Investigations on the Effect of Metal Oxides on the Photocatalytic Properties of Bismuth Vanadate

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1. Abstract: Bismuth Vanadate ($BiVO_4$), with its bandgap of 2.4-eV, is a promising photocatalyst because of its ability to effectively split water using light to produce hydrogen fuel. However, its photocatalytic properties are currently not high enough for it to compete with existing solar systems. In order to improve bismuth vanadate, metal oxide catalysts would be added to the bismuth vanadate. Multiple techniques were employed to synthesize $BiVO_4$ such as the slurry method, the mixing method, the layering method, and the spin coating method. Bismuth vanadate would then be drop-cast onto Fluorine-doped tin oxide plates and its photocatalytic effects increased by over 100% by mixing metal oxide catalysts such as nickel, copper, iron, and cobalt nitrates, with the BiVO4 spots. The SEAL (Solar Energy Activity Laboratory) kit was then used in order to measure the current produced by each individual photocatalysts, allowing comparisons to be drawn between the original and improved samples.

2. Background

Solar energy is currently one leading environmentally friendly source of energy for human consumption; however, there is currently no feasible method to store the energy created, with present techniques requiring expensive supercapacitors or large and unwieldy batteries. A lesser-known procedure is to convert solar energy into storable chemical fuel cells by using solar energy to split water into oxygen and hydrogen, which can then be utilized as hydrogen fuel. [1] Unfortunately, the water-splitting reaction is energy-intensive and typically does not produce enough hydrogen to make up for the energy used to split the water.

In order to make this method more efficient, a suitable material must be found in order to catalyze the water splitting reaction. While several photocatalysts can split water, there are cost-related issues associated with many of these materials, such as gold and tantalum. Viable photocatalysts must be earth-abundant, scalable, and efficiently catalyze the water-splitting reaction[2]. Additionally, these photocatalysts must also have a band gap small enough to efficiently absorb sunlight.

Dr. Jay Winkler, the director of the Beckman Institute Laser Resource Center at the California Institute of Technology, developed a method to test the viability of various metal oxides as photocatalysts through the SEAL kit (Solar Energy Activity Laboratory). In order to use the SEAL kit, metal nitrates must first be drop-cast onto a FTO (fluorine-doped tin oxide) plate and annealed at 500°C to create a metal oxide. The FTO plate is then immersed in an electrolyte solution, typically a 0.1M NaOH solution, and illuminated by LED lights. The LED lights cause the metal oxide to be excited and release electrons, generating current. An integrator unit then measures the current produced and the electrons are returned to a graphite counter electrode. A computer-based program can then create a chart of the current produced by each metal oxide on the FTO plate. While results using this procedure can vary slightly, it is able to give an initial understanding of the properties of photocatalysts.

Bismuth vanadate, with its 2.4-eV band gap, is a fairly inexpensive material made of earth-abundant elements and has recently been established as a potential photoanode material for water splitting. [3] Early work on $BiVO_4$ focused mainly on using $BiVO_4$ to degrade organic compounds but it has recently been used to create electrodes for photoanodes. Despite the fact that bismuth vanadate photoanodes have poor charge transport properties and high electron-hole recombination[3], the addition of various metal oxides can help alleviate its problems. Additionally because of $BiVO_4$'s inability to be soluble in water, there are currently several approaches in synthesizing undoped $BiVO_4$ photoanodes on FTO glass plates. [3, 4, 5, 6] However, $BiVO_4$'s photocatalytic properties vary widely based on an assortment of factors: vanadium salt, annealing time, solvent, drop-casting method, and concentration.[3] As a result, it is necessary to develop an effective and reliable method to synthesize $BiVO_4$ that can be tested using the SEAL kit.

The photocurrent of bismuth vanadate photoanodes can be improved by the addition of various metal oxides. [4] For this reason, nickel, iron, copper, and cobalt's effects on $BiVO_4$ were investigated. [5,6] Bismuth vanadate is known for being an unstable compound in basic solutions [7]

and the addition of various metal oxides onto it could also improve its ability to resist corrosion.

