

Testing for Photoactivity of Different Combinations of Metal Oxides for Water Oxidation

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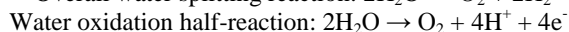
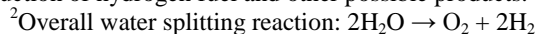
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ABSTRACT: Because of the detrimental effects of fossil fuels on the environment, metal oxides are a viable option for using visible light to catalyze a reaction for water-splitting. One of the main problems of finding these alternative energy sources is that they must be cost-efficient and effective. Homogenous mixtures and differing combinations of common metal oxides, specifically Fe₂O₃ and BiVO₄, were explored to determine if the mixtures complement each other and help increase their photoactivity. Different parameters were tested to determine which spotting technique worked best and which metal oxide was a better catalyst for the water oxidation reaction through the use of the SEAL (Solar Energy Activity Lab) kit. This kit measures the photocurrent of each metal oxide by submerging plates spotted with metal oxides in an electrolytic solution and illuminating them with light-emitting diode (LED) lights to replicate visible light from sunlight. Through this research, different ratios and combinations of metal oxides were shown to help increase photoactivity and catalyze water oxidation.

1. INTRODUCTION

Solar fuels have been a highly researched topic because of greenhouse gases that are raising the Earth's average surface temperature and disrupting normal ecological patterns.¹ Each passing year, energy consumption increases as does the world population.⁶ Because of today's energy dependent society, finding alternative energy sources, such as the sun, is a pressing issue that warrants further research. Some of the main benefits in converting the sun's power to chemical energy is its abundance and accessibility. In fact, all the energy used in a year is less than the amount of energy produced by the sun in one hour¹, making it reasonable to tap into this source to replace and limit CO₂ emissions. Currently, solar panels are gaining popularity, but they are limited to only sunny days and can only be useful during daylight.

One solution is to use the photocatalytic ability of certain metal oxides to accelerate the water oxidation reaction. To test the photoactivity of the metal oxides, the SEAL kit shines LED lights to duplicate visible light from the sun. When the metal oxide spots are illuminated by the LED lights, they catalyze water-splitting where protons, electrons, oxygen, and hydrogen gas are produced. This reaction can allow the production of hydrogen fuel and other possible products.



The SEAL kit operates by measuring the photocurrent produced by the metal oxide when electrons are released in the electrolytic solution. When a strong photocurrent is measured by the program, it suggests that the specified metal oxide can be used as a potential catalyst for water-splitting.

Although metal oxides are a promising start, by themselves they are limited and lack crucial elements to make

them efficient. Doping metals has been found to be successful because the impurities change the band gap, augmenting the photoactivity of the metal itself. In an effort to replicate this procedure, metals were paired together and mixed in differing ratios to see how the overall activity could be improved. Several techniques were tested to improve the procedure of spotting metal oxides, such as identifying the importance of surface area, methods of drying the metal solutions, and different spotting patterns. For example, samples were compared to see if mixing the solutions of the different metals in their aqueous form before drying or creating layers changed photoactivity. Colors and wavelengths of the metals were taken into account in order to improve the efficiency. Because BiVO₄ spots took a while to lower the dark current to below 0.5 V, CoO was layered on top for its characteristic dark color to absorb the light. Mixed metal oxides and improved spotting techniques proved to be promising in finding a reliable photocatalyst.

2. MATERIALS AND METHODS

2.1 Creating Fe₂O₃ and BiVO₄ Standards

In order to protect the integrity of the samples being tested on a plate, a control was needed to prove the catalytic potential of the sample in a relative setting because of the control's known effectiveness. Fe₂O₃ has a small band gap³ at around 2.18 eV,⁴ making it a logical control to begin with. Solutions of 0.25 M, 0.2 M, 0.1 M, and 0.05 M were created with Fe(NO₃)₃, and Fe₂O₃ can easily crystallize if dried too fast, so the FTO plates with Fe₂O₃ were dried at a temperature of 40 °C on a hot plate. Before the use of the ozone cleaner, glycerol was used with 10% by volume.

