

Testing the Photocurrent of Earth-Abundant Mixed Metal Oxides for Solar-Driven Water Oxidation.

Angelina Ye^{*1}, Samuel R. LeFevre², Eamon Patamasing²

¹Northwood High School with Concordia SEAL, Concordia University, Concordia, Irvine, California 92612, United States

²Crescenta Valley High School, Community Ave, La Crescenta, California 91214, United States

ABSTRACT: To affordably utilize sunlight as a renewable energy source, earth-abundant metal oxides are needed as photoanodes for photoelectrochemical water splitting. However, since individual metal oxides have not performed well in previous tests, this experiment focused on various mixed metal oxides in different ratios. Using the Solar Energy Activity Laboratory apparatus, the prepared materials were analyzed in terms of the photocurrent produced when illuminated with visible light-emitting LEDs in a two-electrode system. The experimental data demonstrated that bismuth vanadate had the highest photoactivity when cobalt(II) oxide was layered on top to act as a catalyst. It was also seen that lanthanum(III) oxide increased the photoactivity of iron(III) oxide. Other metal oxide combinations and ratios tested resulted in lower photoactivity, suggesting that specific mixed metal ratios are necessary for larger photocurrent. The high results from the bismuth vanadate and cobalt oxide indicate that an additional catalyst may be necessary or at least better than a metal oxide semiconductor alone.

1. INTRODUCTION

Atmospheric CO₂ is quickly rising to potentially concerning levels due to the current rates of fossil fuel consumption.¹ As such, alternative renewable energy resources are necessary, and solar energy is attractive because of its abundant availability.¹⁻³ Though solar panels have been developed and distributed internationally, their lack of energy storage limits solar-powered electricity usage to times when the sun is out, which can be less than 12 hours even in sunny areas.¹ To create a constant solar energy source, photocatalytic water splitting can be used to store solar energy in chemical bonds via the production of hydrogen fuel (H₂) and environmentally-friendly oxygen gas (O₂).¹⁻⁵ However, the current challenge for photocatalytic water splitting lies in the need for cost-efficient photoelectrodes and catalysts to effectively produce enough hydrogen fuel to meet the world's energy demand.^{1,2}

The approach taken in this experiment for solar-driven water splitting was based on a photoelectrochemical (PEC) device, where the semiconductor is directly in contact with the electrolyte. The charge carriers produced from sunlight on the semiconductor move to the semiconductor-electrolyte interface before traveling to the hydrogen- or oxygen-evolution catalyst, which ultimately splits water through a redox reaction.⁴

Earth-abundant metal oxide semiconductors with sufficiently energetic charge carriers are good potential photoelectrodes, particularly as photoanodes because of their cost-effective stability in oxygen evolution.³ Specifically, hematite (α -Fe₂O₃) has been studied for its optimal band gap of 2-2.2 eV and high photoactivity, however its short hole lifetime and carrier recombination in hematite photoanodes cause a high overpotential that prevents it from being a viable material for water splitting due to its inefficiency.^{5,6} Bismuth vanadate (BiVO₄) has also been tested due to its light absorption

properties,⁷ as well as the highly catalytic cobalt oxide that works well on top of a semiconductor photoanode.^{8,9} However, mixed metal oxides are more promising in terms of photoanodes compared to individual metal oxides, because of their combination of metal oxides with different properties (e.g. light absorption and catalytic ability).¹⁰

The Solar Energy Activity Laboratory (SEAL) apparatus tests for photoanode semiconductors by analyzing the photocurrent produced (Figure 1).¹¹ For this research, the SEAL kit will be used to test various mixtures and ratios of metal oxides such as bismuth vanadate, cobalt(II) oxide, iron(III) oxide, lanthanum(III) oxide, and other transition metal oxides. The objective of this research is to analyze the effects of mixing metal oxides on their ability to produce photocurrent when irradiated with artificial sunlight in the form of LEDs.

2. EXPERIMENTAL SECTION

2.1. Preparation and Testing of Metal Oxides

To create the metal oxides, metal nitrate salts were dissolved in deionized water to a 0.1 molarity (with the exception of iron(III) nitrate and ammonium metavanadate). These solutions were drop casted in a checkerboard fashion (Figure 2) as 10 μ L spots onto 3-inch square ozone-cleaned fluorine-doped tin oxide (FTO) coated glass plates with a 20 or 100 microliter pipette. The plates were then placed on a hot plate to dry before being annealed with an Evenheat Set-Pro kiln at 500 °C to convert the metal nitrates to metal oxides.

