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Variability in the Fabrication Process of BiVO₄ Photoanodes

An Honors Program Project Presented to
the Faculty of the Undergraduate
College of Integrated Science and Engineering
James Madison University

by Lauren Michelle Phillips

May 2015

Accepted by the faculty of the Department of Engineering, James Madison University, in partial fulfillment of the requirements for the Honors Program.

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PUBLIC PRESENTATION

This work is accepted for presentation, in part or in full, at the Madison Engineering xChange on April 18, 2015 .

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Acknowledgements

First and foremost I would like to thank my project advisors, Dr. Keith Holland and Dr. David Lawrence.

I would also like to thank Dr. Sam Morton and Dr. Adebayo Ogundipe for their guidance and advice throughout my honors project.

My completion of this project could not have been accomplished without the support from my research mentees-Kylie Britt and Rachel Berry, and my peer- Bartlett Jones. I would like to thank James Madison University's Center for Material Science for access to equipment integral to the completion of my project.

Abstract

Hydrogen gas produced from the photoelectrochemical (PEC) decomposition of water, using sunlight as an energy source, is a promising approach for sustainable fuel production. This decomposition of water is also called artificial photosynthesis. A device that accomplished this process is sometimes called an artificial leaf, which mimics nature inasmuch as it stores solar energy as a chemical fuel (e.g., hydrogen) by splitting water, in this way imitating natural photosynthesis. In 2009, Dr. Keith Holland and Dr. David Lawrence of James Madison University (JMU) initiated a research program to investigate materials for the photoelectrochemical decomposition of water into hydrogen and oxygen, which is a critical component of the artificial leaf concept for the production of solar derived fuels. Significant research is still required to develop the efficient and low-cost semiconducting photocatalyst materials required for PEC water decomposition. Recently, bismuth vanadate, BiVO_4 , has been identified as a potential low-cost and stable semiconducting oxide for the photooxidation of water. While numerous studies regarding the PEC performance of BiVO_4 have been reported in existing literature, few studies about manufacturing variability have been reported. Variability in the performance of the photoanodes has been observed during previous studies at James Madison University. This study investigates one potential cause of variability in the manufacturing process- slight variations in the Bi:V ratio in precursor solutions used to fabricate the thin-film photoanodes. Small and controlled variations in the precursor solutions during the manufacturing process were observed to produce no significant effect on the PEC performance.

Introduction

With increasing concerns over fossil fuel depletion, rising energy costs, and the cumulative effects of CO₂ emissions, solar energy provides an attractive energy alternative. The challenge with utilizing solar energy is storing the converted energy. One method of storing solar energy is to use a photovoltaic (PV) cell to convert sunlight to electricity and using a battery to store the converted energy. The negative repercussion with this system is the costly and toxic materials, and short lifetime of the system. An alternative to using batteries to store the energy is to convert sunlight to a chemical based fuel. The combustion of H₂, a chemical based fuel, results in only pure water as a byproduct, making this a clean fuel. Materials have been researched to convert sunlight to hydrogen. Previous studies completed at JMU (2) have shown PEC performance variations. Sources of variability have not yet been identified, but slight variations in precursor solutions during the manufacturing process could have an effect on the PEC performance. This project was initiated to investigate the effects of slight variations in the precursor solution composition on the PEC performance of BiVO₄ photoanodes.

Literature Review

In less than two hours, the sun delivers more energy to the Earth than all humans will consume within a year. In 2007, Global energy consumption was estimated to be 13 TW while the sun supplies the earth with 120,000 TW of unutilized power (3). Being able to capture, store, and transport this energy would be a step towards meeting worldwide energy concerns. With increasing concerns over fossil fuel depletion, rising energy costs, and the cumulative effects of CO₂ emissions, solar energy provides an attractive energy alternative. The challenge with utilizing solar energy is storing the converted energy. One method of storing solar energy is to use a photovoltaic (PV) cell to convert sunlight to electricity and using an electrochemical battery to store the converted energy. However, large energy capacity battery systems can be costly and frequent cycling, resulting from intermittent solar resource availability, reduces the useful life. Further, since they are often comprised of environmentally toxic materials, significant costs are incurred in recycling or disposal at the end of life.

An alternative to using electrochemical batteries is to convert captured solar energy to a chemical based fuel, such as hydrogen (H₂). The combustion of H₂ with oxygen (O₂) results in the release of energy and the formation of pure water as a byproduct, making it ideal as clean fuel, since no pollutant or greenhouse gases are released during its combustion (4).

Allen Bard and Marye Anne Fox (1994) described solar energy, when converted to hydrogen, as the “Holy Grail” of renewable energy. They identified the following set of parameters for a successful solar energy to hydrogen fuel conversion system:

- i. Conversion efficiency of at least 10 %
- ii. Materials will not be consumed or degraded under irradiation for at least 10 years
- iii. Photochemical reactions performed with a recyclable catalyst
- iv. Be cost competitive with traditional fossil fuels

Numerous research groups have demonstrated the materials that can produce the desired conversion efficiencies (5) (6); however, these materials are often consumed or destroyed during the solar energy to hydrogen fuel conversion process. To date, a suitable combination of materials that meets all of these criteria has not been discovered.

Solar energy can be converted to a chemical based fuel by splitting water into oxygen, O₂, and hydrogen, H₂. The photodriven conversion of liquid water to gaseous hydrogen and oxygen can be expressed as a general equation (Equation 1).



Solar hydrogen can be derived using three main methods:

- i. Electrolysis of water using a solar cell and metal electrodes,
- ii. Powdered photocatalyst
- iii. Semiconductor Liquid Junction

These methods are briefly described, below.

i. Electrolysis

Electrolysis is the simplest method to harness solar energy. Two metal electrodes, the anode and the cathode, are immersed in water form an electrolysis cell. A power supply, such as a photovoltaic panel, provides the voltage bias necessary to decompose water into its constituents

and the electrical current necessary to sustain the decomposition reaction. The necessary voltage required to split water is approximately 1.23 V. Through electrolysis, including photolysis, oxygen is evolved on the anode, positive electrode, and hydrogen is evolved on the cathode, negative electrode. Although this system is simple, it is inefficient at converting all of the incident solar energy into stored hydrogen fuel energy. Furthermore, the photovoltaic (PV) panels and platinum electrodes are expensive. Figure 1 shows a simple schematic of electrolysis using a solar cell and two metal electrodes.

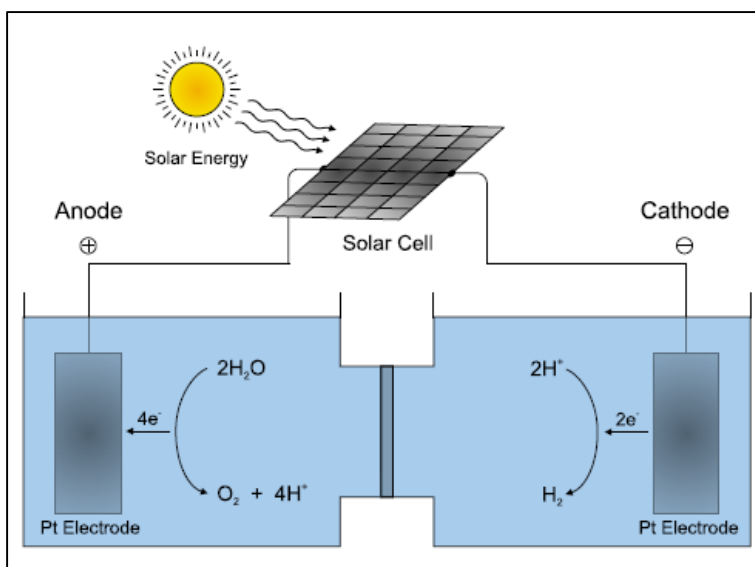


Figure 1: Electrolysis using a solar cell and two metal electrodes (7)

ii. Powdered Photocatalyst

Using a powdered photocatalyst, or particles, to decompose water, is a simple task. Unlike the electrolysis method, solar energy is incident on small semiconductor particles that are suspended in the water. The oxidation and reduction of water (i.e., the conversion of water into O_2 and H_2 , respectively), occur at the surface of these particles. This method is easy to scale up to large application (8). Once the decomposition reaction occurs, hydrogen can be collected by means of

selectively permeable membranes. A primary limitation of the powdered photocatalyst system is that recombination of photogenerated hydrogen and oxygen can occur in the water suspension, thus reducing the efficiency of the solar energy to hydrogen fuel production rates. Methods are currently being researched to reduce such recombination. A simple schematic of a particle photocatalyst system can be seen in Figure 2, below.

