

The 21st Century Solar Army¹

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Thank you, Barbara Grosz, for that very nice introduction. I don't know who invited me to give this talk because I'm not sure how the Society works. It's very mysterious, but whoever did, thank you very much. I've been coming to these wonderful meetings since I was elected in 2000. I just love them. I've made lots of great friends and now I have an opportunity (at last!) to speak to people my own age.

Let's get off and running. There's lots of sunlight; we've got to figure out how to use it productively to make fuels and chemicals. We *are* going to stop using oil, gas, and coal, maybe not in this century but certainly in the next. Therefore, it's about time we started working on renewables. Fortunately, we have four great resources: sunlight, seawater, nitrogen from the air, and carbon dioxide. Starting with these resources, we will have to figure out how to make everything—not only fuel but also pharmaceuticals and polymers. Everything that we now get on the cheap from oil, gas, and coal, we will have to learn to make ourselves. So let's get started.

I'm sure you're familiar with silicon solar cells, which people put on their roofs to generate electricity. We have had silicon solar cells with 10% conversion efficiencies for some time, and now we have 21%-efficient silicon solar cells but very few people are using them. We also have 28%-efficient gallium arsenide, but even with 10%-efficient silicon, we could provide electricity to much of our country. Nate Lewis and I picked out a part of the country to cover with silicon solar cells, a part where nobody lives (we think!), but if any of you in the audience live in that region, we will be happy to move you to Las Vegas. Just kidding! We must find better ways to power the planet.

So, what are we doing? We are covering wasted spaces with solar cells. At Caltech, for example, we have several solar power stations. We put solar cells on the roofs of parking garages to generate electricity, which we sell to Los Angeles during the day and buy back at night. I

1 Read on 24 April 2014.

can tell you that lots of universities are now converting to solar; for example, Arizona State has a big solar footprint, and Occidental College, which is close to Caltech, has a solar power station. Even the Pope is installing solar!

The big challenge in the field is to store solar energy by making fuel, which can be made by splitting water into hydrogen and oxygen.² Good solar water splitters will need to include components that absorb all the light that reaches the earth's surface filtered by the ozone layer. We started with molecular light absorbers to do this job but soon realized they're not going to make it in the long run, so now we use semiconductors with variable bandgaps to capture solar photons.

Upon light excitation in a semiconductor, one electron and one hole are separated briefly. However, chemistry involves multiproton and multielectron processes, such as splitting water into hydrogen and oxygen. So, we have to couple the electrons and holes that are generated in semiconductors with catalysts to drive the desired chemical reactions. We will need to make integrated photoanodes and photocathodes to put into solar water splitting devices.³

Andy Maverick and I laid out the territory for solar water splitting by molecular absorbers and catalysts many years ago.⁴ Since then, I've trained many brilliant students who like to show the old guy up; turns out two, Nate Lewis and Dan Nocera, are solar gurus. These guys wrote a big paper on solar fuels in the *Proceedings of the National Academy of Sciences*.⁵ Of course I responded by writing a one-page paper that summarizes all the important points they attempted to make.⁶ I'm just kidding! Give me a break; I love my former students.

In the late '90s, John Turner's group at the National Renewable Energy Laboratory (NREL) made a big advance.⁷ He and his NREL coworkers showed us that artificial photosynthesis is not just a pipe dream: they constructed a solar-driven device that split water over 10 times more efficiently than can be done by green plants. So natural photosynthesis, which we've been living on since the beginning of civilization, can be improved!

2 H. B. Gray, "Powering the Plant with Solar Fuel," *Nature Chemistry* 1 (2009): 7.

3 J. R. McKone, N. S. Lewis, and H. B. Gray, "Will Solar-Driven Water-Splitting Devices See the Light of Day?" *Chem. Mater.* 26 (2014): 407–14.

4 H. B. Gray and A. W. Maverick, "Solar Chemistry of Metal Complexes," *Science* 214 (1981): 1201–5.

5 N. S. Lewis and D. G. Nocera, "Powering the Planet: Chemical Challenges in Solar Energy Utilization," *Proc. Natl. Acad. Sci. U.S.A.* 103 (2006): 15729–35.

