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Involving Students in a Collaborative Project To Help Discover Inexpensive, Stable Materials for Solar Photoelectrolysis

Paige N. Anunson,[†] Gates R. Winkler,[‡] Jay R. Winkler,[‡] Bruce A. Parkinson,[§] and Jennifer D. Schuttlefield Christus[†,*]

[†]Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, Wisconsin 54901, United States

[‡]Beckman Institute, California Institute of Technology, Pasadena, California 91125, United States

[§]Department of Chemistry and School of Energy Resources, University of Wyoming, Laramie, Wyoming 82071, United States

Ⓢ *Supporting Information*

ABSTRACT: In general, laboratory experiments focus on traditional chemical disciplines. While this approach allows students the ability to learn and explore fundamental concepts in a specific area, it does not always encourage students to explore interdisciplinary science. Often little transfer of knowledge from one area to another is observed, as students are given step-by-step instructions on how to complete their task with little involvement or problem solving. Herein, we provide an example of a real-time research laboratory experiment that is aimed at individual's exploration and development, with the scientific goal of discovering inexpensive, stable oxide semiconductors that can efficiently photoelectrolyze water to a useable fuel, hydrogen. Students create unique metal oxide semiconductors combinations, scan the samples for photoactivity using a purchased scan station, and report their findings to a collaborative database. A distinctive feature of the project is its ability to be implemented in a variety of educational levels with a breadth and depth of material covered accordingly. Currently, kits are being used in secondary education classrooms, at undergraduate institutions, or as outreach activities. The project provides students and scientists from different disciplines the opportunity to collaborate in research pertaining to clean energy and the global energy crisis.

KEYWORDS: *High School/Introductory Chemistry, Upper-Division Undergraduate, Public Understanding/Outreach, Interdisciplinary/Multidisciplinary, Inquiry-Based/Discovery Learning, Combinatorial Chemistry, Electrochemistry, Semiconductors, Solid State Chemistry, Undergraduate Research*

■ INTRODUCTION

Inexpensive methods are needed to produce enough energy to satisfy the growing global energy demand without further harming the environment. Alternative energy sources such as wind-powered generators, solar cells, and nuclear reactors produce some of the world's electricity, but unfortunately not enough power is being generated to offset the continued need to burn fossil fuels. While it is likely that a combination of many alternative forms of energy will be needed to successfully offset current fossil fuel usage, sunlight is the only renewable energy source that has the potential to provide enough clean energy to support the needs of future generations. The problem with solar power is that the source is intermittent, which means that a storable fuel needs to be produced. The direct photoelectrolysis of water with sunlight to produce hydrogen is the most promising method for energy storage. Hydrogen produced from water is sought after because it is a storable, carbon-neutral, energy-dense molecule.[1] The only byproduct produced in the reversible cycle of hydrogen combustion is water, providing an environmentally friendly option to carbon dioxide production from fossil fuel combustion.

Currently, water splitting can be accomplished with conventional solar cells connected to commercial electrolyzers; however, both of these components are quite costly. Therefore, the development of a single, cost-effective device for splitting water directly with sunlight would provide a potential solution to the energy problem. To date, there is no known material that can efficiently and inexpensively photoelectrolyze water while remaining stable under illumination in an electrolyte solution for many years, which is necessary to justify the expense of building a photoelectrolysis system. As a result, a simple and high-throughput method to identify materials is needed. Most likely, the material will be a combination of metal-oxide semiconductors.[2,3] Given that there are approximately 60 metals in the periodic table, thousands of potentially photoactive semiconducting oxide compositions are possible when mixed in varying ratios. The photoactivity of these materials can also be influenced by variables such as deposition method, composition of the precursor materials, and firing temperature and time, which increases the possible number of combinations that need to be investigated.

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Previously, small libraries of tungsten-based oxides were generated via electrodeposition and screened for photoactivity using an electrochemical screening system.[4,5] Metal-oxide combinations have also been produced through the sol gel method and thin film deposition techniques (see Woodhouse[5] and references therein), but these techniques are costly and time-consuming. Alternatively, Woodhouse and Parkinson,[3,6−9] and Lewis and co-workers[10] used inkjet printing, which allowed more combinations to be screened for photoactivity at a quicker pace. The combinatorial method is well suited to discover new catalysts because it is inexpensive and allows for a high throughput of samples. It has previously been used successfully in undergraduate organic chemistry laboratories.[11,12]

