

Mixing copper nitrate, iron nitrate, and nickel nitrate with BiVO₄ to improve the photo-activity of BiVO₄

Helen Choi*[†], Tiffany Kim[†], Justin Cheng[†]

[†]SEAL Summer Outreach Program, Beckman Institute, California Institute of Technology, Pasadena, California, 91125

ABSTRACT: Bismuth vanadate (BiVO₄) is a promising, earth-abundant photo-catalyst used in water-splitting to produce solar fuels, but BiVO₄ is not an adequate large-scale catalyst in its unmodified form. To increase the catalyst efficiency, bismuth vanadate can be mixed with other materials or synthesized in alternative manners. Here, photo-catalysts were evaluated with the SEAL (Solar Energy Activity Laboratory) kit, which is designed to test potential photo-catalysts' water oxidation ability by measuring current resulting from light exposure. Bismuth vanadate solutions were drop casted onto plates to be later annealed and tested using the SEAL kit. The bismuth vanadate solutions were made in a variety of tactics to drop cast bismuth vanadate investigated, including suspending in glycerol, making a slurry out of triton X, and mixing bismuth nitrate with different vanadium salts and solvents. The mixing method using nitric acid to dissolve ammonium meta-vanadate and the bismuth (III) nitrate synthesizing the bismuth vanadate resulted in the greatest activity. The rapid corrosion issue of the solution was resolved by mixing various metal oxides like cobalt nitrate, copper nitrate, iron nitrate, or nickel nitrate to the solution.

1. BACKGROUND

The huge amount of energy the world consumes every day is overwhelmingly provided by non-renewable fuel sources such as coal and oil. According to the United States Energy Information Agency, in 15 years the overall global energy consumption is expected to rise 50 percent compared to 2005's energy consumption, mostly in the fossil-fuel sector.^[1] This problem can be ameliorated by acquiring a new method to convert energy from the sun using artificial photosynthesis to split water for fuel. With the discovery of efficient and powerful light absorbing materials and redox catalysts, we will be able to convert solar energy to chemical energy stored in the form of hydrogen fuel. These discoveries can be utilized within a sunlight-powered device capable of producing solar fuels to contribute greatly to fulfilling the world's energy appetite.

The SEAL (Solar Energy Activity Lab) kit was designed as a simple-to-use, high-throughput method to test earth-abundant materials for light absorbing and oxygen evolution catalysis properties. To test the various photo-catalysts, the SEAL Kit flashes light from each point on a 64 LED array to illuminate the catalyst spots and measure the photocurrent. Before testing, materials are drop-cast onto a transparent conducting fluorine doped tin oxide (FTO) plate. Then, the plate is annealed to change the metal salts into metal oxides. Next, the plate is immersed in an electrochemical cell containing the electrolyte solution, commonly sodium hydroxide.^[2] The computer that is connect-

ed to the SEAL Kit then shows the false color image of the photo-electrolysis activity and records current readings.

Bismuth vanadate is an inexpensive, light-absorbing photo-anode material that is capable of splitting water using solar energy. Electrodeposited bismuth vanadate has shown promise as a light absorber and photo-catalyst.^[3,4] However, BiVO₄ has drawbacks, including high electron-hole recombination, poor charge transport properties, and inadequate water oxidation kinetics.^[4] Certain methods used for this research were the spin-coating method, mixing method, slurry method, and layering method.^[5,6]

2. METHODS

2.1 Slurry method of preparing bismuth vanadate solution. The first combination to be tested was bismuth vanadium oxide with glycerol. First, 0.41 g of BiVO₄ was used to make 25 mL of .05M solution, and stirred. Next, the BiVO₄ particles were weighed and placed into a 25mL volumetric flask. In a fume hood setting, glycerol (C₃H₈O₃) was added to the mark in the flask while constantly swirling and mixing the flask around so that the materials dissolved and mixed. Since glycerol has very high viscosity, use of a stirring magnet and a stirring plate are necessary to achieve full mixture. Next, each spot was spot-casted 10 microliters with a micropipette on the Fluorine doped Tin Oxide (FTO) glass using a checkerboard pattern. The spot-casted plate was air-dried and followed instructions in steps 2.3 and 2.4. The second combination was bismuth vanadium oxide with Triton X and deionized water, using the

slurry method. First of all, 0.41g BiVO_4 oxide was weighed and placed into the 25mL volumetric flask. Then, deionized water was poured into the 25mL mark in the same flask. 1.25mL of Triton X was pipetted into the flask as well, using a P1000 micropipette. The solution was sonicated for 12 minutes and stirred until homogenous. Lastly, the solution was annealed and tested as in following steps 2.3 and 2.4 after the spotted areas were completely air-dried.

