Unassisted Photoelectrochemical Solar-to-Hydrogen on CuBi2O4 Photocathodes Using Glycerol as a Sacrificial Oxidant

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Unassisted Photoelectrochemical Solar-to-Hydrogen on CuBi$_2$O$_4$ Photocathodes Using Glycerol as a Sacrificial Oxidant

An Honors Thesis submitted to fulfill the requirements for Honors Studies in Biochemistry

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**Introduction**

The need to decarbonize society has driven the development of alternative energy technologies. Solar panels are capable of generating electricity at large scale and at competitive costs to fossil fuels, such as coal or natural gas. However, they are only capable of generating electricity when the sun is out. It is therefore necessary to understand how to store that energy for on-demand use. It is also desirable that the storage be portable, lightweight, and compatible with transportation infrastructure like fossil fuels are. A very desirable chemical fuel is H$_2$ which can be produced simply by water electrolysis. Production of H$_2$ can be achieved through photoelectrochemical (PEC) water splitting. PEC allows for the undeviating conversion of sunlight to H$_2$ and O$_2$ without producing harmful pollutants like carbon dioxide. Devices that facilitate PEC water splitting resemble the structure of biological membranes that drive photosynthesis (Berg). They are generally composed of a photoanode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$) and a photocathode ($2e^+ + 2\text{H}^+ \rightarrow \text{H}_2$) (Minggu).

Photoelectrochemical solar energy to fuels conversion is an artificial analogy to natural photosynthesis. That is, to capture energy from sunlight and store that energy is some form of chemical bond through various reactions. For any type of artificial photosynthesis, both a catalyst and light absorber are necessary for specific chemical reactions. The light absorber captures and directs excited electrons and holes from the absorption of sunlight to catalysts for the desired anode and cathode reactions. Previously, the PEC cell was being used to perform water splitting in hopes to generate hydrogen. However, water splitting was replaced with the combination of hydrogen evolution glycerol oxidation (Schichtl). This replacement was made due to the significant reduction in overall cell potential required for the total cell reaction. Water splitting requires 2V to occur. However, H$_2$+glycerol oxidation requires 0.6-0.8V to occur. This difference in voltage is desirable for hydrogen production. Thus, a light absorber is needed that operates within the voltage range of H$_2$+glycerol oxidation. CuBi$_2$O$_4$ is the chosen light absorber considering it gives 0.8V (Kang).
Background

Scientists are on the chase to discover the most efficient way of converting sunlight into energy in the forms of either environment friendly chemical fuels or electrical power. This idea of turning sunlight into forms of clean, efficient energy is capitalized on using the photoelectric effect. The photoelectric effect can best be described as a phenomenon in which matter, typically a metal, absorbs light radiation. This radiation then causes charged electrons from within the metal to be excited. As a result, these electrons are ejected from the metal and can then go and do work. Photovoltaics have become a particular interest in achieving this sunlight to energy production (Gratzel). Photovoltaic (PV) apparatuses achieve this conversion using a particular medium known as a semiconductor (“Photovoltaics”).

Semiconductors are interesting materials as they can be electrical conductors in certain situations; however, in others they may not produce any electrical current at all. This is the exact reason why they are of great importance in PV experiments; They are able to manipulate the electrical currents in a system. All molecules have LUMO (lowest unoccupied molecular orbital) levels and HOMO (highest occupied molecular orbital) levels. The difference in these two levels dictate the exact amount of energy that is needed to excite an electron from the LUMO level to the HOMO level. Semiconductors are no different. All materials have LUMO and HOMO levels as well. Semiconductors manipulate electrical conduction in a system through the difference in their LUMO levels and their HOMO levels. The distance between these levels, called band-gaps, dictates whether a material is a conductor, semiconductor, or insulator. A conductor is a material that has a minimal to no band gap. Since there is no barrier to overcome, conductors allow for continuous electron movement between the LUMO and HOMO levels. That is, electrons freely move between the conduction band and valence band. An insulator is a material that produces no electrical current. This is because insulators have very large band gaps. Because of these very large band gaps, it is not feasible to excite electrons enough to overcome the band gap barrier and produce a current. Semiconductors, however, have a small to intermediate band gap (0.5-3.0 eV). This is what allows for semiconductor to act as either a conductor or an insulator in differing
situations. The composition of semiconductors can be altered to further facilitate current production. These alterations are more formally known as dopants. Dopants can either result in p-type semiconductors or n-type semiconductors. P-type semiconductors are unique in that they have electron holes on their surface which act as charge carries. On the other hand, n-type semiconductors have mainly electrons that carry a negative charge on their surfaces (“Semiconductor”).