Here, the combinatorial approach has been modified to fit into multiple levels of educational curricula creating a cadre or "Solar Army" of students to screen for potential catalysis using inexpensive kits constructed out of LEGO Mindstorms or a light emitting diode (LED) array. The kits scan for photoactivity of mixed metal-oxide semiconductors that students themselves create. LEGO Mindstorms kits have effectively been used as scientific tools in the past. The Mindstorms kit was used as a spectrophotometer for studying adsorption chemistry[13,14] and as an interface to control a high-throughput thin layer chromatography (TLC) and ambient mass spectrometer.[15] Additionally, it has been shown that it is exciting for students to perform scientific experiments with toys they used as children.[16] Educational experiments using LEGOs have been published by the University of Wisconsin Madison Materials Research Science and Engineering Center.[16]

Herein, we describe a real research laboratory experiment that was created to be fun, exciting, and unintimidating to students, with a goal of finding a suitable semiconducting material to photoelectrolyze water. The experiment can be integrated into a high school curriculum, at many different levels of the college curriculum, and also used in after-school clubs or during one-day workshops for students. As a real research project, it provides students the opportunity to explore how real research works in a hands-on manner. Open-ended experiments or projects with no "correct" answer have been developed in the past,[17−22] yet none to our knowledge that are focused on solving the global energy problem via the photoelectrolysis of water. Furthermore, it is our hope that the project helps foster excitement for science in the minds of young students by giving them a chance to help solve a problem that greatly impacts their future.

■ THE FUNDAMENTALS

The production of hydrogen and oxygen from water has long been a primary research objective in the area of solar energy.[3,23] Oxygen evolution was observed as early as 1968 when a rutile electrode in solution was illuminated,[24] but it was Fujishima and Honda who, in a series of experiments using the n-type semiconductor rutile form of TiO_2, tied this evolution to water photoelectrolysis.[25,26] Using a semiconductor and the sun's energy to drive the electrolysis of water, represented by eq 1, is the ideal method to split water into a storable, useable fuel.

$$2H_2O(l) \rightarrow O_2(g) + 2H_2(g) \quad (1)$$

The reaction can be divided into two half reactions that can be carried out independently at the anode and cathode. The anode is the electrode where the oxidation occurs; the half reaction that corresponds to this process for water splitting is shown by eq 2:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^\circ_{red} = 1.23\ V \quad (2)$$

The opposite process, reduction, occurs at the cathode and is shown in eq 3:

$$4H^+(aq) + 4e^- \rightarrow 2H_2(g) \qquad E^\circ_{red} = 0.00\ V \quad (3)$$

The overall calculated cell potential would then be −1.23 V as shown by eq 4:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0\ V - 1.23\ V = -1.23\ V \quad (4)$$

Therefore, for water splitting to occur, a voltage greater than 1.23 V must be generated, which would preferably be generated by sunlight. Ideal photovoltaic devices can use light in the near-IR region with photon energies of 1.23 eV or greater to produce this voltage.[27] A substantial portion of the solar spectrum includes photons above this energy threshold; thus, the use of sunlight as an energy source to split water is thermodynamically possible.

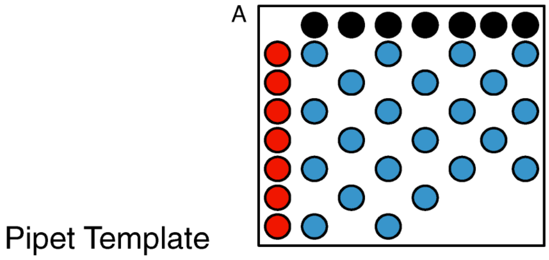
For water splitting to occur; a semiconductor must meet a set of criteria, including these as follows: the material must be accessible (inexpensive and abundant), light absorbing, stable, and have catalytic activity for the splitting of water into hydrogen and oxygen.[8] Metal-oxide semiconductors are ideal candidates owing to their demonstrated ability in the natural world to remain stable through years of weathering and because of their ability to generate e^-/h^+ (electron−hole) pairs when incident photons have energy that is greater than that of the band gap.[28−31]