2.2 Mixing method of preparing bismuth vanadate solution.

2.2.1 Using sodium meta-vanadate. The third combination was the bismuth (II) nitrate and sodium meta-vanadate using the mixing method. Unlike the previous combinations, for this couple, .05M and .025M both were created and tested. First, 0.61g $\text{BiN}_3\text{O}_9 \cdot 5\text{H}_2\text{O}$ and 0.15g NaO_3V were weighed to synthesize 25mL of .5M of BiVO_4 . Second, both weighed particles were placed in a clean 25mL volumetric flask and deionized water was added to the mark on the flask. The solution was mixed by swirling the flask. This solution dissolved comparably faster and more easily. A portion of the solution was taken into a graduated cylinder and deionized water was added in 1:1 ratio with the solution to make .025M bismuth vanadate. Lastly, the two different molarity solutions were spotted in separate spots and air-dried, annealed, and tested like described in steps 2.3 and 2.4. Using the solution made by the third combination, the .05M of the solution was spotted and air-dried. Next, the spotted FTO glass plate was annealed under the same conditions as the before steps. Then, another layer of different metal oxides like Co, Cu, and Ni after making .05M solution of the three metal oxides were spot-cast on the previous layer. Each spot should have one metal oxide layered and air-dried in order for the plate to get annealed as described in steps 2.3 and 2.4.

The mixing method was also tested with the same materials as the previous experiment. Instead of waiting for the bismuth vanadate to air-dry and anneal to spot metal oxides on top, the mixing method had the metal oxides directly mixed with the bismuth vanadate (one 20mL vial per each metal oxide added with bismuth vanadate). The metal oxide added with bismuth vanadate was spot-casted in the checkerboard pattern. Next, the plate continued the air-dry, annealing, and testing procedure in steps 2.3 and 2.4.

2.2.2 Using ammonium meta-vanadate. The fourth combination was bismuth (III) vanadate with ammonium meta-vanadate. First, 0.06g NH_4VO_3 and 0.24g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were weighed and placed in the 10mL volumetric flask in order to make .05M of BiVO_4 . Four different solvents were used to dissolve the chemicals: 2M nitric acid, 10% acetic acid with deionized water, acetyl-acetone with 0.1M NaOH, and acetone with water. On each three vials the same amount of the chemicals were added and the each solvent was used for each vial to compare and find out the best method to synthesize the solution. The spin-coating method was used to place the three different solutions (all solutions except the one using acetyl-acetone as the solvent) on three half sliced FTO plates that were taped with scotch tape on the upper front surface of the FTO plate. After the solutions were placed on top of the FTO plate and spin-coated, the tape was removed and the plate was placed

on top of the hot plate at 300°C for between 5 to 15 minutes. Finally, the plate was annealed and tested like described in the following paragraphs.

2.3 Annealing FTO plates. The spotted plates were air-dried and annealed under 500°C for 5 hours for all the slurry methods and the sodium meta-vanadate FTO plates. The ammonium meta-vanadate solutions from step 2.2.2 were annealed at 500°C for 2 hours. The second annealing process for the metal oxides followed the method used for the respective bismuth vanadate.

2.4 Testing using the SEAL kit. A clean 125*65mm crystallization dish had a graphite counter electrode attached on the inner side of the dish that did not touch the inner ground surface in the dish. Enough 0.1M NaOH, which is the most commonly used electrolyte, was poured in to just sink the graphite in the plate, and the FTO plate was to be placed in the NaOH. The annealed FTO plate was placed in the dish with 0.1M NaOH and ran through the SEAL kit according to the user's manual.

3. RESULTS

3.1 Bismuth vanadate solutions. The first bismuth vanadate solution synthesized and tested was bismuth vanadium oxide dissolved in glycerol. The solution was sticky and hard to mix. The test results from the SEAL kit's Solar Materials Discovery (SMD) software for the first solution ranged relatively low (Figure 1).

