

PLEASE CONTINUE TO THE NEXT PAGE...

Solar Fuel II: The Quest for Catalysts

by Harry B. Gray



Sunlight, leaves, and water can make clean energy. They can also make pretty pictures, as in this cyanotype, also called a “sun print.”

We know how to make electricity from sunlight. You can buy a silicon solar array with a 30-year guarantee, put it on your roof, and make your electric meter run backwards. And if you turn off the lights at night, and do other nice things instead, you'll get a check at the end of the month instead of a bill. And you'll be happy. So why don't we just convert the entire planet now, using technology that we have? There are two big problems. The first is it's not cheap. The cost of photovoltaic solar power is at best maybe 25 cents per kilowatt hour, which is several times the cost of traditional sources—fossil fuels, nuclear, and so on. Of course, oil is going up fast, and so if oil hits three or four hundred dollars per barrel, solar at its current price will be a bargain. But before then, if we could get the cost of solar conversion down to about 10 cents a kilowatt hour, people would start to buy in large numbers, and we could convert the planet to run on solar electricity.

But there's a bigger problem. Even if we had all the cheap photovoltaics we could ever need, we can't store electricity in large quantities—you either use it or lose it. So I'm going to talk about using solar cells to make chemical fuel. If we could make fuel when the sun is shining, we could use it after dark, and the storage problem would be solved. Specifically, I'll talk about splitting water molecules. If you start with two molecules of water, H_2O , and add energy—ZAP!—you can make two molecules of hydrogen, H_2 , which you can compress and store, and one molecule of oxygen, O_2 , which you release to the atmosphere. We did this as little kids when we put two electrodes in a beaker of water and hooked them up to a battery. We got hydrogen gas bubbling up from the cathode and oxygen gas bubbling up from the anode. We want to do the same thing as grownups, but using the sun as our energy source instead of a battery, and we need to scale it up a little. In a solar-powered world, we'd run the H_2 through fuel cells, which generate electricity by recombining hydro-

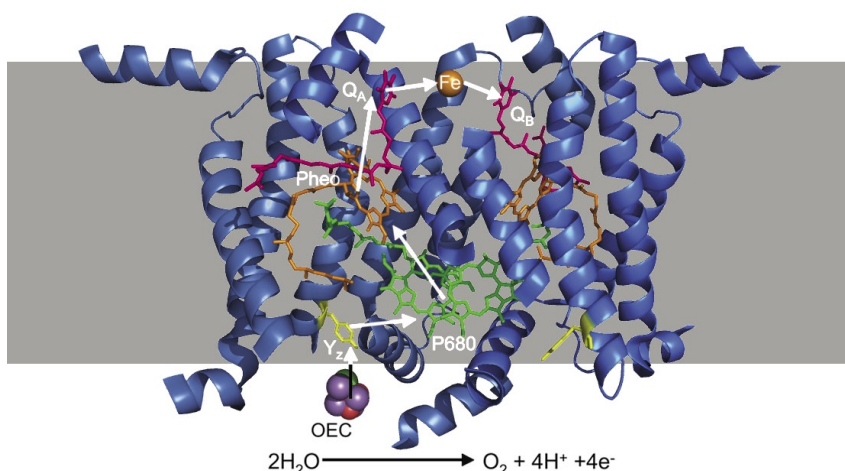
There isn't enough platinum on the planet to meet our energy needs, even if we used every single atom. And we need to save some for jewelry and best-selling albums. . . .

Which leads to the big unanswered question: What are the H₂- and O₂-making catalysts going to be if they're not going to be platinum?

In green plants, the manganese-containing oxygen-evolving complex (OEC) in Photosystem II (blue ribbons) plucks electrons from water molecules. The electrons hop to a tyrosine (Y_z, yellow), a chlorophyll (P680, green), a pheophytin (Pheo, orange) and two quinones (Q_A and Q_B, magenta), not to mention an iron atom (Fe), and eventually cross the chloroplast's membrane (gray) to a second light-absorbing system, Photosystem I, which reunites them with their protons.

gen and oxygen to make water. We'd use solar energy to split water, store the energy in the H—H bonds we made, and get electrical energy out when we ran the reaction in reverse. The fuel cells would run 24/7, making electricity all the time, and the water splitter would make enough extra hydrogen during the day to power the fuel cells at night.