The band gap is the energy range in a solid in which electrons are unable to reside. It is typically referred to as the energy difference measured in electron volts (eV) from the conduction band to the valence band. The conduction band is the lowest energy band that consists of unoccupied molecular orbitals; in contrast, the highest energy band that consists of occupied molecular orbitals is referred to as the valence band.[27,32] In the case of photoelectrolysis, to excite an electron from the valence band to the conduction band requires enough energy to overcome the band gap (see the Supporting Information and SI Figure 1), where the energy used to excite the electron is solar energy. Once an electron is promoted from the valence band to the conduction band, a hole, h^+, or positively charged vacancy is left in the place of the electron. The movement of these charge carriers (i.e., electrons or holes) to the surface of the semiconductor and electrolyte cause the oxidation or reduction of water depending on the type of semiconductor. For p-type semiconductors, electrons are driven to the surface and are capable of reducing hydrogen ions to hydrogen gas. For n-type semiconductors, holes are driven to the surface and are capable of oxidizing water to oxygen gas (see the Supporting Information and SI Figure 2).[2,3,23,27−30,33]

■ THE EXPERIMENT

The goal of the project is to create unique mixed metal oxides, which are then scanned for potential photoactivity using either the Solar Hydrogen Activity research Kit (SHArK) or Solar Energy Activity Lab (SEAL). These mixed metal oxides create

A



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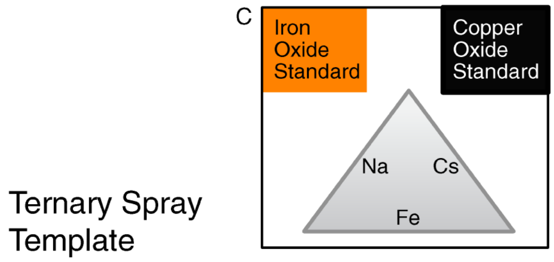

B

Zn:Cu:Cr								
	1	2	3	4	5	6	7	8
1		Cu	Cu	Cu	Cu	Cu	Cu	Cu
2	Fe	1:2:5		1:4:3		1:3:4		1:5:2
3	Fe		4:5:0		5:4:0			
4	Fe	6:3:0		2:4:3		3:3:3		5:2:2
5	Fe		7:1:1		6:1:2			
6	Fe	7:2:0		3:5:1		4:0:5		4:1:4
7	Fe		1:0:1		1:0:0			
8	Fe	1:2:5		1:4:3				

D

Zn:Cu:Cr								
	1	2	3	4	5	6	7	8
1	Fe	Fe	Fe			Cu	Cu	Cu
2	Fe	Fe	Fe			Cu	Cu	Cu
3	Fe	Fe	Fe	0:1:1		Cu	Cu	Cu
4			0:0:1	0:1:1	0:1:0			
5			0:0:1	0:1:1	0:1:0			
6			1:0:1	1:1:1	1:1:0	1:1:0		
7		1:0:1	1:0:1	1:0:0	1:0:0	1:1:0	1:1:0	
8	1:0:1	1:0:1	1:0:1	1:0:1	1:0:0	1:1:0	1:1:0	1:1:0

Figure 1. (A) An example of where samples in varying ratios are deposited onto the fluorine-doped tin oxide (FTO) conductive glass plates. The red circles represent where the standard, iron oxide, is placed and the black circles represent where the standard, copper oxide, is deposited. The blue dots represent where the mixtures can be deposited. (B) Corresponding template is shown that describes the ratios of metal precursors deposited for Zn, Cu, and Cr to a total of 10 μL. (C) The template used for ternary combinations of spraying with the standards in the corners. (D) Corresponding template of the ratios deposited over the area of the FTO plate for a ternary mixture of zinc, copper, and chromium oxides.

multimetal semiconductors, which if determined to be n-type could potentially produce O_2, and if determined to be p-type could potentially produce H_2. Students are allowed to create combinations based off of the background provided to them by the instructor, meaning students should keep in mind that in order for these combinations to replace current energy sources the metals used need to be earth abundant and inexpensive. Additionally, they are looking for combinations that are catalytic to water photoelectrolysis (band gap in the range of 1.6−2.4 eV),[2,3,10,23,27,34] and stable in sunlight and aqueous solution over many years.[8] If students are not sure of what metals to combine, an online collaborative database was established so that students can upload their experiments, as well as search prior results. Here one can find combinations to replicate or that can be avoided if no photoactivity was observed. Students use all of these factors to help them make their decision on what they would like to deposit. The metal salt precursors are deposited by the students as described below in combinations ranging from single metals to multimetal combinations (mixtures of 3, 4, 5, etc.).