6 Gray, "Powering the Plant with Solar Fuel," 7.

7 O. Khaselev and J. A. Turner, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," *Science* 280 (1998): 425–7.

The Turner group built a 12%-efficient water splitting solar cell. They used two semiconductors: gallium arsenide, a low bandgap material that absorbs red photons, and gallium indium phosphide, a higher bandgap semiconductor that absorbs blue photons. These two photons generate two electrons, meeting two protons at the interface to make hydrogen. The generated holes move through the circuit to a platinum electrode where water is oxidized to oxygen. In a tandem cell of this type, 18% is as good as you can do. Remarkably, Turner's group achieved 12% conversion of solar photons to electricity.

Now, this talk would be over before the red light comes on were it not for one startling fact: You can't scale up the Turner cell, as it would cost a fortune. Nate Lewis and I estimated that the device would cost \$50,000 per square meter. The materials are very precious: platinum, for example, shouldn't be used in solar devices, as we need it for jewelry and bestselling albums. We've got better uses for platinum than putting it in solar cells!

So in the late '90s, I decided to go back into the solar field. With colleagues from Caltech and MIT, I put together a team to work on earth-abundant materials that could be used as components of solar water splitting devices. Our goal: to replace platinum, iridium, ruthenium, and other rare metals with elements such as iron and cobalt, which will be available forever. Because an efficient solar water splitting device will have to be scaled up worldwide, vast quantities of absorber and catalyst materials will be needed.

With support from the National Science Foundation, our team began working on methods and materials to advance solar fuels science.⁸ We designed a device that could work with cheap materials—disordered materials. In crystalline materials after photons are absorbed, long-lasting electron hole separation is possible, which allows time to do chemistry. With distorted materials, after light absorption, the electrons and holes don't move very far apart. They tend to recombine to make heat, so we have a real problem: specifically, how can we make disordered materials work? One solution is a device with long and skinny photoanodes and photocathodes. The long photoelectrodes will be able to absorb most of the incoming light, and because they are so skinny, the generated electrons and holes will have a chance to reach catalysts at the surfaces to do the desired chemistry.

In early work, we designed an integrated photocathode with a catalyst made from an abundant metal. Nature couldn't afford platinum, so she used iron as a catalyst for hydrogen evolution in enzymes called

8 CCI Solar website: <http://www.ccisolar.caltech.edu/>

hydrogenases. We thought the iron hydrogenases might be a good place to start, so we put them on silicon photocathodes. However, they degraded rapidly because they're wimpy organic molecules.

Then people told me: "Well, Harry, just take out the active site made of iron—and use that as the catalyst." My reply: "In 45 years of doing bioinorganic chemistry, I've learned one important lesson—that when you take the active sites out of metalloenzymes, they don't work anymore!" They need the warm and friendly protein environment with hydrogen bonds and noncovalent interactions to tune the site for function. So we went to Plan B—making nonbiological molecular catalysts containing iron, cobalt, nickel or other elements that could be scaled up for hydrogen production. This work was very successful; we now have more than 30 molecular catalysts that work well.⁹

A very active nickel catalyst was made at the Pacific Northwest National Laboratory by Dan DuBois and his group, and a cobalt catalyst was developed at Caltech and in France.¹⁰ Even more promising than these molecular catalysts are heterogeneous materials made from nickel and molybdenum (i.e., *NiMo catalysts*). If you put NiMo on silicon microrods, the integrated Si-NiMo photocathode works almost as well as ones with platinum.¹¹ Even better, at Penn State, Ray Schaak made a nickel phosphide catalyst, which works extremely well¹²; and more recently at Caltech, Chris Roske has found that cobalt phosphide (CoP) catalyzes hydrogen evolution for hours at relatively positive potentials in acidic solutions. We now have a CoP-Si photocathode that works nearly as well as platinum on silicon for hydrogen production.¹³

So, what is left to do? The grand challenge is to find efficient and robust catalytic photoanodes to oxidize water to oxygen, which will produce the electrons and protons needed to make hydrogen. We have used tungsten oxide with catalysts, but the bandgap is too high. It is a yellow material that doesn't absorb enough visible light; its bandgap is 2.5 electron volts (eV), but the sweet spot for a photoanode is 1.9 eV.

9 J. R. McKone et al., "Earth-Abundant Hydrogen Evolution Electrocatalysts," *Chem. Sci.* 5 (2014): 865–78.

10 J. R. McKone et al., "Earth-Abundant Hydrogen Evolution Electrocatalysts," 865–78.

11 E. Warren et al., "Hydrogen-Evolution Characteristics of Ni–Mo-Coated, Radial Junction, n⁺p-Silicon Microwire Array Photocathodes," *Energy Environ. Sci.* 5 (2012): 9653–61.