The Swedes and the Norwegians will be happy about this, because they can make their fuel in the summer, when the sun never goes down, and they can run their houses and everything else in the winter, when the sun never comes up. Here in California, we'd have solar-fuel plants along the Pacific Ocean, next to water-purification plants. We'd need an enormously abundant water supply to make hydrogen on the scale we'd need to run L.A., and so in a dream scenario, we'd have a big solar-fuel plant splitting seawater into O₂ and H₂. (We wouldn't even need to desalinate the water first! We need a certain amount of salt in the water—we call it an electrolyte—to make the reaction work.) We'd run the hydrogen through a big electric-power facility next door, and then we'd send the clean, fresh water that comes out of the fuel cells into the municipal water system. So we'd



Structure after K. N. Ferreira, et al., *Science*, Volume 303, pp. 1831–38, March 19, 2004. Rendering by Gretchen Keller.

solve the energy crisis and the water crisis at the same time. There are technical details to work out, and I don't know if anybody has done any serious engineering studies on it, but that's my dream.

We know we can make fuel from sunlight, because nature does it. That's where we get all the fossil fuels we have now. The sun has been shining on plants for a long, long time, and their photosynthetic system is highly optimized. The system transforms carbon dioxide into carbohydrates—sugars and starches, which plants use to store energy, and cellulose, from which plants make their cell walls. Over millions of years, these carbohydrates have become coal, oil, and natural gas.

NATURE'S WAY: FRAGILE ORGANIC MOLECULES

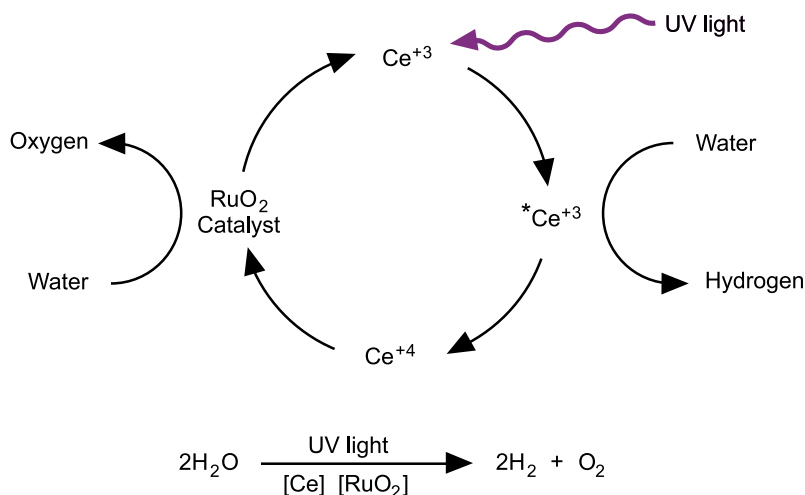
The photosynthetic machinery lives in organelles called chloroplasts, whose membranes contain green chlorophyll molecules. Photosynthesis starts with a chlorophyll molecule absorbing a photon of sunlight. This excites an electron, which hops off the chlorophyll molecule and gets siphoned away by a chain of electron carriers. The charge separation is vital—otherwise, the negatively charged electron would quickly lose the extra energy it picked up from the sunlight by falling back into the “hole,” or positive charge, left on the chlorophyll.

Green plants have no use for electricity—they want to make carbohydrates. So the hole on the chlorophyll molecule gets filled by an electron from a handy water molecule, which then releases a proton. (A proton, of course, is all that's left of a hydrogen atom once you've stolen its electron.) The chlorophyll is now ready to absorb another photon, and the light-harvesting process repeats. Meanwhile, the newly liberated proton gets pumped across the chloroplast's membrane, where other enzymes reunite it with the electron that was siphoned away from the chlorophyll molecule, and use the reconstituted hydrogen atom to reduce carbon dioxide to carbohydrates. “Reduction,” in the chemical sense, means to add one electron or more to an atom or molecule. When a hydrogen atom is the reducing agent, a proton often comes along for the ride.