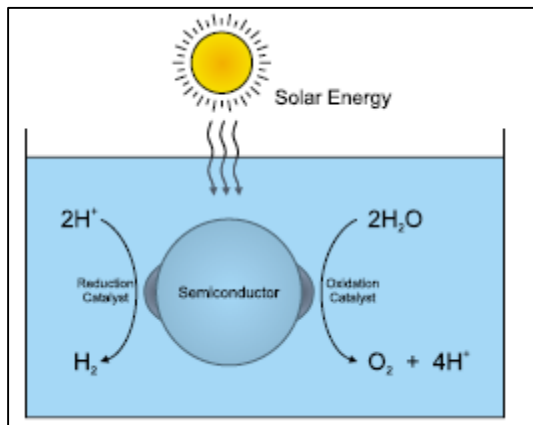


Figure 2: Simple schematic of powdered photocatalyst system (7)

iii. Semiconductor liquid junction

A semiconductor liquid junction (SCLJ) combines aspects of the powdered photocatalyst and electrolysis methods. Ideally, in the SCLJ approach, two electrodes coated with photosensitive semiconducting materials are submerged in water. Using this approach, solar energy is utilized by the semiconducting material or photocatalyst to decompose the water at the semiconductor-liquid interface. In theory, such direct conversion of solar energy, without the reliance on conversion via PV panels, as in the electrolysis approach, can more effectively utilize the available photons of solar energy (7). Although the ideal SCLJ system is comprised of two photoactive semiconductor materials, this is not required. Alternatively, one semiconducting

material can be used as the anode or cathode, while the other electrode is a metal, typically platinum. Figure 3 shows a SCLJ system using two semiconductors.

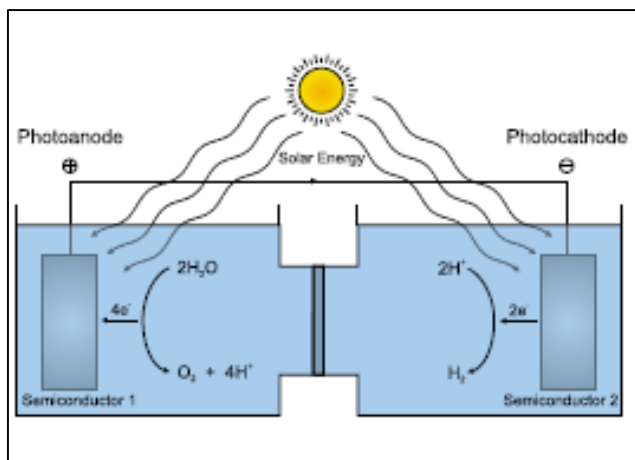
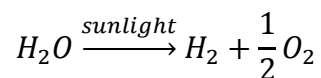


Figure 3: SCLJ system using two semiconductors (7)

In a practical implementation of this approach, the photoanode and photocathode could be coated on opposite sides of the same substrate, to create an “artificial leaf”. When immersed in water and illuminated with sunlight, hydrogen would be evolved on one side of the leaf, and oxygen on the opposite.

Artificial Photosynthesis or Photoelectrochemical Decomposition

Artificial photosynthesis mimics the process plants use to produce molecular forms of Hydrogen and Oxygen. This method follows the SCLJ system. Plants perform a conversion through photosynthesis to convert CO₂ and water to oxygen and carbohydrates (9). Carbohydrates are nature’s way to store the hydrogen from the water splitting reaction (1).



$$E^0 = 1.23V$$

A band gap describes the energy difference (in electron volts) of the valence band and the conduction band in semiconductors. For example, at least 1.23 eV of energy is required to split water, therefore the energy gap of the semiconductor material must be larger than this value to successfully evolve hydrogen and oxygen.

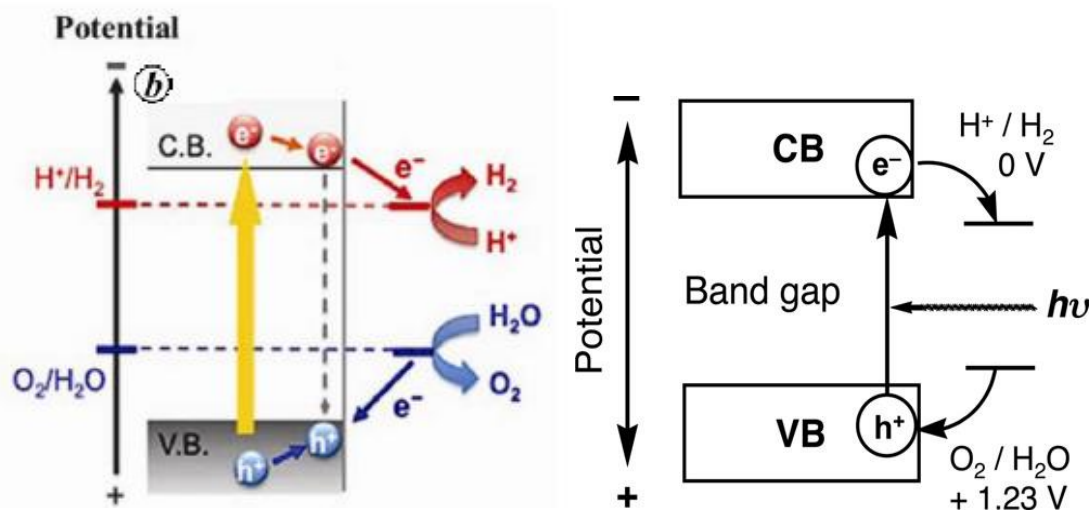


Figure 4: energy level requirements (a) Maitra et al 2014 (9) (b) Kudo et al (8)

This potential difference, 1.23 eV, is equivalent to the energy radiated from the sun at a wavelength of 1000 nm. If an electrochemical system utilized solar energy effectively, it should be possible to split water with visible light (10). For artificial photosynthesis to occur, the following steps must occur (8).

- i. absorb photons in the semiconductor to form electron- hole pairs
- ii. charge separation and migration of photogenerated carriers to the semiconductors surface
- iii. surface chemical reactions
- iv. The photodriven conversion of liquid water to gaseous hydrogen and oxygen

The semiconductor material must absorb the sunlight transmitted through the water (5). Once the light is absorbed, electron-hole pairs will be formed. Charges (electrons and holes) must migrate from their position in the thin film to the surface of the film. Materials with ideal crystal structures allow for easy charge migration (6). This will increase carrier lifetime, i.e. the length of time charges can move without recombining. Once charges reach the surface of their respective electrodes, surface chemical reactions will occur (11). Electrons and holes at active sites on the surface of the semiconductor will recombine with each other if reduction and oxidation (redox) reactions do not occur. Redox reactions occur when electrons are transferred from one species to another. After redox reactions occur, gaseous hydrogen and oxygen will form on the cathode and anode, respectively (12).

Materials for SCLJ

Materials suitable to successfully create a SCLJ system are still being researched. Some common materials that have been identified as potential PEC photoanodes are Titanium Dioxide (TiO_2), Tungsten Oxide (WO_3), Iron Oxide (Hematite) (Fe_2O_3), Bismuth Vanadate (BiVO_4). Numerous other oxide and non-oxide materials have also been considered (5) (6). Each material has its advantages and disadvantages.

Titanium Dioxide (TiO_2)

In 1972, Honda and Fujishima published research using Titanium Dioxide as a material to decompose water. This novel work sparked interest in the photolysis of water. Due to a large bandgap, 3.2 eV (8), Titanium Dioxide is only active in the UV region of the solar spectrum. A small external voltage bias must be applied to the anodes. TiO_2 is very stable in all ranges of pH

solution (7), making the thin films versatile. Due to its versatility in solutions, it is typically used to purify water, because it oxidizes organic material (8).

Tungsten Oxide (WO₃)

Tungsten Oxide has a smaller band gap than TiO₂, 2.8 eV (9), and is active in slightly longer wavelengths of the solar spectrum. It is, however, not stable in acidic solutions (7). While the material is limited in its spectral response, and solution stability, research is still being completed to improve the performance through the use of colored dyes and material additives.

Iron Oxide (Hematite) (Fe₂O₃)

Hematite has a smaller bandgap, at 2.2 eV (9), and is active in the visible light range. Hematite is not stable in acidic solutions (7), and lacks the ability to provide a long carrier lifetime. Carrier lifetime refers to how long the charges (holes and electrons) stay active, until they reach the surface of the material to react with the solution. This poor carrier lifetime limits the efficiency of this material. Recent works have suggested that carrier lifetime can be improved with selective coatings, dye sensitization, and nanostructuring (12).

Bismuth Vanadate (BiVO₄)

Bismuth vanadate has recently emerged as a promising material for use as a photoanode (13). Bismuth vanadate with a monoclinic scheelite structure has a high activity as a visible light driven photocatalyst (14). The bandgap for bismuth vanadate is 2.4 eV (13), and it has been shown to have good charge carrier properties and has exhibited stability in a wide variety of conditions.

