Troubleshooting SHArK 3.0 while Testing for Photoactivity of Metal Oxides

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Supporting Information

ABSTRACT: To test the photoactivity of certain metal oxides as catalysts in splitting water, several different Solar Army kits are employed. The Solar Hydrogen Activity research Kit (SHArK) was used to study different metal oxides in set ratios or spot sizes. The spots were annealed to an FTO (Fluorine-doped Tin Oxide) plate and tested in the kit utilizing a green laser that acts as the light source. Currently, the kit is under beta testing and a variety of techniques must be applied in order to ensure precise results. There are many factors that could affect the SHArK kit and result in inaccurate, abnormal scans. In order to increase the accuracy of the results and eliminate any outside variables, adjustments were made to the SHArK kit and the procedure for scanning the metal oxides. Testing the kit will help in finding better ways to use the instrument in detecting the most efficient and inexpensive metal oxides, which catalyze the water-splitting reaction by the power of solar energy to create hydrogen fuel.

1. INTRODUCTION

With the constant use of fossil fuels, the world's greatest challenge today is in finding a clean and renewable source of energy to depend on (1, 2). Above all other energy sources, solar energy is said to best meet the global demand for energy (3). In order for the energy to be used extensively, the solar power must be converted into a storable form of energy (3). Through photoelectrolysis, the solar energy can be converted into chemical energy in the form of hydrogen fuel. Hydrogen fuel is sought after because in the reversible cycle of hydrogen combustion, the only byproduct is clean water (3). While this can be done with current solar cells in the market today, most of materials used are often costly and rare (3). Because of this, much of the research focuses on finding cost-effective and earth abundant materials in the form of metal oxides that could split water on contact with sunlight. (3)

The Solar Hydrogen Activity research Kit (SHArK) is just one of the kits used to detect photoactivity of the potential metal oxides. Multimetal solutions are made and deposited onto an FTO plate in different combinations and ratios. After firing, each plate is scanned by a green laser, which acts as the light source in order for photoelectrolysis to occur. Variables such as deposition method, controlled evaporation, firing temperature, the semiconductor's band gap, and other factors that may have affected the results were noted.

However, with the SHArK kit, different methods like silk screening, drop pipetting, and spray pyrolysis in varying patterns can be tested. The SHArK kit itself has evolved from the original SHArK to become the current SHArK 3.0 with improvements in its infrastructure and software. As the current kit is under beta testing and is relatively new, it is expected that problems will arise during testing. Different variables can affect the accuracy of the results and cause sudden changes that result in noise. At this point, each variable must be tested to get the kit to work properly. Some of the variables, such as lighting, solution molarity, sodium hydroxide solution contamination, and circuit connections were explored in order to reduce chances for error in the data. Other factors, such as malfunctions within the kit itself must be verified in order to continue testing plates. Troubleshooting the kit is essential as a whole in getting accurate and precise results from each plate and scan.

2. THE EXPERIMENT
2.1 The Setup

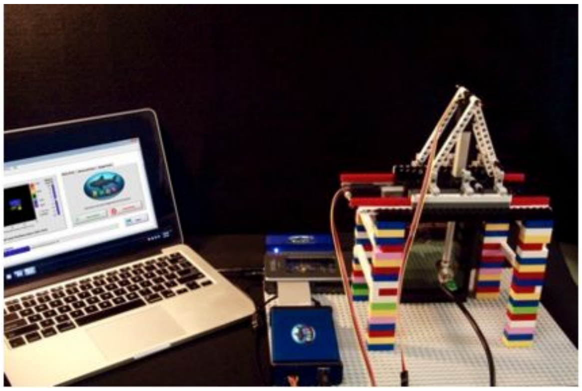

Figure 1: SHArK kit setup. At left is a Mac with Windows desktop. The computer used during the program was a Windows HP laptop. The first step of this project was assembling the LEGO® stand, seen here, and connect the wiring correctly.

The SHArK kit was first built using LEGOS® in order to create the stand that held the actuators for moving the green laser. With the SHArK manual, the structure was assembled accordingly. Once the structure had been set up, the electronics were attached. The two blue SHArK electronics boxes were connected by a National Instruments MyRIO box and then connected to a Windows computer, where the data was received. Each spotted FTO plate that was run was put into sodium hydroxide solution inside a 3D printed holder. A copper tape was attached to the FTO plate across the top. The alligator clips which were connected to the NI Instrument MyRIO box were then attached with one to the holder and one to the FTO plate accordingly.