Meanwhile, the water molecules' oxygen atoms have to go somewhere, so a manganese catalyst on the inside of the chloroplast's membrane puts the leftover oxygen atoms together in pairs to generate the O₂ that we breathe. The chloroplast winds up with four electrons and four protons on one side of its membrane, and one molecule of O₂ on the other. All of the charges balance, no atom is left behind, and everybody's happy.

We don't need to make carbohydrates, we just want to make H₂. Even so, figuring out a way to mimic photosynthesis is going to be one of the biggest challenges for chemists in this century. Over 20 years ago Eli Greenbaum, working at the Oak

The granddaddy of inorganic solar-fuel makers was developed in the 1950s. Ultraviolet light kicks a cerium ion (Ce^{+3}) into an excited state ($^*\text{Ce}^{+3}$), which promptly sheds the extra energy and an electron by jolting a hydrogen atom off a water molecule to become Ce^{+4} . The catalyst scrounges replacement electrons from other water molecules, liberating oxygen.



Ridge National Laboratory in Oak Ridge, Tennessee, took the chloroplasts out of green leaves and dipped them into a platinum solution until they were thinly coated with the metal. Then he dried them off and put them in a flask of water. When he shone sunlight on the flask, he got H_2 off the platinum surface, and the marvelous manganese catalyst made O_2 . The catch is that once he took the chloroplasts out of the green leaves, they could no longer repair themselves. Protein molecules are fragile things, and any oxidant strong enough to turn water into O_2 will make short work of them. The process makes very energetic states of O_2 , which, with the other powerful oxidants involved, including the manganese catalyst itself, oxidize the component proteins into useless organic glop within 30 minutes. But a leaf is a wonderful synthetic factory that just rebuilds the apparatus back again. So after Eli exposed his chloroplasts to sunlight for a few hours, all he had left was an ugly sludge in the bottom of the flask—something that I have seen many times.

THE HARD WAY: INDESTRUCTIBLE INORGANICS

So why not make an inorganic mimic of photosynthesis that contains no proteins and never poops out? This field took off in the 1950s, when several independent researchers developed a cerium-based water-splitting system. In it, light hits a cerium ion, Ce^{+3} , converting it into Ce^{+4} and kicking out an electron that reduces water to H_2 . Then a ruthenium dioxide catalyst strips an electron from a water molecule to make O_2 and give you back Ce^{+3} so the cycle can begin again. This system will run forever, because it is made of hard, inorganic components. The only problem is it requires deep ultraviolet light, and no deep ultraviolet light gets through the ozone layer. This system doesn't split any water at the surface of the earth, but it's great in space. So when we have to vamoose to another

planet, because of all the problems here, we will take a lot of cerium with us and a little bit of ruthenium dioxide, and we'll be just fine.

Nate Lewis, who is now Caltech's Argyros Professor and professor of chemistry, was an undergraduate in my group in 1977, and he knew he could do better. He and grad student Kent Mann [PhD '77] developed a binuclear rhodium system—if you put two rhodium atoms together, they interact to absorb lots of visible light. In fact, they will absorb red light, the lowest-energy visible light that reaches Earth's surface. Kent and Nate shone light on their rhodium-rhodium system, and sure enough, hydrogen streamed out in a beautiful way. This was an important milestone in the solar-fuel field, because it was the first time anyone had ever made H_2 from sunlight, with an inorganic catalyst, in a homogenous system that actually stored energy. However, we could never get the quantum yield of hydrogen—the number of H_2 molecules we made per photon absorbed—to be better than one percent. Unfortunately, you have to have a quantum yield in the 50–70 percent range in order to have any chance of a reasonable efficiency for the process as a whole. After years of studying the mechanism, we figured out that there was a very inefficient step in it that limited our H_2 production, so the rhodium pair went the way of all systems.