3. Methods:

3.1 Materials.

$Bi(NO_3)_3$ x $5H_2O$, NH_4VO_3, and $NaVO_3$ were used to synthesize $BiVO_4$. NaOH, Fluorine doped Tin Oxide glass substrates, epoxy, copper tape, copper wire, and a graphite rod were necessary in order to utilize the SEAL kit. Iron nitrate, copper nitrate, cobalt nitrate, nickel nitrate were used for the mixing and layering methods. 2M HNO_3, 10% CH_3COOH, and acetone were used for spin coating. Triton X and glycerol were used to create slurry solutions. Acetone was used to rinse glassware.

3.2 Slurry Preparation.

Two 25 ml volumetric flasks were obtained. 0.6 g. of $Bi(NO_3)_3$ x $5H_2O$ was added along with 0.15 g. of $NaVO_3$ to one of the volumetric flasks. Water was added until the two solids completely dissolved when swirled. Glycerol was then added until the 25 mL mark, resulting in a 0.05M solution. The second volumetric flask was filled with water until the two solids completely dissolved when swirled. 1.25 mL of Triton X was then added into the solution and water was added until the 25 mL mark, also creating a 0.05M solution. The two solutions were then drop-cast onto two different FTO plates in a checkerboard pattern (Fig 1) with 5 µL on each spot.

3.3 Mixing & Layering Methods.

1.2 g. of $Bi(NO_3)_3$ x $5H_2O$ was dissolved in 5 mL of 2M HNO_3 and water was added to the 25 mL mark. 0.1 M $NaVO_3$ solution was then created by adding 0.3 g. of $NaVO_3$ along with 25 mL of water to a volumetric flask. 10 mL of each solution was then mixed together and the resulting solution was then drop cast onto an FTO plate with 5 µL on each spot.

Afterwards, 3 µL of the 0.1M $Bi(NO_3)_3$ x $5H_2O$ solution was drop cast onto a new FTO plate for the layering method. This plate would then be left to anneal for 5 hours at 500°C at atmospheric pressure before 3 µL of the 0.1 M $NaVO_3$ solution was drop cast onto the previous $Bi(NO_3)$ x $5H_2O$ spots.

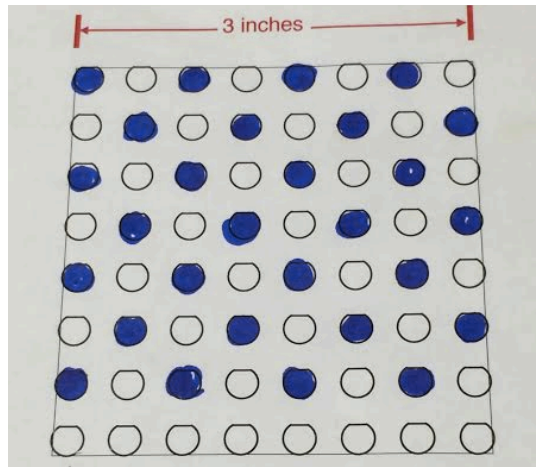

Fig. 1 Solutions were drop-cast onto an FTO plate. The blue spots signify where each sample goes.

Add 0.46 g. of $Co(NO_3)_3$ x 6 H_2O to 25 mL of water in a volumetric flask. Add 0.47 g. of $Cu(NO_3)_2$ to 25 mL of water in a volumetric flask Add 0.47 g. of $Ni(NO_3)_2$ to 25 mL of water in a volumetric flask. This will create a 0.1 M of each metal nitrate solution. Add 10 mL of the cobalt nitrate solution to 10 mL of a 0.1 M $Bi(NO_3)_3$ x $5H_2O$ and $NaVO_3$ solution created using the mixing method. Repeat with the copper and nickel nitrate. Drop cast the three remaining solutions onto an FTO plate following the pattern in Fig. 2 and anneal for 5 hours at 500°C.

1.2 g. of $Bi(NO_3)_3$ x $5H_2O$ was dissolved in 5 mL of 2M HNO_3 and water was added to the 25 mL mark. 0.1 M NH_4VO_3 solution was then created by adding 0.15 g. of NH_4VO_3 along with 25 mL of water to a volumetric flask. 10 mL of each solution was then mixed together and the resulting solution was then drop cast onto an FTO plate with 5 µL on each spot.

