



The next time you groan when it's time to mow your lawn, take a second first to marvel at a blade of grass. Plants are so commonplace that it's easy to take their wizardry for granted. When they absorb sunlight, they immediately squirrel away almost all of that energy by using it to knit together a chemical fuel they use later to grow and multiply. It sounds so simple. Yet it's anything but. Modern society runs on fossil fuels precisely because researchers have never managed to duplicate the chemical mastery of a fescue. Now, with the side effects of our massive-scale use of fossil fuels piling up (climate change, acidified oceans, oil spills, and so on), researchers around the globe are struggling to play catch-up with biology in hopes of harnessing the sun's energy to synthesize gasoline or other fuels that are the bedrock of modern society.

Humans, of course, already have ways to capture solar energy. Today's photovoltaic solar cells typically trap 10% to 20% of the energy in sunlight and convert it to electricity, and PV prices continue to drop. But because electricity is difficult to store on a large scale, the effort to store sunlight's energy in chemical fuels has risen to one of the grand challenges of the 21st century. "You're talking about turning the energy world on its head. Today we turn hydrocarbon fuels into electricity. But in the future, we need to find a way to turn electricity [from sunlight] into fuels," says Daniel DuBois, a chemist at the Pacific Northwest National Laboratory in Richland, Washington.

The problem is daunting. Energy production is the world's largest enterprise. Today the world consumes power at an average rate of 17.75 trillion watts, or 17.75 terawatts, 85% of which starts out as fossil fuels, coal, oil, and natural gas. Thanks to rising populations and incomes, by 2050 the world's demand for power is expected to at least double. To keep fossil fuels from stepping in to fill that need, with potentially devastating side effects, any new solar fuels technology will have to provide power just as cheaply, and it must have the potential to work on an equally massive scale.

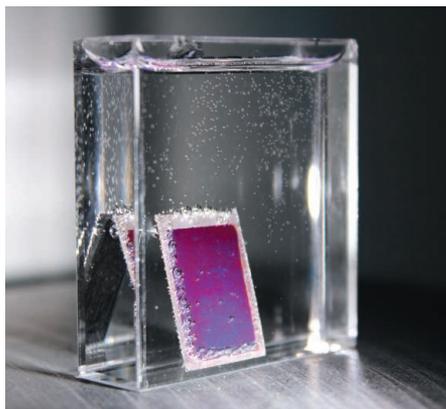
Enter artificial photosynthesis. Researchers around the globe are working to combine materials that capture sunlight with catalysts that can harness solar energy to synthesize fuels. This dream has been pursued for

decades. But recent strides are adding new zip to the field. "In the last 5 to 10 years, there has been amazing progress," DuBois says. Anthony Rappé, a chemist at Colorado State University, Fort Collins, agrees. However, he adds, "the bottom line is we're not there yet."

Molecular shuffle

To get there, most artificial photosynthesis researchers look to natural photosynthesis for inspiration. During photosynthesis, plants absorb sunlight, water, and CO_2 . Then they use two protein complexes—called photosystem I and II—to split water and synthesize fuel. First, in photosystem II, energy in sunlight splits two water molecules into four hydrogen ions (H^+), four electrons, and a molecule of oxygen (O_2). The O_2 wafts away as waste; the protons and electrons are sent to photosystem I and used to energize the coenzyme NADP to NADPH, which in turn is used to help synthesize sugars—a key series of metabolic steps.

Of course, artificial photosynthesis researchers aim to make fuel not for plants but for planes, trains, and automobiles. So after splitting water into H^+ , electrons, and oxygen molecules, most make very different use of those ingredients. Some researchers are working to combine the protons and electrons with carbon dioxide (CO_2) to make methane gas and other hydrocarbon fuels (see sidebar, p. 927). But most are working on what they believe is a simpler approach: combining the pieces they get from splitting pairs of water molecules into molecules of O_2 and hydrogen gas (H_2). That H_2 can then either be burned in



The splits. An artificial leaf harnesses energy in sunlight to split water into oxygen and hydrogen.