But there is hope. In 1998, John Turner at the National Renewable Energy Laboratory (NREL), in Golden, Colorado, built a device that is far, far more efficient than natural photosynthesis or almost anything else. (Incidentally, John got into the photoelectrochemical water-splitting racket while he was a postdoc with Fred Anson (BS '54), Caltech's Gilloon Professor of Chemistry, Emeritus, from 1977 to 1979.) John's world-record water-splitter has two layers of semiconductors—gallium arsenide and gallium indium phosphide. Gallium arsenide absorbs reddish light, and gallium indium phosphide absorbs bluish light, so this tandem array absorbs most of the sunlight that

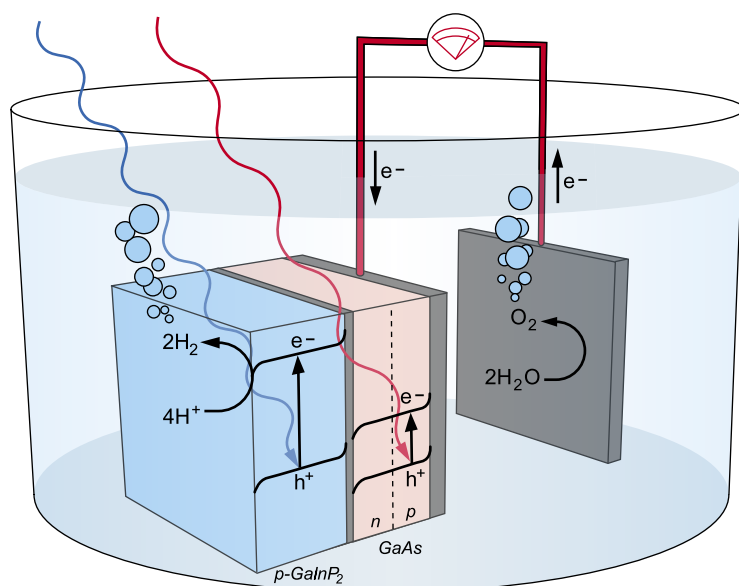
comes in. H_2 molecules form on the gallium indium phosphide surface, sucking electrons out of a platinum electrode and creating holes that in turn pull electrons from water molecules, thereby oxidizing water to O_2 . (To oxidize something in an electrochemical sense means to remove electrons from it—or add holes to it, which is the same thing.) The system works beautifully. Its overall efficiency is better than 10 percent—and, because of wavelength and thermodynamic considerations and so forth, 18 percent is about as high as you can get. So the good news is that John's wonderful water splitter is efficient; the bad news is that John's wonderful water splitter costs \$10,000 per square centimeter to make.

So now all we have to do is build something similar out of cheap, Earth-abundant materials. Not platinum. There isn't enough platinum on the planet to meet our energy needs, even if we used every single atom. And we need to save some for jewelry and best-selling albums. Gallium is probably OK, but not arsenic, which is toxic. We need something environmentally friendly that will do as well as NREL's wonderful cell. To find it, we have formed an unholy alliance with our East Coast branch, MIT. We call this alliance Powering the Planet, a very modest sort of title, and the MIT head is Dan Nocera [PhD '84], a former grad student of mine. He works with Kit Cummins and Jonas Peters, who used to be a professor here at Caltech but recently defected to MIT because they clearly need the help, as you will see momentarily.

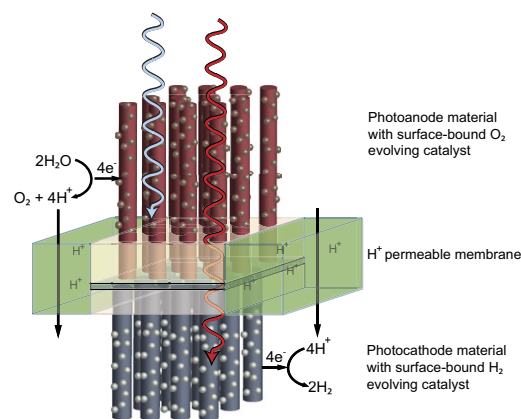
POWERING THE PLANET

We are collaborating to build a nanorod-catalyst device to split water. A membrane in the device acts like the chloroplast's membrane, keeping the O_2 -making and H_2 -making sides of the system