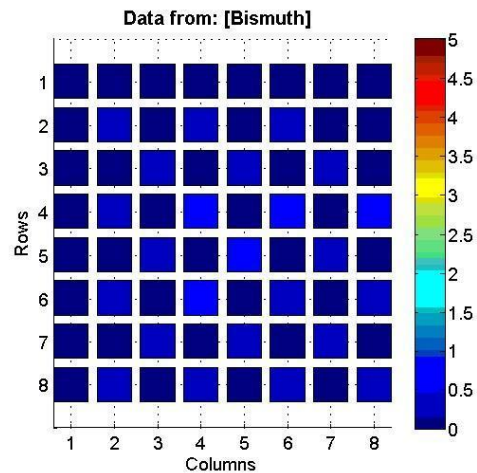


Figure 1. Photocurrent of Bismuth vanadium oxide dissolved in glycerol (.05M) tested and measured using the Solar Materials Discovery (SMD) software. Conducted relatively low photocurrents and drop-casted in checkerboard pattern.

The second bismuth vanadate solution was created using bismuth vanadium oxide with triton X and deionized water. The solution was difficult to spot cast because the spots spread rapidly. The photo-activity of the second solution shown in the results was a little better than the first solution but was still relatively low (Figure 2).

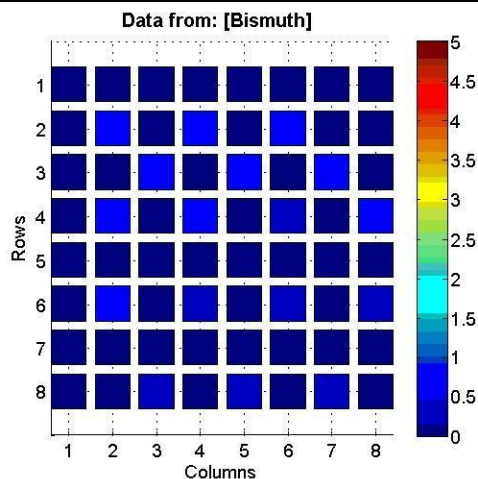


Figure 2. Photocurrent of Bismuth vanadium oxide dissolved in Triton X and deionized water (.05M) measured and tested using the Solar Materials Discovery (SMD) software. Produced higher energy than the Fig. 1 and drop casted in checker-board pattern.

The third combination was bismuth (II) nitrate and sodium meta-vanadate mixed in deionized water. The solution was comparably easier to synthesize than the previous two solutions. However, the third solution produced the least amount of energy among the three solutions (Figure 3).

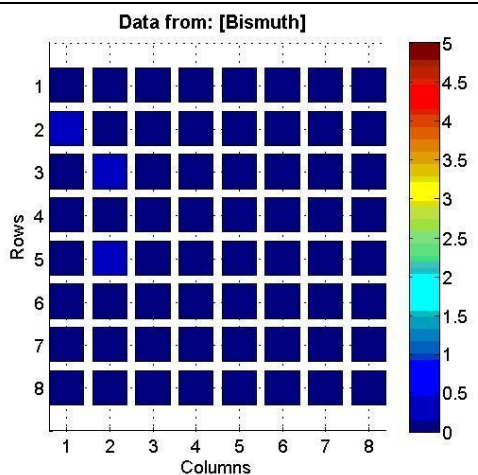


Figure 3. Photocurrent of Bismuth (III) nitrate and sodium meta-vanadate dissolved in deionized water to make .05M BiVO₄. Tested and measured using the SMD software from the SEAL kit, produced least amount of energy. And was drop-casted in Checker-board pattern.

Lastly, the fourth mixture contained bismuth (III) nitrate and ammonium meta-vanadate dissolved in 2M nitric acid. The first scanned performance of the fourth solution was great, producing high photocurrents (Figure 4).

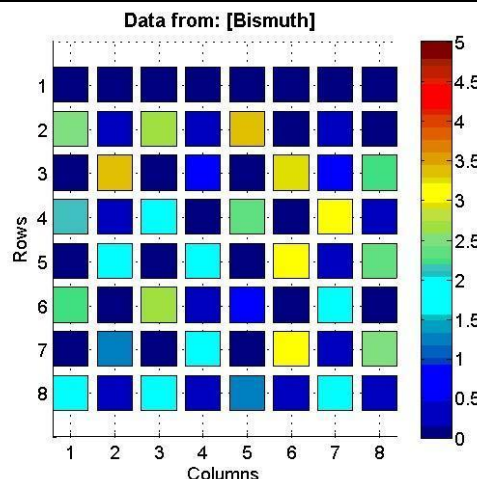


Figure 4. Photocurrent of Bismuth (III) nitrate and ammonium meta-vanadate (.05M) dissolved in 2M nitric acid when tested the first time using the SMD software. Produced most amount of photo-activity compared to the other bismuth vanadate solutions and drop-casted in Checker-board pattern.