To create the unique metal-oxide semiconductors, students first deposit metal salt precursor solutions (e.g., metal nitrates, acetates, or chloride salts) of their choosing onto fluorine doped tin oxide (FTO) conductive glass substrates (3.0-mm 8-Ω SnO_2:F, Hartford Glass). The combinations can be deposited a variety of different ways, including pipetting, spray deposition with inexpensive airbrushes or glass atomizers, or by using an inkjet printer in which the ink in the cartridges is replaced by precursor solutions. The most common and easy method is the pipet method. By following this method, students are able to practice the concepts of record keeping, molarity, concentration, and stoichiometry. (See the Supporting Information for more details.) The internal standards, iron and copper oxides, are deposited on every plate. The concentrations of the precursor solutions for the standards are typically 0.04 M. α-Fe_2O_3 has been shown to be a consistent n-type material, producing a photocurrent under positive applied bias. Copper(II) oxide functions as the p-type standard as it has consistently produced a photocurrent under negative applied bias.[3,32]

Before deposition of any precursor solutions, the FTO glass substrates (working electrode) must be cleaned with a diluted soap and rinsed with distilled water. After the rinsing step, methanol or ethanol can be used to make the plate slightly hydrophobic for optimal beading of the spots. Once the plate is dry, the metal precursor solutions are deposited. Solutions can be premixed in a well plate or added to the FTO glass substrate in a layer-by-layer fashion. If students are pipetting, spot sizes range from 5 to 15 μL, with the optimal spot size being ∼10 μL. An example of how metal precursors are deposited using a pipet and combined in varying ratios is shown in Figure 1A,B. Concentrations of the precursors generally range from 0.04 to 0.20 M. Students spot the combinations onto the plate over the area that would be illuminated by the scan station (scan stations are described in more detail below). Students must know which scan station they are using prior to the experiment, so that they can accurately deposit their combinations. Students can create their own template as long as they record all details, which emphases good laboratory notebook keeping procedures. Using the pipet method allows students to examine approximately 30−58 unique compositions per plate. The template shown in Figure 1A,B has open space on the plate, which serves two purposes. First, this allows students to check to make sure that the instrument is working properly, as no signal should be observed in these locations. Second, an area is needed for students to attach a contact so that the plate can be connected to the scan station. After the combinations are applied to the plate, it is then heated on a hot plate at ∼100 °C to remove the solvent and dry the combinations prior to firing. Once the combinations have dried, the glass substrate is fired at 500−550 °C up to 12 hours, allowing the precursor solutions to decompose into potential metal-oxide semiconductors.

The precursor solutions can also be deposited via spray deposition using inexpensive airbrushes (Central Pneumatic, model 47791) or glass atomizers (Chemglass, CG-1180). As with the pipet method, templates are created by individual users after choosing to deposit their samples via spray deposition. An

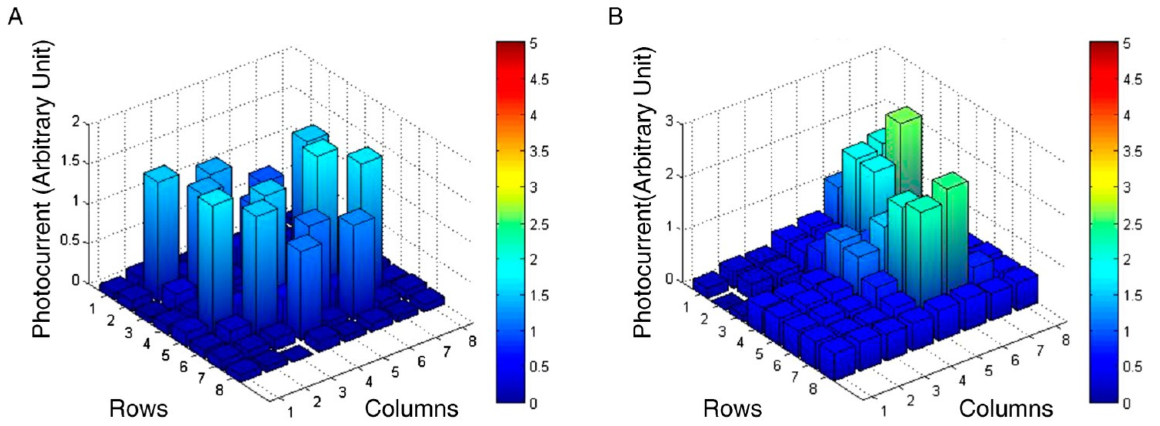

Figure 2. (A) no changes (B) Student-acquired data that shows the photocurrent response from a mixture of the metals: zinc, copper, and potassium. The standards iron oxide (upper left corner) and copper oxide (upper right corner). No bias was applied.