The NREL water-splitting cell uses two semiconductors (blue and pink) to absorb two wavelengths of visible light that, combined, give electrons enough energy to reduce hydrogen. (For a fuller explanation of what this means, and what the letters *n* and *p* signify, see "Solar Fuel I," which begins on page 20.) The intermediate, lower-energy electrons recombine with holes in the conductive layer between the semiconductors.



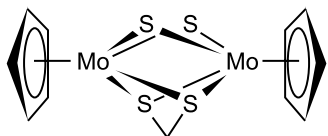
The National Science Foundation–supported Caltech-MIT “Powering the Planet” design will use two sets of light-absorbing nanorods to get the necessary energy boost.



away from each other. This is important for several reasons, including the fact that we don't want the two gases recombining explosively. Embedded in the membrane are silicon nanorods to harvest the sunlight, and several grad students and postdocs in Nate Lewis's group are working on that part. The nanorods stick out of both sides of the membrane, and will be coated with a different catalyst on each side of it. High-energy blue light gets absorbed on the anode side of the membrane, making holes that interact with a catalyst—perhaps a metal oxide, like zinc oxide or titanium dioxide—to make O_2 . Lower-energy red light gets absorbed on the cathode side of the membrane, where another catalyst reunites the electrons (those that have worked their way down from the anode end of the nanorod, plus the nearby ones the red light has knocked loose) with the naked protons that have diffused through the membrane to make H_2 .

Nate's group and my group are working on the H_2 catalyst, which we have a pretty good idea how to make. The stickler is the oxygen side. This is the problem that comes up over and over and over again in solar-fuel formation, the fact that nobody has ever developed a good molecular catalyst for the oxidation of water to O_2 . Since we have no clue, really, how to make the catalyst for the O_2 anode, we naturally assigned that part to MIT.

Which leads to the big unanswered question: What are the H_2 - and O_2 -making catalysts going to be if they're not going to be platinum? Platinum is our old friend. It does everything. It catalyzes the oxidation of water to O_2 , and the reduction of protons to H_2 . But we've got to replace platinum, because there's not enough of it in the world, and we can't do what nature does. Nature uses big proteins. The ones that split off hydrogen from water are called hydrogenases, and their catalytic sites are pairs of iron atoms—a simple, Earth-abundant material. Marcetta Darensbourg at Texas A&M and Tom Rauchfuss at the University of Illinois at Urbana-Champaign have built the main parts

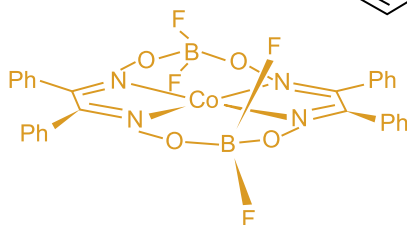
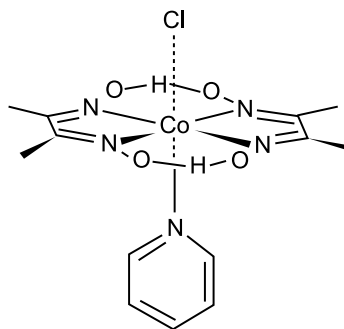


Three candidate hydrogen-making catalysts.

Above: A two-molybdenum molecule made at the Pacific Northwest National Laboratory.

Above, right: A cobalt complex from France.

Right: Caltech's contender, which also contains cobalt.



of these active sites that have the correct geometry without being surrounded by proteins, and they don't work very well. This is the story of inorganic mimics of proteins—the proteins tune the active sites' properties in very subtle and brilliant ways, which we have not figured out how to do.