3.2 The rapid corrosion of the BiVO₄. Although bismuth (III) nitrate added with ammonium meta-vanadate worked best among the synthesized BiVO₄, its performance dropped severely after one SEAL kit run. The same plate's activity declined incredibly fast with some visible color change from bright yellow to yellow-green (Figure 5).

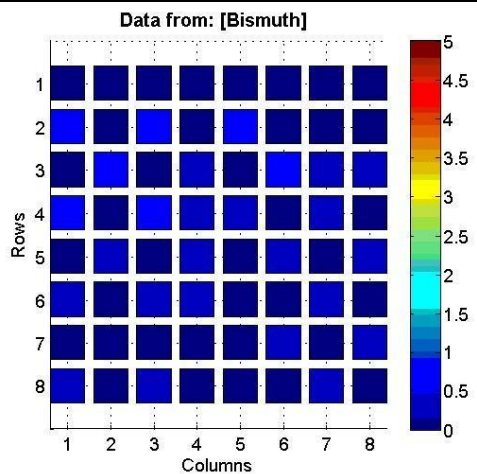


Figure 5. Photocurrent of Bismuth (III) nitrate and ammonium meta-vanadate (.05M) dissolved in 2M nitric acid when tested the second time. Severely declined amount of energy produced compared to the first trial which proved the rapid corrosion issue of the solution using the SMD software. Checker-board pattern drop-casted.

3.3 Various solvents used for the solution.

3.3.1 Mixing method. The most energy producing solvent among 2M nitric acid (Figure 6), 10% acetic acid, acetone, and acetyl-acetone for bismuth(III) nitrate and ammonium meta-vanadate was the 2M nitric acid which conducted the highest current (Figure 7). It dissolved the most and had bright yellow spots after annealing.

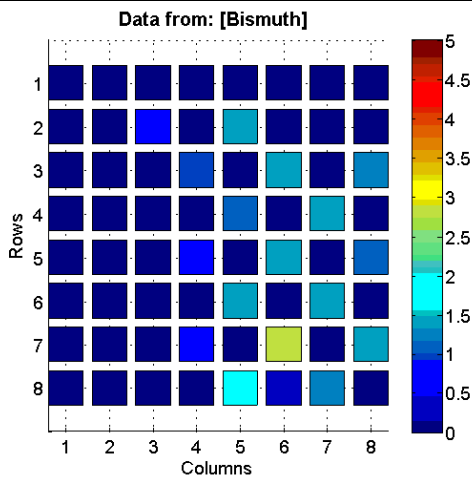


Figure 6. The photocurrent of the fourth solution drop casted on a FTO plate. Image saved from the SMD software of SEAL kit. Produced great amount of energy.

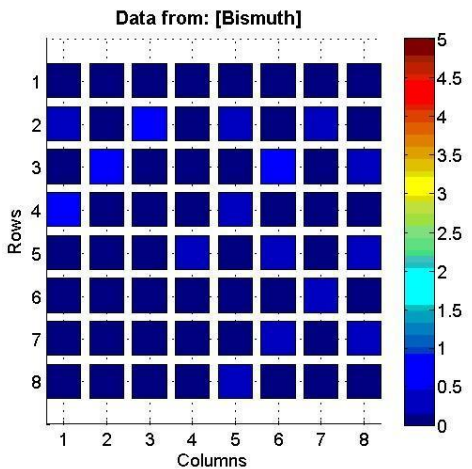


Figure 7. One full FTO plate drop casted with two different solutions: one was Bismuth (III) nitrate and ammonium meta-vanadate dissolved in acetone with water and another was dissolved in acetic acid and deionized water (both solutions had the same concentration of 0.05M). Neither one is better in conducting energy than the 2M nitric acid.

3.3.2 Spin-coating method. The various solvents with the Bismuth (III) nitrate and ammonium meta-vanadate were spin-coated as well to see if there were any difference of the performances of the photo-catalysts. The spin-coating method did not result in as much energy as the layering method did (Figure 8).