Fabrication Methods

At JMU, Thin films of Bismuth Vanadate have been deposited using Ultrasonic Spray Pyrolysis (USP). This method is convenient, fast and economical technique to prepare films (14). The ultrasonic spray pyrolysis method is one of multiple chemical solution based synthesis techniques, including metal-organic decomposition, drop casting, spin coating, and dip-coating. BiVO₄ has also been fabricated using electrochemical deposition techniques and vacuum deposition methods (13).

Conclusion

There are many methods to improve the photoelectrochemical properties of thin films. It has been shown that high temperature annealing improves PEC performance in BiVO₄ thin films (13). Annealing thin films promotes formation of the monoclinic scheelite crystal structure (2). Thin films can be annealed in air and also a 3% hydrogen atmosphere. A research group at James Madison University studied the effects of tungsten doping on bismuth vanadate thin films. While some groups saw an improvement of PEC performance in the thin films, Holland *et al* results showed a decrease of performance. Performance variability was noted throughout the photoanodes, in the doped and undoped samples. This led to the proposal that the performance variability should be addressed before further research. It was identified that the source of the variability might occur during the spray pyrolysis BiVO₄ deposition process. Two likely sources are slight variations in the nozzle height and the chemical composition of the precursor solutions.

Problem Statement

In this work, the effect of slight precursor composition variations in the film deposition process on the PEC performance of BiVO₄ photoanodes was investigated. This was done in an attempt to isolate a potential source of PEC performance variability that may be attributed to the fabrication process.

Procedures

To investigate the effects of precursor solution variability on thin-film BiVO_4 photoanodes produced via the ultrasonic spray pyrolysis method, a total of twelve different photoanodes were fabricated. These twelve samples were produced according to the fabrication methods outlined in the following sections. The PEC performance and material characteristics of these twelve samples were evaluated according to the testing methods described in the following sections.

Bismuth Vanadate Photoanode Fabrication

As previously described, the thin-film photoanodes are produced by nebulizing a precursor solution containing bismuth and vanadium compounds. To prepare the precursor solution for the ultrasonic spray deposition process, stock solutions of bismuth nitrate and vanadium oxysulfate were made. The bismuth source was a solution of 0.04 M Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.999%, Alfa Aesar)) in 0.5 M HNO_3 (Fisher Scientific). A solution of 0.04 M vanadium oxysulfate ($\text{VOSO}_4 \cdot 3.5\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich)) in 0.5 M HNO_3 was prepared as the vanadium source. The precursor solutions were then prepared from these stock solutions by mixing the stock solutions in specific ratios to make the precursor solutions. Once deposited on the heated substrates, the bismuth nitrate reacts with vanadium oxysulfate, to form bismuth vanadate, and volatile byproducts that are carried away by exhaust gasses. Three precursor solution ratios were mixed from stock solutions: 1 Bi: 1 V, 1.005 Bi: 0.995 V, 0.995 Bi: 1.005 V. The 1 Bi: 1 V stock solution was mixed by combining 20 mL of the of bismuth nitrate and 20 mL vanadium oxysulfate; The 1.005 Bi: 0.995 V stock solution was mixed by combining 20.1 mL of the of bismuth nitrate and 19.9 mL vanadium oxysulfate; The 0.995 Bi: 1.005 V stock solution was mixed by combining 19.9 mL of the of bismuth nitrate and 20.1 mL vanadium

oxysulfate. Approximately 10 mL of the precursor solutions were used for each thin-film deposition, or fabrication, process. Before every deposition run, the precursor solution was refilled to ensure trial consistency.

Test samples were produced for characterization using a variety of methods, including PEC performance, film thickness measurements, film morphology characterizations. For tests that did not require measurement the photoelectrochemical properties of the samples (i.e. film thickness, morphology), the thin-film was deposited on glass microscope slides. This was chosen as the substrate for such tests due to the inexpensive nature of glass slides. For measuring the electrical properties of the samples, glass substrates coated with a thin, nominally transparent layer of fluorine doped tin oxide (FTO) were used. In particular, TEC 7, a manufacturer's designation for the FTO coated glass substrates, were used for consistency with studies in the literature. In the past, JMU researchers have determined that FTO provides the best interface with the BiVO₄ thin film, as opposed to tin doped indium oxide (ITO), an alternative transparent conducting material reported in the literature.

In preparation for deposition, all glassware and deposition system components were cleaned. Substrates on which the BiVO₄ was to be deposited were cleaned to ensure that no residue (e.g. dust or fingerprints) was left on them. To begin the cleaning process, substrates were placed in an acetone bath. The acetone was agitated by an ultrasonic cleaner for approximately ten minutes. The substrates were then mechanically scrubbed, using a q-tip, with a solution of Dawn dish detergent and water. The cleaned substrates were then placed in another ultrasonic bath

containing deionized water for approximately ten minutes. Once the substrate cleaning process was completed, they were stored in isopropyl alcohol (IPA).

For each BiVO_4 deposition run, one glass slide and two TEC 7 (25 mm by 13 mm) substrates were placed on a hotplate at 425 °C. Caution was taken to ensure substrates did not shatter when plated on the hot surface. The nozzle of the ultrasonic spray pyrolysis device was positioned 3mm above the substrates. The substrates were then positioned in line with the nozzle. The nozzle, when activated, swept back and forth linearly over a deposition area with a travel distance of approximately 1.5 inches. For each deposition performed in this study, the substrates were always placed in the same position on the hot-plate surface, as seen in Figure 5.

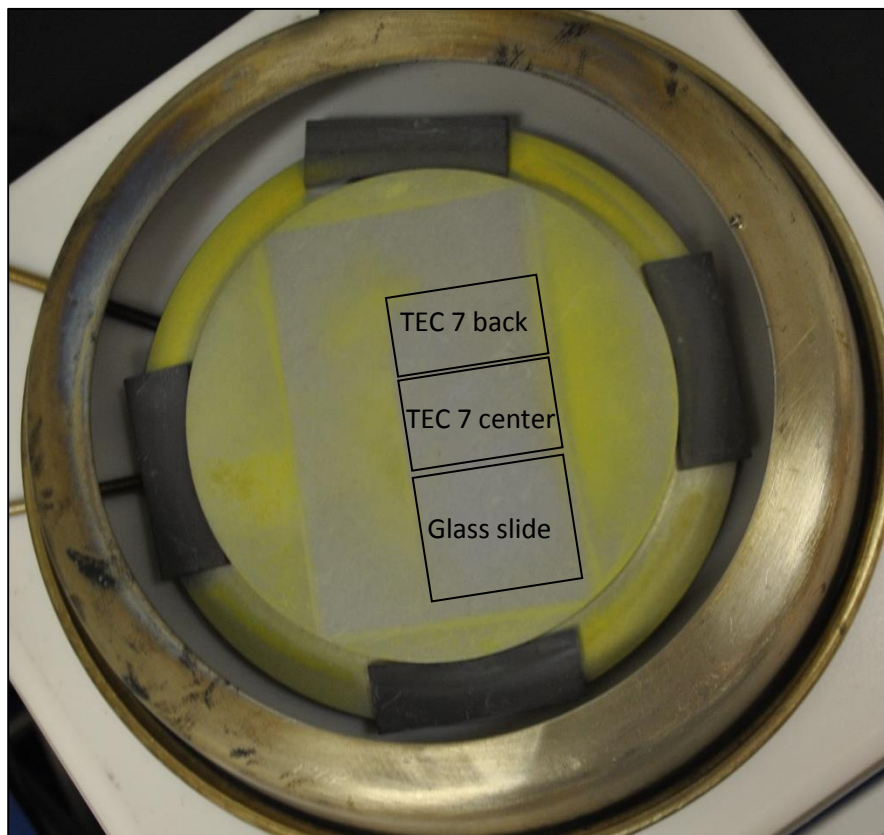


Figure 5: Sample orientation on the hot plate used during deposition

Approximately 10 mL of the precursor solution was then placed over the ultrasonic transducer. Small droplets of the precursor solution were formed via ultrasonic nebulization, which causes small vapor droplets to form at the air-liquid interface due to the agitation provided by the ultrasonic transducer. To date, at JMU, this droplet formation has been achieved by using ultrasonic nebulizer operating at 1.7 MHz to agitate the liquid precursor. The droplets formed by the nebulizer are then carried to the substrate using dry, bottled air as a carrier gas at a flow rate of 6.9 L/min for 10 minutes. Figure 6 shows the setup for the ultrasonic spray pyrolysis apparatus. The image on the left shows the ultrasonic transducer and the carrier gas while the image on the right shows how the precursor solution mist is directed to the substrate through the translating nozzle above the substrate on the hotplate surface.