The semiconductor of interest here is CuBi\textsubscript{2}O\textsubscript{4}, copper bismuthate. CuBi\textsubscript{2}O\textsubscript{4} is a p-type semiconductor. When light radiation hits CuBi\textsubscript{2}O\textsubscript{4}, three possible outcomes can result. The light radiation can either be absorbed by the semiconductor, can be reflected off the surface, or can be transmitted through the semiconductor. Out of the three possible outcomes, the most desirable is that the light radiation, photons, are absorbed into the material. This is because only through absorption of photons is the semiconductor able to produce electrical power (“Absorption of Light”). When photons are absorbed, an electron in the semiconductor’s valence band can be excited into its conduction band producing an electron-hole pair. Both the excited electron and the hole created can contribute to the electrical conduction of the semiconductor. The most important factor here is the energy of the photon, E, being absorbed. For light, \( E = h \nu = hc/\lambda \), where \( h \) is Planck’s constant \( 6.62608 \times 10^{-34} \frac{m^2 kg}{s} \), \( c \) is the speed of light \( 2.99792 \times 10^8 \frac{m}{s} \), \( \nu \) and \( \lambda \) are the frequency and wavelength of the photon. The minimum amount of energy needed to excite an electron into the conduction band equal to the band gap of the material. Photons with less energy are not able to excite electrons between the bands. (“Band Gap”).

An excited electron is driven to equilibrate by recombining with a hole. A chemical reaction can use the excited electron to make products – chemical work. Some of the energy absorbed from a photon can be lost to heat as the electron and hole diffuse around the material, but they will still have an energy difference of at least the band gap to drive a chemical reaction. Excited electrons can return to the ground state in a number of ways. Electrons can recombine with the same hole that was generated by the photoexcitation, or another hole in the semiconductor. The energy is generally lost to heat but can also sometimes generate light – this
is the operating principal of a light emitting diode. Electrons can also fall and be used for some other unwanted chemical process, such as corrosion of the material. The favorable possibility is that excited electrons in the semiconductor can be directed to perform the chemical reduction of reactants at a liquid interface. That is precisely what we are studying here. The idea is to create a well-characterized semiconductor made out of CuBi$_2$O$_4$ that can function as a photocathode in a PEC cell to run the cathodic hydrogen evolution reaction for water splitting. CuBi$_2$O$_4$ as a potential photocathode will partake in a series of reductive processes to ultimately assist in generating H$_2$. This series of reductive processes will need to be assisted by a catalyst such as platinum, which organizes protons in the form of platinum-hydride bonds on the surface. This helps to direct electrons to reduce protons to form H$_2$.

**Literature Review**

CuBi$_2$O$_4$ is typically prepared through electrodeposition. The electrodeposition is performed using a potentiostat. Wired to the potentiostat are three electrodes in a working cell with a particular solution. The working electrode is the FTO film being electrodeposited with Cu/Bi. The reference electrode is an Ag/AgCl electrode, and the counter electrode is Pt. The electrodeposition is typically carried out in a DMSO and ethylene glycol solution containing Bi(NO$_3$)$_3$, Cu(NO$_3$)$_2$, and KClO$_4$. After electrodeposition, the film is annealed to form CuBi$_2$O$_4$. After annealing, Pt is then photodeposited onto the CuBi$_2$O$_4$. Pt is necessary as an electrocatalyst for the CuBi$_2$O$_4$ films to facilitate H$_2$ production (Kang).