12 E. J. Popczun et al., "Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction," *J. Am. Chem. Soc.* 135 (2013): 9267–70.

13 C. W. Roske et al., "Comparison of the Performance of CoP-Coated and Pt-Coated Radial Junction n⁺p-Silicon Microwire-Array Photocathodes for the Sunlight-Driven Reduction of Water to H₂(g)," *J. Phys. Chem. Lett.* 6 (2015): 1679–83.

The good news is that we found a way to incorporate molecular nitrogen into the interior of tungsten oxide to lower its band gap to 1.9 eV!¹⁴ Our discovery could be a game changer if we can find general ways to incorporate inert atoms and molecules into metal oxides to tune bandgaps to optimize performance.

Our nitrogen-doped tungsten oxide photoanode works for solar water splitting over the entire visible region, but only in combination with rare metal oxide catalysts.¹⁵ We need active and robust water oxidation catalysts made from earth-abundant elements. Once again, we appeal to nature. Nature's catalyst is a manganese-calcium oxide cluster complex, but to date, no synthetic manganese-calcium oxide material works well for water oxidation.

What are we to do? We need to solve this problem! I have gone out on a limb and announced that the world's greatest water-oxidation catalyst hasn't been discovered yet. It's going to be an oxide containing three or four metals, maybe five. Some time ago, I decided to search for the magic oxide in a certain region of the periodic table. For the life of me, I can't figure out why I picked that particular region, but I did. Then of course I had to cross out all the rare elements because devices made from them would not be scalable. Even then, billions of possible combinations exist! So again, what to do?

I could use either robots or students in this search. All of my life, I've loved to work with students, so I started a Solar Army. Lots of students enlisted in the first year, and now thousands of kids worldwide are searching for new materials and interacting via the Web. We have brigades all across North America (and a few overseas as well). We send each brigade a Solar Army search kit with an LED scan station made at Caltech. The students work with simple chemicals from high school laboratories, make them into amorphous metal oxides, spot them on conducting glass plates, slap them onto the 8 x 8 scan station, irradiate them, and read out their performance for water oxidation in real time.¹⁶

We all get together on a regular basis, the kids make presentations, they tell us which metals are looking promising, and they check the stability of certain formulations. Graduate students and postdocs in our CCI Solar Program are also looking for better mixed-metal water oxidation catalysts. At Caltech, we are developing a method called *pulsed laser*

14 Q. Mi et al., "Thermally Stable N₂-Intercalated WO₃ Photoanodes for Water Oxidation," *J. Am. Chem. Soc.* 134 (2012): 18318–24.

15 Q. Mi et al., "Thermally Stable N₂-Intercalated WO₃ Photoanodes for Water Oxidation," 18318–24.

16 J. R. McKone et al., "The Solar Army: A Case Study in Outreach Based on Solar Photoelectrochemistry," *Rev. Adv. Sci. Eng.* 3 (2014): 288–303.

ablation in liquids (PLAL) that can be used to synthesize metal oxide nanoparticles. We focus a high-powered laser on a metal target, exploding it and forming a high-temperature (3000–7000 K) plasma, which upon cooling deposits nanoparticles. By putting other metal salts in the irradiated solution, we obtain mixed-metal nanoparticles whose sizes can be tuned by varying the laser pulse energy.^{17,18} We have made several highly active water-oxidation catalysts containing some of the metals studied by students in the Solar Army. The best one is a nickel-iron-titanium-lanthanum-layered double hydroxide.¹⁸ We make this catalyst by PLAL with an iron target and nickel nitrate, along with other metal salts in solution.

Time to wrap up: the red light is on! I have many colleagues to thank. Those on the CCI Solar Advisory Board have been particularly helpful (the CCI Solar Fuels Program is supported by NSF CHE-1305124), and kudos to our alumni, who now occupy positions in industry, government laboratories, and universities all over the world. I am confident that together we will make steady progress toward the goal of renewable energy to power our planet.

17 J. D. Blakemore et al., “CO₃O₄ Nanoparticle Water-Oxidation Catalysts Made by Pulsed-Laser Ablation in Liquids,” *ACS Catal.* 3 (2013): 2497–2500.

18 B. M. Hunter et al., “Highly Active Mixed-Metal Nanosheet Water Oxidation Catalysts Made by Pulsed-Laser Ablation in Liquids,” *J. Am. Chem. Soc.* 136 (2014): 13118–21.