Harry Gray's Legacy to the Children of the World

by Jorge Colón

Dedicated to Harry Gray on his 81st birthday

In February 2011, I participated in the American Association for the Advancement of Science (AAAS) Annual Conference held in Washington, DC. At the conference, I attended a symposium titled, *Powering the Planet: Generation of Clean Fuels from Sunlight and Water* organized by Harry B. Gray, the Arnold O. Beckman Professor of Chemistry and Founding Director of the Beckman Institute at the California Institute of Technology (Caltech). I'd known Harry since he was my mentor during the two years (1990-1992) that I was a National Science Foundation (NSF) Postdoctoral Fellow at Caltech. At the AAAS symposium, Harry talked about the Solar Army, the outreach branch of the Center for Chemical Innovation in Solar Fuels (CCI-Solar, www.ccisolar.caltech.edu), an NSF-funded consortium of 13 universities and 19 laboratories centered at Caltech and headed by him. I joined the Solar Army right after that symposium. This is a story about the Solar Army from an international perspective and of how, through the transforming power of scientific research done by thousands of students around the world, Harry is leaving a lasting legacy to the children of the world.

I decided to attend Harry's symposium because I was very interested in the use of solar energy as an alternative energy source. Around 2005, I started to integrate the topics of the energy crisis, global warming, and solar energy in my talks about my research at the Río Piedras campus of the University of Puerto Rico (UPR). I followed very closely the increased awareness on these topics brought by the documentary "An Inconvenient Truth" by former US Vice-President Al Gore, and I was pleased when the 2007 Nobel Prize was awarded to Gore and to the Intergovernmental Panel on Climate Change (IPCC). Global warming and climate change threaten islands in the Caribbean region, including my country of Puerto Rico. Several studies have concluded that small islands will confront the consequences of climate change first. IPCC had indicated in the Fourth Assessment report in 2007 that "small islands... have characteristics which make them especially vulnerable to the effects of climate change, sea-level rise, and extreme events". So I was particularly eager to hear what Harry and the rest of the speakers at the 2011 AAAS symposium had to say about generating clean fuels from sunlight and water.

Jorge Colón (right) and Harry Gray at the CCI Solar Annual Meeting, on 6 Feb 2016

At the symposium, Harry talked, in his characteristically enthusiastic manner, about the CCI-Solar program. He explained that the Center's aim was to study the fundamentals of using solar energy to split water into oxygen and protons, which are then used to make hydrogen fuel. This is one of the "Holy Grails" of 21st Century Chemistry: the conversion of solar energy into chemical fuel. More energy reaches Earth each hour from the sun than all the fossil fuel energy consumed in the planet in a year. Producing cheap hydrogen can provide energy on a 24-7 basis, contrary to silicon-based photovoltaic cells that only work during the day, when the sun shines. In order to do that, Harry explained that we must mimic Nature, which is able to catalyze both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) required for the conversion of solar energy into chemical fuel by water splitting using earth-abundant materials. Contrary to Nature, scientists commonly use expensive catalysts such as platinum to accomplish this. Replacing platinum with cheaper alternatives (such as cobalt, iron, or nickel) would provide the opportunity to make solar energy competitive with fossil fuels.

A big part of the CCI-Solar program effort is to understand the critical science needed to discover and optimize new catalysts for these reactions. However, obtaining efficient catalysts based on earth-abundant materials is still a daunting task. In his talk Harry explained CCI-Solar efforts to obtain new, more efficient, and cheaper catalysts. But when Harry became really enthusiastic during his talk was at the end, when he talked about the Solar Army.

In 2007, the Bruce Parkinson research group at the University of Wyoming pioneered a combinatorial,

chemistry-based method to quickly produce and test the catalytic properties of new mixed-metal oxide semiconductors using widely available components and a LEGO Mindstorms® building set. The kits developed by the Bruce Parkinson research group were called the Solar Hydrogen Activity Research Kits (SHArK). The kits were in beta stage at eight institutions thanks to a Dreyfus Grant when Bruce joined the CCI. Jennifer Schuttefield Christus started then as postdoctoral research associate with Bruce and both worked to distribute the kits nationally. Jennifer worked with the CCI to get the SHArK sites up and running in California with the help of Jillian Dempsey, then a graduate student in Harry's group, and James McKone, then a graduate student of both Harry and Nate Lewis. Harry established the CCI Solar Army in 2009 after a public lecture at Caltech in which he demonstrated the apparatus developed by the Parkinson research group. He invited the public to take a closer look at the apparatus and said that they would be drafted into "our army" of solar energy researchers. Following Harry's public lecture, the CCI received numerous phone calls and e-mails from community members eager to have their children recruited into the "Solar Army", and so the Solar Army was born (see dx.doi.org/10.1166.rase.2014.1076).