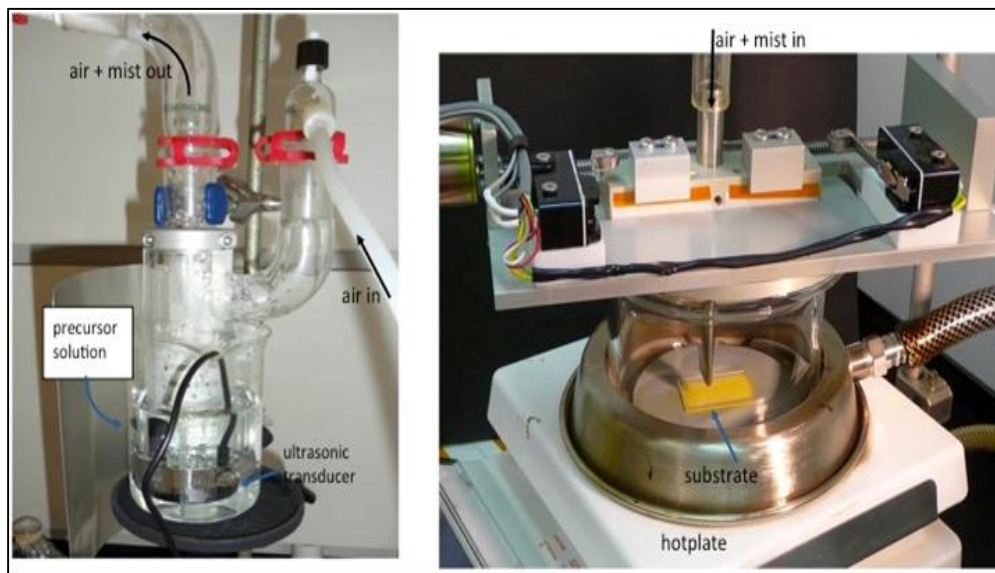


Figure 6: Ultrasonic Spray Pyrolysis apparatus

Once the thin films were formed, they were removed from the hot plate carefully (as to not damage the film formed or induce shattering of the glass substrates) and allowed to cool in ambient room air. The produced thin films then received two annealing treatments – once in an

air environment and then in a reducing hydrogen atmosphere. It has been shown that annealing BiVO₄ thin films in air (at 500 °C for 3 hours) promotes the formation of the desired photoactive monoclinic scheelite phase (15). Annealing in a reducing environment (Air + 3 % hydrogen, 375 °C, 3 hours) has been demonstrated to increase the number of oxygen vacancies in the material, which is believed to result in increased electron transport through the material (15).

Once annealed, samples for photoelectrochemical testing were prepared by affixing a wire to the exposed FTO substrate using a two-part silver epoxy (Epoxy Technology EE129-4). Samples were then baked for 75 minutes at 97 °C to cure the silver epoxy. Resistance measurements were performed to ensure conductivity between the conducting substrate and the wire. Finally, the wires and exposed conducting substrate were coated with clear insulating epoxy (2 Ton insulating epoxy, Devcon) resulting in a BiVO₄ photoanode samples with exposed surface areas ranging from 0.84 to 1.5 cm². Figure 7 illustrates the silver epoxy, clear epoxy, and exposed area of a BiVO₄ photoanode.

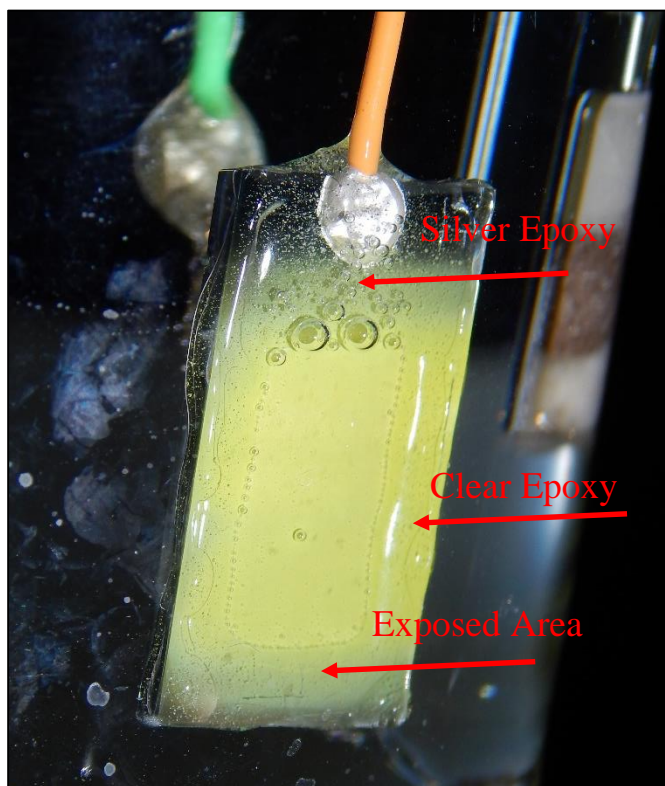


Figure 7: Illustration of the silver epoxy, clear epoxy, and exposed area of a BiVO₄ photoanode that is immersed in Na₂SO₄ electrolyte solution for PEC testing

Photoelectrochemical Testing

Photoelectrochemical (PEC) testing is used to characterize the ability of the material to oxidize water in the presence of sunlight. The reaction rate for oxygen production is directly proportional to that for hydrogen production. That is, for every O₂ molecule produced, two H₂ molecules are produced. One method of characterizing the PEC performance is to measure the rate and total amount of oxygen (or hydrogen) produced. However, such a system to capture and monitor gas evolution rates was not available for this investigation. An alternative method for testing the photoelectrochemical performance of thin-films is to measure their electrical characteristics in a three-electrode electrochemical cell. Because the water splitting process results in the transfer of

ions, which in turn requires the transfer of electrons between the anode and cathode of the electrochemical cell, the electrical current produced is directly proportional to the hydrogen and oxygen evolution rate. Therefore, higher currents in the presence of sunlight indicate a greater oxygen evolution rate and a higher light energy to hydrogen conversion efficiency.

Photoelectrochemical measurements were performed in a three electrode cell containing a 0.5 M Na_2SO_4 (99.5%, Fisher Scientific) electrolyte with a phosphate buffer (pH 7.00 ± 0.02 at 25 °C, Micro Essentials Laboratory). Because pure, deionized water is not electrically conductive, an electrolyte solution is required for ion transport through the solution. However, the ions within the electrolyte solution must not be oxidized or reduced at a potential lower than the redox potential of water. The Na_2SO_4 solution meets this criterion, unlike NaCl , which will cause the formation of Cl_2 , instead of O_2 at the photoanode. Photoanodes of the produced BiVO_4 films served as the working electrodes for the electrochemical cell. A 4 M KCl Ag/AgCl electrode (Accumet, Fisher Scientific) was used as a reference electrode and a platinum mesh served as the counter electrode. All potential measurements reported herein are with respect to the Ag/AgCl reference electrode.

A Keithley 2400 SourceMeter configured as a potentiostat was used to perform linear sweep voltammetry at a sweep rate of 10 mV s^{-1} . A potentiostat is a power supply that maintains a desired set potential between the sample (or working electrode) and the reference electrode by continuously adjusting the potential applied across the working electrode and the counter electrode. For these tests, it was programmed to perform a linear sweep from -0.5 V to 1.5 V across the working electrode with respect to the reference electrode. Voltammograms, or

measurements of current vs. applied potential, were obtained for all of the samples when illuminated by simulated solar radiation with an intensity of 0.1 W cm^{-2} at the sample surface. The simulated solar illumination was produced with an Oriel 96000, 150 W solar simulator (Newport) with an AM1.5 filter. The three electrode cell was placed 25.4 cm away from the solar simulator to ensure the photoanode would receive approximately 0.1 W/cm^2 . A pyranometer was used to confirm that the irradiance from the solar simulator was in fact 0.1 W/cm^2 , ensuring that the testing setup mimicked natural sunlight.

Both front side illumination and through-substrate illumination conditions were investigated and compared to dark current measurements. The front side of the sample is the side with the exposed thin film. The back side of the sample is the TEC 7 substrate. Illumination from both sides of the BiVO_4 films were performed to study the electron transport through the BiVO_4 film. During each test, as the applied bias was varied from -0.5 V to 1.5 V , the light from the solar simulator was intermittently blocked using an automated shutter system. The shutter closes and opens at 0.05 V bias voltage intervals to obtain the dark current of the sample, for a total of 20 on off cycles. The dark current obtained represents the current that is not produced due to the incident light. To compare the photoelectrochemical performance of the different size BiVO_4 photoanode samples, the measured current was normalized by the area exposed to the electrolyte solution to obtain photocurrent density, J (mA/cm^2).

All electrodes were rinsed in deionized (DI) water and dried with N_2 gas prior to PEC testing. The solar simulator was turned on and allowed to warm up. The three electrodes (BiVO_4 photoanode, platinum mesh counter electrode, and reference electrode) were placed in

approximately 200 mL of the electrolyte solution. The photoanode was placed directly in the middle of the beam from the solar simulator. The reference electrode was tested to ensure a flow of KCl electrode solution through the frit. All electrodes were connected to the Keithley Sourcemeter. A LabVIEW™ interface that was programmed to control the Keithley Sourcemeter, record data, as well as control the shutter was used to collect the data. A screenshot of the LabVIEW interface used can be seen below (Figure 8) along with a picture of the PEC testing setup (Figure 9).

