



Experimentation and Troubleshooting with SHArK 3.0 for Testing the Photoactivity of Metal Oxides

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Abstract

The SHArK 3.0, introduced February of 2016, is the Solar Hydrogen Activity research Kit. Constructed with the LEGO Mindstorm Kit, SHArK 3.0 functions as a means for high school and undergraduate students to test the photoactivity of metal oxides. Photocurrent results obtained from these scans would determine how effectively metal oxide semiconductors could facilitate the process of photoelectrolyzing water, thus identifying potential photocatalysts for the production of hydrogen fuel as an energy source. In this process, metal solutions are deposited on to thin FTO plates, fired at 500°C, and submerged in an electrolyte solution of an electrochemical cell. SHArK 3.0 has supplanted the gearing system and mirrors of previous models with a pair of linear actuators rastering a laser for a high-resolution scan. In this research study, different methods of drop-pipetting metal nitrate solutions are analyzed, with varieties in the selection and ratio of metals, as well as the size and concentration of spots. As this kit is still in beta-phase, there are numerous glitches with SHArK 3.0 that have produced inaccurate photocurrent results. In this article, such issues are troubleshoot through numerous means, including alterations in ambient light as well as other changes in procedure.

INTRODUCTION

Simply put, alternative energy research will impact every living species on the planet. In the twenty-first century, the most impending global crisis is climate change. Due to the vast scale of burning fossil fuels such as oil, gas, and coal, excessive amounts of carbon dioxide are being released into the atmosphere at faster rates than plants and trees can absorb. Such drastic carbon emission has caused the overall temperature of earth to rise, resulting in unprecedented weather changes that threaten all living species. In fact, the average carbon footprint of the United States is approximately fifty tons of CO₂ per year, nearly five times greater than the global average [1]. Fortunately, alternative energy sources offer great potential as replacements for fossil fuels.

Among these alternative forms of energy, solar energy has a great capability to supply enough power to sustain our future generations. However, because solar energy is intermittent, the obstacle of producing a storable fuel must be overcome before it can supplant fossil fuels and be implemented on a global scale. The most effective way of facilitating this process is by photoelectrolyzing water with sunlight, $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$, to yield hydrogen fuel and oxygen with the production of water as an eco-friendly byproduct [2]. The current operation for generating solar energy is costly and unpractical for wide-scale use, but a promising new method has been proposed in recent years: discover a stable, inexpensive, and abundant metal-oxide semiconductor, with a small band gap appropriate for absorbing sunlight, to catalyze a water splitting reaction [3]. Given that there are endless possibilities

for combining and testing metal oxide materials, this is where SHArK 3.0 comes into play [4].

SHArK 3.0, constructed with the LEGO Mindstorm Kit, stands for Solar Hydrogen Activity research Kit. Produced for use by the “Solar Army”, SHArK 3.0 allows for scanning the photoactivity of mixed metal oxides. Unlike previous models of SHArK, SHArK 3.0 provides a more comprehensive, high-resolution scan of photocurrent due to its incorporation of linear actuators for rastering a laser, allowing one to determine how well different combinations of mixed metal oxides would work as catalysts for photoelectrolysis. There are numerous deposition methods of metal oxide materials, such as ink-jet printing and silk-screening. In this particular research study, drop-pipetting metal nitrate solutions onto thin FTO plates was the primary procedure followed, with strategic modifications in the preference and ratio of metals, as well as the size and concentration of the deposited spots [5].

As a high school student, it is clear to see how SHArK 3.0 can be integrated into the high school or undergraduate curriculum as a form of research study. However, as SHArK 3.0 is still in the beta-phase, much trouble-shooting is still required to ensure consistency in detecting photoactivity. This article, in particular, will focus on different methods for improving the efficiency and function of this kit. Regardless, SHArK 3.0 definitely holds great potential to be widely-distributed as a laboratory experiment for resolving our global energy crisis.