3.4 Vanadium Salt and Annealing Time

Bismuth nitrate was added with ammonium metavanadate in equal concentrations (0.5M) and dissolved using 2M nitric acid. The resulting solution was then spotted using the checkerboard pattern and annealed in a kiln at 500°C for 2 hours.

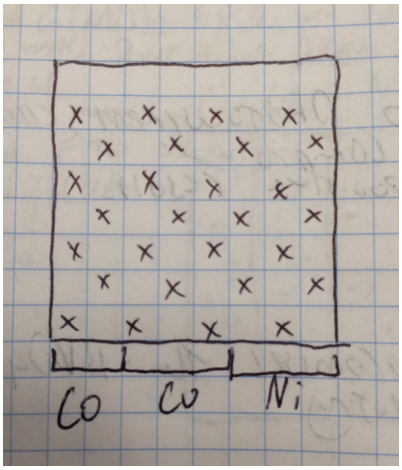

Fig. 2 Solutions were drop-cast onto the FTO plate. The X's mark where each sample goes.

3.5 Spin-coating

Solutions of bismuth nitrate and ammonium metavanadate were created using different solvents. 0.05M of Bismuth Nitrate and Ammonium Metavanadate solutions were created using 2M nitric acid in a 10 mL volumetric flask. Another solution was created using 5 mL of acetone and 5 mL of water as the solvent and the last solution was created using 10% acetic acid.

The FTO plates were then split in half. An etcher was used to cut a line in the middle of the nonconductive side of the FTO plate. Water was then administered to the cut and pressure was applied to allow the FTO plate to snap in half. This was repeated until 3 halves were obtained.

A spincoater was then set up at 1000 rpm for 6 seconds. The nitric acid solution would be dropped onto the FTO plate using a pipet. After the cycle is completed, the FTO plate is then set to dry on a hot plate at 200°C for 5-10 minutes. This was repeated with the other 2 FTO plates. The spincoater would then be set to run for 16 seconds and each plate would be spun once more with their respective solutions.

3.6 SEM/EDS

A portion of the FTO glass from Sample 5 was broken off. To do so, an etcher would vertically etch a deep line on the nonconductive side of the FTO plate, splitting the FTO plate into two halves. Distilled water would be added to wet the line. Half of the glass would be placed onto a hard surface and force was applied to allow the FTO plate to snap in half. This process would be repeated until a 3/8 in x 3/8 in sample was created. An FEI Nova NanoSEM 450 was used to investigate the composition of the bismuth vanadate.

3.7 Testing

An etcher would be used on the nonconductive side of the FTO plate to etch MC-## (##=the page number in the lab notebook). Cut around 1 inch of copper tape and 10 cm of copper wire. Cut 1 cm of the rubber shielding off each side of the copper wire and cover one tip of the copper wire with the copper tape. Tape the copper tape onto the top right corner of the FTO plate. Apply nonconductive epoxy to cover all parts of the copper tape. Wait for 5 minutes or until the epoxy dries.

Add ~100 mL of 0.1M NaOH into a 1550 mm x 75 mm Pyrex glass crystallization dish. Put the FTO plate into the crystallization dish and put the dish on top of the LED lights. Line up the spots with the LED lights and run the SMD program. Apply 0.1 V and check to make sure the dark current is below 0.5 V. Run the program for 3 cycles and save the data.

4. Results

Sample 1 and Sample 2 were both created using the slurry method. Sample 1 exhibited a high surface tension and viscosity, making it difficult to drop=cast. Sample 2 had a low surface tension and failed to properly adhere to the FTO plate.

Sample 3 and Sample 4 both resulted in brown-black colored spots and produced low photocurrent.

Sample 7 and Sample 9 had extremely uneven layers of bismuth vanadate and Sample 8 had an even layer but all three of the spin-coated FTO plates produced low photocurrent.

Sample 5 exhibited a high photocurrent during the first day it was tested. However, its photocurrent rapidly diminished from an average of 2 μA after it was tested a second time the next day. A high dark current (~6V) was noticed on the first day of testing Sample 5.

