Troubleshooting the Solar Hydrogen Activity Research Kit 3.0

Hannah Park

ABSTRACT: The SHArK (Solar Hydrogen Activity research Kit) 3.0 was developed as a mechanism to detect promising photocatalysts that can effectively split water in order to produce hydrogen fuel. Thin films of metal nitrates in various ratios are placed onto fluorine-doped tin oxide plates through various methods including drop-pipetting. By utilizing a kiln, these metal nitrates on the plates become metal oxides. SHArK 3.0 then shines a green laser to detect the photoactivity of the respective metal oxides. Various parts including two linear actuators, a 3D-printed sample holder with an FTO plate, and MyRIO by National Instruments work together to perform and display the data from the scans. However, while SHArK 3.0 is an improvement from previous models, changes are still needed in order to optimize the kit. Numerous variables including various concentrations of metal oxides, restriction of ambient lighting, and sizes of spots were tested with the hopes of yielding an improved scan. By creating plates and testing them while manipulating different variables, efforts were made to produce viable data. Improvements to SHArK 3.0 will make it possible to test the potential photocatalysts for current when exposed to light. The presence of photoactivity is a necessary quality for a catalyst that uses energy from the sun to split water.

1. INTRODUCTION

With the rapid depletion of fossil fuels, the world's primary energy source, the need for an alternative energy source for human consumption becomes increasingly urgent. Solar energy is one of many environmentally friendly energy sources, in addition to nuclear reactors and wind-powered generators. Solar energy can hence be utilized to drive the water-splitting reaction to create hydrogen fuel, which would be easier to store than solar energy.[1] A proposed solution is to use sunlight to produce hydrogen fuel through the photoelectrolysis of water. By splitting water into hydrogen and oxygen gas, hydrogen gas can be employed as an environmentally friendly fuel.[2]

However, this water-splitting reaction requires a suitable photocatalyst to speed up the reaction. The development of a cost-effective device that would enable this hydrolysis to occur could solve the energy problem by making solar energy a more viable alternative to fossil fuels.[1] Combinations of metal-oxide semiconductors are likely a suitable photocatalyst to solve this issue.[3] However, with about 60 metals on the periodic table, the endless combinations of photoactive semiconducting oxide ratios make the possibilities limitless. Additionally, by altering other variables including solution concentration and deposition methods, even more possibilities are presented.

At the University of Wyoming, SHArK (Solar Hydrogen Activity research Kit) was developed by Bruce Parkinson as a mechanism to test the effectiveness of metal oxides as photocatalysts.[4] A "Solar Army" of students is needed to test all of the combinations of metal oxides that would be effective photocatalysts. They utilize inexpensive kits with materials including LEGO Mindstorms which had an intricate gearing system which tilted two mirrors to move a laser on the surface of a sample dropped onto a FTO plate.[1] This kit's gearing system was prone to having backlash, and the process took approximately two hours.[5] After upgrades and innovations to both the kit and the software necessary to run SHArK, SHArK 3.0, developed by Lenore Kubie, was released in February 2016. SHArK 3.0 uses LEGO-compatible linear actuators which allow for greater accuracy of the scanner and shorter scanning times.[5] Additionally, improvements to the collection and storage of data allow instantaneous results to be communicated to and from other SHArK users through its global database.

When using SHArK 3.0, metal nitrates of various ratios and concentrations are prepared on an FTO (fluorine-doped tin oxide) plate and kilned.[6] Afterwards, the FTO plate is placed into a sample holder which contains an electrolyte solution. Next, the various components of SHArK 3.0 are connected, consequently allowing the computer-based program to begin a scan. As the green laser scans the sample in a spiral motion, the results from the scan demonstrating the photocurrent of the sample are displayed on the SHArK scanner.

Due to the recent release of SHArK 3.0, the kit is currently undergoing beta-testing.[5] Noisy scans prevent the data from the scans from consistently correlating with the spots seen on the actual plates.