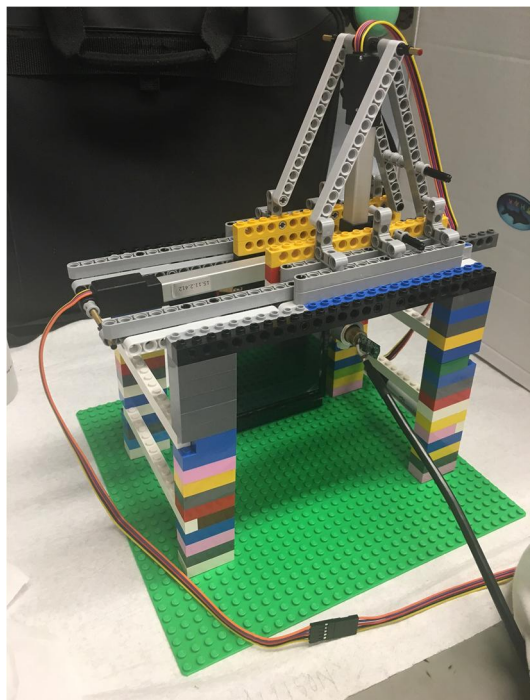


Figure 1: Image of SHArK 3.0.

METHODS

The primary objective of the SHArK is to test the photoactivity of mixed metal oxides for potential use as a semiconductor for catalyzing solar-driven water splitting. When considering the appropriate metal oxide material to use in this experiment, it is important to keep in mind that the ideal photocatalyst must be also be inexpensive and abundant on earth for prospective use on a global level. Additionally, these metals can be categorized in two ways; n-type metals, such as iron, could be used to produce oxygen, while p-type metals, such as copper, could be used to produce hydrogen.³ This study, in particular, is focused on drop-pipetting metal nitrates onto fluorine doped tin oxide conductive glass substrates. SHArK 3.0 measures photoactivity based on an arbitrary scale represented by color, with red signifying the generation of high photocurrent.

Materials

FTO (fluorine doped tin oxide glass substrates), copper tape, and 0.1 M NaOH solution were required for use of SHArK 3.0. $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, and $\text{La}(\text{NO}_3)_3$ were the primary metal oxides tested for photocurrent, with concentrations of 0.04 M, 0.05 M, and 0.10 M.

Plate Preparation

With the pipette method, single-metal and combinations of multi-metal nitrates were deposited onto FTO plates. Before the deposition process, each plate was etched on the top left corner of the nonconductive side, in the format SK-##. The FTO plate was then cleaned with soap and distilled water, and rinsed with isopropanol in order to change the hydrophobicity of the plate, ensuring uniformity with the spots. Next, metal salts were measured out, transferred to 10 mL volumetric flasks, and dissolved with distilled water until a homogeneous solution was achieved, according to measurements obtained through stoichiometry. These single metal or multi-metal nitrate solutions were pipetted onto the plates, with spot sizes ranging anywhere from 5- 300 μL . The purpose of such variations in the material, concentration, and size of spots was to determine how these different variables affected photocurrent results. In addition to the variety of metals deposited onto the plate, it is important to always spot solutions of iron (III) nitrate and copper (II) nitrate as well to maintain a consistent standard in all of the scans. To finish the process, the plate was then dried via a hot plate at $\sim 65^\circ\text{C}$ and annealed in a kiln at 500°C .

Scanning the Sample

Once the plate was out of the kiln, it was prepped for scanning. A strip of copper tape was placed above the spots on the plate, parallel to the top edge. The plate was then placed into a 3D-printed sample holder, with the conductive side facing the glass panel. 0.1 M NaOH solution was added until all the spots were completely submerged. This step was performed with caution such that the copper tape never came in contact with the electrolyte solution. Alligator clips were attached to both the plate and the conductive glass of the sample holder. The former functions as the working electrode and the latter as the counter electrode of the electrochemical cell. Once everything was connected to the SHArK system, the SHArK software was utilized to obtain the photocurrent results of the metal oxide semiconductors. In this process, the LEGO Mindstorm Kit would raster a laser across the surface of the sample holder, on the side with the conductive glass, to scan the substances on the plate. Most scans were completed on the basic setting, lasting 55 minutes each time. Advanced scans would require 2 hours to complete.

RESULTS

Unfortunately, most scans completed using the SHArK Software presented with a lot of noise until the source of the errors was traced to the electronics box. The kit had failed to detect the location of the metal oxides, let alone their

photoactivity. As a result, few of the photocurrent graphs resembled the actual pattern of spots pipetted onto the plates until a new electronics box was obtained.

For example, plates SK-01 through SK-16, scanned with the defective device, presented with inaccurate scans. SK-01 and SK-02, two plates containing nine spots of 5 μL 0.1 M $\text{Fe}(\text{NO}_3)_3$, had better photocurrent results than most, with mainly black backgrounds stippled with random spots of color. Similar results occurred for SK-11, a standard plate of 0.05 M $\text{Fe}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$, but the scans nonetheless did not reflect the contents of the plate (as evident in Figures 2 and 3). With the exception of those three, all other scans leading up to SK-16 presented with lots of noise (Figure 4).



