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Discovering Inexpensive, Effective Catalysts for Solar Energy Conversion: An Authentic Research Laboratory Experience

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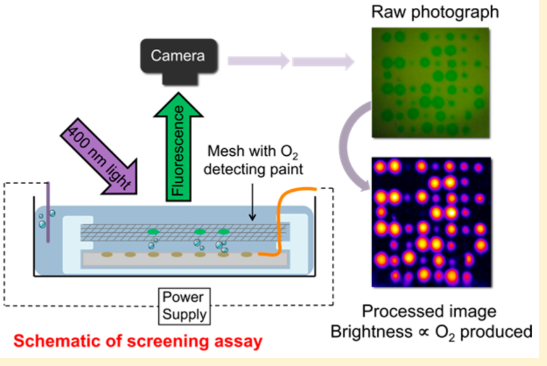
Supporting Information

ABSTRACT: Electrochemical water oxidation is a major focus of solar energy conversion efforts. A new laboratory experiment has been developed that utilizes real-time, hands-on research to discover catalysts for solar energy conversion. The HARPOON, or Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization, experiment allows an array of mixed-metal oxide compositions to be analyzed in parallel to test their activity as water oxidation catalysts. Students create unique combinations of mixed-metal oxide materials, which are then analyzed utilizing a simple, inexpensive system that detects the amount of oxygen evolved during electrolysis. This experiment has the flexibility to be implemented at a variety of educational levels with the depth and breadth of the material covered accordingly. Concepts such as stoichiometry, materials, solutions, and fluorescence can be emphasized, while the research-like experience strengthens students' independence, critical-thinking skills, and excitement for science. An online questionnaire was developed to measure various effects of the experiment on students, including learning gains, attitudes toward chemistry, and motivation to pursue a career in scientific research. The assessment results indicate positive gains for students in their understanding of the social nature of scientific work, scientific literacy, and interest in pursuing additional research opportunities.



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INTRODUCTION

Considerable recent attention has been directed to the development of real-time laboratory research experiments or experiments that are open-ended in nature.[1−8] While many inquiry-based experiments focus on projects that are exploratory in nature, few are true research experiences.[2−8] An important example of a real-time research experiment is the SEAL/SHArK project described by Anunson et al., which focuses on renewable energy and student involvement in the discovery of materials for the photoelectrolysis of water.[1] The success of this distributed research project to engage thousands of students in research and obtain meaningful scientific results provided the inspiration behind the HARPOON project described herein.

Developing environmentally sustainable energy sources is a global challenge, and the need to use abundant resources, such as solar energy and water, to produce chemical fuels has increased the urgency to optimize all aspects of the photoelectrochemical water splitting reaction (Scheme 1). The HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) experiment, described in this report, focuses on

Scheme 1. Reaction Steps for the Splitting of Water in a Photoelectrochemical Cell

Anodic water oxidation half reaction: $$2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad (1)$$

Cathodic hydrogen evolution half reaction: $$4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2(g) \quad (2)$$

Water splitting reaction: $$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \quad (3)$$

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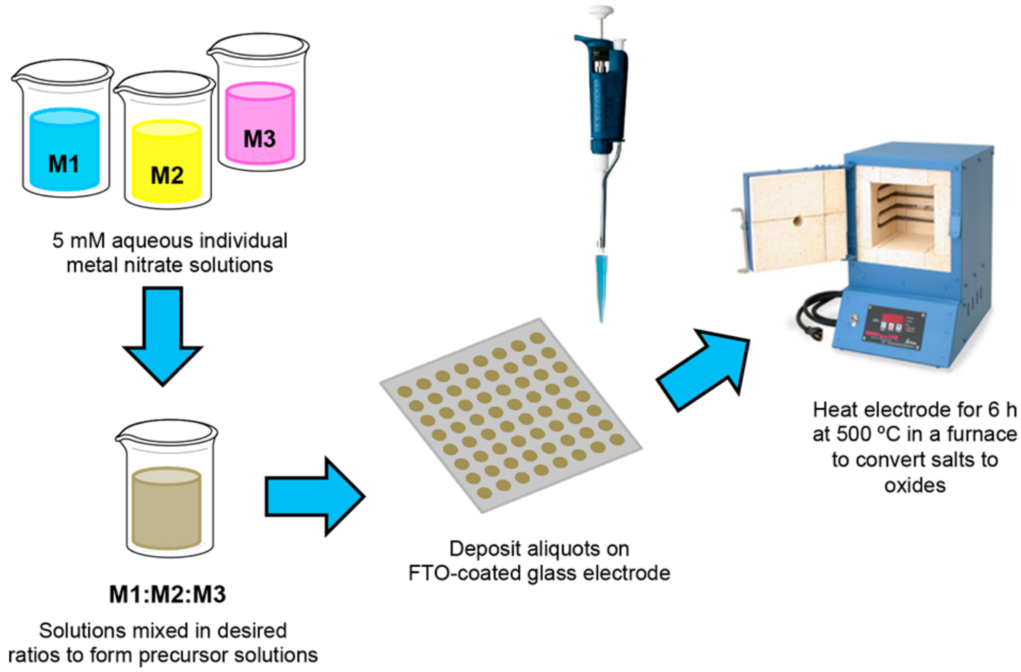