2.2 Method
2.2.1 Spotting

Out of the methods mentioned, drop pipetting was the technique used to apply metal salt solutions to FTO plates. The pattern of solution application was varied in spot size, shape, number and volume. Each pattern of spots was annealed onto the FTO plate and ran in the SHArK kit. In order to create the spots, solutions of differing metals were created. Using metals including copper(II) nitrate, iron(III) nitrate, cobalt(II) nitrate, nickel(II) nitrate, zinc(II) nitrate, lanthanum(III) nitrate, and others, spots of distinct combinations and ratios were created. A typical plate was made in a chosen pattern or design. The concentrations for the solutions made ranged from 0.04 M to 0.1 M. Each of these variables were tested in the SHArK kit as each could change the readings of photoactivity seen in the scan data.

2.2.2 Iron and Copper Standards

For each plate, iron and copper standards were made. This was because the copper acted as a low (negative) standard while the iron acted as a high (positive) standard. This way, the range of photoactivity could be tested to ensure accurate results. The kit's laser adjusts according to the high and low points on the plate when scanning the metal oxides and their photoactivity. Iron and copper standards are important in ensuring that the scans match up and act as a good test sample for scanning.

2.3 Scanning

To scan the plate, software was downloaded from a USB drive, with two applications being used: the SHArK Scanner and the SHArK Viewer. The SHArK Scanner application was opened and "Start Raster" was pressed to begin a basic scan that lasted about 55 minutes and scanned the whole surface of the plate for photoactivity of the spots. An advanced scan provided the option of applying a bias voltage and also gave more control over the scanning process and the laser's scanning speed, however this takes a while longer in order to finish. In order to test whether the scans had any effect on troubleshooting the kit, both types of scans were tested. Scanning results showed spots with photoactivity as a red, orange, or yellow color, while no photoactivity either shows up as blue, purple, or black. The setup involved a 3D printed sample well holding the plate vertically. The green laser scanned the sample plate point by point in a repeated pattern of squares moving from the center to the outermost edge. Finally, after the scan was completed, the plate was removed and rinsed with distilled water. The results were then saved online and recorded in the SHArK Viewer, where results from different SHArK kit locations are archived.

3. TROUBLESHOOTING

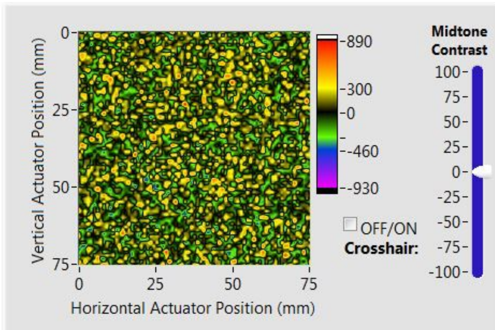

Figure 2: Example of a noisy scan.

3.1 Lighting and Positioning

The first few weeks of research focused on troubleshooting the kit and determining the source(s) that could have resulted in "noise" (see Figure 2) in the scan results. The first problem faced during scanning with the kit was a change in the environment. At first, it was thought to be the changing from one lab bench to another that affected the scan results, making them more noisy. However, after testing with a cardboard box and turning off the lights, there was still noise, eliminating the factor. Different positions were used in order to test the factors of lighting. However, despite the variable reduction, scans still appeared noisy.

3.2 Laser Scanning and Wiring Setup

Figure 3: Alligator clips attached to kit (white wire--black wire in the kit used for this experiment--is attached to the FTO glass cover of holder, while red wire is attached to copper tape on FTO sample glass plate).

The next factors tested were the laser and the wiring of the SHArK kit. During scanning, the laser began pointing off from the desired scan area of the plate. In order to adjust this, extensions to the rainbow-colored actuator cables were added. Following this, the ring holding the laser was tightened. After these adjustments the laser began pointing in the correct direction. In addition to the the laser positioning, the next variable investigated was the setup of the alligator clips (see Figure 3). In fact, the correct attachment of the alligator clips was the opposite: with the black wire (white wire in the Figure 3) attached to the FTO sample plate, and the red wire attached to the holder's front cover. In addition, the alligator clips had to be attached in such a way that the half of the clip with the wire was touching the FTO side of the sample plate and the FTO glass cover so that data could correctly be sent to the computer. Alligator clips were checked to make sure they were dry and that sodium hydroxide did not reach them.