To create the electrode, about 0.5 inches were stripped off of the ends of an insulated copper wire approximately 4 inches long. One end was then adhered to the top right corner of the plate with a strip of copper tape, which was then covered with 5-minute epoxy.

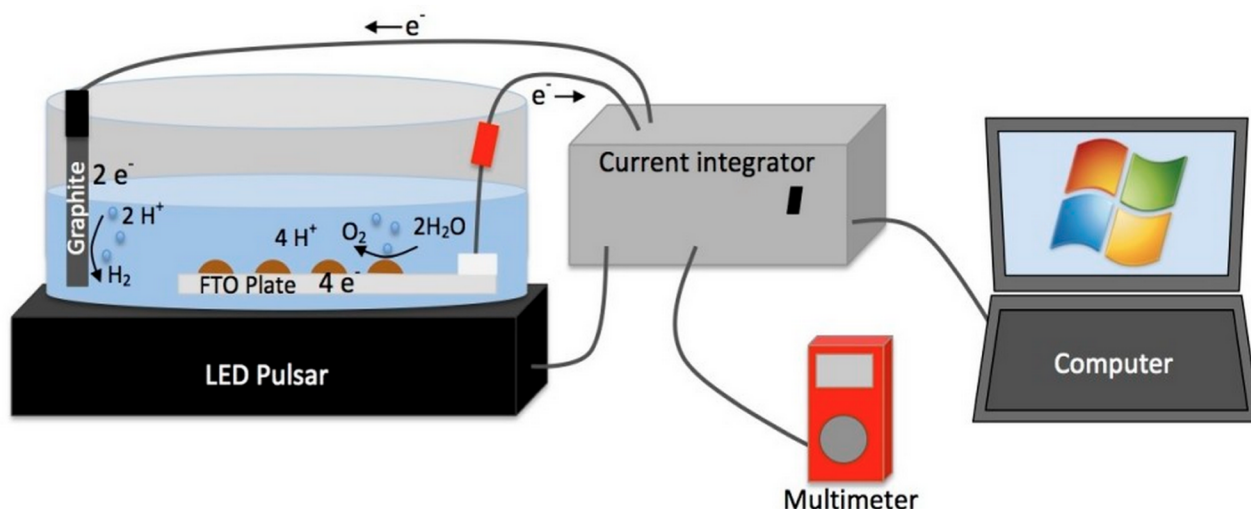


Figure 1. The SEAL kit while testing (SMD program not shown)¹².

After the epoxy dried, the electrode was placed into a glass crystallization dish and covered with 0.1 M NaOH solution. A graphite rod was taped to the side of the dish. After turning on the current integrator and the Solar Materials Discovery (SMD) computer program, the exposed wire attached to the plate was then connected to the working electrode from the integrator while the counter electrode was clipped to the graphite rod. With a forward bias of 0.100 V and a dark current less than 0.5 V, the SEAL apparatus was set to perform a 3-cycle scan. When scanning, the metal oxides were illuminated with LED pulses (OVLEW1CB9, Optek Technology, Inc.) lasting 100 ms to produce photocurrent detected by the current integrator.

by dissolving 2.02 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 25 mL of water. Similarly, the 0.1 M cobalt(II) nitrate solution was created through diluting a 0.2 M solution consisting of 1.46 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 25 mL of water. The 0.1 M bismuth nitrate solution consisted of 1.21 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 2 mL of 2 M nitric acid and enough water for a 25 mL solution. The 0.05 M ammonium metavanadate solution was made of 0.15 g NH_4VO_3 in 25 mL of water while the 0.1 M ammonium metavanadate solution was prepared with 0.29 g NH_4VO_3 in 25 mL of water. The 0.1 M zinc nitrate solution was obtained by dissolving 0.38 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20 mL of water. The 0.2 M lanthanum(III) nitrate solution was created by dissolving 0.43 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 5 mL of water.