When identifying the appropriate setup and manipulating the numerous variables, consistent data can be acquired to maximize success in using the SHArK 3.0 kit and to begin identification of effective photoelectrocatalysts.

2. METHODS

2.1 Procedure

2.1.1 SHArK 3.0 Setup

The SHArK 3.0 manual was carefully followed to properly assemble the pieces of the kit which included the LEGO bricks, linear actuators, and a MyRIO by National Instruments. The LEGO Mindstorms was constructed. The x and y actuators were attached using various pegs and a top carriage. The laser was secured to the y-axis actuator. To continue setting up the remainder of the SHArK 3.0, the linear actuator extension cables, blue electronics box, MyRIO by National Instruments, and computer were connected by following the SHArK 3.0 manual. From the included flash drive, the SHArK viewer and scanner software were downloaded onto a Windows 7 computer.

2.1.2 Preparing a 0.1 M Iron (III) Nitrate Solution

A 0.1 M iron (III) nitrate solution was created initially to be used as a standard. First, a 10.0 mL volumetric flask was obtained. Into the volumetric flask was placed 0.40 g of $Fe(NO_3)_3$ x $9H_2O$ and approximately 5 mL of deionized water. The flask was swirled to dissolve the salt before more water was added to the 10 mL line. The aqueous solution was transferred to a labeled vial.

2.1.3 Preparing a Plate

First, a 3 in x 3 in FTO plate was obtained. Next, deionized water was used to clean the plate. Acetone was used to rinse the plate and help it dry faster. The plate was labelled by etching “SK-#” on the top left corner of the nonconductive side of the plate. Next, a 10 µL pipet was used to spot nine identical spots in a 3 x 3 pattern. Next, after the spots were dried on a hot plate, they were annealed in a kiln at 500°C for 3 hours.

2.1.4 Making 0.1 M NaOH solution

First, a 250 mL volumetric flask was obtained. 1.0 g of NaOH was added to create a 250 mL solution of 0.1 M NaOH. Distilled water was added and swirled to dissolve the solid NaOH, until the 250 mL line was reached. Afterwards, it was transferred to a labeled bottle.

2.1.5 Running a Scan

A strip of copper tape was first placed across the top edge of the FTO plate. The FTO plate with the sample was placed in the slot of the 3D-printed sample holder, with the spots facing the glass of the sample holder. The sample was attached to the SHArK electronics box by clipping the black alligator clip to the copper tape on the plate, and the red alligator clip to the FTO glass of the sample holder. The electrochemical cell (sample holder) was filled with 0.1 M NaOH through the cylindrical spout on the side of the sample holder in order to prevent the electronics from getting wet. The solution level remained below the copper tape so that the alligator clips and copper tape were not touched by the solution. The sample holder was then attached to the LEGO base to secure it. On the computer, the SHArK scanner was opened and the “Start Raster” button was clicked to begin a 55 minute basic scan.

2.2 Troubleshooting

2.2.1 Altering the Height of NaOH when Scanning

The height of NaOH was altered to ensure that the copper tape and alligator tips would not be touched by the NaOH to create false readings. The level of NaOH in the sample holder was never poured to be higher than 1.5 centimeters from the top of the FTO plate. The level of NaOH was later made to just barely cover the spots on the plates.

2.2.2 Drying the Alligator Clips

The alligator clips were dried by a Kimwipe each time before they were attached to the FTO plate prior to running a scan. After snapping the LEGO structure into place on the LEGO base, the alligator clips were dried one more time with a Kimwipe.

2.2.3 Orientation of the LEGO Mindstorm

The orientation of the LEGO Mindstorm structure was arranged so that the structure was to the right of the computer, with the laser facing the right. It was then altered so that the laser pointed at the wall. Next, the LEGO Mindstorm structure was moved to the left of the computer.