3.3 Solution Purity and Molarity

One potential variable that could have led to the noisy scans was the solution purity. Tiny, floating specks were noticed in the solutions made. In addition, after firing in the kiln, the spots did not seem to be properly annealed. Specks came off the spots when placed in the sodium hydroxide solution, which may have affected the scan results. In order to get rid of the floating specks, the concentration of the solutions was dropped from 0.1 M to 0.05 M and later to 0.04 M. While changes in the spots were seen as they were better annealed, scans still did not change from the continuous noisy pattern seen before. Different spot sizes were tested varying from 5 microliters to 600 microliters, however no changes in results appeared.

3.4 Sodium Hydroxide and Copper Tape

Another factor tested was sodium hydroxide contamination. A new sodium hydroxide solution was made. Problems were also thought to have occurred because of left over sodium hydroxide that might have been trapped in the baffles of the holder. For this reason, washing the holder down with deionized water is important to prevent contamination.

Isopropyl alcohol was used to clean the front FTO glass cover of the holder to prevent other particles from getting into the sodium hydroxide. At first, this reduced a lot of the noise, but scans later returned to the original noise seen before. Copper tape also posed a problem, as copper tape in contact with sodium hydroxide would likely cause the setup to short circuit. The sodium hydroxide formed a cusp with the liquid climbing up the edges of the holder and touching the copper tape. Smaller pieces of conductive copper tape were placed on the FTO plate to reduce the chance of contact made between the plate and the solution.

3.5 Update and Electronics

By the fourth week of scanning, no changes in noisy scans were seen. An update was made at the beginning of the week and tested, but with no changes in the noisy scans. A scan was then conducted with a solar cell, with the same exact results. The problem was concluded to be rooted in the electronics of the kit, especially since the scan results had no similarity to the solar cell being tested. A new SHArK electronics box was obtained. The plate, SK-17 (see Figure 4) was scanned and results dramatically improved.

4. RESULTS

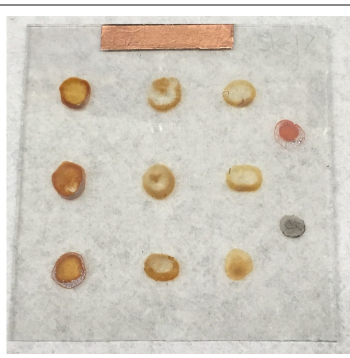

Figure 4: A picture of plate SK-17. The solutions on the plate are a mixture of 0.04 M iron(III) nitrate, 0.04 M nickel(II) nitrate and 0.04 M zinc nitrate. The three spots in column one (far left) were a 4:1:1 ratio of the metal salts, respectively. The spots in column two had a ratio of 1:4:1, and the spots in column three were in a 1:1:4 ratio. The fourth column (far right) contained a 0.04 M iron(III) nitrate spot above a 0.04 M copper(II) nitrate spot.

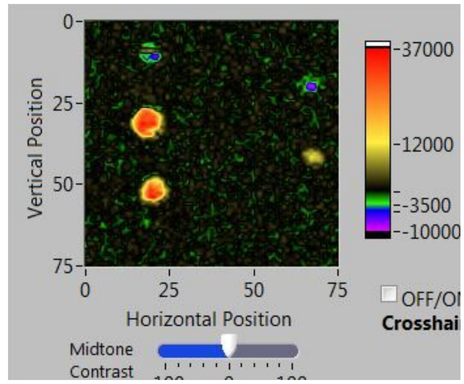

Figure 5: The following image after shows the results of plate SK-17 using the new SHArK electronics box.

All scans, prior to the replacement of the electronics box, were noisy. However, when the SHArK electronics box was switched, results greatly improved. Plate SK-17 (Figure 4), was the first plate scanned following scans of other plates that showed photocurrent in the scans. It was much more successful compared to the other plates in showing photoactivity. Following the SHArK electronics box changes, scans zeroed out noise that was seen before. Scans of other plates were made. A scan of a solar cell was done matching with the position of the solar cell during the scan.