For BiVO₄, 0.1 M solutions of Bi(NO₃)₃ and NH₄VO₃ were mixed in equal volumes, and the orange BiVO₃

precipitate formed. The plate was put into the kiln at 500 °C for 3 hours, and the oxide form BiVO_4 was created. The high photoactivity of BiVO_4 , with a band gap of 2.4 eV,⁵ caused the resting dark current in the NaOH solution to be well above 0.5 μA prior to testing. After continued tests of negative results with BiVO_4 made of equal volumes of 0.1 M $\text{Bi}(\text{NO}_3)_3$ and 0.05 M NH_4VO_3 , a new 0.1 M $\text{Bi}(\text{NO}_3)_3$ was created with mild success. Different ratios of 0.1 M $\text{Bi}(\text{NO}_3)_3$ and 0.05 M NH_4VO_3 were tested. A cardboard box was placed on top of the kit in order to lower the dark current.

2.2 Cleaning Plates: Ozone Cleaner

A vinyl template that had the same pattern as the grid of LED lights on the SEAL kit was placed on top of a plate cleaned with deionized water, acetone, and isopropyl alcohol. Droplets of water helped stick the template to the plate, and the plate was placed in the ozone cleaner for 10 minutes to ensure a thorough cleaning. The ozone cleaner was used to help create an even layer of metal oxides by making the surface hydrophilic prior to spotting the plates with the solutions. The ozone cleaner consisted of a UV lamp where the UV rays reacted with oxygen to create ozone which interacted with the impurities on the plate that made it hydrophobic. When the microscopic dirt was removed from the plate, the plate became hydrophilic. The holes on where the LED lights should illuminate were exposed to the ozone and became hydrophilic, but the portions not exposed remained hydrophobic. When spotting the metal solutions onto the plate after the cleaning, more reliable circles were created and the accumulation of the salts on the outer rings of the spots were reduced. This allowed the LED to shine directly onto a uniform layer of metal oxide rather than an uneven one.

2.3 Drying Techniques

In order to avoid crystallization of the metal salt solutions, samples were dried on the hot plate at 40 °C. Ribbed structures were produced from crystallization because of incorrect drying procedures. Mixing the metals before spotting or spotting one metal then pipetting the other on top after drying were compared. In most experiments with BiVO_4 being tested, 10 μL of BiVO_4 was pipetted first, let dry at 40 °C, and 5 μL of the secondary metal was spotted on top with another drying time before being placed in the kiln.

2.4 Spotting Plates and Testing Plates

A variety of 0.1 M solutions of transition metals (most in the first row of transition metals or period 4 on the periodic table) were tested. On plates where BiVO_4 was paired with another metal, separate layering with drying times in between were applied. When homogenous mixtures were created, the salt solutions were mixed together in a well with a pipette tip, then spotted with a micropipette. Most plates were in the following

checkerboard pattern:

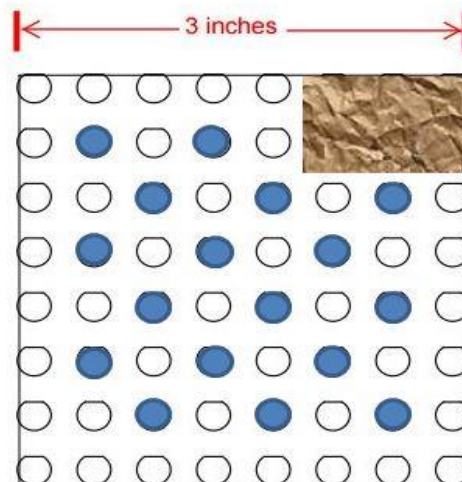
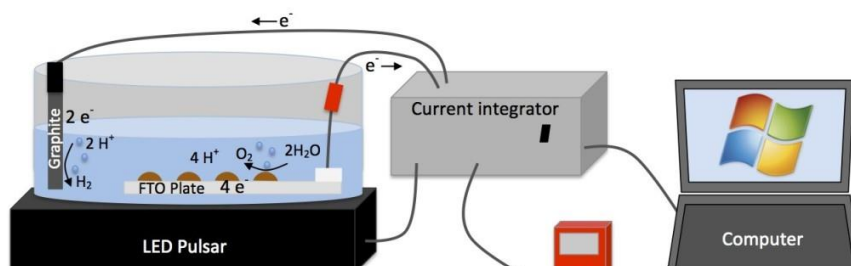


Figure 3: The blue spots represent the checkerboard pattern the metal solutions were spotted on after being treated in the ozone cleaner. The rectangle on the upper-right corner represents the insulated wire covered in copper tape and epoxy.