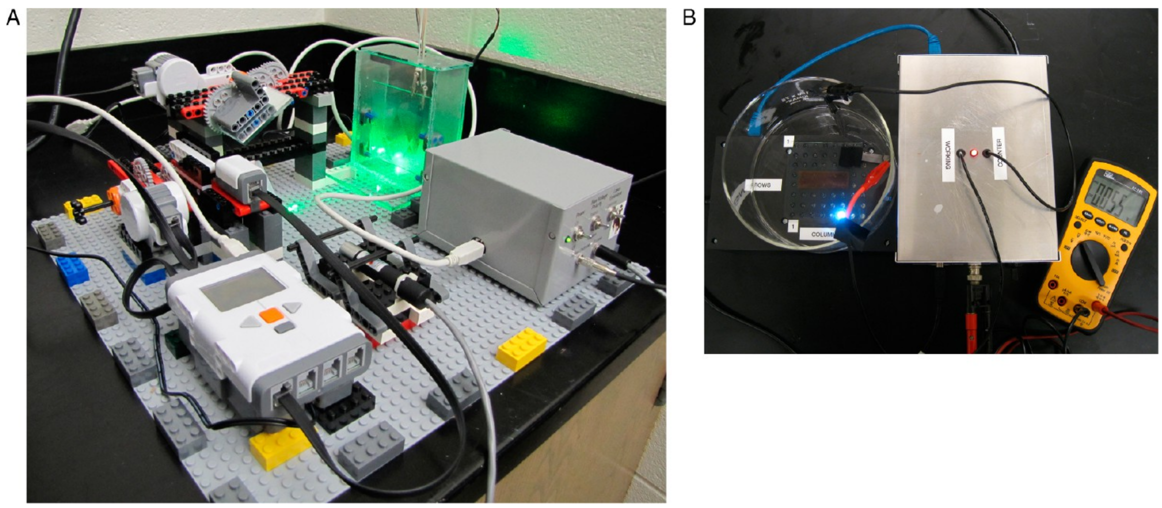

Figure 3. The two scan stations used in the Solar Army. (A) The LEGO scan station (SHArK) (B) The light emitting diode (LED) scan station (SEAL) recently deployed.[35] See ref 36 for ordering information on both stations.

example of a template and how the ratios are deposited via spray deposition is shown in Figure 1C,D. An advantage to this method is that it allows for thin film gradients to be investigated, thus yielding potentially more combinations than the pipet method. As with the previous method, the internal standards (i.e., iron and copper oxide) are spray deposited to the corners of the glass substrate, and again are included on each plate tested. An inert gas, such as compressed nitrogen, is used to power the airbrush to deposit the precursor solutions. To successfully accomplish spray deposition, the glass substrates are mounted on a hot plate that is heated at 300 °C. The precursors are applied using quick swipes of the sprayer, approximately 3 in. away from the glass substrate. Masks are used to direct the deposition to certain areas on the plate. Concentrations of the precursors are generally 0.25−0.35 M. The application technique can be adjusted to achieve the desired thickness and coverage, depending on the precursor being deposited. As with the pipet method, after all of the combinations have been deposited, the plates are fired at temperatures in the range of 500−550 °C.

Post firing, students must prepare their plates for scanning. A metal wire is attached to the conductive side of the glass via silver conductive epoxy and is sealed with clear, nonconductive epoxy in an area where no samples were deposited. Alternatively, conductive graphite tape can be used as a connector, which is attached to a clean area and coated with regular or liquid electrical tape that is allowed to dry. Once the contact has been made, the students attach their plates to the scan stations via alligator clips and scan their combinations for photoactivity using the SEAL or SHArK scan stations.