Figure 1. Schematic of individual steps for preparing a mixed-metal oxide catalyst array from metal salt precursor solutions.

one part of this challenge: the discovery of catalysts for the oxidation half reaction (Scheme 1, eq 1), which is known as the water oxidation or oxygen evolution reaction (OER). The experiment utilizes direct detection of the oxygen evolved by mixed-metal oxide materials during electrochemical water oxidation to assess catalyst activity. The project provides an accessible and exciting means to introduce students to chemical research and an important scientific problem.

Of the two water-splitting half-reactions, the anodic water oxidation half-reaction (Scheme 1, eq 1) is particularly challenging.[9] In this reaction, two molecules of water are converted into O_2, together with the release of four protons and four electrons. The protons and electrons can then be used to produce fuel (i.e., H_2) in the cathodic reaction (Scheme 1, eq 2).

The thermodynamic difficulty of the anodic reaction, 1.23 V vs NHE (at pH 0.0), is compounded by the need for substantial overpotentials, typically >0.40 V, to drive the reaction to useful rates.[10] This additional potential requirement reduces the efficiency of solar energy utilization. Therefore, identifying electrocatalysts able to reduce the kinetic barriers for water oxidation is crucial to advance solar fuel technology.[11−13] Promising electrocatalysts must also be stable under highly oxidizing conditions, solar irradiation, and in contact with aqueous solutions over long periods of time.[1,12,14−22]

Currently, the most active water oxidation catalysts employ precious metal oxides, such as iridium or ruthenium oxides, but the high cost of these materials limits their utility.[13,15,16,20−24] While a single nonprecious-metal oxide cannot rival the catalytic activity of these expensive materials, mixed-metal oxides of nonprecious metals are a promising class of catalysts for water oxidation in alkaline electrolyte[25−29] because they are economically viable and often exhibit the stability necessary for widespread use.[1,12,14−22,24,30]

The challenge is that with millions of possible mixed-metal oxide compositions and no guiding theory[31] for the selection of optimal metal combinations and their relative proportions, the task of identifying the best water oxidation electrocatalysts is daunting.[1,10,12,14,15,17−22] Combinatorial screening methods are an attractive approach to address this challenge,[1,10,12,14,15,17,18,20−23,26,31,32] and involving students in this discovery process presents the opportunity to screen large numbers of compositions while offering students the chance to learn about renewable energy and participate in real scientific research.

In addition to aiding the search for new catalysts, HARPOON can be used to introduce or reinforce numerous chemical concepts. Many students will have previously seen a water splitting demonstration in a science class, for example, using the graphite in pencils and a battery.[33] The HARPOON experiment exposes students to the phenomena behind the bubbles observed in this demo and can emphasize three areas of chemistry that often receive limited attention in traditional undergraduate coursework: inorganic materials chemistry, electrochemistry, and electrocatalysis. Other scientific topics explored by the HARPOON experiment are amenable to intro/general chemistry, inorganic chemistry, analytical chemistry, and special-topics courses, or units focused on energy. This flexibility gives the experiment the distinctive ability to be distributed at a variety of educational levels. Herein, we describe a fluorescence-based combinatorial experiment to directly detect oxygen evolution from unique mixed-metal oxide combinations. The distribution of this experiment to students across the country can provide a means of obtaining information on potential water oxidation catalysts, which can then be collaboratively collected in an online database for mass distribution of testing and the dissemination of results. Assessment has shown that students exposed to the HARPOON experiment are more aware of the challenges and social interactions inherent in scientific research as well as understanding how scientists work on real problems, conduct research and analyze data, and integrate chemistry theory and practice.