So we don't go with this mimic-of-the-biological-stuff approach, at least for hydrogen. Dan Nocera and Nate Lewis organized a Gordon Research Conference on solar fuels in 2007 that assessed all the inorganic, nonplatinum hydrogen catalysts around. Three winners came out. One is a dimolybdenum system that Dan DuBois at the Pacific Northwest National Laboratory has worked on, and one is a cobalt system that Vincent Artero and Marc Fontecave at the Université Joseph Fourier in Grenoble, France, developed. The third was originally developed at Iowa State in the 1980s by Jim Espenson [BS '58], was recently improved by Xile Hu when he was a postdoc here at Caltech, and is now being worked on in my lab by grad student Jillian Dempsey. The DuBois molecule and the Caltech one are both very good. They operate at very close to the optimum voltage to make H_2 . This is a critical feature, because if the system's voltage is more than the optimum, the extra energy is wasted. And if the voltage is insufficient, the reaction doesn't go at all. But Dan's molecule contains sulfur, which can be nasty, and ours is easier to make, so we think the Caltech one looks like a real winner.

Jillian is well along to working out its mechanism, using the laser flash-quench techniques pioneered by Faculty Associate in Chemistry Jay Winkler [PhD '84], who oddly enough also used to be a grad student of mine. The question is whether it takes two cobalt hydrides crashing together to split off H_2 , or whether an incoming proton can pluck the hydrogen atom off a single cobalt hydride—in other words, does each cobalt atom act alone, or do you need to have them work in pairs? The distinction is very important, because if we want to improve the catalytic rates so that

they are really fast, *really* fast, approaching the biological rates, we have to design our molecules to fit the mechanism. At this point, it looks like it's two cobalts diffusing toward each other, in which case we want to design a system that tethers them together and will reduce the diffusion time tremendously. The hydrogenase enzyme spits out some 6,000 H_2 molecules per second; our best cobalt catalyst is not as active, but our tethered systems may be the answer.

Last summer Carolyn Valdez, a Summer Undergraduate Research Fellowship (SURF) student in our group who had just finished her freshman year at Caltech, made such a tethered binuclear cobalt system with Jillian. It looks very promising. It's not quite right yet—we still need to tune the voltage a little—but so far, it looks extremely good. I think we're well on the way to having a very active, Earth-abundant catalyst for making H_2 .

JUST ONE SMALL PROBLEM . . .

The problem, as I said, is water oxidation. The MIT side. And, to be fair to them, this is by far the toughest problem. We haven't improved on molecular catalysts for water oxidation in a quarter of a century. The best thing we've got is a blue Ru-bpy (pronounced "roo-bippy," as in "you bet your bippy") dimer introduced by Tom Meyer at the University of North Carolina, Chapel Hill, in 1982. Ru-bpy is a molecule my lab has been studying for a very long time. There's even a drink at the Ath named for it. Ru-bpy is short for ruthenium-bipyridine—an Ru^{+2} ion sitting at the center of an array of organic molecules called bipyridines that are really good at absorbing light. Postdoc Kristine Kilså in my lab made Ru-bpy systems that, combined with the proper catalysts, could produce H_2 with yields approaching 80 percent. But on the O_2 side, Ru-bpy systems are terrible. (Oxygen production from water by Ru-bpy systems is one of those reactions that runs much, much better in the journals than it does in the lab.) Whereas the O_2 -producing manganese catalyst in green leaves turns over in thousandths of a second, generating tremendous amounts of oxygen so that we can live on this planet, Meyer's famous blue dimer turns over only a few times each day. I think "rolls over" is a better way to describe it. And it only produces 10 to 25 O_2 molecules before it craps out altogether. It's likely that the problem is our old friend, oxidative degradation. It's much easier to oxidize the bipyridines than to oxidize water, so it is hard to avoid bipyridine oxidation to carbon dioxide.