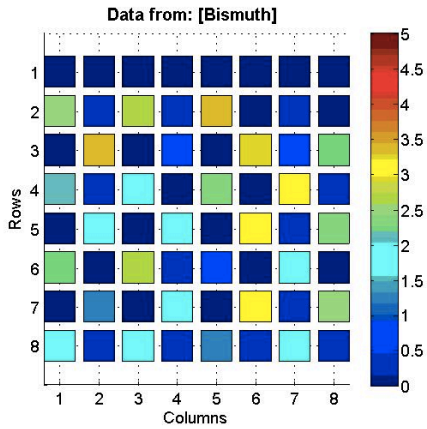

Fig. 3 Results of the current produced by Sample 5, a standard bismuth vanadate plate created using ammonium metavanadate, the first time it was tested.

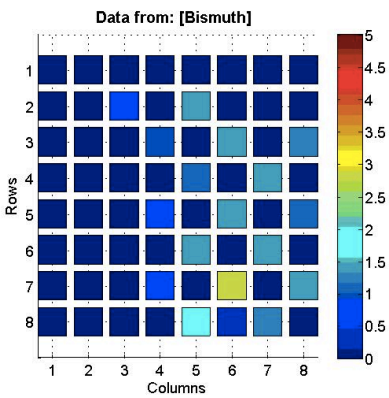

Fig. 4 Results of the current produced by the second trial of Sample 5: a standard bismuth vanadate plate created using ammonium metavanadate.

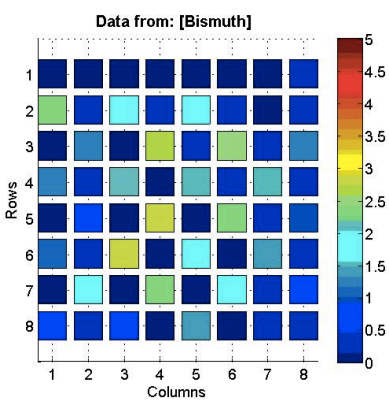

Fig. 5 Results of the current produced by Sample 6: a bismuth vanadate plate layered with cobalt, copper, iron, and nickel

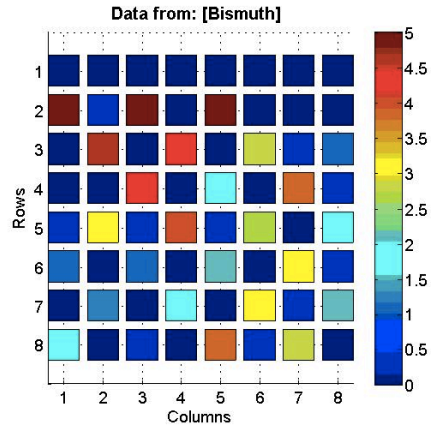

Fig. 6 Results of the current produced by Sample 10: a bismuth vanadate plate mixed with cobalt, copper, iron, and nickel

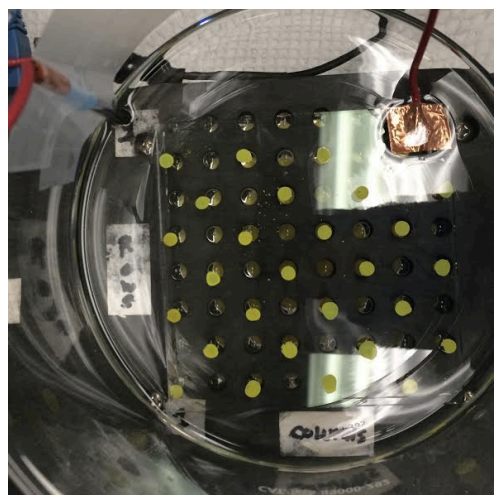

Fig. 7 The color of Sample 5's spots beginning to turn from a bright yellow into a yellow-green color in 0.1M NaOH