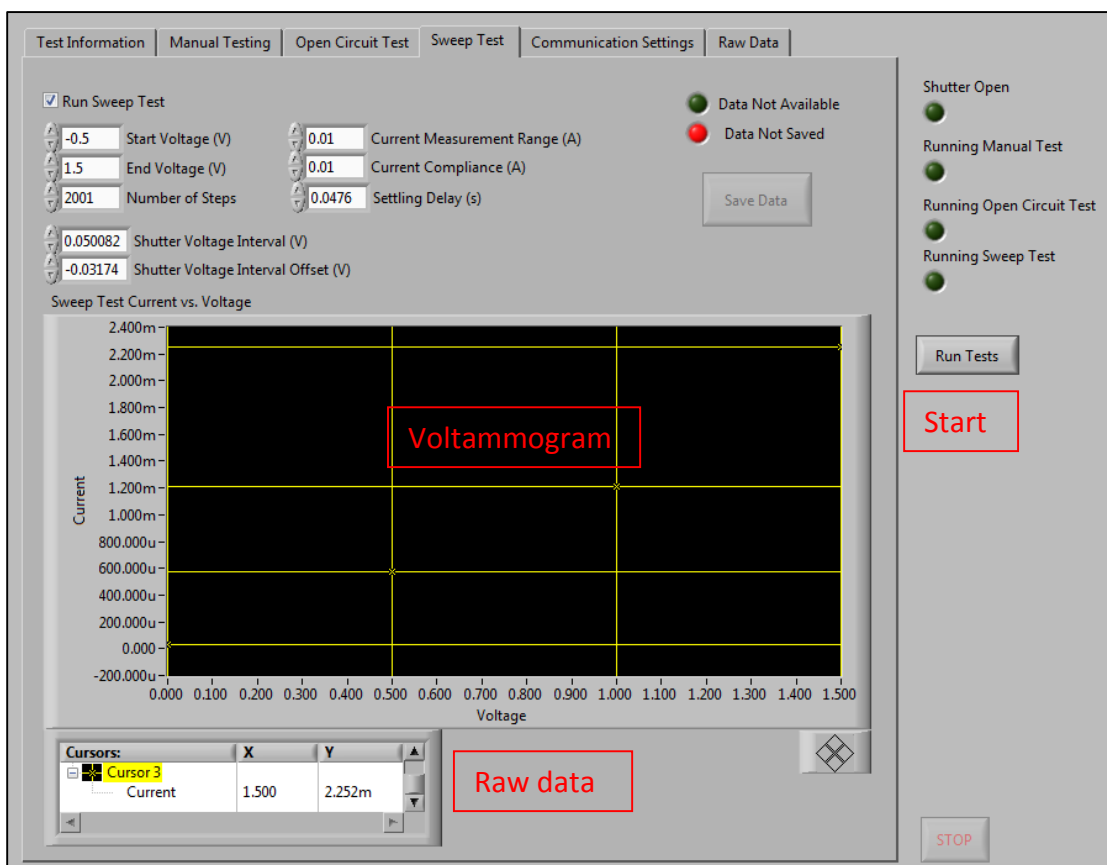


Figure 8: Data Acquisition Control Panel

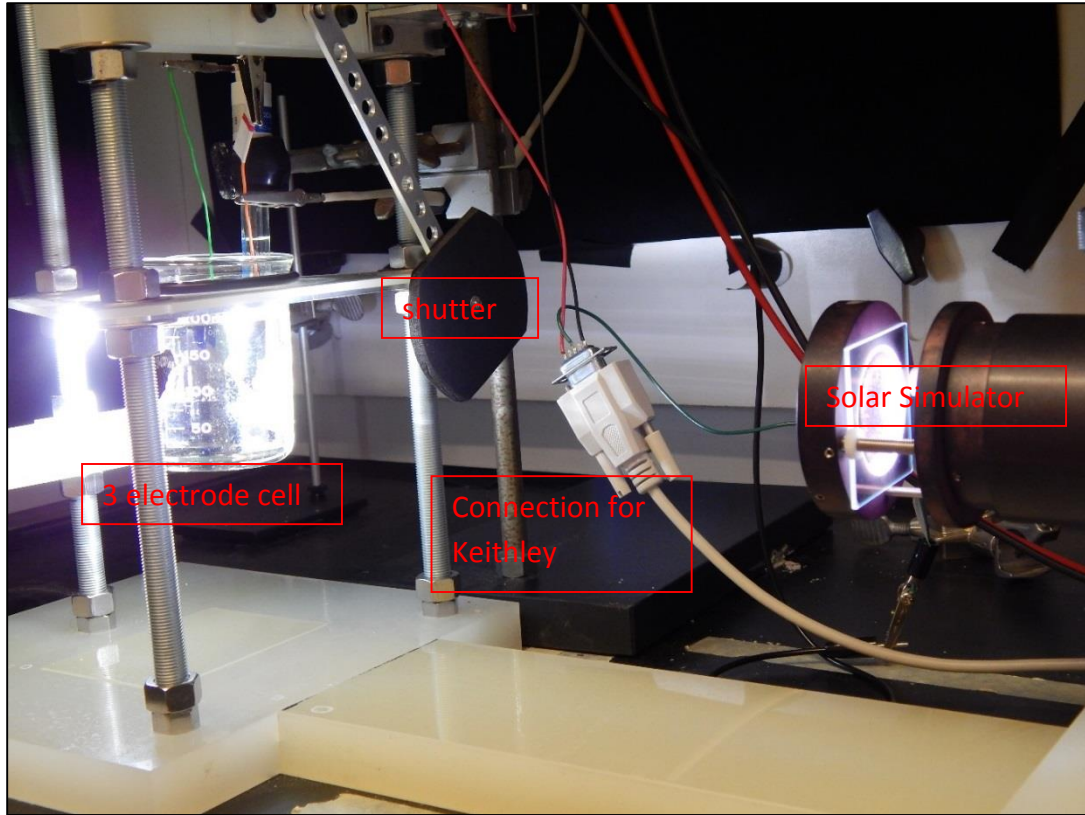


Figure 9: Photoelectrical chemical testing setup

Once data acquisition was completed for a sample, the resulting raw data files were saved. This procedure was completed for every sample for the front and back side illumination conditions. Once a PEC test was completed, each electrode was rinsed in DI water and dried in N_2 gas. The electrolyte solution was covered and the solar simulator was turned off.

Material Characterization

Thickness measurements were taken using a KLA Tencor P-7 surface profiler. Glass slides from deposition runs were used to measure the thickness of the films by removing a tiny portion of the thin-film to expose the glass substrate. This was done by making a small scratch down the edge of the sample. This scratch allows the apparatus to measure the thickness of the film with respect

to the exposed glass slide. A small stylus is dragged across the surface of the thin film, as illustrated schematically in Figure 10a, and the height of the stylus is recorded. The difference between the height of the glass and the height of the rough BiVO_4 material is used to determine the film thickness. Thickness measurements are taken seven times (Figure 10b) per sample, to ensure that a representative average thickness was obtained for each sample.

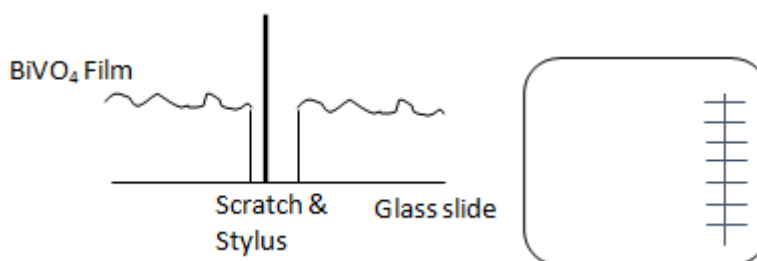


Figure 10: Surface thickness measurement (a) stylus and (b) locations on slides

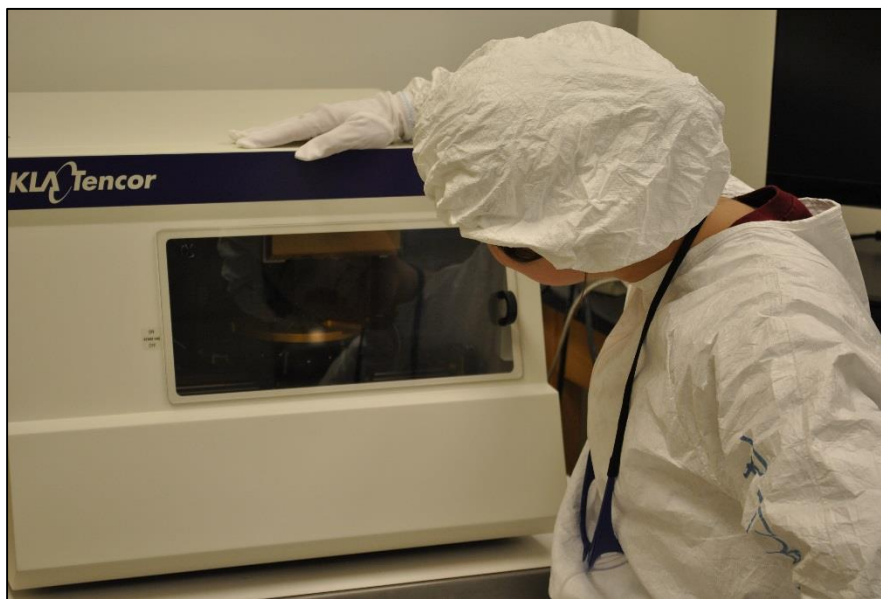


Figure 11: Lauren Phillips performing thickness measurements

A LEO 1430VP scanning electron microscope (SEM) with an Oxford energy dispersive X-ray spectrometer system (EDS) was used to analyze film morphology and chemical composition. For