After being spotted with the metal, the plates were kilned at 500 °C for 3 hours. This kilning process annealed the spots onto the plate and created the oxide form of the metals. A piece of insulated wire, with their ends removed, was attached to a kilned plate by adhesive copper tape. Then, 5 minute epoxy was placed on the copper tape, making sure none of the tape was exposed. After drying for 5-10 minutes, the finished plate was placed in a crystallizing dish on top of the LED pulsar array unit and covered with 0.1 M NaOH. A graphite rod (acting as the counter electrode) was connected and placed in the electrolyte. The current integrator unit's alligator clips were attached to the exposed wire on the plate and the graphite rod. A voltage of 0.1 μA was applied to the solution by the integrator unit, and the plate was not tested until the dark current was below 0.5 μA (for most of the tests, plates were all ran at around 0.3 μA). The Solar Materials Discovery (SMD) software measured the photocurrent of the metal samples.



3. RESULTS

3.1 Mixed Metals of BiVO₄

3.1.1 BiVO₄ and CoO

On the first plate testing BiVO₄ and CoO, 0.1 M BiVO₄ and Co(NO₃)₂ were spotted. After testing, the average photoactivity of the 8 μL BiVO₄: 2 μL CoO was 7.52 μA whereas the 8.5 μL BiVO₄: 1.5 μL CoO was slightly lower with 7.50 μA. For the same pattern, BiVO₄ and Cr₂O₃ had average values of 3.36 μA and 2.72 μA respectively. BiVO₄ alone had an average value of 3.69 μA, a much lower value than the mixed metals of BiVO₄ and CoO (Figure 4). Drying methods were explored for BiVO₄ and CoO, and the most positive results were when Co(NO₃)₂ was spotted on top of already dry BiVO₄. Varied ratios of BiVO₄ and CoO were tested with 1%, 10%, 20%, 30%, and 40% of 0.1 M solutions of Co(NO₃)₂ with BiVO₄. The general trend was that as the percentage of CoO increased. The photoactivity increased as well, with 40% CoO having the highest average with 6.30 μA. More ratios were tested with 40%, 50%, 60%, 70% and 80% CoO. As the percentage of CoO increased, the spot's photoactivity decreased where 40% had an average value of 2.87 μA and 80% had an average value of 0.59 μA (Figure 5). The plate with the higher ratios was tested on the Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization (HARPOON) kit. The highest levels of oxygen evolution were found at 80% CoO.

3.1.2 BiVO₄ and ZnO

For the first plate studying layering of BiVO₄ and ZnO, 10 μL of BiVO₄ was dried and 5 μL of 0.1 M solutions of Zn(NO₃)₂ and ZnSO₄. The two different salts of zinc were used to see if being a sulfate or nitrate changed its photoactivity. After kilning, the zinc spots were clear and were similar looking to the normal BiVO₄ spots. Unlike the BiVO₄ and CoO, it took a while to lower the dark current and required a cardboard box to cover the kit. ZnSO₄ performed the best (even better than BiVO₄) with an average value of 7.20 μA and Zn(NO₃)₂ had an average value of 3.12 μA (See Figure 6 for results). When the experiment was repeated, the nitrate form reacted better than the sulfate form, which made the difference between the two salts inconclusive.