Harry described at the symposium how, in the Solar Army, they recruit school kids to do experiments in solar energy and solar fuels. This army of students is engaged in several activities which spearhead the outreach efforts of the CCI-Solar program. Initially, the efforts concentrated on two activities for students. One is called *Juice from Juice* (JfJ), a demonstration experiment in which students construct a dye-sensitized solar cell (DSSCs) that, instead of using expensive ruthenium-based dyes as solar energy absorbers, uses juice that students extract from blackberries, which are rich in anthocyanin molecules that serve as cheaper dyes for the cell. DSSCs were pioneered by Michael Grätzel of the École Polytechnique Fédérale de Lausanne in Switzerland. There were already commercial kits to prepare DSSCs based on fruit juice, but at the CCI-Solar program they developed a kit that contained a prepared nanoparticle TiO_2 semiconductor paste, which in DSSC kits from other sources needed to be prepared after purchasing the kit, making the CCI-Solar kits more attractive to teachers.

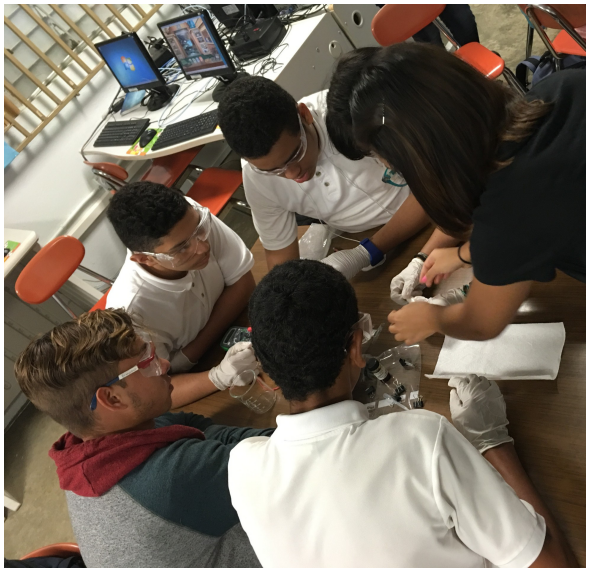
The second component of the Solar Army's initial outreach efforts consisted in engaging students in a real-time research laboratory experiment to discover new catalysts for the hydrogen evolution reaction (HER), initially using the SHArK kits. Later, at Caltech, Jay Winkler and his son Gates devised a quick way to test these types of materials based on an LED array coupled to a photoelectrochemical setup (the Solar Energy Activity Lab (SEAL) kit). Both this kit and the SHArK kit were taken by CCI graduate students to dozens of schools throughout California, Wyoming, and other sites for students to use them to discover new catalysts. Mixed-metal oxides can be cheap semiconductor materials with catalytic properties, but there are millions of possible metal combinations. The idea is that students, while helping to discover the best combinations, would gain interest in chemistry and science and pursue STEM careers. Already a discovery of a Fe, Cr, Al oxide made by an undergraduate student with a SHArK kit has resulted in three papers in peer-reviewed scientific journals. Harry believes that discovering new catalysts based on earth-abundant materials should not only involve scientists at top research universities, but also schoolchildren and undergraduate students. Kids can be the best ambassadors promoting solar energy. In addition, he believes that getting a child interested in a science or engineering career instead of becoming a lawyer is worth the effort!

After I attended the AAAS symposium I wrote to Harry to tell him how happy I was to hear his talk. He wrote me back and told me "We would like to have a Caribbean Brigade of the CCI Solar Army!". He put me in contact with Siddharth Dasgupta, managing director of the CCI. When I attended the American Chemical Society National Meeting in Anaheim, California, in March 2011, I took the opportunity to travel to Pasadena and meet Siddharth and some of the Caltech graduate students and post-docs involved in the CCI outreach efforts. They told me how in the summer they performed JfJ workshops for teachers and that those teachers were given JfJ kits to perform those workshops for their own students during the school year. In addition, they told me how CCI graduate students involved in these outreach efforts would visit, once a week for about two months, different schools after school hours to mentor groups of five to six students involved in doing the SEAL experiments. The results of all those experiments were sent

online to a central database at Caltech, where students could see which experiments demonstrated the best catalysts and could search which mixed-metal oxides had been previously tested, to help them decide which new metal combinations to test. Furthermore, the CCI sponsors a summer internship program for high-school students to attend Caltech and work on the SEAL experiment. Both the SHArK and the SEAL experiments have many variables that can be explored and therefore the students can get involved in real research to optimize variables to obtain the best catalysts for HER. The SHArK and SEAL experiments were later described in a *Journal of Chemical Education* publication in 2013 (see dx.doi.org/10.1021/ed300574x). Solar Army groups from throughout California meet once a year at a SEAL Conference to present their results. Upon hearing all of this and the enthusiasm with which the graduate students described the Solar Army, I was hooked. I decided to come back to Puerto Rico and establish the Caribbean Brigade of the CCI Solar Army as Harry had suggested. I recruited Professor Juan López Garriga and his student Samirah Mercado, who both ran a successful outreach effort called *Science on Wheels* at the UPR-Mayagüez campus, to join the Caribbean Brigade, and started planning its launch in Puerto Rico. We decided to have two teams in Puerto Rico, one at UPR-Río Piedras and one at UPR-Mayagüez.