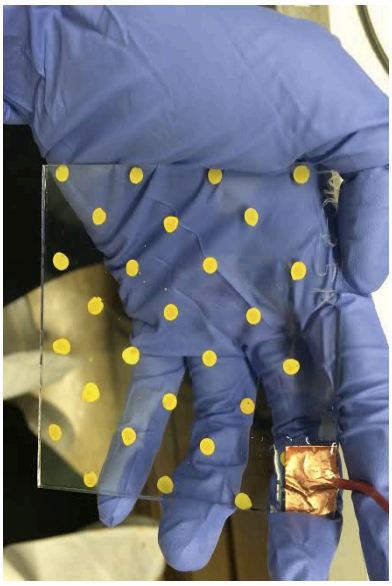

Fig. 8 Original color of Sample 5, a FTO plate drop-cast with bismuth vanadate

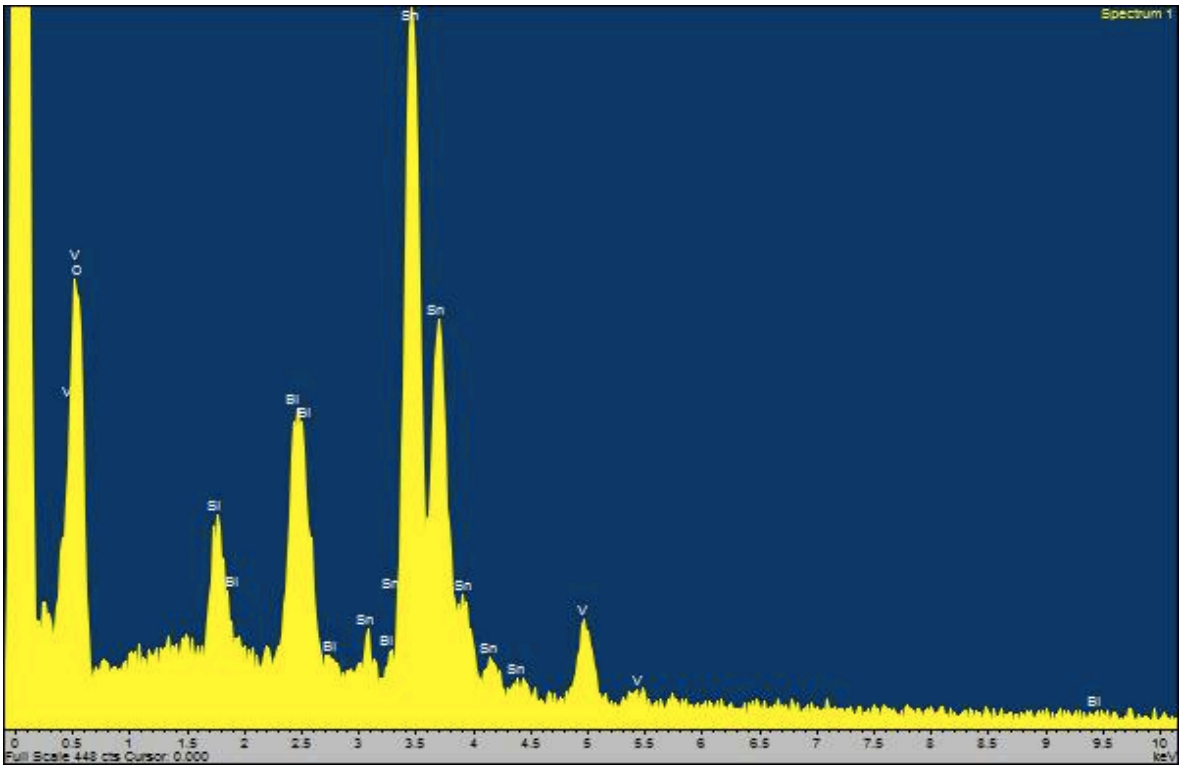

Fig. 9 Sample 5 was investigated using a scanning electron microscope (SEM). Elemental analysis of Sample 5 using energy-dispersive X-ray spectroscopy showed bismuth and vanadium in equal proportions.

Sample #	Vanadium Salt	Concentration	Color	Mixing or Layering	Metal Added	Average Photocurrent (μA)
Sample 1 Glycerol	$NaVO_3$	0.05M	Yellow	Mixing	N/A	0.3
Sample 2 Triton X	$NaVO_3$	0.05M	Yellow	Mixing	N/A	0.25
Sample 3	$NaVO_3$	0.05M	Black/ Brown	Mixing	Co, Cu, Ni	0.05
Sample 4	$NaVO_3$	0.05M	Black/ Brown	Layering	Co, Cu, Ni	0.05
Sample 5*	NH_4VO_3	0.05M	Bright Yellow	Layering	N/A	3 → 2
Sample 6*	NH_4VO_3	0.05M	Red Blue Yellow Green	Layering	Co, Cu, Fe, Ni	2.7
Sample 7 Spincoat 2M Nitric	NH_4VO_3	0.05M	Brown/ Yellow	Mixing	N/A	0.03
Sample 8 Spincoat Acetone	NH_4VO_3	0.05M	Yellow	Mixing	N/A	0.03
Sample 9 Spincoat Acetic Acid	NH_4VO_3	0.05M	Yellow w/ Black specks	Mixing	N/A	0.03
Sample 10*	NH_4VO_3	0.05	Yellow Red Blue Green	Mixing	Co, Cu, Fe, Ni	4.4