3.2 Mixed Metals of Fe₂O₃

3.2.1 0.2 M Solutions of Fe(NO₃)₃ and Co(NO₃)₂

CoO spots were noticed to change into a dark black color while Fe₂O₃ crystallized, creating hematite. When placed in NaOH, the iron spots flaked away, making them unusable for testing. Metals created separate layers because they were not mixed beforehand but rather spotted on top of each other. All iron-cobalt spots were relatively the same value at 0.44 μA, slightly lower than the iron standard spots at 0.61 μA (See Figure 7 for results). When the experiment was repeated with the two metals mixed, prior to spotting, results remained the same.

3.2.2 0.2 M Fe(NO₃)₃, CrCl₃, and Co(NO₃)₂

After kilning, all spots came with high crystallization making them flake off into the solution. Cr₂O₃ had a green-silver tinge and CoO had a black color. All results were highly negative

with the average value being 0.24 μA while the iron standard had an average value of 0.71 μA (See Figure 8 for results).

3.2.4 0.05 M Fe(NO₃)₃ and 0.05 M La(NO₃)₃

Because doping metals with lanthanum proved successful for other researchers, 0.05 M Fe(NO₃)₃ and 0.05 M La(NO₃)₃ were mixed. 10% lanthanum was compared with 1%. Hematite formation was found on the edges of the spots but not the center after the kilning process. Lanthanum spots were translucent and had no effect on the color of iron. The average value for 10% lanthanum was 0.16 μA, while the average value for 1% was 1.11 μA. The 1% lanthanum produced better results than the iron standard with an average value of 0.86 μA (See Figure 9 for results).

3.3 Standard Solutions

3.3.1 Fe₂O₃ Standard

The 0.05 M solution was found to be the most effective. The 0.2 M and 0.25 M solutions crystallized into hematite easily, making them unusable for testing as the salt flaked away into the 0.1 M NaOH solution. These solutions also did not dry in a reasonable amount of time, sometimes taking days to complete. Solutions of 0.1 M and 0.05 M were most effective, with 0.05 M drying the fastest and consistently producing the least crystallized version of Fe₂O₃. After testing, the best results showed a photocurrent in the 1.5 - 2 μA range (Figure 1). The use of 10% by volume of glycerol helped produce thick spots that were suitable for testing, but the results were overall very negative, making glycerol an unreliable option.

3.3.2 BiVO₄ Standard

For the 0.1 M solutions of Bi(NO₃)₃ and NH₄VO₃, the average photocurrent was 7.33 μA (Figure 2). After many tests where BiVO₄ performed abnormally weak, the 0.1 M NH₄VO₃ solution was thought to be contaminated with V₂O₅ and was purified (with its concentration decreased down to 0.05 M). 2 μL of Bi(NO₃)₃ combined with 8 μL NH₄VO₃ was the most photoactive, with its photocurrent at the normal 6 - 8 μA range. Because of how photoactive BiVO₄ was, it would react in the ambient light which would make the dark current way above the recommended 0.5 μA.

3.4 Ozone Cleaner

The FTO plates were placed in the ozone cleaner for 10 minutes prior to spotting the metal solutions. More reliable circles were created and the accumulation of the salts on the outer rings of the spots were reduced. This allowed the LED to shine directly onto a uniform layer of metal oxide rather than an uneven one. The longer the plate remained in the cleaner, the more circular the spots turned out.

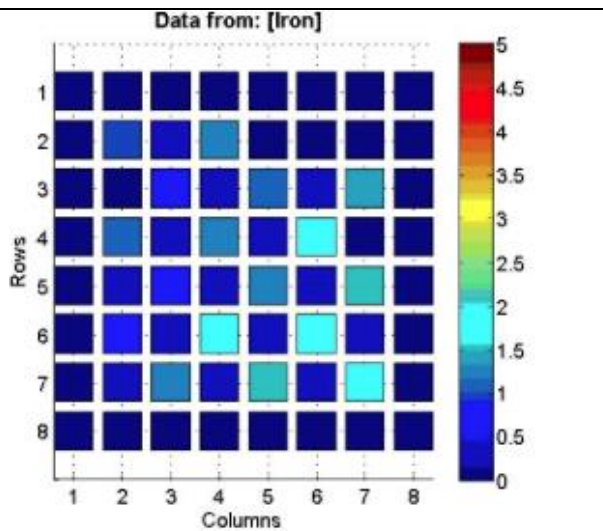


Figure 1: 0.05 M $\text{Fe}(\text{NO}_3)_3$ was spotted in a checkerboard pattern. Light blue squares indicate photocurrent at those spots is 1.5 - 2 μA .