2.2.4 Changing Ambient Light

A cardboard box was arranged on a shelf above the SHArK 3.0 to block out ambient lighting from the ceiling lights. Additionally, a scan was run with the lights off.

2.2.5 Using New NaOH for Each Scan

The NaOH was disposed of after each scan to prevent contamination. After disposing of the NaOH into the base waste container, the sample well was cleaned with distilled water. A new solution of NaOH was then placed into the sample well for the next scan.

2.2.6 Cleaning the Sample Well

The inside of the glass of the sample well was cleaned prior to each scan to prevent contamination.

First, the glass was rinsed with distilled water. The glass was then rinsed with isopropyl alcohol. The sample well was placed, upside down, on a stack of paper towels to dry for approximately 20 minutes.

2.2.7 Changing Concentrations

The molarities of the different solutions used on the FTO plate samples were altered to make the spots stay on the plates more definitively. The molarity of all of the solutions were lowered from 0.1 M to 0.05 M through dilution. The 0.05 M solutions were all then diluted to 0.04 M.

2.2.8 Testing the Solar Cell

A scan was run on a solar cell to test the functionality of the SHArK 3.0's electronics. A voltmeter was used, with the red wire touching the positive side of the solar cell and the black wire touching the negative side of the solar cell, in order to ensure the solar cell worked properly. The solar cell was then attached to the LEGO Mindstorm where the sample well would have been placed. Tape was used to secure the solar cell in place in a vertical orientation, with the positive part of the solar cell on the bottom and the negative part of the solar cell on top. A black bag was placed behind the solar cell to create a solid, dark background to allow for the results on the scan to be seen more clearly.

3. RESULTS

Plates SK-1 and SK-2 were scanned in SHArK 3.0. The results of these scans showed colorful specks on a black background, as shown in Figure 1.

Scans for SK-3 to SK-19 all exhibited a plethora of colorful spots covering the entire scan, demonstrating a high degree of noise, similar to Figure 2. When SK-1 and SK-2 were run by the SHArK 3.0 again, they exhibited much more noise than when the initial scans were performed.

SK-11 was a standard plate with three spots of $Fe(NO_3)_3$ and three spots of $Cu(NO_3)_2$. When initially scanned, it demonstrated some noise, but considerably less than for the scans up to this point (Figure 1). SK-11 had a similar scan of predominant black and some colorful specks, as did SK-1 and SK-2. However, when it was run again, the scan was completely different, showing the plethora of colorful spots covering the entire scan (Figure 2).

All of the scans exhibited a large amount of noise, so a solar cell was scanned on SHArK 3.0 to check that the electronics box was properly functioning. The scan exhibited a large amount of noise, which should not have happened when scanning the solar cell (Figure 3). This demonstrated that the electronics box was broken.

With the new SHArK 3.0 electronics box that functions properly, the scans demonstrated less noise. When SK-11 was scanned again, it demonstrated much less noise (Figure 4). This showed a functioning scan of SK-11. Also, when the solar cell was scanned again, the scan demonstrated that the SHArK was working properly (Figure 5).

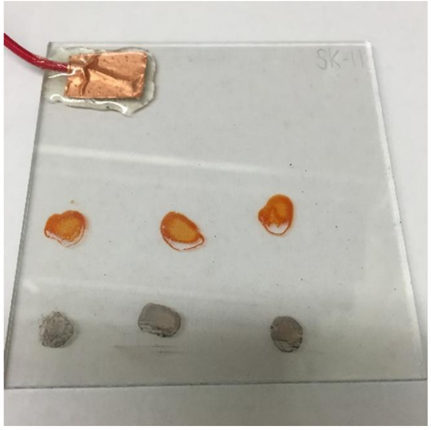

Figure 1A. Plate SK-11 was a plate with three horizontal spots of $Fe(NO_3)_3$ and with three horizontal spots of $Cu(NO_3)_2$ below them.