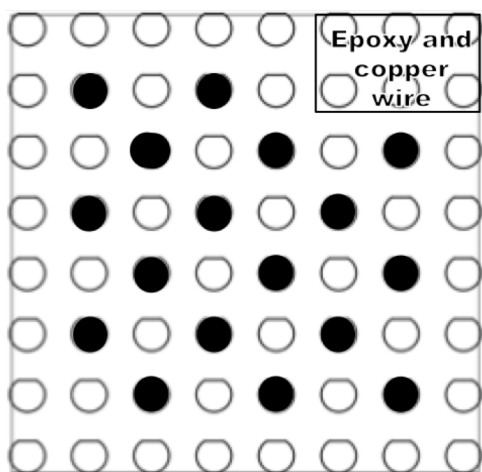


Figure 2. The pattern used to spot the FTO plates with 10 μL of metal nitrate/sulfate solution.

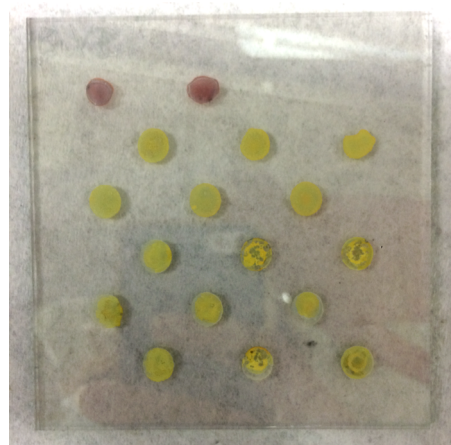


Figure 3. FTO plate with 0.1 M bismuth vanadate (yellow) and 0.05 M iron oxide control spots (red).

2.2. Preparation of Metal Nitrate Solutions

The 0.05 M iron(III) nitrate solution was prepared by diluting a previously made 0.2 M iron(III) nitrate solution, which was made

2.3 Preparation of Metal Oxides.

The different metal oxide combinations used were iron(III) oxide, iron(III) oxide mixed with 1% lanthanum(III) oxide by volume, bismuth vanadate with bismuth and vanadium in a 1:1 ratio, bis-

mium vanadate with bismuth and vanadium in a 2:8 ratio, bismuth vanadate mixed with cobalt(II) oxide in varying concentrations, 1:1 bismuth vanadate with cobalt(II) oxide layered on top, 2:8 bismuth vanadate with cobalt(II) oxide layered on top, 2:8 bismuth vanadate with zinc oxide made with zinc sulfate layered on top, and 2:8 bismuth vanadate with zinc oxide made with zinc nitrate layered on top.

Unless otherwise specified, the amount of metal oxide layered on top of bismuth vanadate was 5 μL .

3. RESULTS

3.1. Individual Metal Oxides

For the iron oxide, the highest photocurrent was 1.27 μA , produced by the spots made with 0.05 M iron(III) nitrate, which appeared solid, rust-red. However, the iron oxide control spots made with the same solution on other plates usually did not go past 1 μA .

The highest bismuth vanadate photocurrent with a 1:1 ratio of bismuth nitrate and ammonium metavanadate was 7.33 μA . The more time that passed after the bismuth nitrate and ammonium metavanadate solutions were made, the lower the photocurrent of the bismuth vanadate created with the solutions, ending up with photocurrent around 2 μA . Replacing the solutions only resulted in 2.94 μA when in a 1:1 ratio, but the new solutions in a 2:8 ratio of bismuth nitrate and ammonium metavanadate resulted in 7.44 μA (Table 1).

Table 1. Photocurrent of different ratios of bismuth nitrate and ammonium metavanadate.

$\text{Bi}(\text{NO}_3)_3:\text{NH}_4\text{VO}_3$ (μL)	Photocurrent (μA)
8:2	0.83
6:4	2.08
5:5	2.94
4:6	5.61
2:8	7.44

3.2. Iron oxide with lanthanum oxide

Mixing iron oxide with 1% of lanthanum oxide helped improve the photocurrent. For the specific plate, the iron oxide with 1% lanthanum oxide produced 1.11 μA , while iron oxide alone had 0.86 μA .