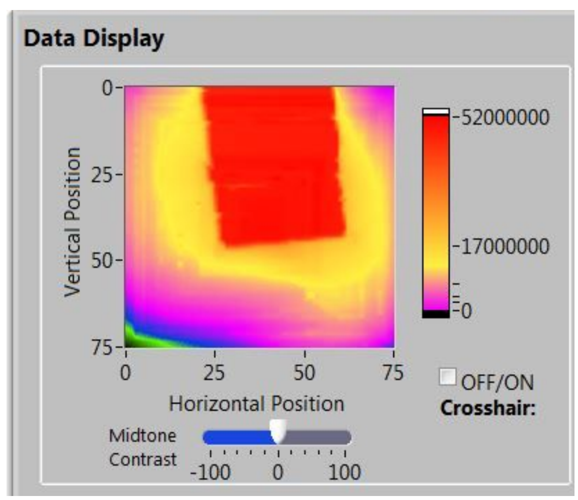

Figure 6: A scan of a solar cell after the replacement of the electronics box. The results appeared accurate to the orientation of the solar cell along with the photocurrent present.

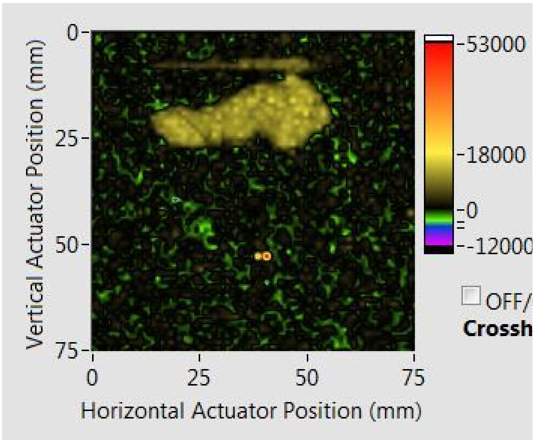

Figure 7: Results with red wire lead, or alligator clip, attached to sample plate and black wire lead to FTO cover.

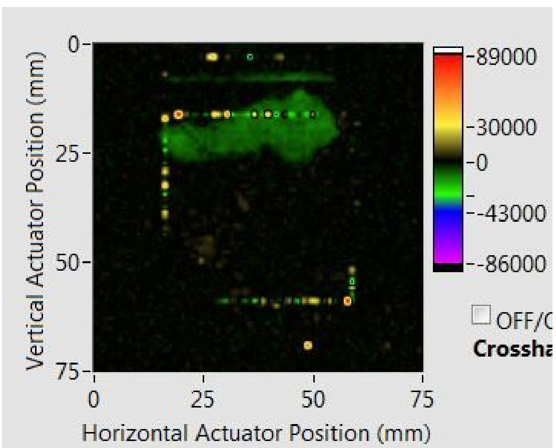

Figure 8: Results with red wire lead, or alligator clip, to FTO cover and black wire lead to sample plate.

Figure 9: Plate SK-18; includes one big spot of 99% iron(III) nitrate and 1% lanthanum(III) nitrate, and a faint spot of copper that was picked up in scans at the beginning.

Interestingly, however, the scale of the photocurrent levels of the scans was quite high. The arbitrary units used reached the millions rather than the thousands as seen in typical scans. While this could affect scan results, photoactivity was still detected. Another scan was also done of plate SK-18, with results as shown in Figure 7. While slightly dusty in color, the plate showed photocurrent present in the scan. The change of alligator clips, seemed to have affected the results as well, making the photocurrent appear negative (Figure 8). This change of leads seemed to affect the results, though photocurrent was still visible.

5. CONCLUSION

Different methods and factors of spotting greatly affected the outcome of the spots as they annealed to the FTO plates. Varying factors such as lighting, solution purity, molarity, wiring, and sodium hydroxide contamination could have affected the scanning. After these factors were eliminated through troubleshooting, the problem was discovered to be within the kit's electronics box. However, the experiment tested different factors that could very well have caused problems. Troubleshooting the kit brought attention to many variables that could lead to inaccurate results. Looking further into finding ways for noise reduction is essential to the experiment and helped in better understanding the kit. It can also be concluded that photocurrent, if present, will show up in the scan, as seen in SK-17 and SK-18 plates. In conclusion, different variables must be tested and eliminated before further experimentation can be done with the kit to ensure accurate results.

ASSOCIATED CONTENT

Supporting Information Placeholder

Details regarding SHArK kit and scanning see SHArK Lab Manual: http://www.uwyo.edu/parkinson/parkinson_research_group/manuals/sharkv3manual.pdf

More information is available at: thesolararmy.org

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