■ THE EXPERIMENT

Recently, a method was developed for rapidly identifying mixed-metal oxide compositions that are active water oxidation

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electrocatalysts.[12,34] This method has been modified into a laboratory experiment for undergraduate and high school students. The HARPOON experiment assesses an array of mixed-metal oxide compositions in parallel for activity as water oxidation catalysts via their ability to produce oxygen (O_2) under a suitable applied potential. A general schematic of the steps students must take to prepare a sample is shown in Figure 1. Students start by creating unique mixed-metal salt combinations which are deposited onto fluorine-doped tin oxide (FTO) conductive glass plates (3.0 mm 8-Ω SnO_2:F, Hartford Glass), which serve as the working electrodes in the experiment. Students choose their unique mixed-metal combinations using information provided to them by their instructor, and instructors should emphasize the importance of selecting earth-abundant, cost-effective materials for testing, as well as choosing at least one redox-active metal.[1,10,12,15−17,19,22] Examples of metal salts that can be used in the experiment are given in Box 1. Students can

Box 1. Examples of Relatively Inexpensive Metal Nitrate Salts[a] That Can Be Used in the Experiment

Copper(II) nitrate
Calcium nitrate
Aluminum nitrate
Nickel(II) nitrate
Strontium nitrate
Cobalt(II) nitrate
Barium nitrate
Iron(III) nitrate
Zinc nitrate
Gallium nitrate[b]
Cerium(III) nitrate[b]
Bismuth nitrate[b]
Magnesium nitrate
Chromium(III) nitrate
Manganese(II) nitrate

[a]This list contains salts that have been used successfully in the HARPOON experiment. It is also possible to use acetate and chloride salts, but these have not been explored as thoroughly.

[b]It is recommended that HNO_3 is included in the solution to prevent precipitation.

follow a provided template or create their own templates. The latter gives students additional experience in method development, stoichiometry, and record keeping.

Initially, students determine the conductive FTO side of the glass electrode using a multimeter. After the FTO-coated side is washed with distilled water and then rinsed with methanol, the plate is dried and positioned over the spotting template (see below and the Supporting Information documents Spotting Template, Pre-lab, Student Handout, and Instruction Manual for examples). Students should also mark the glass side of the electrode using a scribe or a glass-etching tool for identification purposes after the creation of their materials.

To create the array of mixed-metal oxides, students combine metal salt precursor solutions (e.g., 0.005 M solutions of metal nitrate, chloride, or acetate salts) in desired ratios using pipets or syringes. Aliquots (1−10 μL range can be used) of these mixed metal solutions are deposited on the FTO side of the glass electrode. Once the combinations are deposited, the samples are fired in a kiln or furnace for 6 h at a temperature of 500 °C to convert the metal salts to metal oxides.

A 2:4:4 Ni−Fe−Co oxide is included on every electrode array. This mixed-metal oxide has been determined to consistently perform as an oxygen evolution catalyst.[12] Cobalt and nickel oxides individually, and in mixed-metal oxides, have been widely studied as electrocatalysts for water oxidation,[12,13,26,28,29,35−49] and the 2:4:4 Ni−Fe−Co oxide provides a consistent material to compare materials against in the search for higher performing OER catalysts. This catalyst is included on each electrode to ensure the validity of comparisons of compositions within and across different electrodes and also across data collected by different researchers.