The scan is accomplished using an electrochemical cell with a working and counter electrode. The working electrode is the FTO conductive glass substrate and the counter electrode is a graphite rod. The working and counter electrodes are submerged in a dilute electrolyte (e.g., 0.1 M KOH or NaOH) and connected to the system. Software is provided and used to acquire the photocurrent reading for each combination deposited on the working electrode. The results are recorded using a data acquisition box, which has been previously described in the literature.[35] After students obtain results, they examine their data for "hits". A "hit" is either a bright spot for the SHArK station or a tall (red) bar for the SEAL station. The results from either station can be uploaded and viewed on the project's Web site.[36] Examples of data obtained from the SEAL scan station are shown in Figure 2. The graph shown in Figure 2A is a calibration performed for the scan station. Iron oxide is deposited randomly across the plate so that students can test their scan station. Once it has been confirmed that it is working, students scan their own unique combinations. An example of student-collected data is shown in Figure 2B. This mixture consists of zinc oxide, copper oxide, and potassium oxide. At the upper left (rows 1−3, columns 1−3) is the response from the copper oxide standard. In the upper right (rows 1−3, columns 6−8) is the response from the iron oxide standard. In the middle (rows 4−7, columns 2−7) are unique combinations. Students compare their unique combinations to the standard responses. If the unique combinations perform better than the standards, then the combination is reported as a "hit" and should be investigated further by research scientists involved with the Center for Chemical Innovation (CCI) Solar Fuels, or by the research group that discovered the combination, if they choose. In Figure 2B, the sample performed equally to that of the standard so it is not a "hit". The photocurrent of each unique combination is examined under no bias as well as under an applied bias (e.g., ± 0.001 to 0.5 V). A positive bias is used to scan for n-type materials and a negative bias is used to scan for p-type materials. (For additional details, see the Supporting Information.)

Schools are encouraged to conduct their own experiments (i.e., deciding what combinations to investigate) and then report their findings to the Web site so that all participating institutions can monitor the most up-to-date results from all collaborating institutions.[36] The Web site is also used as a communication tool that provides a platform for basic information, instructional videos, discussion, troubleshooting, and news.[36] All software and hardware downloads are also available on the Web site. Additional materials have been developed to help participants, such as manuals, tutorials, lectures, worksheets, assessments, and handouts.

The two scan stations, SHArK and SEAL, were developed to achieve high-throughput screening of potentially photoactive semiconductor materials in a simple and inexpensive manner. The SHArK scan station is shown in Figure 3A. It is constructed of mostly commercially available parts, including LEGO Mindstorms kits, LEGOs, a modified 532 nm green laser pointer, and a custom-built electronics box that plugs into a USB port allowing for computer control of the electrode potential, photocurrent data collection, and the pulsing of the laser. An etched glass electrochemical cell was constructed from plate glass and aquarium cement, and electrode holders are constructed from copper wire and alligator clips to connect the FTO glass substrate (working electrode) to the electronics box (see the Supporting Information and SI Figure 3). The software directs the laser to raster over the FTO glass plate in the electrochemical cell, which simultaneously records the photocurrent generated by the materials at each point. A false-color image displays the photocurrent produced by the material as a function of Cartesian position and is then analyzed using the open-source software program ImageJ. Spots of interest or "hits" can be identified by the bright color regions in the false-color image. Again, students are looking for a bright region that is not produced by a standard but instead by a unique semiconductor combination.

The second station, the SEAL kit, is shown in Figure 3B. The kit consists of an 8 × 8 LED array pulser and a potentiostat scanner, which measures photocurrent generated upon illumination of the semiconductor samples by the LEDs.[35] This system is a two electrode system, with a counter electrode (graphite rod) and working electrode (conductive glass plate). The kit, when purchased, includes the following items: counter electrode (graphite rod), FTO conductive glass substrates, data integrator box, USB cords, and the LED array box (see the Supporting Information and SI Figure 4). Other items that are not provided in the kit and that must be purchased separately to run the station include conductive wire, silver epoxy, nonconductive epoxy, a crystallization dish, and voltmeter or multimeter. Links to order additional substrates or other supplies as well as contact information for ordering are available via the Solar Army Web site.[36] The software program allows students to control the applied voltage and adjust the number of scans, which then generates an integrated average of the current produced by the sample when it is illuminated. The software removes any background current prior to producing the final image in a bar graph format (Figure 1A,B). The image and corresponding data (i.e., chemical information, bias applied, etc.) are then saved in a file that is uploaded to the online database.