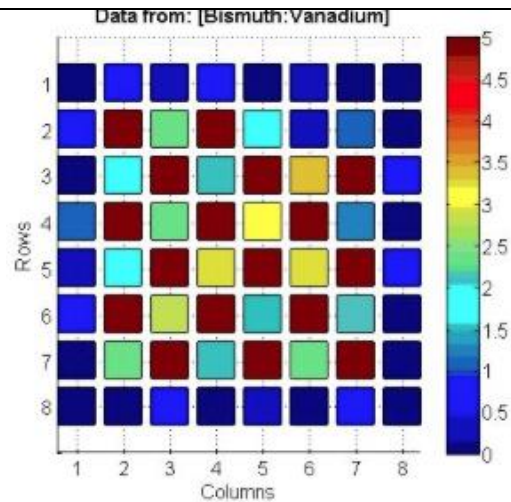


Figure 2: 0.1 M solutions of $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 were mixed in wells and 10 μL of this mixture was spotted on the FTO plate in a checkerboard pattern. The dark red squares represent an average photocurrent of 7.33 μA , indicating high photoactivity.

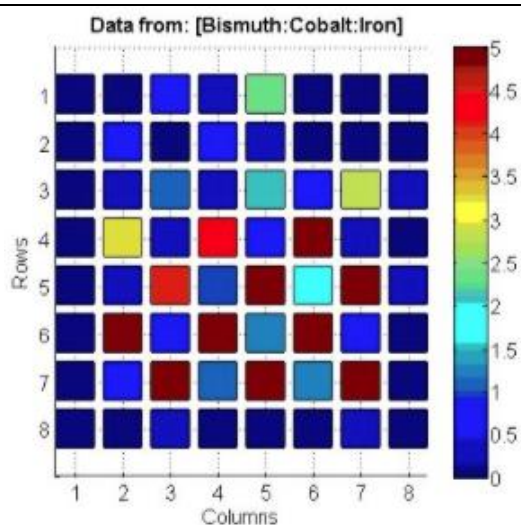


Figure 4: Row 2 consisted of 2 spots of the 0.1 M $\text{Fe}(\text{NO}_3)_3$ standard. Row 3 was made of 1% $\text{Co}(\text{NO}_3)_2$ and the consecutive rows were made up of 10%, 20%, 30%, and 40%. The scale on the right represents the measured photocurrent.

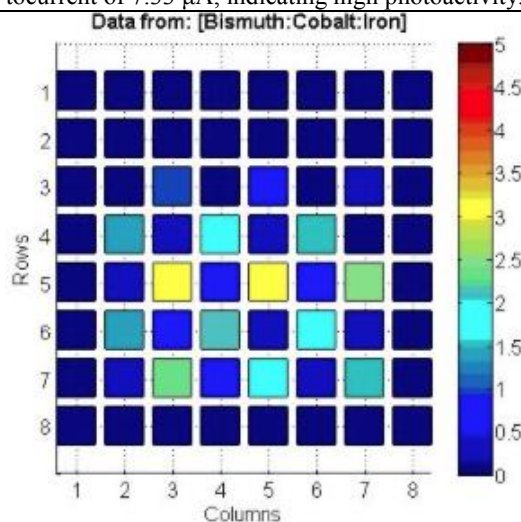


Figure 5: Row 2 consisted of the 0.05 M $\text{Fe}(\text{NO}_3)_3$ standard. The consecutive rows were made of 20%, 40%, 60%, and 80% CoO , respectively. Row 7 was the 0.1 M BiVO_4 standard.