CuBi$_2$O$_4$ has become a semiconductor of interest in photoelectrochemical work due to multiple advantages it presents. First, CuBi$_2$O$_4$ is stated in literature to have a band gap equal to 1.5-1.8 eV. This band gap corresponds to a portion of the visible light spectrum. This meaning that the semiconductor can use visible light to excite its electrons. Second, CuBi$_2$O$_4$ has a more negative potential at its conduction band minimum compared to other semiconductors being
tested. Having such a negative potential at its conduction band minimum, CuBi$_2$O$_4$ is a promising semiconductor for H$_2$ production. Not to mention, it is very inexpensive to produce (Kang).

However, CuBi$_2$O$_4$, along with its many advantages presents limitations as well. In PEC experiments, the actual chemistry is occurring at the interface between the semiconductor and the electrolytic solution. Semiconductors, such as CuBi$_2$O$_4$, with lower band gap energies can present stability issues in certain electrolytic solutions. Also, in conjugation with stability issues, the actual semiconductor surface is also at risk for corrosion in PEC cells. A solution to potentially combat the instability and corrosion potential of CuBi$_2$O$_4$ has been presented. The solution is to incorporate a thin film protection layer onto the semiconductor (Cooper).

Previous work performed by the Coridan research lab was done on CuO. CuO is another semiconductor that was studied for material synthesis work. CuO was studied because it has the same positive features as CuBi$_2$O$_4$. CuO is also inexpensive to produce and can absorb a lot of sunlight due to its low band gap. However, CuO also presents similar limitations in PEC experiments to CuBi$_2$O$_4$. The first limitation is that both CuO and CuBi$_2$O$_4$ have shown to be highly unstable in acidic solutions. The second limitation is neither of the semiconductors can fully facilitate hydrogen evolution on the surface of the material. Thus, a catalyst is needed to facilitate hydrogen production at the surface of the semiconductor. The solution to compensate for these limitations is to introduce a thin film protection layer to the surface of the semiconductor and incorporate Pt onto the surface of the semiconductor to function as the catalyst. The thin film protection layer was investigated for CuO, which dissolves easily in most electrolytes of interest (acid and base). The thin film protection layers are deposited using TiO$_2$. This compound was chosen as it has great stability in an array of electrolytic solutions, including both very basic and very acidic solutions. The TiO$_2$ is incorporated onto the semiconductor through atomic layer deposition (ALD). ALD can deposit materials with atomic precision to
create thin film coatings from gaseous particles (Mehrabi). In that work we showed that we could use thermal annealing to control cracks in the TiO$_2$ layer that will partially expose the semiconductor for making contact with a hydrogen-evolving catalyst such as Pt while maintaining the protective and transparent TiO$_2$ layer elsewhere.

TiO$_2$ was chosen as the thin film because once deposited on the semiconductor, it will allow for electrons to leave the semiconductor (be excited) and go do further reductive work in the system. This is because TiO$_2$ is transparent, meaning it will allow light to pass through it to reach the semiconductor. TiO$_2$, once deposited, also creates a nice, conformal layer which is desirable for a protection layer so that protons from an acidic solution will not be able to reach the semiconductor surface. Thus, corrosion of the material is preventable. TiO$_2$, along with its many advantages as a thin film protection layer, does present limitations to the system. TiO$_2$, once deposited, contributes new resistance to the semiconductor that was previously not there. So, this resistance must be taken into account when fabricating the protection layer. It would be ideal if the protection layer could be bypassed and a cohesive layer of Pt be deposited onto the entirety of the material’s surface. However, this is not feasible. This is because Pt is not transparent and would not allow light to hit the semiconductor. It also wouldn’t protect the semiconductor from corrosion in solution. Hence, the TiO$_2$ protection layer is a necessity in conjunction with the Pt catalyst (Mehrabi).