■ INTEGRATION IN THE CURRICULUM

High School Applications

The experiment can be implemented in after-school clubs or used for AP or introductory chemistry classes during normal classroom laboratory periods. The project has also been used as a "special project" for science fairs, after AP exam projects, or semester-long projects. The context of this experiment provides a platform for educators to discuss renewable energy and the current environmental and energy challenges the world is facing, while conducting a laboratory experiment that is connected to current cutting-edge research in this area of science. Science concepts can be tuned to the level of the students that educators feel is appropriate for their particular classroom. Instructional videos are available on the Web site to help with the assembly of the kits and deposition of combinations.[36] Additionally, a worksheet has been created to provide example problems that are useful for students performing the experiment (see the Supporting Information). To introduce the experiment at the high school level, the best deposition method to facilitate the project in this setting is the pipet technique using Hamilton syringes or micropipets. For after-school implementation, typically students meet for 1−2 h, once a week with 3−4 students per scan station. The first meeting is introductory with basic concepts and the purpose of the CCI project being explained. Solutions are made in the second and third weeks. Deposition can be completed in weeks 4 and 5. The plates should be fired within 24 h of deposition. High schools may choose to purchase their own furnace or use a ceramic art kiln if one is available. Additionally, the high school could possibly partner with local collegiate institutions if a furnace is available. In weeks 5 and 6, students can attach the wires or graphite tape to the glass substrates and scan the plates. After the results are obtained, students analyze their combinations compared to the standards. Students can present research results by creating a poster, writing a lab report, or presenting findings to other students. Additional potential benefits include the possibility of presenting a poster at an American Chemical Society meeting in the high school section. When the project is implemented in the high school curriculum, teachers provide students with an overview of the CCI Solar Fuels project[20] as well as the details of the experiment. Students are allowed to pick from a series of chemicals (e.g., metal salts that are provided by the teacher), create their precursor solutions, and deposit combinations of their choosing onto FTO conductive glass plates. The teacher

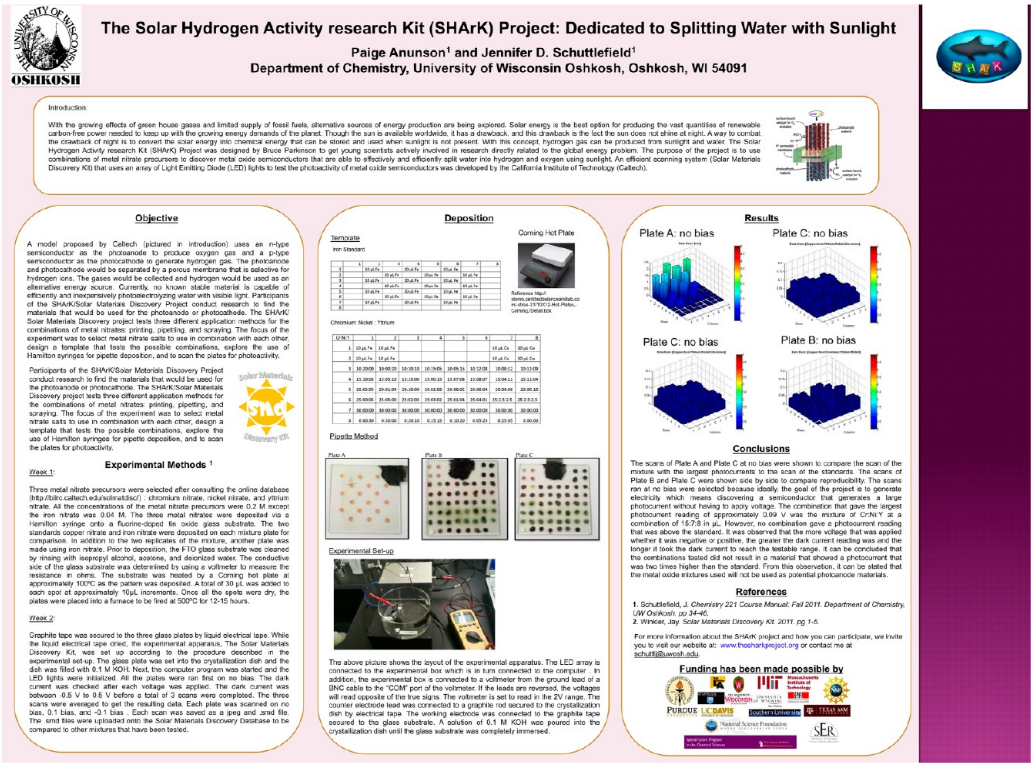

Figure 4. A poster is shown that was submitted for grading using data collected from the SHArK/SEAL project implemented in a sophomore level chemistry course. The students conducted the research over a two week period, where the laboratory class periods last for 3 hours and 20 minutes once a week. Students were required to include background on the project, the experimental process, the data they collected and a discussion of their results.

fires the plates and either allows students to attach the wire or graphite connector to the plates or does so prior to returning the plates to the students. Students scan their combinations during the next lab period and upload their results to the Web site. The entire process generally takes 3−5 lab periods to run one cycle of testing plates. Demonstrations[37−39] or other experiments[37,39,40] can also be used to complement the project.