After the metal precursors have been decomposed into the mixed-metal oxides, the experiment apparatus, consisting of an electrolytic cell modified for O_2 detection, is assembled for analysis. The setup for the experiment is shown in Figure 2, where Figure 2A shows the equipment being used in the experiment, and Figure 2B provides a schematic of the inside of the electrolyte-containing dish to illustrate the assembly of the various components. To attach the power supply to the working electrode, conductive tape (U-line, Catalog no. S-14676) is attached to the conductive side of the glass where no oxide spot is present. The glass plate is then placed in a custom-made acrylic holder, a stainless steel mesh is positioned above the plate, and the assembly is held together with two rubber bands. The stainless steel mesh (Grainger, Catalog no. 3DLP3) is coated with a commercially available, dual-chromophore fast-response pressure-sensitive fluorescent paint (Innovative Scientific Solutions Incorporated, Catalog no. BUNC-12) that changes color in proportion to the partial pressure of oxygen. The fluorescent pressure-sensitive paint works by combining two fluorophores, chemical compounds that can re-emit light upon light excitation, where one fluorophore with green fluorescence is insensitive to O_2 and used as a background reference, and the other fluorophore with red fluorescence is quenched in proportion to the pressure of O_2.[12]

The holder assembly is placed in a suitable dish (e.g., crystallization dish, plastic container, etc.) containing 0.1 M degassed alkaline electrolyte (NaOH or KOH) with the unattached end of the conductive tape extending out of the electrolyte solution and dish. An efficient way to degas the electrolyte is to bubble an inert gas such as N_2 or Ar rapidly through the solution for 20 min before pouring it into the dish where the electrolysis will take place. The power supply has two wires that terminate in alligator clips. To complete the circuit necessary for electrolytic testing, one alligator clip is attached to the conductive tape (which is connected to the FTO-coated glass anode). The other alligator clip is attached to a graphite counter electrode (cathode), and the end of the graphite electrode is immersed in the electrolyte.

Before turning on the power supply and initiating the OER reaction, a final purge of the electrolyte and headspace is carried out using N_2 or Ar gas. A darkened room or box covering the setup is used to enable detection of the fluorescence resulting from illumination of the paint without interference from stray room light (see Supporting Information document Student Handout or Instruction Manual for directions on construction of a "dark room" box).

During the electrolysis, the mesh is illuminated with a commercially available UV-LED flashlight (Esco-Lite 395 nM Ultraviolet LED Flashlight), and the emission is recorded using a digital camera, camera phone, or webcam camera every 30 s for 5−10 min. A yellow filter (Lee Spring, Catalog no. LE100S) is

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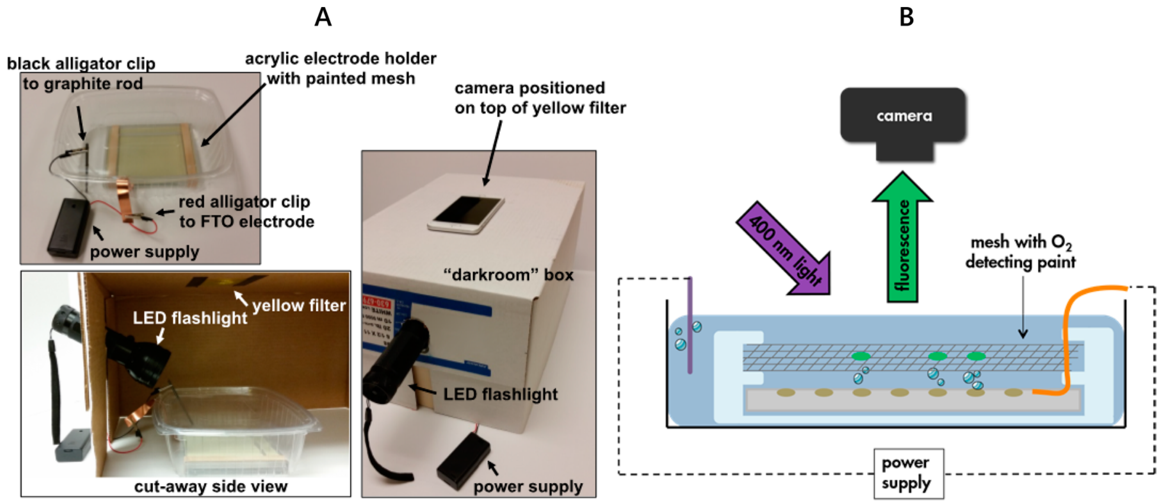

Figure 2. (A) The setup for the HARPOON experiment is shown. Kit components include a UV-LED flashlight, graphite rod, power supply, acrylic holder, painted mesh, and a yellow filter. The camera and "darkroom" box are not included. See ref 50 for ordering information for the experiment kit. (B) Schematic of the HARPOON setup from the side perspective view.