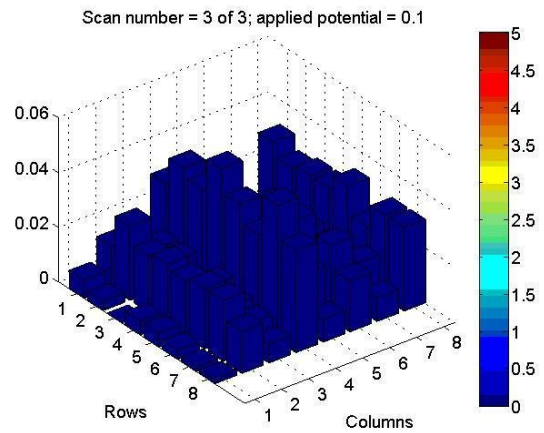


Figure 8. The photo-activity of the spin-coated bismuth (III) nitrate and ammonium meta-vanadate dissolved in acetone and water (.05M). Image from SMD. Very low activity of the solution can be also proven by the fact that the spin-coated solutions were all spotted on a half sized FTO plate. The difference between the FTO plate and the solutions are not visible in the image.

3.4 Adding metal oxides to improve performance.

3.4.1 Layering method. When cobalt, copper, iron, and nickel were layered with this fourth BiVO_4 , copper and iron improved the solution's performance by around 20% while nickel showed no improvements at all and cobalt showed very little improvements (Figure 9). The new solutions with the metal oxides like copper and iron did not corrode like the fourth solution did.

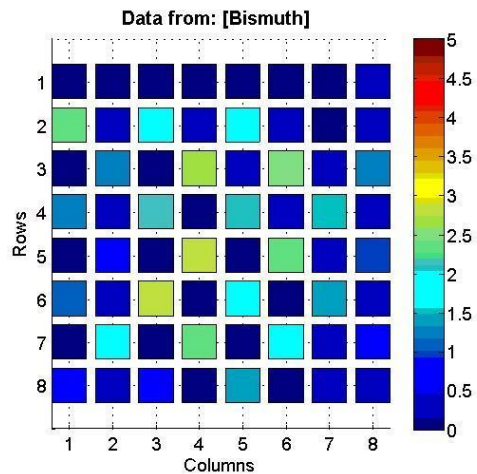


Figure 9. Photocurrent of Bismuth(III) nitrate and ammonium meta-vanadate dissolved in 2M nitric acid (.05M) layered with various metal oxides, including Co, Cu, Fe, and Ni in order (2 columns for each in order). Image from the SMD software used in the SEAL kit. Did not produce as much energy as Figure 4 but is more stable and long-lasting than Figure 4. Checker-board pattern drop-casted.

3.4.2 Mixing method. The mixing method for the metal oxides and the fourth bismuth vanadate solution worked out great. Two FTO plates were drop-casted with the mixed solutions of cobalt nitrate solution, copper nitrate solution, iron nitrate solution, and nickel nitrate solution in order (2 columns for each solution) with the BiVO_4 made like the fourth solution of BiVO_4 . Nickel produced the least amount of energy. Copper and iron oxides have the greater potentials than the other two metal oxides and the mixing method produced more energy than the layering method (Figures 10 and 11).

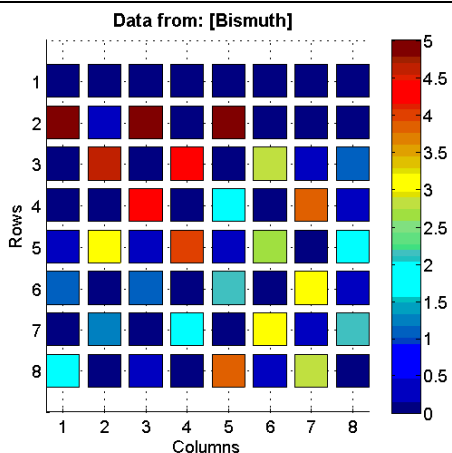


Figure 10. Photoactivity of BiVO_4 (made like the fourth solution of BiVO_4) mixed with Co, Cu, Fe, and Ni in order. Image from SMD of the SEAL kit. Copper and Iron nitrates that turn into oxides after annealing performed the best among the four metal oxides.

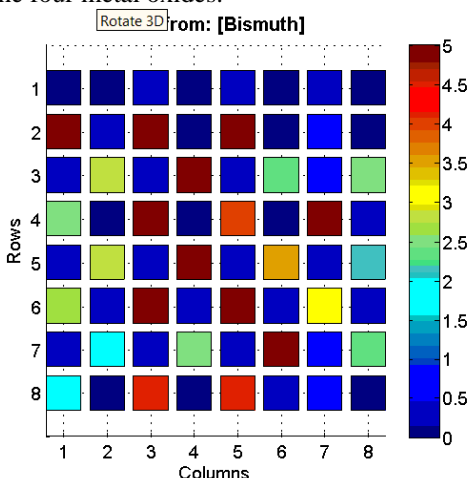


Figure 11. Same composition with Figure 10 but different plates. Similar results with Figure 10 except that its average photocurrents are higher.

