$$m_{\text{FTO}} = \pi (R_{\text{FTO}}^2 - R_{\text{Si}}^2) L \rho_{\text{FTO}} = \pi [(5 \ \mu m)^2 - (4.5 \ \mu m)^2] (100 \ \mu m) \left(\frac{cm}{10^4 \ \mu m}\right)^3 (6.95 \ \frac{g}{cm^3})$$

$$= 1.04 \times 10^{-8} \ g \ \text{wire}^{-1}$$

$$m_{\text{TiO}_2} = \pi (R_{\text{TiO}_2}^2 - R_{\text{FTO+Si}}^2) L \rho_{\text{TiO}_2} = \pi [(6.5 \ \mu m)^2 - (5 \ \mu m)^2] (100 \ \mu m) \left(\frac{cm}{10^4 \ \mu m}\right)^3 (4.23 \ \frac{g}{cm^3})$$

$$= 2.29 \times 10^{-8} \ g \ \text{wire}^{-1}$$

$$m_{\text{wire}} = 1.48 \times 10^{-8} + 1.04 \times 10^{-8} + 2.29 \times 10^{-8} \ g \ \text{wire}^{-1} = 4.81 \times 10^{-8} \ g \ \text{wire}^{-1}$$

The total mass of all photoactive particles in a slurry per cm$^2$ of microwire array wafer used is thus:

$$m_{\text{slurry}} = Nm_{\text{wire}} = (5.13 \times 10^5 \text{ wires cm}^{-2})(4.81 \times 10^{-8} \ g \ \text{wire}^{-1}) = 0.0247 \ g \ cm^{-2}$$
The mass concentration of photoactive particles in a 1 mL slurry per cm$^2$ of microwire array wafer used is thus:

$$\rho_{\text{slurry}} = \frac{Nm_{\text{wire}}}{V_{\text{solvent}}} = \frac{(0.0247 \text{ g cm}^{-2}) (1000 \text{ mL L}^{-1})}{1 \text{ mL}} = 24.7 \text{ g L}^{-1} \text{ cm}^{-2}$$

The approximate volume of one tandem microwire is:

$$V_{\text{wire}} = \pi R_{TiO_2}^2 L = \pi (6.5 \mu m)^2 (100 \mu m) = 13273 \mu m^3 \left( \frac{cm}{10^4 \mu m} \right)^3 = 1.327 \times 10^{-8} \text{ cm}^3$$

The total volume of all photoactive particles in a slurry per cm$^2$ of microwire array wafer used is thus:

$$V_{\text{slurry}} = NV_{\text{wire}} = (5.13 \times 10^5 \text{ cm}^{-2}) (1.327 \times 10^{-8} \text{ cm}^3) \left( \frac{1 \text{ mL}}{1 \text{ cm}^3} \right) = 0.00681 \text{ mL cm}^{-2}$$

The volume fraction of photoactive particles added to 1 mL of solution in a slurry, per cm$^2$ of microwire array wafer used, can be approximated as:

$$\frac{V_{\text{slurry}}}{V_{\text{slurry}} + V_{\text{solvent}}} \approx \frac{V_{\text{slurry}}}{V_{\text{solvent}}} = \frac{0.00681 \text{ mL cm}^{-2}}{1.000 \text{ mL}} = 0.00681 \text{ cm}^{-2} = 0.68\% \text{ cm}^{-2}$$
CURRICULUM VITA
Saumya Gulati
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Education

University of Louisville, KY 2017 - 2023
Doctor of Philosophy, Chemical Engineering GPA: 3.88/4

Coursework: Solar Fuels, Chemical Vapor Deposition, Solid-State Physics, Material Characterization, Transport Phenomena, Electrochemistry

Columbia University, NY 2015 - 2017
Master of Science, Chemical Engineering GPA: 3.63/4


Harcourt Butler Technological Institute, India 2011 - 2015
Bachelor of Technology, Chemical Technology GPA: 4.0/4

Bachelor’s final project: Biodiesel production from jatropha oil

Overview

- Research experience in growth and characterization of micro-photocathodes
- Experience in designing and 3D printing components using CAD software
- Programming experience in solving complex problems using MATLAB
- Comfortable presenting complex data in written, visual, or verbal formats
- Inter-disciplinary research between physics, chemistry, and material science
Research Experience

University of Louisville

Dr. Joshua Spurgeon, Conn Centre for Renewable Energy Research 2017 –2023

*Growth of Silicon (Si) /TiO₂ tandem semiconductor microwire for unassisted water-splitting*