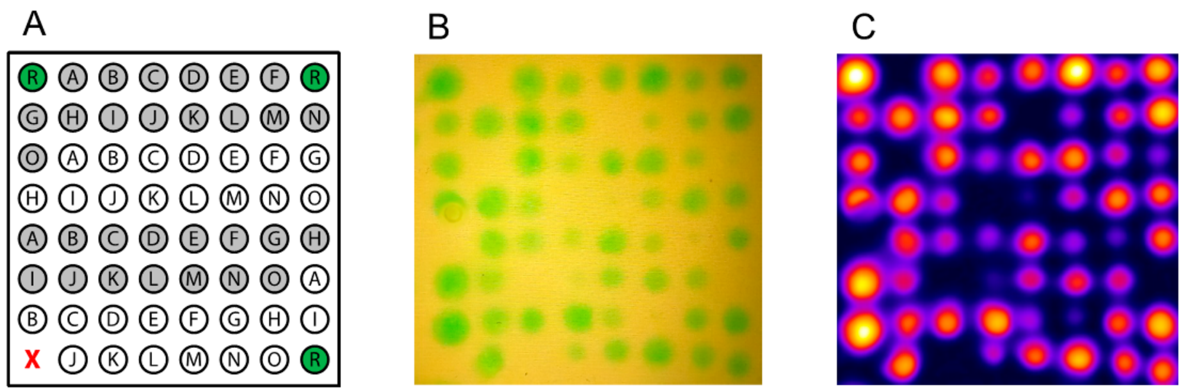

Figure 3. (A) Template for an 8 × 8 catalyst array on an FTO-coated glass electrode. The red X indicates a blank position for the attachment of conductive tape and the positions with an "R" indicate the locations of the Ni−Fe−Co reference material. (B) Raw photograph of the O_2-sensitive paint acquired during electrolysis. Green spots are observed from fluorescence quenching due to O_2-production by catalysts on the underlying array. (C) False-color processed image where brightness is proportional to the amount of O_2 produced at an array position. The image can be used to quantify the activity of each mixed-metal oxide catalyst on the electrode.

positioned between the fluorescent mesh and the camera to absorb the 400 nm light while allowing the emitted light to reach the camera. Where there is an absence of O_2 at the mesh, both the red and green fluorophores emit light, and a yellow-orange color is observed. The competent catalysts in the array produce oxygen that diffuses to the part of the mesh directly above them, and in the presence of this O_2, the red fluorescence is quenched. This catalyst activity is observed as green spots on the mesh. Note that the UV-LED flashlight does not drive the electrolysis reaction, but is essential for illuminating the fluorescent steel mesh and obtaining visible results for O_2 production.[51]

Figure 3A illustrates a template for an 8 × 8 catalyst array, with the green circles labeled "R" indicating the location of the 2:4:4 Ni−Fe−Co reference material to which the rest of the deposited samples can be compared. Figure 3B shows an example of a picture captured while a mesh is being illuminated and electrolysis is occurring. The green spots above the metal oxide spots indicate oxygen evolution, with the more intense spots indicating greater oxygen evolutions and therefore a more effective mixed-metal oxide catalyst. The photographs collected over the 10 min are then processed using the open source program ImageJ[52] to create a false color map image of the intensity of the fluorescence. This map is shown in Figure 3C. The processed digital image in Figure 3C represents the relative activity across the array, with the brightest spots corresponding to the materials that evolved the highest concentration of O_2. The catalyst compositions at these spots are considered "hits" if their brightness is better than the average brightness of the 2:4:4 Ni−Fe−Co reference spots. These compositions are the catalysts that deserve further investigation.

Each composition should be included multiple times on an array to compensate for inherent variability in spot brightness that can arise due to factors which include sample preparation, spot position on the electrode, or sample illumination. For example, in the template shown in Figure 3A, the 2:4:4 Ni−Fe−Co reference is included at three array positions and each test composition is included at four array positions on the electrode. This design ensures that each catalyst composition is tested multiple times and reinforces to students the importance of reproducing experimental results.