Table 1. Table of the various samples tested using the SEAL kit

5. Discussion:

The first goal was to find an effective method to drop-cast bismuth vanadate onto FTO plates to test with the SEAL kit. The first method that we used was the slurry method, which involved creating slurries using either Triton X or glycerol shown in Sample 1 and Sample 2. However, the slurry method only produced a photocurrent of ~0.3, which led to the mixing and layering methods. Both of these methods resulted in near-zero photocurrents, most likely due to an unwanted reaction between the metal nitrate, the sodium metavanadate, and the bismuth nitrate creating a compound that is not a photocatalyst.

The experiments were then repeated using a different vanadium salt: ammonium metavanadate. We believe that because sodium metavanadate is not volatile, the bismuth vanadate that we create still has sodium on the spots, negatively affecting our results. Ammonium metavanadate should become volatile at 500°C, leaving behind the vanadium and creating a pure bismuth vanadate compound. This resulted in a plate with the average photocurrent being at 3 μA. However, this plate (Sample 5) would begin to turn from a bright yellow color to an acidic-green color in electrolyte solution and when it was tested a second time, its average photocurrent decreased

to ~2 μA. It was noticed that the first time the bismuth vanadate was tested; an abnormally high dark current was created. Additionally, while it appeared that the bismuth vanadate underwent some kind of reaction in the NaOH solution, elemental analysis showed that no such reaction took place as both the bismuth and vanadium were in equal quantities. After this, Sample 5 continued to give us a photocurrent of ~2 μA and so this result was thought to be more reliable.

All three spin-coated FTO plates (Sample 7, 8, 9) failed to produce any significant current. While Samples 7 and 9 both looked unlikely to generate current, Sample 8 actually comprised of an even layer of bismuth vanadate. Hence, it is unknown why all three of the spin-coated plates conducted the same current despite the obvious contrasts.

When the various metals were added to the bismuth vanadate through the layering method, as shown in Sample 6, the average photocurrent of the plate increased by around 20%. When the mixing method was tested using the SEAL kit with Sample 10, the results were significantly higher than those of Sample 6. This is most likely due to how the mixing method allows for a more homogenous spot, instead of simply layering two different photocatalysts on top of each other as done through the layering method.

In both situations, the bismuth vanadate layered with copper and iron gave the highest readings while the bismuth vanadate layered with cobalt and nickel barely improved the bismuth vanadate. While iron oxide is known to be a stable and reliable compound for testing in the context of the SEAL kit, copper oxide has no notable properties.

6. Conclusion

While bismuth vanadate is already an efficient photoanode, its catalytic properties can be significantly improved with the addition of copper oxide and iron.

The slurry, mixing, layering, and spin-coating methods were used to synthesize bismuth vanadate. The mixing method produced better results than the other three methods. Additionally, ammonium metavanadate allowed for proper testing of bismuth vanadate, instead of testing bismuth vanadate coupled with sodium when sodium metavanadate was employed. The mixing method also allowed for an effective way to add the metal oxides into the bismuth vanadate spots and improved the catalytic properties of bismuth vanadate for water oxidation by 120%.

Due to time constraints, further experimentation of cobalt, nickel, and various other metals were not possible. However, testing should be done on copper and iron oxide in order to see just how effective they are. Furthermore, nickel oxide was expected to significantly improve the photocatalytic results of bismuth vanadate while no precedent indicated that copper oxide improved the results of bismuth vanadate. More research should be done on the effects of copper oxide on other photocatalysts and to recheck the photocatalytic properties of copper oxide. Additionally, layering the metal nitrates may have the effect of protecting the bismuth nitrate from corroding in a basic electrolyte solution and so more research should be done on bismuth vanadate corrosion.

7. References:

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