- Established setup for reflectance and transmittance measurement of photoactive particles in a cuvette
- Established setup for n/p doping of silicon (Si), growth of conductive oxide layers and hydrothermal synthesis of TiO₂ semiconductor on Si
- Automated processing of current-voltage data obtained experimentally from photocathode/anode
- Designed and 3D printed parts to expedite growth process and characterization of the tandem microwires

*NiATSM molecular catalyst for hydrogen evolution*

- Tested JV performance and characterized the structure of p-Si photocathode with multiple Ni based molecular catalyst

Columbia University

Dr. Daniel Esposito, Columbia University in the city of New York 2015 - 2017

*Quantifying the effects of electrolyte induced inversion layer on p-Si MIS photocathodes*

- Performed scanning photocurrent microscopy and photoelectrochemical (PEC) measurements on platinum decorated silicon electrodes to optimize catalyst loading
- Conducted numerical modeling for metal-insulated semiconductor system to validate the experimental results
- 3D printed setup to study effective diffusion length of electrons on a platinum- Si electrode
- *Course Project* - PEC reactor design for treatment of phosphates from run-off in Lake Erie

Work Experience

Teaching Assistant Aug 2017 - May 2020

- Delivered recitation for undergraduate level chemistry
- Undergraduate-level courses- chemical kinetics, computer application in chemical engineering, material and energy balance, thermodynamics, and unit operations lab

Mentor, Undergraduate/Graduate Research 2017- 2023
• Mentored a student on the use of an integrating sphere for reflectance and transmittance measurement, under the Louisville Science Pathways program
• Mentored a student for a project on metal assisted chemical etching of silicon for microwire growth
• Mentored 3 students working on designing of photomask for etching Si wafers via DRIE and alignment study of the subsequently obtained Si microwires
• Mentored multiple students on various characterization techniques including SEM, EDS, UV-Vis etc.

Undergraduate Tutor @Columbia Aug 2015 - Dec 2016
  • Taught physics, chemistry, and mathematics to student athletes

Skills

• **Programming language** - Java, C, MATLAB
• **Computer Aided Design** - Solidworks, Autodesk Inventor
• **Technical Skills** - Scanning electron microscopy, UV-Vis spectroscopy, Energy-dispersive X-ray spectroscopy, Thermal vapor deposition, Gas chromatography, XPS
• **Finite Element Simulation** - COMSOL (Limited proficiency)

Publications

• **Gulati S**, Mulvehill MC, Thompson TC, Spurgeon JM. “Optical properties and photocatalytic performance of Si/TiO$_2$ tandem semiconductor microwire slurries.” (Submitted)


### Conference Presentations and Posters

<table>
<thead>
<tr>
<th>Conference</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRS Fall meeting, Boston, MA</td>
<td>Nov 2021</td>
</tr>
<tr>
<td>International Solar Fuels conference (Virtual)</td>
<td>July 2021</td>
</tr>
<tr>
<td>MRS Spring meeting (Virtual)</td>
<td>April 2021</td>
</tr>
<tr>
<td>nanoGe Fall meeting (Virtual)</td>
<td>Oct 2020</td>
</tr>
<tr>
<td>Graduate student regional research conference, Louisville, KY</td>
<td>Feb 2020</td>
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<tr>
<td>AIChe Annual Meeting, Orlando, FL</td>
<td>Nov 2019</td>
</tr>
<tr>
<td>HOPE program at NREL Boulder, CO</td>
<td>Jul 2019</td>
</tr>
<tr>
<td>Workshop, Beijing, China</td>
<td>Jul 2016</td>
</tr>
</tbody>
</table>

### Awards and Scholarships

- NSF Thesis Commercialization Enhancement microgrant, KY 2022
- UofL-NSF I-Corps funding, LaunchIt Startup and Innovation Bootcamp, KY 2022
- Graduate student council (GSC), UofL research/travel grant, KY 2019/2021
- 3-minute thesis (3MT) runners up award, KY 2019/2020
- Women in energy spring internship research funding, NY 2017
- Energy and sustainability workshop travel grant, China 2016
- Institute merit scholarship, HBTI Kanpur, India 2013

### Journal Reviewer

- RSC Advances (Publisher-Royal Society of Chemistry) May 2020- present

### Leadership/Volunteering

- Outreach Chair: Columbia Engineering Energy Club Jan - Dec 2016
- Helped organize various information sessions, guest lecturers, networking events for internship opportunities and informal interactive sessions for current students and alumni
- Developed synergetic relations between energy clubs at different schools in Columbia and organize events in collaboration with each group
Society Of Women Engineers: Mar - Sept 2016
- Participated in an outreach event to showcase various science experiments for high school students

- Catered to the elderly residents at Jewish Home Lifecare

Speech Therapist (Amrita School for special kids) Jan - Mar 2014