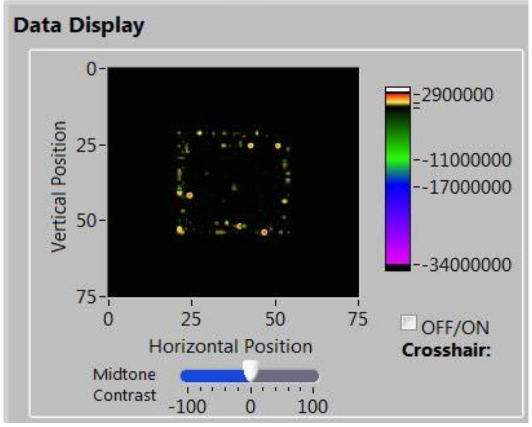

Figure 1B. The scan of SK-11 exhibited noise, but not to the extent of previous scans.

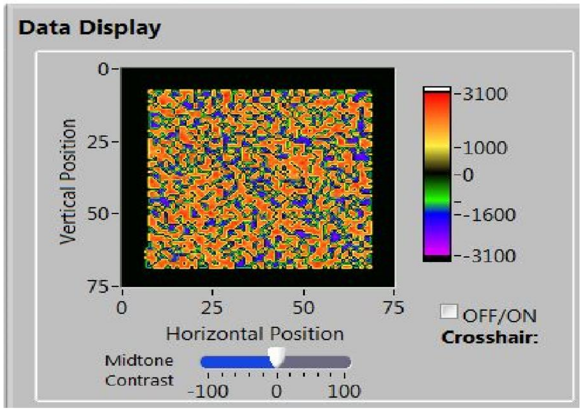

Figure 2. When SK-11 was scanned for a second time, noise dominated the scan to a greater degree.

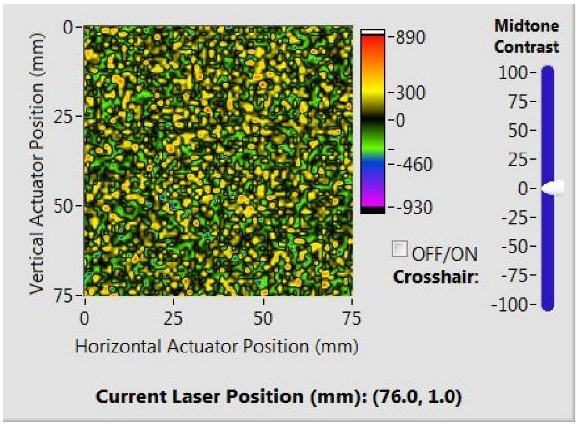

Figure 3. When the solar cell was scanned, noise dominated the scan once again.

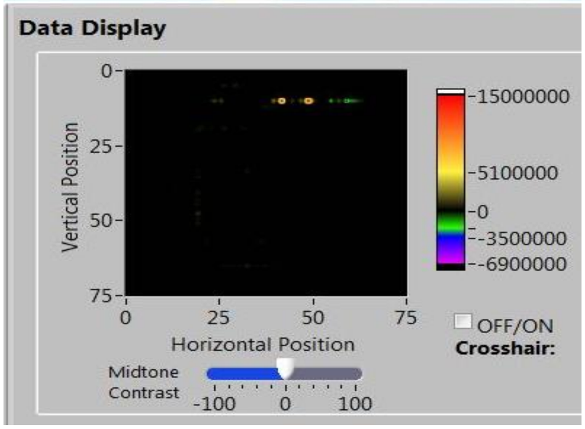

Figure 4. After the new electronics box arrived, SK-11 was scanned again, exhibiting significantly less noise than before.