Siddarth, Jay, and Shane Ardo (then a postdoctoral research associate in Nate Lewis laboratory at Caltech and a member of the CCI-Solar program) visited Puerto Rico in August 2011 and gave JfJ and SEAL workshops, with the help of our graduate students, to about 50 teachers at the UPR-Mayagüez and the UPR-Río Piedras campuses. Then the Caribbean Brigade started visiting schools and, by March 2012, we starting receiving funding from the CCI-Solar program. Later, I became a Co-PI of the CCI.

In the Caribbean Brigade of the CCI Solar Army, we introduce concepts of solar energy as a suitable energy source to underrepresented groups in middle and high schools in Puerto Rico, as well as to undergraduate students and even adults in informal education outreach activities. We have been giving JfJ workshops using DSSC kits sold by Arbor Scientific (http://www.arborsci.com/dye-sensitized-solar-cell-kit-16) and workshops on research to identify new catalysts for HER using the SEAL kit sold by Caltech. Dozens of schools and over 3,000 students have been involved in Puerto Rico so far. Every year, four graduate students (two at each site) participate in giving the workshops with us. Undergraduate students (about four in each site per year) have been collaborating with the graduate students in the



Top: JfJ workshop at the Benjamin Harrison Vocational High School in Cayey, Puerto Rico; Middle: Newly recruited members of the Caribbean Brigade; Bottom: Harry Gray with Mario Ramos Garcés and Jennifer Vargas, members of the Caribbean Brigade, at the CCI-Solar Retreat

program. Several of our undergraduate and graduate students have done summer research internships on solar catalyst development at CCI Universities under the auspices of this program, most recently at Stanford University doing research at Thomas Jaramillo's laboratory. The Solar Army activities have been integrated into the curriculum of the undergraduate General Chemistry and Analytical Chemistry laboratory courses at the University of Puerto Rico-Río Piedras campus. We translated the JfJ materials into Spanish and are in the process of translating the SEAL manual. We participate each year in the CCI-Solar retreat where all Co-PIs and our students meet to discuss the latest results and the plans for the next year. One of the goals of the Caribbean Brigade of the CCI Solar Army is to bring these workshops to other countries in the Caribbean, beginning with Haiti and the Dominican Republic, to help advance solar energy science and science education-related capacity building in our region. Obtaining funding for this goal is our most important challenge.

So far, well over 10,000 students have been involved in Solar Army activities in the United States, Canada, Europe, and Puerto Rico (see map).

Recently, another outreach activity has been introduced in the CCI-Solar Army. This activity allows students to discover new catalysts using the *Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization* (HARPOON) kits, which use fluorescence quenching by oxygen as a function of electrode potential to screen electrocatalysts for the OER (recently described in http://dx.doi.org/10.1021/acs.jchemed.5b00591). We intend to bring this activity to Puerto Rico.

A year ago, world leaders meeting in Paris reached an agreement to limit global warming below 2° C above pre-industrial levels and to try to maintain it below 1.5° C, in order to significantly reduce the risks and impacts of climate change. The agreement followed the adoption earlier last year by the United Nations General Assembly of the resolution "Transforming our world: the 2030 Agenda for Sustainable Development".[1] Goal 13 of this resolution makes a call to "Take urgent action to combat climate change and its impacts", while Goal 7 calls to "Ensure access to affordable, reliable, sustainable and modern energy for all". The Paris agreement recognized that "climate change represents an urgent and potentially irreversible threat to human societies and the planet and thus requires the widest possible cooperation by all countries, and their participation in an effective and appropriate international response, with a view to accelerating the reduction of global greenhouse gas emissions". If the world is to reach the goals of combating climate change and its impacts and ensuring access to clean energy for all, a drastic transition away from fossil fuels to renewable energy sources, particularly solar energy, is needed. The Paris agreement goals must be achieved while satisfying the world energy needs, particular in developing countries, which deserve their chance of improving their quality of life.

Harry Gray's legacy is a Solar Army that is helping to discover the materials needed to increase the possibility of reaching the United Nations 2030 sustainable development goals. The Solar Army is inspiring thousands of students to pursue STEM careers and preparing the new scientists that will solve the global energy crisis and alleviate the climate change crisis. We invite *Chemistry International* readers to join our efforts and collaborate in expanding the Solar Army worldwide. Let's increase the number of students recruited to the Solar Army from tens of thousands to hundreds of thousands of students, or even more. A truly global Solar Army is our best chance of a sustainable future and the best legacy that Harry Gray can leave to the children of the world.

Reference

1. www.un.org/sustainabledevelopment/sustainable-development-goals/

Jorge Colón <jorge.colon10@upr.edu> is Professor of Chemistry at the Río Piedras Campus of the University of Puerto Rico, Secretary-Treasurer of the AAAS-Caribbean Division, Treasurer and Alternate Councilor of the Puerto Rico Section of the American Chemical Society, Associate Member of Division II (Inorganic Chemistry) of IUPAC, member of the "Colegio de Químicos de Puerto Rico", and member of Ciencia Puerto Rico (www.cienciapr.org). For Solar Army information please contact Michelle DeBoever at mchansen@caltech.edu or Jennifer Schuttefield Christus at schuttlj@uwosh.edu.

http://thesolararmy.org and http://sharkscienceoutreach.com