Students are encouraged to conduct their own experiments (i.e., determine what combinations to investigate) and then upload their findings to a database on a website dedicated to the HARPOON project.[50] The website is managed by the

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NSF-funded Center for Chemical Innovation in Solar Fuels whose overall mission statement is to "focus on one of the 'holy-grails' of 21st century chemistry—the efficient and economical conversion of solar energy into stored chemical fuel". CCI Solar investigators are targeting the basic-science underpinnings of the solar-driven decomposition of water into hydrogen and oxygen.[53] The online HARPOON collaborative database allows students to upload their data, both positive and negative results, for further dissemination of their results so that all participating institutions can monitor the up-to-date results from the collaborating institutions. Results from catalyst candidates that are not promising are also useful and should be uploaded so that combinations that do not show activity are not excessively replicated once inactivity is confirmed.

In addition to the database, the HARPOON section of the Solar Army Web site provides information on obtaining a kit (current price and ordering information) as well as background information, resources for running the kit or purchasing replacement components, an example spotting template, the ImageJ macro for data analysis, and relevant journal articles.[50]

INTEGRATION IN THE CURRICULUM

High School Curriculum

The HARPOON experiment implementation into the high school curriculum is similar to previously reported experiments,[1] which can be implemented into after-school chemistry clubs, AP or introductory chemistry laboratory experiments, or as semester long projects. Instructors can provide the students with valuable exposure to experimental science while selecting the amount of background information that is pedagogically appropriate. HARPOON could inspire classroom discussions on renewable energy, sustainability, green chemistry, and the current grand challenges the world is facing. The Next Generation Science Standards (NGSS) and the Common Core State Standards for Mathematics (CCSSM) both call for improving scientific, engineering, and mathematical practices, which include model-based reasoning that engages students in developing and using models, analyzing and interpreting data, and using mathematics and computational thinking.[54,55] The HARPOON experiment addresses all of these practices and specifically addresses the following NGSS standards: HS-PS1-6, HS-PS3-3, HS-ESS3-2, HS-ESS3-4.[54] Further details are provided in the Project Overview Summary included in the Supporting Information.

To conduct the experiment at the high school level, students would first need to be introduced to the basic concepts of water splitting, the mission of finding the "holy grail"[53] and the fundamentals of how the experiment is conducted. The first laboratory experience could include creating precursor solutions, determining templates for deposition, and making the mixed-metal oxide catalyst array by depositing the precursor solutions onto the array. After the catalyst arrays are made, the arrays are fired in a kiln or furnace. After firing and cooling overnight, the sample plates are tested and the data is analyzed. Students can present their results a variety of ways including writing a lab report, creating a poster, or presenting their experience to the class. Students gain experience in developing a method by selecting which metals they would like to combine, creating a template, and depositing the combinations of their choosing. After the combinations are fired, the students gain experience in setting up an experiment, collecting data, and analyzing the data they collected, all of which provide significant experience in the practices specified by the NGSS and CCSSM. The entire process generally can take between 2 and 5 lab periods to analyze one round of combinations and can be paired with demonstrations[56−58] or other lab experiments[1,57,59−61] to reinforce concepts.

HARPOON has been developed with accessibility in mind, and the experiment should be appropriate for implementation within many high schools. However, depending on available resources and the comfort of the instructor, the project could also be adopted as a partnership between a high school and a local college or university. In this arrangement, high school students could benefit from the facilities and expertise provided by the college, and the project could be used to forge relationships between high schools and higher education institutions.

Undergraduate Classroom

The project can be integrated into the curriculum at a variety of levels of undergraduate education and specifically into courses including introductory, analytical, physical or inorganic chemistry, and special topics courses such as materials science or electrochemistry. Pedagogically, HARPOON connects to conceptual chemistry topics including electrochemistry, fluorescence, redox reactions, solution chemistry, materials chemistry, and electrocatalysis or it can be used to expose students to applications of chemistry including sustainability, renewable energy, and green chemistry. The experiment presented here can also be paired with many other projects including the Solar Energy Activity Lab (SEAL), Solar Hydrogen Activity research Kit (SHArK), or other relevant experiments.[1−3,33,59−63]

An advantage to using a versatile project like HARPOON is that it can be modified to emphasize a specific area of interest for a particular course (e.g., pH and solutions for analytical chemistry, materials in inorganic chemistry), and thus, one kit can be used in a variety of courses. Integration of the project requires a minimum of two lab periods. In the first lab period, students choose the different metal combinations they are going to analyze and make their array. The students' arrays are fired in a kiln or furnace prior to the second lab period. In the second lab period of 45−60 min, students assemble the system, purge the chamber, and test the array for oxygen evolution. Once complete, students can analyze their test results either in class or out of class using the free open source[52] software, ImageJ. After analysis, students can either report their findings or prepare and test another array using their results. Supporting Information includes a pre-lab exercise, sample lecture, detailed procedure, background documentation, and system requirements.