examination with a SEM, small fragments were broken from a coated glass slide and a coated TEC7 substrate and attached to a SEM mounting stub. The samples were coated with gold in a low pressure argon environment. This was done to eliminate sample charging during SEM imaging. The morphology of samples was investigated at 2000X-5000X magnification.

Results

Samples produced fall into one of three categories, based on the liquid precursor stoichiometric ratios. Sample identification is presented in Table 1.

Table 1: PEC testing sample names

1 Bi: 1 V	1.005 Bi: 0.995 V	0.995 Bi: 1.005 V
BiVO _x -115	BiVO _x - 118	BiVO _x - 121
BiVO _x - 116	BiVO _x - 119	BiVO _x - 122
BiVO _x - 117	BiVO _x - 120	BiVO _x - 123

Three deposition trials were performed for each Bi:V ratio tested. Each trial was given its own identifier. Samples deposited on TEC7 from the same deposition trial were distinguished by their location on the hot-plate (b- back, c-center) during the deposition process (see Fig. 5).

Sample Area

Areas of samples were approximated by measuring the length and width of the exposed (not covered with 2-ton epoxy) BiVO₄ surface and assuming the area to be rectangular. Figure 12 illustrates the definition of the exposed BiVO₄ surface area.

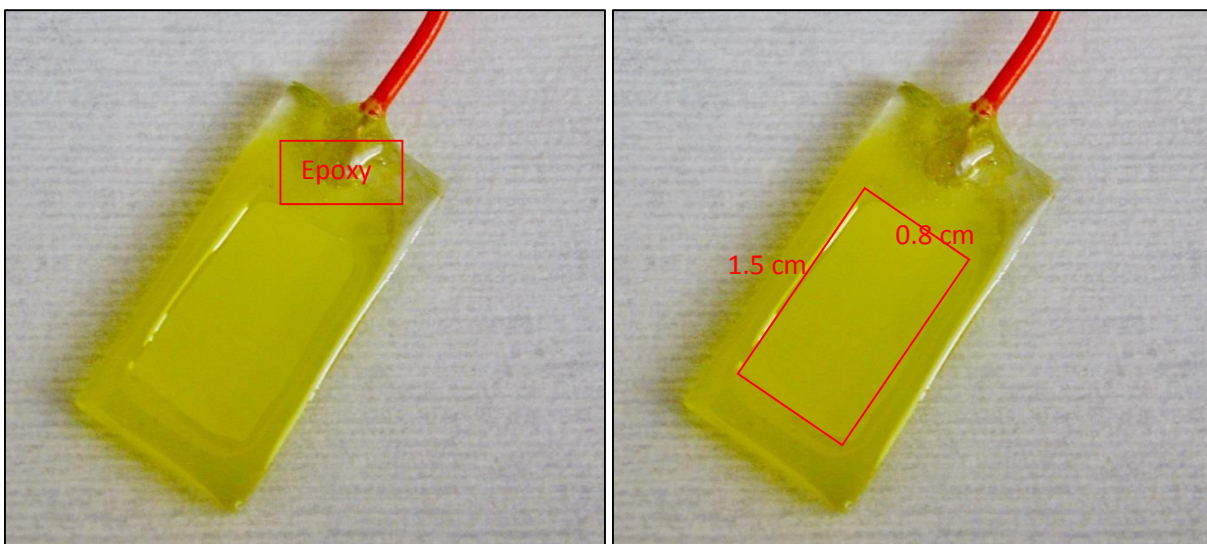


Figure 12: Sample exposed area calculation for BiVO₄-123b

$$Area = Length * width = 0.8 \text{ cm} * 1.5 \text{ cm} = 1.2 \text{ cm}^2$$

The exposed sample areas for all of the fabricated photoanodes are shown in Table 2. Exposed sample areas ranged from approximately 0.84 cm² to 1.5 cm².

Table 2: Exposed sample area

Sample ID	Sample Area (cm ²)	Sample ID	Sample Area (cm ²)
BiVO _x -118c	0.84	BiVO _x -123b	1.2
BiVO _x -118b	1.12	BiVO _x -115b	1.02
BiVO _x -121c	0.98	BiVO _x -115c	1.12
BiVO _x -121b	1.26	BiVO _x -117b	0.91
BiVO _x -119c	1.26	BiVO _x -120b	0.91
BiVO _x -116b	1.12	BiVO _x -122c	1.5

Sample Thickness

Sample thicknesses were determined using a KLA Tencor P-7 surface profiler. Thicknesses were measured from the thin-films deposited on glass from various times in the fabrication processes (post deposition, post air annealing, or post air and hydrogen annealing). This allowed for change

in thicknesses of films during fabrication to be determined. The measured sample thicknesses are shown Table 3, with notes as to stage of fabrication during which when they were recorded.

Table 3: Sample thicknesses raw data

Sample thickness (μm)										
Location	115	116	117	117	118	119	120	121	122	123
1	2.35	1.87	2.42	2.46	1.22	1.84	2.09	1.69	2.51	1.95
2	2.57	2.27	2.11	1.97	1.28	1.89	1.79	1.52	2.83	1.54
3	2.04	1.94	2.3	2.1	2.06	1.91	2.88	2.57	3.68	1.73
4	2.28	1.64	2.12	1.97	2.03	2.12	2.43	1.84	2.23	2.25
5	2.18	2.42	2.36	2.14	1.64	1.59	2.17	1.78	2.62	1.67
6	1.95	2.17	2.29	2.04	2.21	1.68	2.38	1.39	3.81	2.59
7	2.08	2.14	2.51	2.25	1.53	2.09	2.16	1.46	2.58	3.04
Avg.	2.21	2.06	2.30	2.13	1.71	1.87	2.27	1.75	2.89	2.11
stdev	0.211	0.264	0.148	0.175	0.395	0.195	0.340	0.398	0.609	0.548
	As deposited	Air& H2	As deposited	Air& H2	Air& H2	Air& H2	As deposited	After air annealing	As deposited	Air& H2

PEC Performance

The photoelectrochemical performance of each photoanode was determined from the voltammogram data. The raw data from PEC testing was normalized by the exposed sample area to obtain photocurrent density (mA/cm^2) so that all film performances can be compared.

The measured photocurrent density for all samples under front-side illumination at each voltage bias level is shown in Figure 13. The different bias voltage conditions are: 0 V (bottom blue bar), 0.5 V (red bar), 1.0 V (green bar), and 1.5 V (top purple bar). This graph allows for all samples to be compared at multiple bias conditions. The samples fabricated from precursors with the same chemical composition have been grouped together. From this, it is noted that there is wide variability between samples of nominally identical compositions. This is most likely due to variations in uncontrolled aspects of the testing and deposition procedure

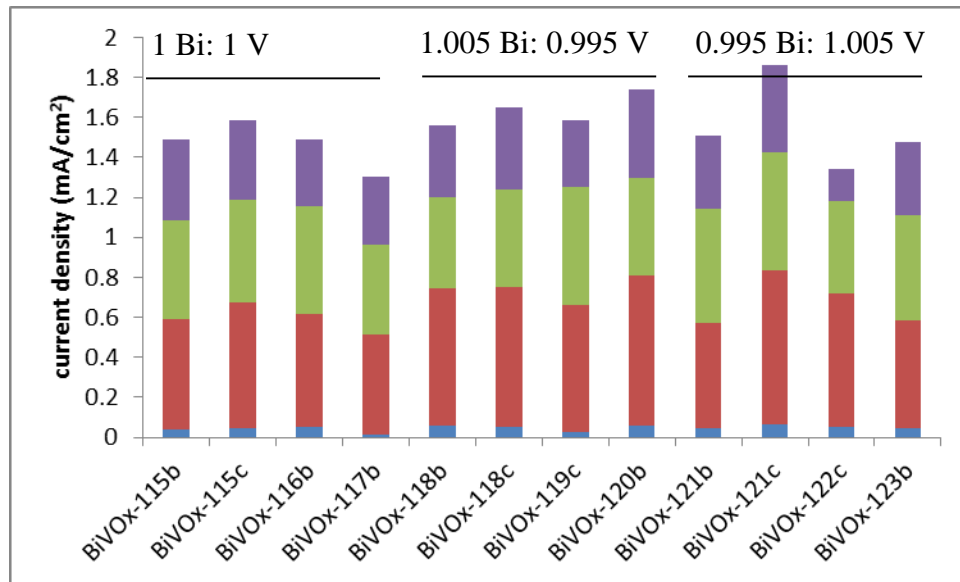


Figure 13: Front side illumination current density

The backside illumination current density graph can be seen in Figure 14. The graph can be read similarly, i.e., the bias conditions are 0 V (bottom blue bar), 0.5 V (red bar), 1.0 V (green bar), and 1.5 V (top purple bar). The backside illumination current density is lower than for front side illumination, as expected due to light absorption and reflection by the glass substrate, and exhibits even greater variability.