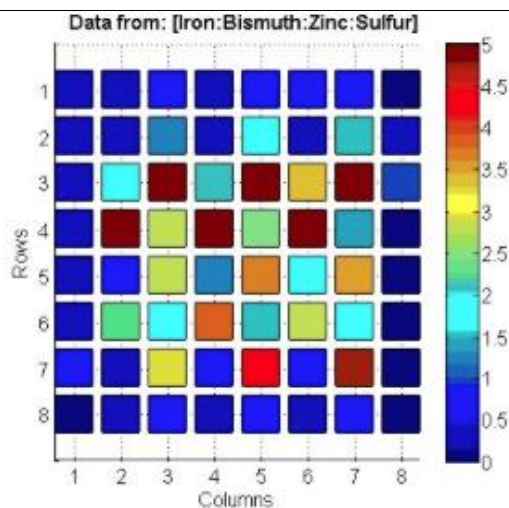


Figure 6: Row 2 consisted of the 0.05 M $\text{Fe}(\text{NO}_3)_3$ standard. Rows 3 and 4 were made of 10 μL BiVO_4 and 5 μL of ZnSO_4 with separate drying times. Rows 5 and 6 were made of the same materials as in rows 3 and 4 but with $\text{Zn}(\text{NO}_3)_2$. Row 7 is the BiVO_4 standard.

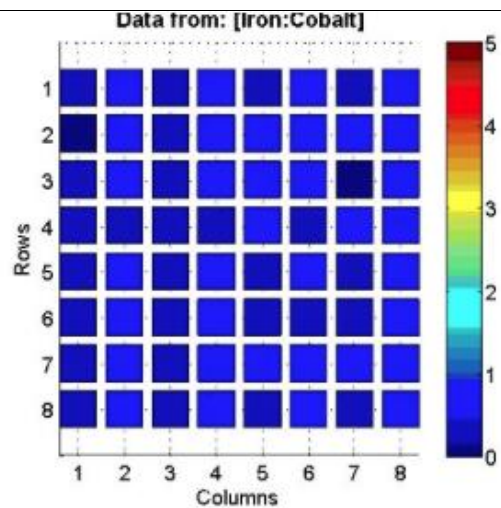


Figure 7: Row 2 consisted of 0.2 M $\text{Fe}(\text{NO}_3)_3$ standard. The consecutive rows were made up of 20%, 40%, 60%, and 80% CoO respectively. Row 7 consists of CoO by itself.

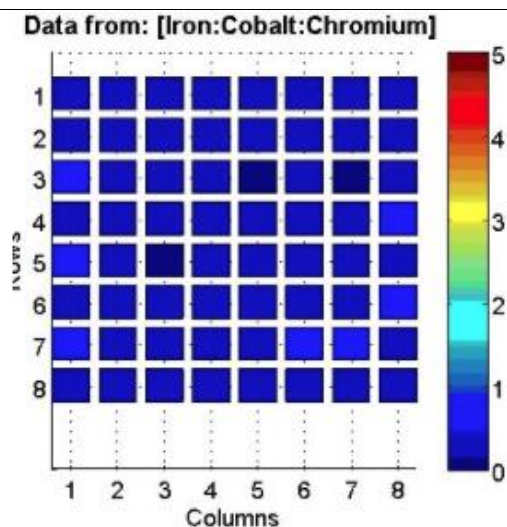


Figure 8A: Refer to Figure 8B for spotting pattern. The scale on the right represents the measured photocurrents.

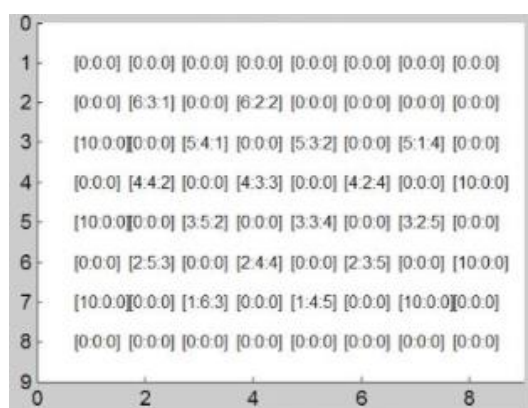


Figure 8B: The image above is the mixing pattern of the plate from Figure 8A. Element 1 was 0.2 M $\text{Fe}(\text{NO}_3)_3$ standard, element 2 was 0.2 M $\text{Co}(\text{NO}_3)_2$, and element 3 was 0.2 M CrCl_3 .