In the Coridan lab, it was determined that annealing can be used as a technique to alter both the oxidative chemistry and volume of a particular material. For instance, Cu$_2$O was annealed and as a result, a volume change was detected as CuO was produced. This is because the ratio of O to Cu increased during the process. The CuO semiconductor then underwent ALD TiO$_2$ deposition. After deposition, the CuO/TiO$_2$ film was annealed again. It was determined that the TiO$_2$ thin film protection layer contracted. These two findings build the
foundation for the current work on CuBi$_2$O$_4$ since the Coridan lab previously determined that the extent to which these contractions and expansions occur can be controlled. These finding are significant in the case of CuBi$_2$O$_4$ because it will allow for the control over how much the TiO$_2$ contracts. As a result of TiO$_2$ contraction, cracks on the surface of the material are made. These cracks then expose the semiconductor that is underneath the protection layer. The cracks that are made are important because they provide space to deposited Pt onto. The Pt needs to be in direct contact with the CuBi$_2$O$_4$ in order to carry out its function as a catalyst (Mehrabi).

Here, I am proposing a solution that will both protect the CuBi$_2$O$_4$ semiconductor and help catalyze the production of hydrogen. The idea is to protect certain areas of the film while placing a catalyst in other areas. To do this, the previous work done on CuO will be translated to CuBi2O4 since it has been shown that the amount of volume change and cracking of the protection layer can be controlled. That is, the expansion of the light absorber and contraction of the protection layer, both due to annealing, will be used to expose certain amounts of the interface to Pt. Pt catalyzes the production of hydrogen due to its structure. The catalyst forms platinum hydrides on its surface. So, when light is shined on the entire semiconductor, it first hits the TiO$_2$, travels to the CuBi$_2$O$_4$, 2 electrons are excited, and as a result the Pt releases 2 hydrogens (Mehrabi).

Other work has been performed in the Coridan research lab pertaining to glycerol electrooxidation. It has been shown that glycerol oxidation is a promising alternative to water oxidation at the anode of the PEC cell. This is because glycerol oxidation requires a much lower input of potential in order to produce H$_2$ compared to water oxidation. Water oxidation typically requires greater than 1.7V in order to attain adequate efficiency. Glycerol oxidation, however, requires only 0.8V in order to attain equivalent efficiency. (Schichtl). An electrocatalyst has already been achieved for this PEC cell. It is a AuPtBi-Ni electrocatalyst. This specific catalyst is
able to assist hydrogen evolution at a much lower overall cell potential in comparison to combining hydrogen evolution and water oxidation. Our hypothesis is that we can build a complete PEC cell that uses CuBi2O4 to drive hydrogen production and glycerol oxidation simultaneously, a much simpler cell design than would be required for the overall water splitting reaction \(2H_2O \rightarrow 2H_2 + O_2\).

**Materials Synthesis**

**FTO Slide and Solution Preparation:**
To begin making the CuBi2O4, FTO electrodes are cut into 1cm x 3cm pieces and washed respectively with acetone, methanol, isopropanol, and HPLC grade water. The dimensions for the FTO slides were chosen with the intention of creating a semiconductor that would fit nicely into the PEC set up as seen below in Figure 8 and that would also give a large enough surface area to absorb light on. After cleaning the FTO films, the films are then be placed into a UVOzone cleaner, conductive side up, for two hours. The UV-Ozone cleaner removes particles from the FTO film that are considered contaminants. It does so by using known wavelengths to excite these contaminant particles. Ozone is produced when O2 inside the cleaner is hit with UV light. The ozone produced then reacts with the contaminant organic molecules and H2O and CO2 that can easily be removed from the sample. While the films are sterilizing, the ethylene glycol solution is prepared for depositing the CuBi2O4 onto the FTO films. The ethylene glycol solution is composed of 50mM copper (ii) nitrate and 100mM bismuth (iii) nitrate. The 50mM copper (ii) nitrate and 100mM bismuth (iii) nitrate concentrations were chosen since the desired ratio of Cu2+ to Bi3+ is 1:2 in CuBi2O4.