Figure 2: Photographic Sample of SK-11. The top row contains 10 μL spots of 0.05 M $\text{Fe}(\text{NO}_3)_3$. The bottom row contains 10 μL spots of 0.05 M $\text{Cu}(\text{NO}_3)_2$.

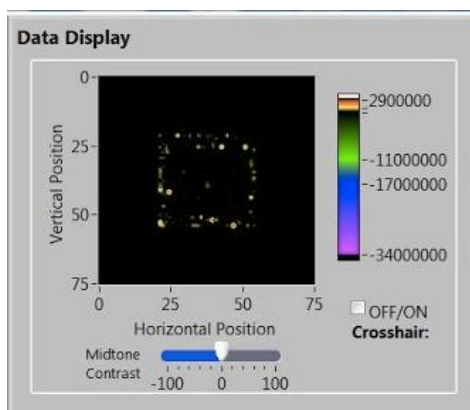


Figure 3: Scan of SK-11, prior to the new electronics box.

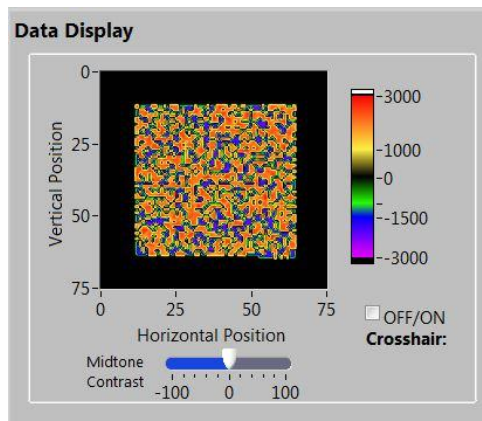


Figure 4: Noisy Scan of SK-05, prior to the new electronics box.

After replacing the electronics box of the kit, results showed great improvement with SK-17, particularly for the 20 μL spots with a 4:1:1 ratio of $\text{Fe}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$. The scan finally resembled the template of the plate, producing bright spots of red and orange on a black background where metal nitrates were pipetted, indicating high levels of photocurrent (Figures 5 and 6). SK-18, a plate with a 300 μL spot of 0.05 M $\text{Fe}(\text{NO}_3)_3$ and 1% $\text{La}(\text{NO}_3)_3$ and a 5 μL spot of $\text{Cu}(\text{NO}_3)_2$, produced promising results as well (Figures 7 and 8).



Figure 5: Photographic Sample of SK-17. The first column features 20 μL spots at a 4:1:1 volume ratio of 0.05 M $\text{Fe}(\text{NO}_3)_3$ to 0.05 M $\text{Ni}(\text{NO}_3)_2$ to 0.05 M $\text{Zn}(\text{NO}_3)_2$. The second column features 20 μL spots at a 1:4:1 volume ratio of 0.05 M $\text{Fe}(\text{NO}_3)_3$ to 0.05 M $\text{Ni}(\text{NO}_3)_2$ to 0.05 M $\text{Zn}(\text{NO}_3)_2$. The third column features 20 μL spots at a 1:1:4 volume ratio of 0.05 M $\text{Fe}(\text{NO}_3)_3$ to 0.05 M $\text{Ni}(\text{NO}_3)_2$ to 0.05 M $\text{Zn}(\text{NO}_3)_2$. In the last column, 0.05 M $\text{Fe}(\text{NO}_3)_3$ was spotted on top and 0.05 M $\text{Cu}(\text{NO}_3)_2$ was spotted below at 20 μL as well, to function as standards.

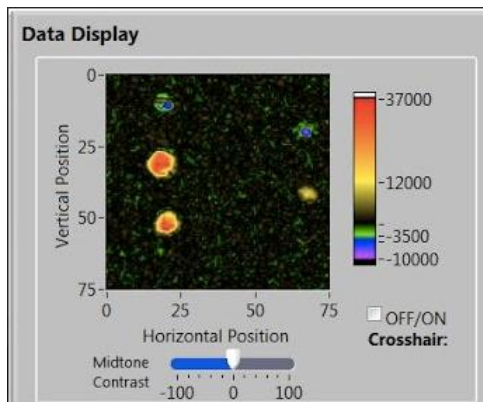


Figure 6: Scan of SK-17 with the new electronics box.