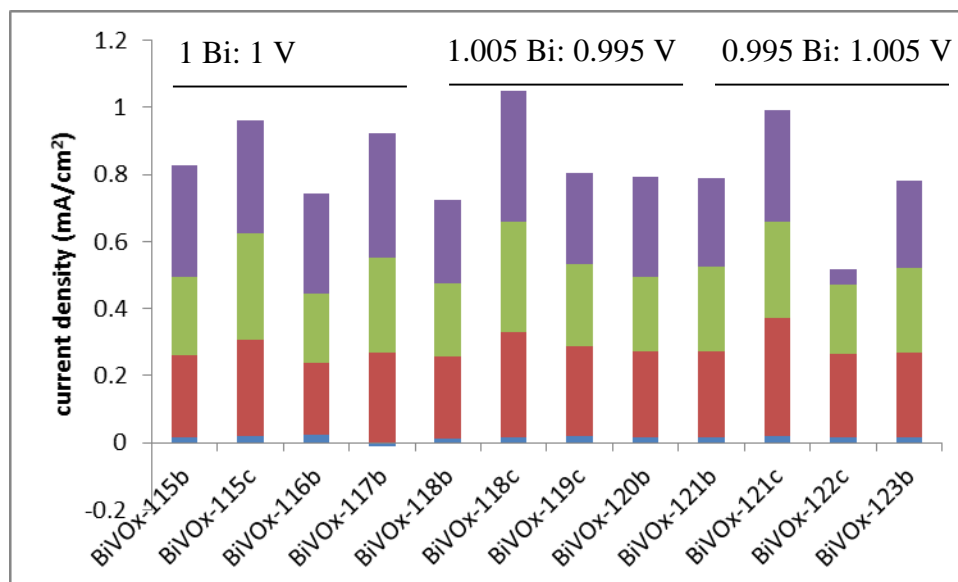


Figure 14: Backside illumination current density

Scanning Electron Microscopy

A scanning electron microscope (SEM) was used to characterize the morphology of the spray deposited BiVO₄ thin-films. It is typical for bismuth vanadate films to have a high surface roughness & complex morphology (2), as illustrated in Figure 15, which presents an SEM images obtained at 2000X-5000X magnification for sample BiVOx-117b. The small, partial spherical structures are consistent with morphologies of USP deposited films investigated in prior studies. It is believed that such a complex, highly porous morphology of the resulting films significantly enhances the surface area available for the photooxidation processes and may help to explain the state-of-the-art performance obtained from such samples.

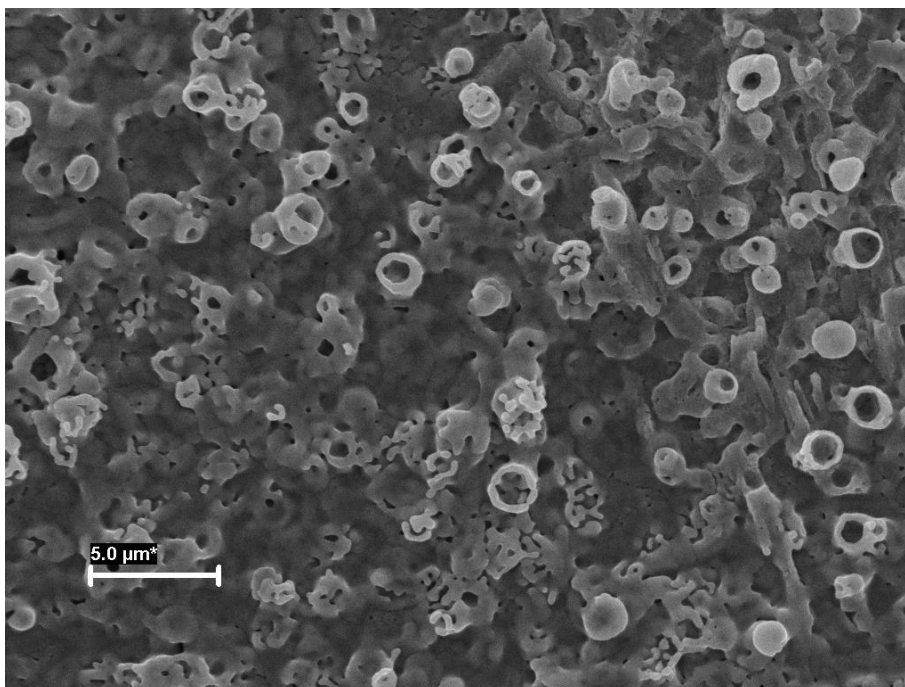


Figure 15: SEM image for BiVO₄-117b

Energy dispersive X-ray spectroscopy (EDS) was used to determine the chemical composition of the resulting BiVO₄ films. EDS measurements confirmed that the atomic composition of the deposited thin films were as expected. Table 4 shows the EDS results from the BiVO_x-117b sample.

Table 4: Energy Dispersive X-ray spectroscopy raw data for sample 117b (TEC 7)

<i>Trial 1</i>		<i>Trial 2</i>		<i>Trial 3</i>	
Element	Atomic %	Element	Atomic %	Element	Atomic %
O	57.09	O	58.41	O	55.92
V	14.66	V	14.85	V	14.24
Sn	12.14	Sn	12.13	Sn	13.52
Au	1.43	-	-	Au	1.92
Bi	14.67	Bi	14.61	Bi	14.4

Table 4 shows the elements detected and their atomic proportions from three different locations on sample BiVO_x-117b. This method, using EDS to determine chemical composition, is non-ideal for rough samples. As seen in Figure 15, BiVO₄ samples have a rough surface. The traces of tin (Sn) result from the FTO (Fluorine doped tin oxide) substrate. The traces of gold (Au) are from the gold coating that is applied prior to SEM analysis. The ratio of bismuth to vanadium is approximately 1:1. The chemical composition for BiVO_x-117b was intended to be 1:1 and within the uncertainty of the EDS measurement. The ratio of bismuth (and vanadium) to oxygen is approximately 1:4. The measured chemical composition of the film is consistent with the desired stoichiometric BiVO₄ composition. The variability in the measured composition is attributed to the film surface roughness, which can reduce the accuracy of EDS measurements. SEM imaging and EDS measurements of films with Bi:V ratios of 1.005:0.995 and 0.995:1.005 have not yet been completed.

Analysis

After raw data was organized into meaningful charts and graphs, the results were analyzed.

Sample thickness results were organized based on chemical compositions.

Table 5: Sample Thicknesses data organized by chemical composition

Film Thicknesses	1:1 Ratio	Bismuth rich	Vanadium Rich
Average (μm)	2.18	1.95	2.25
Standard deviation	0.10	0.24	0.48

Variations can be seen in the film thicknesses. This is likely due uncontrolled factors in the deposition process (e.g. the rate of atomization of the precursor by the ultrasonic transducer).

The PEC current density graphs shown in the results section (Figure 13- Figure 14) showed no discernable trends with respect to chemical composition. Thus, it was concluded that small, controlled variations had little effect on the PEC performance. To further investigate the results, graphs were created based on film thickness and substrate location during deposition.

Figures 16 and 17 show PEC performance of films from low thickness (BiVO_x -118c) to high thickness (BiVO_x -122c).