At this point, the heating plate is turned on to maximum temperature, which is around 500°C. A glass petri dish is then placed on the hot plate. The dish is then allowed to heat for two minutes. After two minutes, a clean FTO slide is placed onto the petri dish using tongs. It is
imperative that the conductive side of the FTO slide is facing up. The FTO slide is allowed to heat for two minutes or until it reaches 400°C or higher. A temperature reading gun is used to measure the temperature. Once the FTO slide has reached the desired temperature, the Cu<sup>2+</sup>/Bi<sup>3+</sup> solution is ready to be sprayed on.
Spray Pyrolysis Technique:

Figure 1. A pictorial representation of the spray pyrolysis technique.

The Cu/Bi solution is added into the glass container that is attached to the spray gun. The glass container is first massed. To properly achieve the solution needed to spray Cu$^{2+}$ and Bi$^{3+}$,
ensure that the total solution is 1-part Cu$^{2+}$/Bi$^{3+}$ solution and 1-part deionized water. The ratio that typically allows for optimal output of the spray gun is 7g Cu$^{2+}$/Bi$^{3+}$ solution and 7g deionized water. To ensure that the spray gun is spraying properly, a quick spray is performed into an empty beaker.

The spray gun is held a distance of 15cm to 18cm away from the FTO film. The first spray is a 30 second spray. The spray gun is moved in a forward to backward motion to ensure that the entire film is being coated by the spray. After the 30 second spray is complete, a 2minute hold period follows. After the hold period, the film is sprayed once again for a 30 second spray. This process is repeated for either a total of 2 spray/hold cycles or 4 spray/hold cycles. After the last hold period, the slide is allowed to heat for another 2 minutes. Then the petri dish containing the slide is placed onto the benchtop to cool for 4 minutes. After cooling, the slide is then placed into a new petri dish and etched with an appropriate label on the backside.
Image 1. Cu$^{2+}$/Bi$^{3+}$ sprayed FTO films before annealing. These films underwent 4 cycles of the spray/hold periods.

Annealing:

The Cu$^{2+}$/Bi$^{3+}$ sprayed FTO films are then placed onto a microscope slide. The films on the slide are then placed into the furnace. The temperature is set to 500°C and the slides are heated for 5 hours. Annealing the Cu$^{2+}$/Bi$^{3+}$ sprayed FTO films is a crucial step as this is how CuBi$_2$O$_4$ is formed. The CuBi$_2$O$_4$ is formed by the Cu$^{2+}$ and Bi$^{3+}$ reacting with O$_2$ in the air.
Annealing is a heating process that ultimately alters the physical properties of the electrode. It heats the electrode so that its hardness is reduced which in turn allows for the electrode to be more workable in a PEC cell experiment. Annealing, however, can also alter the chemical properties of the electrode.

**Image 2.** The Cu$^{2+}$/Bi$^{3+}$ sprayed FTO film on the left is what the film looks like before annealing. The Cu$^{2+}$/Bi$^{3+}$ sprayed FTO film on the right shows what the film looks like after annealing. The film on the right is then CuBi$_2$O$_4$.