Undergraduate Independent Study Research

The HARPOON experiment provides a way for undergraduates to gain insight into a research project and to participate in an established research community. It serves to expand the undergraduate students' knowledge by allowing them to apply previously learned concepts to their research. Students have the opportunity to learn about renewable energy, as well as focus on an interesting aspect of the experiment. For example, they may be interested in the oxygen evolving reaction (OER) capability of manganese because it is their favorite element, or they may want to know what happens when the pH of the electrolyte is varied. Questions such as these can be explored as research projects, which provide students with a vested interest in the work. Lastly, students can be exposed to many surface science techniques if they identify a promising electrocatalytic material. Techniques such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) or X-ray diffraction (XRD) can be employed to further characterize the materials to

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investigate the active structure. The research value of this type of undergraduate research experience has been demonstrated in the previously reported SHArK project, wherein an undergraduate researcher identified a new, functional solar water-splitting oxide that has been the subject of follow-up studies.[1,17,19] Analogous opportunities are anticipated through the HARPOON project.

Outreach

The HARPOON experiment can be performed as a special event demonstration for novice participants and can also be used to teach students about data collection in a "science" day workshop. For these outreach events, students could participate by testing previously prepared arrays and then analyze the data. Students could identify any "hits" on their particular plate and discuss with the workshop mentors or leaders what the results mean and how they compare to experiments in the database from students conducting experiments at all participating institutions. This venue again provides a platform for a discussion on a variety of topics including chemistry content, scientific theory, modeling, renewable energy, sustainability and research. It can also be paired with other demonstrations to illustrate the concepts of solar energy and water splitting.[56,58,60−65]

■ ASSESSMENT

Previous studies have shown that research-type laboratory experiences can expose students to previously absent aspects of curricula, such as experimental design and applying textbook knowledge to a real situation. Many higher-education institutions have incorporated more open-ended, self-designed, research-like experiences at a variety of curricular levels.[2,3,5−8,66−69] Assessments of these authentic research-based experiences provide evidence for increased interest in chemistry, as well as increased interested in pursuing further research experiences.[7] Students also reported gains in learning about lab concepts, using the scientific method, and thinking critically.[7]

The HARPOON experiment was implemented at the Milwaukee School of Engineering (MSOE) for undergraduate students enrolled in a second 10-week term of general chemistry (Chemistry II, 4 credit hours, n = 37), where the primary topics include precipitation, kinetics, equilibrium, acid/base and electrochemistry. At MSOE, each student had 3 h of lecture and one 2 h lab period each week. The lab sections contained between 15 and 20 students, which consisted of primarily engineering majors in their first or second year of college. The course was ∼79% male and 21% female with three students abstaining from answering the question. Students in the course identified as mostly Caucasian or European, with ∼6% identifying as Asian American, ∼6% identifying as Hispanic, and ∼3% identifying with either Native American or African American.

The experiment was implemented over three weeks. In the first week of lab, students deposited their unique combinations of mixed-metal oxides, downloaded the software, and practiced data analysis by analyzing a sample data set. In the second week of lab, students assembled the HARPOON scan station and tested their specific combinations. They analyzed their data in the third week. Students were asked to complete an online survey at the end of their experience. The results were then analyzed by the Center for STEM Education at the University of Colorado at Colorado Springs.