Table 2. Photocurrent of different amounts of cobalt(II) oxide with bismuth vanadate

Percent of CoO	Photocurrent (μA)
0% CoO	0.62
1% CoO	2.01
10% CoO	4.37
20% CoO	5.27
30% CoO	5.99
40% CoO	6.30

3.3. Bismuth Vanadate and Cobalt Oxide

For mixing bismuth vanadate and cobalt oxide, the highest photocurrent was produced by 40% cobalt oxide (Table 2). However, the photocurrent varied extremely depending on how old the bismuth vanadate was and how well it was made. The photocurrent for cobalt oxide layered on bismuth vanadate changed based on the microliters of cobalt(II) nitrate drop casted on top of 10 μL of bismuth vanadate. The largest photocurrent was produced by lower amounts of cobalt oxide on top (Table 3). Layering created higher photocurrent compared to mixing (Table 4).

Table 3. Photocurrent for different amount of cobalt(II) nitrate on top of bismuth vanadate.

Amount of $\text{Co}(\text{NO}_3)_2$ (μL)	Photocurrent (μA)
0	8.19
1	7.12
2	6.49
3	4.25
4	3.55
5	4.20

Table 4. Photocurrent for different preparation of cobalt(II) nitrate with bismuth vanadate

Preparation method	Photocurrent (μA)
Layered	6.05
Mixed	1.19
BiVO_4	5.23

3.4. Bismuth Vanadate and Others

Zinc sulfate spotted on top of bismuth vanadate produced higher photocurrent than zinc nitrate spotted on top of bismuth vanadate; 7.20 μA compared to 3.12 μA . The spots with zinc sulfate actually performed better than the bismuth vanadate spotted on the same plate (Table 5).

Table 3. Photocurrent for different solutions of zinc layered on top of bismuth vanadate.

Solution spotted on BiVO_4	Photocurrent (μA)
ZnSO_4	7.20
$\text{Zn}(\text{NO}_3)_2$	3.12
BiVO_4 alone	4.13

4. DISCUSSION

4.1. Iron Oxide and Iron Oxide with Lanthanum Oxide

The iron oxide performed worse than expected; iron oxide has been known to produce a photocurrent of around 1.5 μA when the

spot appears a solid rust-red color, as the spots tested appeared. This may have been because of the SEAL kit, however this is unlikely since it detected the high photocurrent from bismuth vanadate. Thus, the problem with the iron oxide may have been from the iron(III) nitrate solution, but this is currently unknown.

For the lanthanum oxide-iron oxide combination, lanthanum oxide seems to improve the photoactivity of iron oxide, but it does not increase the photocurrent drastically. Also, since lanthanum is a rather expensive element further down the periodic table, it does not seem conducive to a cheap metal oxide semiconductor.

4.2. Bismuth Vanadate

The bismuth vanadate was incredibly inconsistent in terms of performance over time. A week after making the bismuth nitrate and ammonium metavanadate solutions, the bismuth vanadate made with the solutions had dramatically lower photocurrent uncharacteristic of bismuth vanadate (Figure 4) that was partly fixed by the creation of new solutions. However, the new solutions still did not meet the original photocurrent of the first plate of bismuth vana-