**Clean Up:**

After spraying is complete, the excess ethylene glycol solution is properly discarded. The spray gun is then cleaned by filling the glass with deionized water and spraying the water into an empty beaker. Next, isopropanol is sprayed into the beaker followed by another round of deionized water. The tip of the gun is dried and then the gun is properly stored.
**Materials Characterization**

X-ray Photoelectron Spectroscopy (XPS) is an analytical technique used in many laboratories to investigate the composition of a material’s surface. It provides information about composition, oxidation state, and structure pertaining to the sample of interest. XPS applications are only of concern to the surfaces of materials. This is because XPS utilizes a low energy source of x-ray which can only penetrate so deep into the material. Once the x-ray hits the material, electrons absorb different energies and are then excited. Once excited, the electrons are ejected as photoelectrons. The energy it took to eject a particular photoelectron is known and well defined. From there, the kinetic energy and work function can both be calculated. Finally, the binding energy can be calculated from the known energy to produce the photoelectron, kinetic energy, and work function. This binding energy is what allows for the determination of the particular components and their oxidation states in the surface of a material. Peaks present on a XPS spectrum indicates the presence of a certain element whereas the area under the peak indicated the amount of the element present. Therefore, by using XPS, it can be determined if and how much CuBi$_2$O$_4$ is being formed (Skoog).

X-ray Diffraction (XRD) is also an analytical technique used in laboratories to determine the structure of crystalline molecules. XRD does so by utilizing Bragg’s Law. First, light is shown onto the sample and a certain angle. Once the light hits the sample, it will either penetrate deeper into the sample or be scattered off the sample’s surface. The light that is scattered off the surface hits a detector and then can create interference. The detector then analyzes the intensities of the interferences which allows for the determination of how particular atoms are arranged in the material (Skoog). Hence, the structure of CuBi$_2$O$_4$ can be characterized. Scanning Electron Microscopy (SEM) is an analytical technique that allows for the visualization of the CuBi$_2$O$_4$. 
SEM uses a beam of electrons to flow around and through the material in order to produce an image.

The XPS data for Cu 2p below in Figure 2 shows that in four different variations of material synthesis, Cu 2p was found to be in the composition of two of the materials’ surfaces. This has to do with the variations in annealing and ALD of the protection layer. It is expected that Cu would be present in the CBO-anneal version as there is no protection layer. This version is simply confirming that Cu was successfully deposited as a result of the spray pyrolysis technique. However, in the CBO-anneal-ALD version, there is no presence of Cu on the surface. This was expected. There being no Cu on the material’s surface means that the TiO₂ protection layer is working. It is preventing any of the CuBi₂O₄ from getting to the surface. Interestingly, the CBO-anneal-ALD-anneal version did not show Cu to be present on the material’s surface. This is more than likely due to the material not actually forming deep enough of cracks to expose certain areas of the semiconductor. The four CBO films underwent 4 cycles of the spray/hold periods and then varied in the subsequent steps of annealing and ALD.
Figure 2. XPS Spectra of Cu 2p detection on CuBi\textsubscript{2}O\textsubscript{4} sprayed semiconductors
The XPS data in Figure 3 shows that Bi 4f was present in three of the four semiconductors made. The top trial, CBO-anneal, in purple presented peaks so large that the scale had to be minimized to 0.1 times of the original spectrum. This trial simply shows that Bi was successfully deposited through the spray pyrolysis technique. The CBO-anneal-ALD version shows that no Bi was present at the surface. This was expected. Once the TiO$_2$ protection layer is deposited, no materials from beneath should reach the surface. This trial confirmed that the protection layer was deposited successfully. The CBO-ALD-anneal version and CBO-anneal-ALD-anneal version show that annealing the sample after the protection layer is deposited, allows for Bi to reach the surface. Initially the results seemed promising; however, after comparing to the CBO-anneal-ALD-anneal version of Cu in Figure 3, it can be inferred that a new issue has presented. The Bi reaches the surface; however, Cu does not. Because of this it can be inferred that the TiO$_2$ layer isn’t actually cracking enough to expose small areas of the semiconductor underneath. Instead, Bi reaching the surface could be due to Bi being potentially miscible in TiO$_2$. All four variations of the CuBi$_2$O$_4$ semiconductors made were made via 4 cycles of the spray/hold periods. It’s evident that the CBO-anneal variation presents the most Bi 4f at the surface. The process of annealing is what allows for the components in the material to move towards the surface; therefore, that is why no Bi 4f was present on the surface in the CBOanneal-ALD variation.
Figure 3. XPS Spectra of Bi 4f detection on CuBi$_2$O$_4$ sprayed semiconductors
The XPS data in Figure 4 shows that Ti 2p was present in three of the semiconductors made. Ti 2p was present here in the three samples that underwent ALD of the protection layer, TiO$_2$. This data was completely expected; however, its significance is that it shows the protection layer was successfully deposited in all ALD trials. All four variations of the CuBi$_2$O$_4$ semiconductors made were made via 4 cycles of the spray/hold periods.