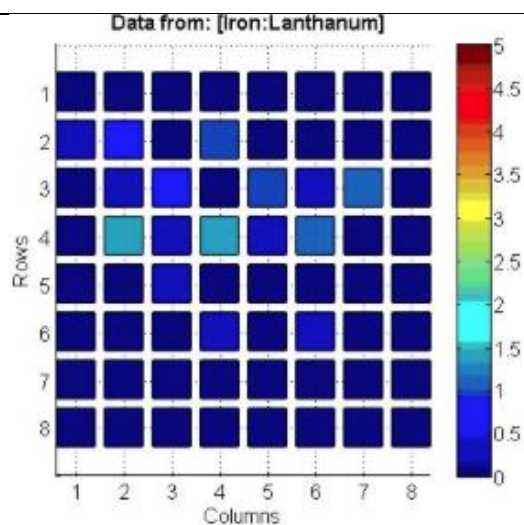


Figure 9: Row 2 consisted of 0.05 M $\text{Fe}(\text{NO}_3)_3$ standard. Rows 3 and 4 consisted of 1% lanthanum, and rows 5 and 6 consisted of 10% lanthanum. Row 7 consisted of 100% lanthanum.

5. DISCUSSION

5.1 Mixed Metals with BiVO_4

Out of all the mixed metal oxides, BiVO_4 and CoO performed consistently the best. In order to produce the most positive results, $\text{Co}(\text{NO}_3)_2$ was spotted on top of dried BiVO_4 spots where BiVO_4 acted as a semiconductor and CoO acted as a catalyst. When the LED light shined on BiVO_4 , it bypassed the band gap exciting the electrons which allowed the CoO to catalyze the redox reaction. Cobalt's black color and being able to cover the whole BiVO_4 spot prevented BiVO_4 from reacting with the ambient light. This negated the need for a cardboard box to lower the dark current. ZnSO_4 had similar photocurrent values as CoO when mixed with BiVO_4 because ZnO it acted as a catalyst for the redox reaction like CoO . Although they were not photoreactive alone, when paired with BiVO_4 , cobalt and zinc performed well in the high red range (6 - 7 μA). ZnO required a longer period of lowering the dark current (unlike CoO) because it lacks the black color of cobalt that was able to absorb the ambient light and prevent BiVO_4 from reacting.

5.2 Mixed Metals with Fe_2O_3

Although Fe_2O_3 worked well alone, it lacked the strong catalytic ability of BiVO_4 and often crystallized when drying, impeding its performance. Specific drying procedures were employed in order to create good spots of iron, but they were unreliable in consistently creating workable spots. The likely reason why 0.05 M worked the best is it prevented some of the crystallization because of the low molarity. Fe_2O_3 lacked the strong catalytic ability to work well with the other metals tested, which made it unsuitable for continued testing.

5.3 Ozone Cleaner and Drying Techniques

The ozone cleaner helped reduce the accumulation of metal oxides on the edges of the spots and created even, more circular spots. This made testing the spots easier because more light could hit the evenly distributed spots more consistently than uneven spots. Although it did not reduce crystallization in the Fe_2O_3 spots as hoped, it made spotting the solutions on the plate easier after being in the cleaner for 10 minutes. When placing the solution on the desired location, the solution retained a circular shape rather than spreading all over the plate.

New drying techniques, such as drying one metal before the other, helped increase the photoactivity of the spots and increased the chance of the movement of electrons, especially in the case of BiVO₄ and CoO. As the surface area of the spot increased, so did the chance for it to be excited by the LED lights. Since a larger portion of the spot was able to be hit by the lights, it had a higher chance of being photoreactive. The ozone cleaner helped create consistent solution thicknesses and uniform circular patterns on each spot.

ACKNOWLEDGMENT

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