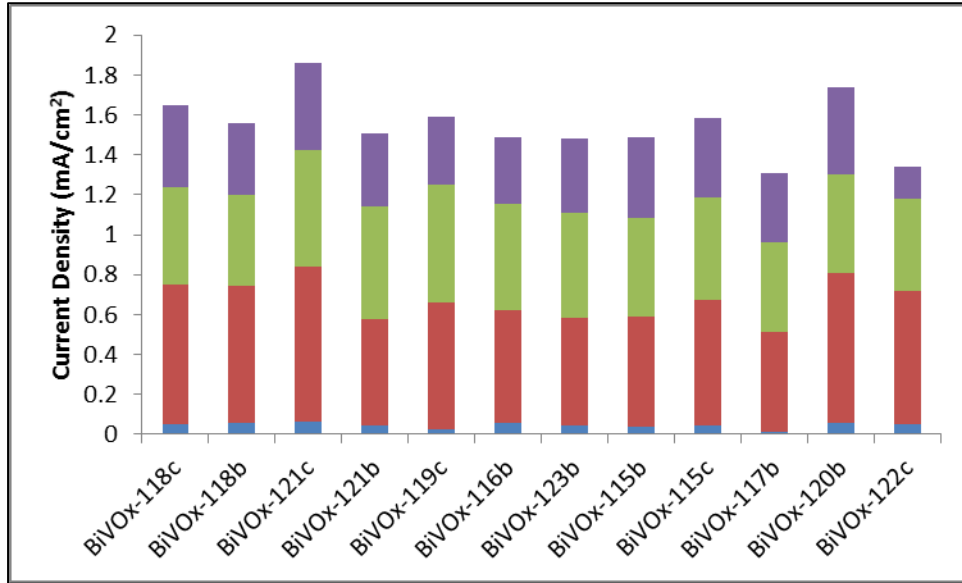


Figure 16: Front side illumination, organized from low to high film thickness

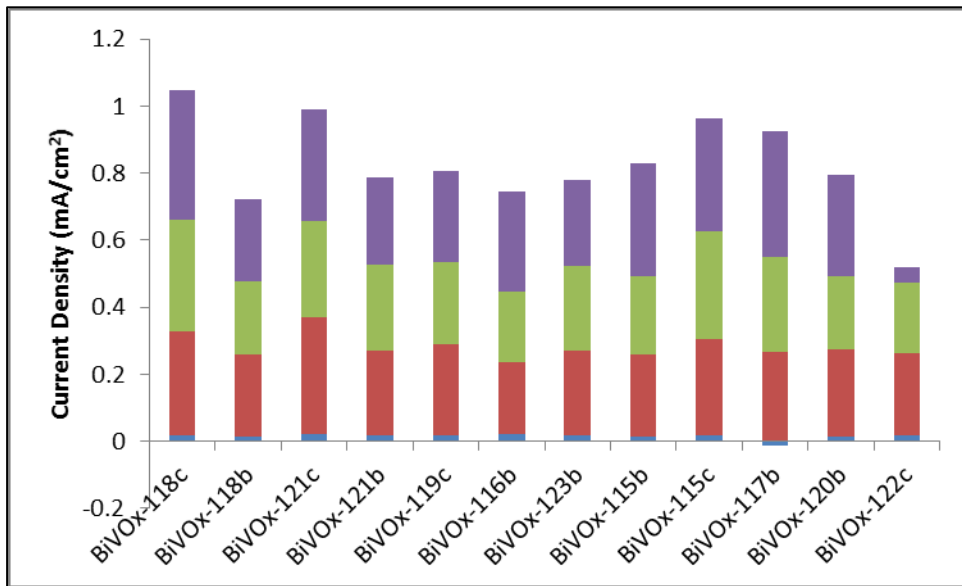


Figure 17: back side illumination, organized from low to high film thickness

As seen in Figures 16 and 17, little correlation between film thickness and PEC performance could be easily ascertained from the data. A slight decrease in PEC performance with thickness increase may be present, but is not significant compared to the sample-to-sample variations measured.

Samples that were created in the same deposition trial were also compared based on their location in the deposition chamber during the deposition process, as described in Figure 5. It can be seen in both front side illumination (Figure 18) and back side illumination (Figure 19) that the TEC 7 substrate placed in the ‘center’ position exhibited slightly higher photocurrents relative to those placed at the ‘front’ position.

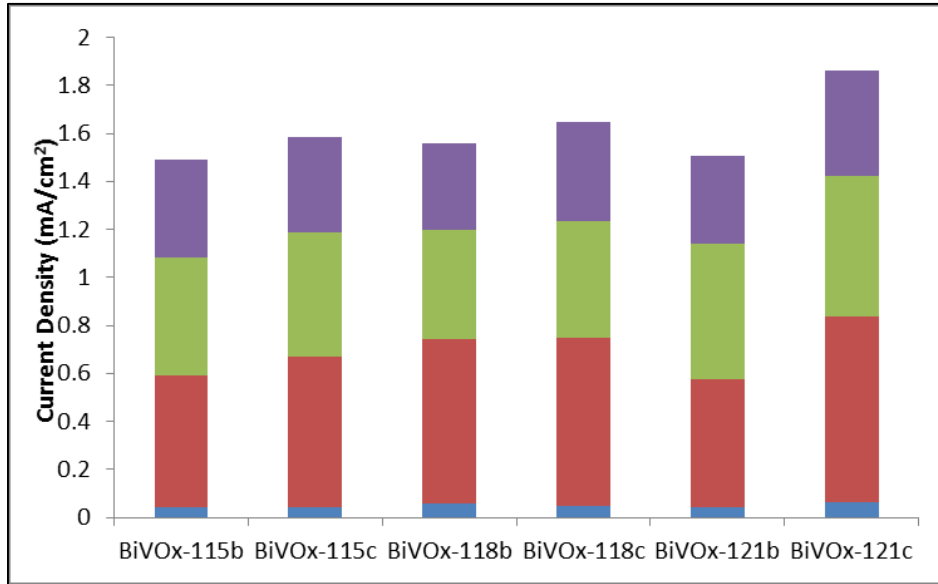


Figure 18: Front side illumination current density, organized by deposition placement

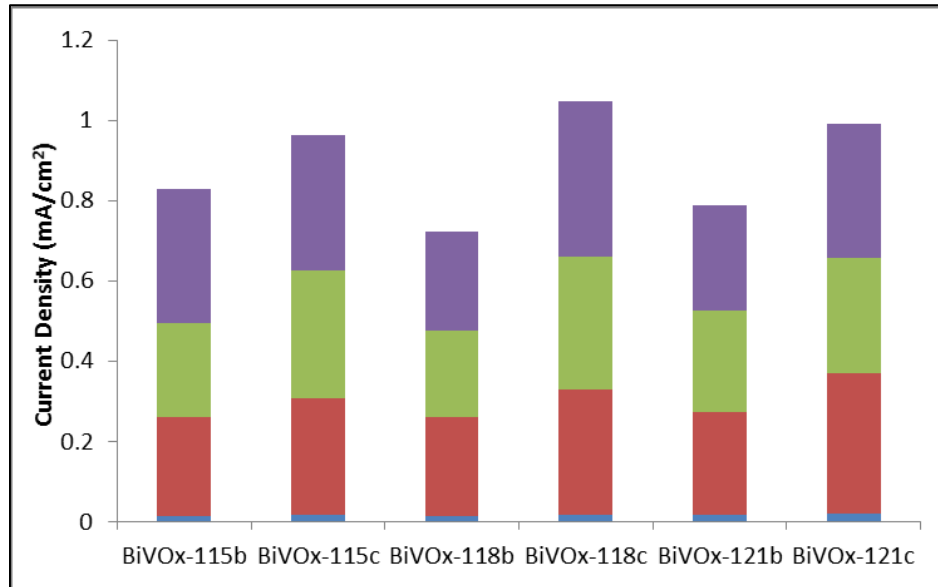


Figure 19: Back side illumination current density, organized by deposition placement

There is not strong enough evidence from this project to make conclusions that samples placed in the ‘center’ during the deposition runs perform better, based on the limited number of samples produced; however, the data presented indicates that location within the deposition chamber may be more strongly correlated with PEC performance than the chemical precursor composition variations. Such performance variations may arise from temperature gradients or droplet flow patterns near the center of the deposition chamber, which may impact the formation of the BiVO₄ film. Further investigation into the substrate placement is recommended to identify potential sources of performance variations.

Conclusion

Twelve BiVO_4 photoanodes were fabricated to investigate the effects of slight precursor stoichiometry variations on the PEC performance. Precursor ratios of 1 Bi:1V, 1.005 Bi:1 V, and 1 Bi:1.005 V, were investigated. Based on the results presented herein, slight variations in the Bi:V ratio in the precursor solutions exhibited little to no effect on the PEC performance.

Further investigation is suggested to determine the source of variability. Trends in data indicate that the position of the substrate within the deposition chamber may be correlated with the resulting PEC performance of the photoanodes. Specifically, substrates located at the center of the deposition chamber exhibited slightly increased performance relative to those positioned at the front of the chamber. Additional suggestions to improve the procedures and, to potentially identify the sources of sample variability are to standardize the surface area measurement for photocurrent normalization and to standardize the method in which photoanodes are placed in the 3 electrode cell and aligned with the solar simulator for PEC testing.

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Relevant Sources

Some relevant sources have been included for further investigation.

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