4. DISCUSSION

4.1 Reasons of different results to different combinations to make BiVO_4 .

4.1.1 The Glycerol and Triton X solution's problems. Compared to the all the solutes used, bismuth(III) nitrate and ammonium meta-vanadate were combined to form the photo-catalyst with the highest current. Glycerol with

bismuth vanadium oxide was not active due to the high viscosity of the glycerol which disabled the solute (bismuth vanadium oxide) to completely dissolve in the solvent (glycerol). Triton X's low surface tension made the spot-casting difficult and the spots uneven, which resulted a low activity graph from the SEAL kit.

4.1.2 Sodium meta-vanadate. The sodium meta-vanadate dissolved in deionized water conducted lower energy than expected even with copper, cobalt, and nickel added. This was because of the fact that the sodium meta-vanadate with bismuth (III) nitrate leaves some sodium in the spots even after the annealing process.

4.1.3 Ammonium meta-vanadate. Despite that, the ammonium in the ammonium meta-vanadate is volatile and eventually leaves only bismuth vanadate in the spots after the annealing process. The change in color of the spots from yellow to green-yellow affected the activity of the spots greatly, so we first wondered if we had some chemicals left in the solution that might have made something new rather than bismuth vanadate.

4.1.3.1 SEM and EDS. By using one of the best (bismuth (III) nitrate and ammonium meta-vanadate mixed in 2M nitric acid) spot-casted plate that was tested twice and proving that the activity declined significantly after the first trial, the SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive X-Ray Spectroscopy) analysis helped us figure out that the spot-casted solution that was tested was bismuth vanadate with no ammonium in it (Figure 12). The elemental ratio of bismuth to vanadium found from the elemental composition found by the EDS was 1:1. The ammonium in the ammonium meta-vanadate became volatile and not shown in the EDS analysis because at the annealing process as discussed previously, the ammonium evaporated out from the solution into the air. This proved that the correct bismuth vanadate solution was producing maximum photocurrent during the first trial only, so the quick corrosion of bismuth vanadate was due to the reaction with the electrolyte (0.1M NaOH) which caused the dark current to remain high and unstable.

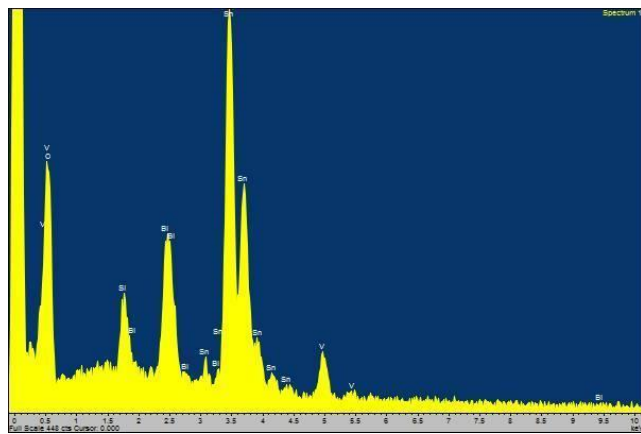


Figure 12. The picture of the EDS analysis work on the electron composition. (Other electrons beside the Bi, V, and O were from the carbon tape and FTO plate used)

4.2 Metal Oxides with BiVO₄. Metal oxides like copper and iron improved the photo-activity of the catalyst (BiVO₄) and reduced the sudden decrease in the activity as well because the metal oxides made the oxygen evolution available.^[7]

5. CONCLUSION

The bismuth (III) nitrate with ammonium meta-vanadate dissolved in 2M nitric acid conducted high photocurrents as a BiVO₄. However, it corroded very quickly after one scan performance with the SEAL kit. The annealed bright yellow spots of BiVO₄ turned into neon green after the spots contacted with 0.1M of NaOH, the electrolyte used to scan the spots with the SEAL kit. By mixing copper nitrate solution and iron nitrate solution with BiVO₄ separately, the performance of BiVO₄ with the metal oxides improved by 20% and became more stable. The reason why BiVO₄ corrodes so quickly can be further investigated by using different salts and electrolytes. Also, various methods like changing the order of layering can be further discovered and tested to see the difference in the order of layering.

6. ACKNOWLEDGMENT

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