The online survey instrument combined items from the Survey of Undergraduate Research Experience (SURE)[68] and the Student Subjective Science Attitude Change Measure (SSSACM).[70−80] The survey consisted of 79 questions including student demographic information. The SURE portion of the survey asked students to rate their interest and motivation to pursue scientific research, to indicate their level of knowledge gain as a result of the lab project, and had some questions about the student lab experience including feedback on the teacher and other students. The SSSACM section included 12 statements that students were asked to rate on a 6-point Likert scale. The statements measured an increase in motivation to pursue science and an increase in interest in pursuing a science career. Another 15 questions asked students to indicate the level of knowledge gain for each of several topics, with 1 indicating "no gain", and 5 indicating a "very large gain". Finally, there were 7 open-ended questions asking about their experience, the change in their knowledge about renewable energy, and the change in their view about the world's energy problems. All students reported some type of benefit or gain from their participation on the experiment, with the majority of our findings in agreement with previously published assessment on authentic research-based experiences in the laboratory.[7]

Students were surveyed about their plans after finishing their undergraduate (UG) degree. More than half of the students who responded planned to pursue further education after completing their UG degree, including a Ph.D., Master's degree, or going to a professional school such as medical school. While the number of students who are considering furthering their education beyond UG degrees is high relative to a typical introductory class (∼5% of college students in the U.S. in 2013−2014 went on to receive master's or doctor's degree[81]), students still were impacted by their lab experience and reported overall gains in their understanding of how the scientific process works. Specifically, students reported the experiment was effective at helping them understand the role of supporting evidence for making scientific claims, how to perform data analysis, how research occurs, and how scientists work on real-world problems.

From the analysis of the student responses, the experiment appeared to effectively support student understanding of the nature of research and the use of scientific knowledge, but interestingly, a major difference was observed for students who reported that they intended to pursue a career in scientific research versus those who did not. The more research-oriented students reported that the largest benefit they perceived from participating in the lab experience was (i) becoming part of a learning community; (ii) understanding chemistry research; and (iii) developing a tolerance for obstacles faced in the research process. The students who did not identify as research-oriented were not swayed to pursue a career in scientific research, but they were able to attain a better understanding of the scientific process. While the experience was effective in exposing research-oriented students to the challenges and social interactions inherent in scientific research, the nonresearch oriented students indicated that the project was effective in exposing them to the nature of scientific inquiry, data analysis, and giving priority to data-based evidence. Though the project did not effect change in these students' intent to pursue a scientific research career, the benefits experienced by these students are very important to creating scientifically literate undergraduates and community members. Additionally, ∼74% of participants reported that their level of interest to continue to pursue learning science increased after the lab, which again can lead to critically thinking, problem-solving citizens who use data-based evidence to make decisions.

Finally, the HARPOON experiment was effective in improving student understanding of chemical processes and how these processes relate to the world's energy challenges. The majority of

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students reported a medium to large gain in their understanding of various chemical education topics related to energy production. Additionally, 57% of the students participating in the project reported that they are between likely and very likely to participate in another research experiment like HARPOON, which could potentially lead to increasing the number of students pursuing research opportunities either in their careers or in graduate school. As the students participated in the experiment over the course of a few weeks, they became more aware of the importance, challenges, and nature of scientific research, which is an experience that they can carry with them into their chosen career fields regardless of the discipline.

■ CONCLUSIONS

One of the current grand challenges is for society to meet the global energy need in a sustainable and environmentally friendly way. Lab experiments provide an ideal platform to introduce the ideas of current renewable energy technology and sustainability, while providing students with hands-on learning experiences that reinforce topics concurrently being covered in class. Here, we developed a real-time research experience aimed at discovering inexpensive and stable mixed-metal oxides that are efficient water oxidation catalysts, while providing a platform for students to learn about many chemical concepts, renewable energy, and sustainability. 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. Assessment data collected indicates that exposure to the HARPOON experiment provides an effective method of exposing research-oriented students to the challenges and social interactions inherent in scientific research and that the main impacts from the experience on nonresearch oriented students appeared to be increased gains in understanding how scientists work on real problems, conduct research/analyze data, and integrate chemistry theory and practice. Lastly, the experiment increased interest for students to seek out or choose to work on another research project in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00591.

- Data workup spreadsheet (XLSX)
- Project overview including supplemental experimental details; Instructor notes (PDF)
- Lid template (PDF)
- HARPOON kit instruction manual; Spotting template (PDF)
- Laboratory handout (student and instructor versions); Sample lab report worksheet (PDF)
- Pre-lab assignment (PDF)
- Sample lecture (PDF)

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Notes

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