Undergraduate Classroom

At the undergraduate level, the project can be integrated into the curriculum in a variety of ways. It can be used as an undergraduate research independent study project or as laboratory experiments in introductory, analytical, inorganic, or physical chemistry, and materials science courses. This experiment provides a platform to discuss sustainability, renewable energy, and current research in the area of photoelectrochemistry; it can potentially be paired with other relevant experiments.[30,41−50] Scientific concepts can be tuned to the specific area of interest, depending on the focus of the particular course (e.g., stoichiometry in introductory chemistry, or materials in inorganic chemistry). Integrating the project into a laboratory course generally requires a two-lab period commitment. In the first lab period, students pick the metals to test, design a template for their plates and deposit their unique combinations. Suggested combinations can be provided to the students. A variety of precursor solutions can either be prepared by students or can be premade to speed up the deposition process.After the precursor solutions are made, students spot the combinations on a heated FTO conductive glass substrate. After the samples and standards are deposited, the instructor or TA fires the plates and mounts a connection (e.g., wire or graphite tape) to the plate enabling the plate can be connected to the system. During the second lab period, students scan the plates for photoactivity. One scan station will support 2−3 students. In one lab period, for students using the SEAL kit, data can be obtained by the end of a laboratory period (~4 plates scanned). A group of three students scan an individual plate per student and a "group" test plate of only the standard iron oxide to determine whether the scan station is functional. For students using the SHArK scan station, results from one plate will not be obtained until the next day as a typical run takes between 6−8 h per plate. After results are obtained, students compare their combinations to the standards deposited on their plates to determine the photoactivity of the combinations. The instructor or TA then uploads the results to the online database. The results of the lab can be reported in a laboratory report or using other scientific communication, such as making a poster. An example of a student's poster from a second-year-level analytical chemistry class at the University of Wisconsin−Oshkosh is shown in Figure 4.

Independent Study

As a research or independent study project, students are able to use the same fundamentals given in the other curriculum approaches. Participating in the "Solar Army" as a research project allows students to format and shape it into something they are particularly interested in investigating (e.g., very interested in Zn). For instance, if the student wishes to test the effects of layering (i.e., spotting one metal precursor at a time and allowing it to dry before the next is added) versus premixing the precursor solutions prior to deposition, the student would have more time and freedom to conduct such research. Also, after a potential photoactive material has been identified, the student would be able to conduct further characterization of the sample using techniques such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), and ultraviolet−visible (UV−vis) spectroscopy. Lastly, experiments can also be performed by students on their catalysts to determine whether photoelectrolysis is occurring by checking for the evolution of gases, such as O_2.[49,51]

Outreach

This project can also be used as a demonstration to young students (i.e., fourth grade and up) to teach them about chemistry, energy, climate issues, and the scientific method. The project can be performed as a workshop in a "science" day event or as a special event in the classroom. Teachers and students are able to participate in the research project in a limited manner. Typically students are allowed to set up the kit and run a scan of a plate in which previous samples have been deposited. Students then analyze the plate to identify any "hits" relative to the standards on the plate. Leaders of the workshop then help students to understand and compare their results to experiments in the database from students conducting experiments around the world. This can provide students with a taste of the real research problem of finding an inexpensive, effective photocatalyst for photoelectrolysis, and increases awareness of the growing energy and climate issues. Other experiments can easily be paired with this demonstration to reinforce the concepts of water splitting[41,43,44,46,49,52,53] and solar energy.[54,55]

CONCLUSIONS

In addition to the goal of finding a suitable semiconducting material to photoelectrolyze water, the project presented here is aimed at fostering excitement for science in the minds of students. This project was developed to be fun, exciting, and unintimidating to high school and undergraduate students while providing them with the opportunity to participate in a real research project and attempt to solve the global energy problem. This project provides a platform for learning how to problem solve, perform research, use Web-based tools, and communicate scientific research, as well as learning how to collaborate with peers from all over the world and having the opportunity to be part of a larger scientific community. These will all be necessary skills for future scientists to have as they work to solve problems that the upcoming generations of the world will face. To date, over 70 institutions, from high schools to research institutions, have and continue to participate in the project.

ASSOCIATED CONTENT

Supporting Information

Laboratory handout; supplemental experimental details; example worksheet. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: schuttlj@uwosh.edu.

Notes

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