**Figure 4. XPS Spectra of Ti 2p detection on CuBi$_2$O$_4$ sprayed semiconductors**
Image 3. SEM Image of a CuBi$_2$O$_4$ sample that underwent 4 cycles of the spray/hold period, had TiO$_2$ deposited onto it, and then annealed. The bubbling seen below is due to the material boiling during the actual spray. It is evident that cracking did not occur on this sample. This is potentially due to the miscible properties of Bi in TiO$_2$ (Yao).
Image 4. SEM Image of a CuBi$_2$O$_4$ sample that underwent 4 cycles of the spray/hold period, annealed, and then had TiO$_2$ deposited onto it. The hole like structures on the surface are most likely attributed to the oxidation of Cu$^{2+}$ and Bi$^{3+}$. This meaning that the CuBi$_2$O$_4$ was not completely oxidized during annealing before the protection layer was deposited.
Image 5. SEM Image of a CuBi$_2$O$_4$ sample that underwent 4 cycles of the spray/hold period, had TiO$_2$ deposited onto it, and then annealed. This sample compared to Image 3 looks as if the surface was protected from oxidation of Cu$^{2+}$ and Bi$^{3+}$ because of the TiO$_2$. That is potentially why the surface morphology looks rather different in this trail; however, it is unknown exactly how the incomplete oxidation contributed to the surface chemistry.
Figure 5. XRD Spectra shows that CuBi$_2$O$_4$ was formed as a result of spray pyrolysis on FTO films followed by annealing.
Conclusion

The goal was to determine a way to fabricate a CuBi$_2$O$_4$ semiconductor in order for it to serve as a photocathode in a PEC and facilitate the hydrogen production reaction ($2e^\# + 2H^+ \rightarrow H_2$). The idea was to mimic previous work done by the Coridan lab on CuO. It was determined that the amount of volume change of the semiconductor and cracking of the protection layer can be controlled. Thus, the goal was to use the expansion of the light absorber and the contraction of the protection layer, both due to annealing, to expose certain amounts of the interface such that Pt could be deposited. The semiconductor with the protection layer of TiO$_2$ was successfully fabricated. However, cracking in the protection layer was not achieved. One potential reason is the miscibility of Bi in TiO$_2$. Once TiO$_2$ is deposited onto the surface of the CuBi$_2$O$_4$ and annealed, Cu is not present on the surface while Bi is. This is not due to cracking. If cracking in the protection layer had occurred, both would be present on the surface. Instead, Bi alone is present on the surface. The most plausible reason for this finding is that Cu is completely immiscible in TiO$_2$ whereas Bi potentially forms Bi$_2$O$_3$ when in contact with TiO$_2$. It has been shown that cracking in the TiO$_2$ is certainly possible. It was achieved using CuO. Therefore, in order to fabricate a CuBi$_2$O$_4$ semiconductor that has both a working protection layer and sparsely deposited Pt catalyst that can be incorporated into a PEC cell, the miscibility issue of Bi in TiO$_2$ must be addressed. Thus, future work target this issue and ultimately involve testing the efficacy of the integrated photocathode in generating H$_2$ from sunlight.
Works Cited