After many years of hard work, the structure of nature's manganese catalyst was finally solved by two teams working independently. Jim Barber of Imperial College London and Wolfram Saenger at the Free University of Berlin managed to grow crystals of the assembly of proteins containing

the manganese catalyst and do X-ray diffraction studies on them, so we know, roughly, what it looks like. So people now have ideas about how the mechanism might work, but I'm sure they're wrong, because we have never learned *anything really definitive* about mechanisms by solving these big structures. Mechanistic studies take many years and involve an enormous amount of effort. We still don't know how the nitrogenase catalyst works—nitrogenase is what bacteria use to convert N_2 into ammonia and eventually amino acids—and Doug Rees, the Dickinson Professor of Chemistry, solved that structure here at Caltech 15 years ago.

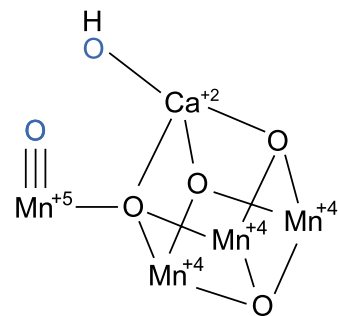
But we knew one thing, long before the structure had been solved. The catalyst has four manganese ions, so we will probably need four metal atoms—one for each electron in the double bond of the O_2 molecule. Otherwise, it's too much punishment for one metal atom to take; it's much easier to make four holes on four atoms than to strip four electrons off a single atom. Multielectron reactions are very hard to do, and they need very elaborate structures to keep everything in the right place. That's why the only good water-oxidation catalyst we have is the one in green leaves that nature evolved.

My group is taking a different approach. We believe that if we take an enzyme that will reduce O_2 by four electrons, we should be able to tweak it, through protein engineering, into a catalyst that will oxidize water. Its catalytic center is already set up for a four-electron, four-proton reaction, and all the atoms are already in the right positions—the intermediate states in the oxygen-reduction reaction must be very similar to what we would need to go backwards and generate O_2 instead of consuming it.

Grad student Kyle Lancaster in my group has decided to work on a beautiful, blue protein called copper efflux oxidase, because three of its four copper atoms form a catalytic center that reduces O_2 to water. Kyle can grow this protein in *E.*



The sands of time are running out on fossil fuels, but with silicon nanorods, the future may be the times of sand. From left: Kyle Lancaster, Carolyn Valdez, Harry Gray, Jillian Dempsey, and Jay Winkler contemplate this conundrum.



Photosystem II's manganese-based oxygen-evolving complex has three manganese (Mn) atoms, four oxygen (O) atoms, and a calcium (Ca) atom at the corners of a cube, plus a fourth manganese atom in a higher oxidation state that acts as the wedge in the water splitter to make an O_2 molecule out of the two oxygen atoms shown in blue. How that cube and the protein drapery around it make this happen is anybody's guess.

coli, and we may even call on Frances Arnold, the Dickinson Professor of Chemical Engineering and Biochemistry, to help us through a directed-evolution strategy; another of our collaborators, Corey Wilson at Yale, likely will contribute to this effort. (Corey is currently a Gordon Moore Scholar here at Caltech.) The trick will be to change the voltage at which the system operates from one that supports the reduction of O_2 to a much higher one that will support the oxidation of water.

Some time in this century, we're going to stop taking from nature and start paying back. We're going to be able to take the components of our atmosphere—carbon dioxide, nitrogen, and oxygen—combine them with seawater and, with sunlight as our energy source, make not only fuels, electricity, and pure water, but pretty much everything else you can think of: plastics, pharmaceuticals, and food. I really believe that this is where we're headed, and that this will be the Century of Chemistry. So you can see there's a lot riding on the ability to create O_2 from water, and I hope we can make it work. □

Harry Barkus Gray got his PhD in 1960 at Northwestern University under professors Fred Basolo and Ralph Pearson, who cowrote the "bible" of inorganic chemistry. Gray came to Caltech as a full professor in 1966, and is the Beckman Professor of Chemistry and the founding director of the Beckman Institute. He has published 17 books and more than 730 research papers. He has received innumerable awards for his work in inorganic photochemistry and bioinorganic chemistry, including the National Medal of Science in 1986 from President Reagan, the Priestley Medal from the American Chemical Society in 1991, and the Wolf Prize in 2004.

This article was edited by Douglas L. Smith.