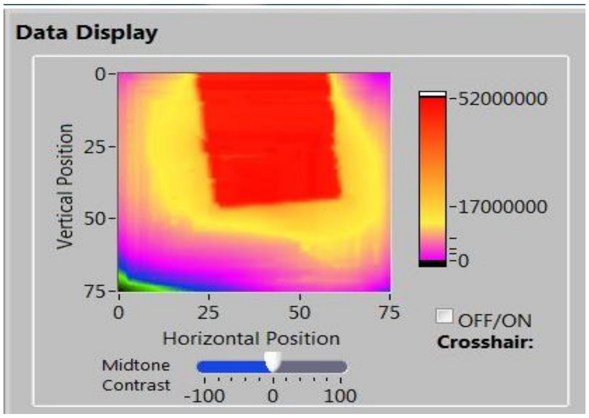

Figure 5. With the new electronics box, the solar cell demonstrated that the SHArK 3.0 functioned properly.

---

4. DISCUSSION

The primary goal was to discover the appropriate metal nitrate to find a high photocurrent. In order to accomplish this, various plates were spotted using different metals including nickel (II) and cobalt (II) nitrates. These metal nitrates were spotted on plates labeled “SK-#” in a 0.1 M concentration. Different pipet sizes were utilized to alter the sizes of the spots and see which sizes of spots would produce scans with high photocurrent. However, the scans conducted were very noisy and the data was unreadable. The metal oxides were also mixed in various ratios and spotted onto plates. When the data continued to be unreadable, the concentrations of the metal solutions were lowered at first to 0.05M and then eventually to 0.04M.

Regardless of what size pipets were used or what metal solutions were spotted onto the plates, the scans on the plates had noisy, unreadable data. The goal then shifted to focusing on obtaining a better scan to see the data. Since some scans of the same plate, such as of SK-11, produced different results, it was necessary to alter numerous variables to find the ideal scanning setup.

Many variables were altered to conduct a more effective scan. First, a cardboard box was placed above the SHArK 3.0 to reduce the ambient lighting to make a darker scanning environment. Additional variables that were altered included the following: orientation of SHArK 3.0 laser, linear actuator extension cables, cleaning the glass of the sample well, and using new NaOH.

Despite the adjusting of different variables, the scans produced noisy, unreadable data. Scanning the solar cell produced noisy scans, which confirmed that the electronics box was not functioning properly. The SHArK 3.0 electronics box was not functioning, so a new one was obtained. With the new electronics box, the noise was significantly reduced. The functionality of the electronics box was confirmed by the new scan of the solar cell. In the future, close attention should be given to the additional variables that were tested, as they all contribute to the scan produced by SHArK 3.0.

ACKNOWLEDGMENTS

The author would like to thank Professor Harry Gray and California Institute of Technology for providing the resources and laboratory for the research that was conducted. Also, thanks to Allison Moore for supporting the research conducted; Asia Leong, Melody Wu, and Vera Qu for their contributions to the research; and Lenore Kubie for developing SHArK 3.0.

REFERENCES

(1) Anunson, P. N.; Winkler, G. R.; Winkler, J. R.; Parkinson, B. A.; Christus, J. D. S. *J. Chem. Educ. Journal of Chemical Education* **2013**, *90* (10), 1333.
(2) Lewis, N. S.; Nocera, D. G. *Proceedings of the National Academy of Sciences* **2006**, *103* (43), 15729.
(3) Osterloh, F. A.; Parkinson, B. A. *Mater. Res. Soc. Bull.* **2011**, 36, 17-22.
(4) Woodhouse, M.; Parkinson, B. A. Combinatorial Approaches for the Identification and Optimization of Oxide Semiconductors for Efficient Solar Photoelectrolysis. Chem. Soc. Rev. **2009**, 38, 197−210.
(5) SHArK | The Solar Army http://thesolararmy.org/shark/ (accessed Jul 15, 2016).
(6) Rowley, J. G.; Do, T. D.; Cleary, D. A.; Parkinson, B. A. *ACS Appl. Mater. Interfaces ACS Applied Materials & Interfaces* **2014**, *6* (12), 9046.