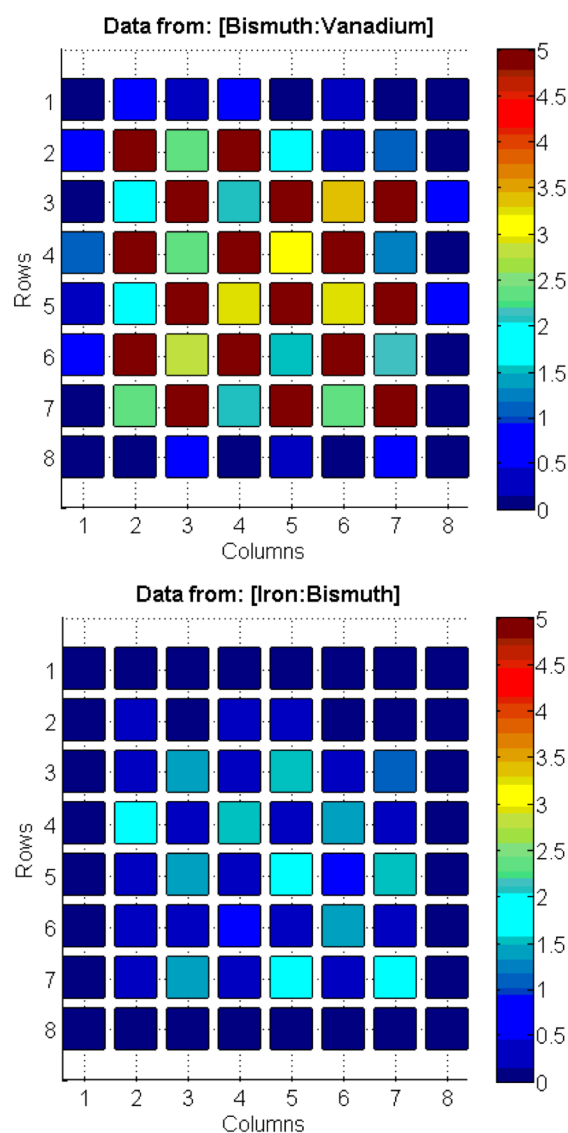


Figure 4. Comparison between bismuth vanadate plate after the solutions were newly made (top) and after a week (bottom).

date. This either could have been the result of the SEAL apparatus breaking after the first plates of bismuth vanadate, or it could be from the metal salts gaining too many impurities. Even with the 2:8 bismuth nitrate to ammonium metavanadate ratio, the photocurrent of the new bismuth vanadate could barely match that of the first plate, meaning that the other results with the new bismuth vanadate may not be entirely accurate.

4.3. Bismuth Vanadate with Cobalt Oxide

The use of cobalt oxide fulfills the catalyst that is typically used with the photoanode for solar-driven water splitting. However, whether layering cobalt oxide on top of bismuth vanadate increases the photocurrent cannot be completely determined because of the fluctuating photoactivity of the bismuth vanadate. In some cases, especially with the low photoactive bismuth vanadate, layering and mixing cobalt oxide with bismuth vanadate performed much better than bismuth vanadate alone. Yet with the 2:8 ratio of bismuth nitrate and ammonium metavanadate, this was not always the case. For most plates, layering cobalt oxide on top of dried bismuth vanadate spots before annealing typically produced larger photocurrent than mixing cobalt oxide and bismuth vanadate, most likely because it used the semiconductor-catalyst model for photoanodes.

Since cobalt oxide is a known oxygen evolution catalyst, the high photocurrent was expected. However, since bismuth vanadate is the light-absorbing semiconductor, it is still a necessary component of the photoanode in order to absorb enough light to bypass the band gap and pass its electrons to the catalyst, which in this case is cobalt oxide. The 40% combination may have shown the best ratio of catalyst and semiconductor when mixed together, while the best layering combination has yet to be found. Tests with the Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization (HARPOON) illustrated that while bismuth vanadate does well absorbing visible light, cobalt oxide is the material that actually completes the water splitting redox half-reaction to produce oxygen and bismuth vanadate does not contribute much in that aspect. With UV light, cobalt oxide is more optimal material for water splitting, but since UV light is only a small fraction of sunlight, the majority of solar energy is not utilized. Because of this, bismuth vanadate is still a crucial part of the photoanode.

4.4 Bismuth Vanadate and Others

Bismuth vanadate had high photocurrent when zinc oxide was spotted on top of it, which could have been because the zinc oxide acted as an oxygen evolution catalyst for bismuth vanadate. But the difference between zinc sulfate and zinc nitrate illustrated the importance solutions make on the final metal oxide. This could possibly mean that the final spots may not be only the metal oxide desired, but with many impurities that can make an extremely large difference on the photocurrent, potentially to the point where it is doubled, as seen with the zinc sulfate and zinc nitrate comparison.

ASSOCIATED CONTENT

Supporting Information

Details of making and testing metal oxides and mixed/layered metal oxides, photoanode semiconductors, water oxidation catalysts, the SEAL kit. This material is available free of charge via the Internet at <http://thesolararmy.org>.

AUTHOR INFORMATION

Corresponding Author

*angelinaye1217@gmail.com

Author Contributions

E. Patamasing and S. R. LeFevre contributed equally to the creation of this work.

Notes

The author declares no competing financial interest.

ACKNOWLEDGMENT

We thank Prof. Harry Gray and California Institute of Technology for funding and providing a laboratory for this research. We also thank Michelle DeBoever and Allison Moore for supporting this research. This work was supported by the National Science Foundation (NSF) through the CCI Solar Fuels Outreach Program (CHE-1305124).

ABBREVIATIONS

SEAL, Solar Energy Activity Laboratory.

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