Figure 7: Photographic Sample of SK-18. The plate contains a 300 μL spot of 0.05 M $\text{Fe}(\text{NO}_3)_3$ with 1% $\text{La}(\text{NO}_3)_3$, and a 5 μL spot of 0.05 M $\text{Cu}(\text{NO}_3)_2$.

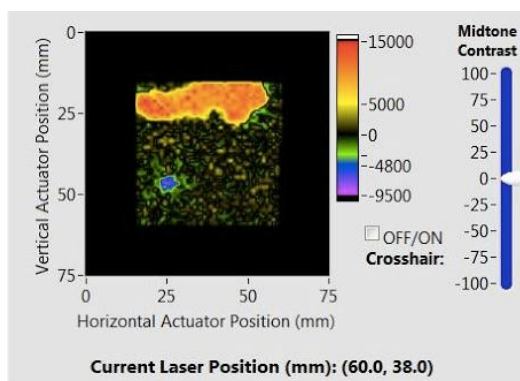


Figure 8: Scan of SK-18 with the new electronics box.

DISCUSSION

For the majority of the first 5 weeks of experimentation with the SHArK 3.0, all scans were

characterized by high rates of noise, with none of the scans resembling the patterns of the metal nitrate spots. Plates featuring $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$, among others, were all tested, but no photoactivity was detected. As a result, most of the study consisted of troubleshooting SHArK as other variables were explored in order to find the source of the issue.

Beginning with the electrolytic solution, the initial concern was that reusing NaOH for multiple scans would risk contamination as spots flaked off during submersion, so 250 mL of 0.1 M NaOH were made every day for the electrochemical cell. However, as this alteration did not yield better results, ambient lighting was the next variable analyzed; SHArK 3.0 is recommended for use in a dimmer surrounding, so a cardboard box was taped over the apparatus to shield the sample holder and laser from the ceiling lights of the laboratory. After observing no visible improvements again, the alligator clips were examined. If the alligator clips or copper tape had come in contact with the NaOH solution, the entire experiment could have been thrown off. Therefore, techniques such as shortening the length of copper tape, drying the clips with Kim wipes, and applying bias were employed. After countless, consistently noisy results with no visible enhancements in the quality of the scans despite procedural changes, all other sources of error were eliminated, and the electronics box of SHArK 3.0 was determined to be the source of the problem.

In order to confirm the hypothesis that the SHArK electronics box was at fault, a solar cell was scanned. With a properly functioning kit, a solar cell should easily be tested to yield high photocurrents (represented by a bright red color on the scan) and visible borders between the cell and its surroundings. As this was not the case, the hypothesis was deemed correct, and a new electronics box was ordered. For example, Figures 9 and 10 illustrate the differences in the scans of the solar cell between the malfunctioning and working apparatuses.

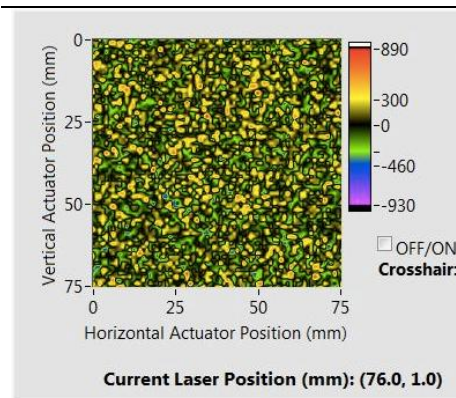


Figure 9: Solar Cell Scan with Old Electronics Box.

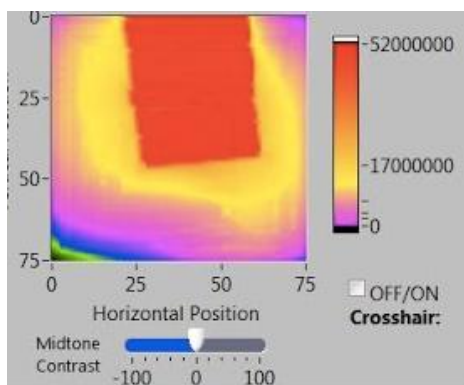


Figure 10: Solar Cell Scan with New Electronics Box.

Because the expected photoactivity of the solar cell was observed with the new electronics box, it held great promise for testing the photocurrent of metal oxide materials. In particular, unlike previous scans completed with the old electronics box, the noise in the new scans canceled out. With the SK-17 plate, for example, the scan finally resembled the template of the plate, producing bright spots of red and orange on a black background where metal nitrate was pipetted. With further testing to ensure consistent quality of the SHArK 3.0 mechanism, this kit can become an invaluable tool for all classroom and laboratory settings.

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