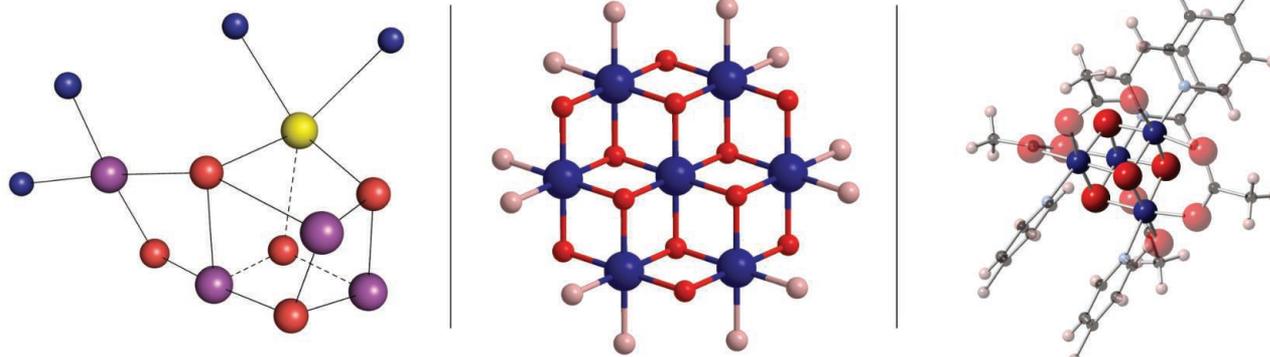
an engine or run through a fuel cell, where the water-splitting reaction runs in reverse: combining two H₂s with O₂ from the air to generate water and electricity.

Although plants split water with seeming ease, it's not a simple task, and it requires electrons to perform an intricate quantum-mechanical dance. Quantum mechanics dictates that electrons can exist only at discrete energy levels—or “bands.” In semiconductors, for example, electrons can sit in either a lower energy state known as the valence band, where they are closely bound to the atom on which they sit, or a more freewheeling energized state in the conduction band. Molecules like chlorophyll in plants act like tiny semiconducting proteins. When they absorb sunlight, they kick an electron from the valence to the conduction band, leaving behind a posi-

In 1972, Japanese researchers took on the challenge by using particles of titanium dioxide to split water. The method was impractical for commercial use because TiO₂, which absorbs only ultraviolet light, could make no use of 95% of the solar spectrum. But the demonstration inspired numerous other water-splitting systems. One setup uses molecular dyes made with ruthenium and other rare metals to absorb a variety of wavelengths of light and pass the charges to metal catalysts. Another, developed by Turner's NREL team, absorbed light with semiconductor wafers made from gallium arsenide (GaAs) and gallium indium phosphide (GaInP). A platinum electrode served as the catalyst to split water and generate O₂, while the semiconductor acted as the electrode to produce H₂.

ple is the quest for H₂-forming catalysts. Natural photosynthesis carries out the reaction using enzymes called hydrogenases, which are built from the abundant elements iron and nickel. The enzymes have evolved until they can knit roughly 9000 pairs of hydrogen atoms into molecular H₂ every second. Many early water-splitting systems performed the same reaction even faster using pure platinum as the catalyst. But platinum is too rare and expensive to be broadly useful.

In recent years, researchers have synthesized numerous compounds aimed at mimicking the core complex of hydrogenases. All work more slowly (if at all), however, largely because they lack parts of the natural protein around the core that optimizes the core's activity. In 2008, Thomas Rauchfuss, a chemist at the University of Illinois, Urbana-



Box step. Natural photosynthesis depends on a molecular cube (left) made from manganese atoms (purple), oxygens (red), and a calcium atom (yellow). The catalyst splits water molecules (blue), generating molecular oxygen. Synthetic versions (center and right) have similar cube-shaped cores.

tively charged electron vacancy called a hole.

The holes are shuttled over to a compound called the oxygen-evolving complex, which grabs two oxygen atoms, holds them close together, and rips out an electron from each to fill the holes. The electron-deficient oxygens regain their stability by combining to form O₂. In an artificial system, the electrons and protons liberated by water splitting then must migrate to a second catalyst, which combines them into two molecules of H₂.

A successful artificial photosynthesis system must therefore meet several demands. It must absorb photons, use the energy to create energized electrons and holes, and steer those charges to two different catalysts to generate H₂ and O₂. It also has to be fast, cheap, and rugged. “This is a much more stringent set of requirements than [those for] photovoltaics,” says John Turner, a water-splitting expert at the National Renewable Energy Laboratory (NREL) in Golden, Colorado.

Unfortunately, these systems, too, had drawbacks. The metals in the best light-absorbing molecular dyes are too rare to be viable as a large-scale technology. To get enough ruthenium to power the world with water splitting, “we would need to harvest 1% of the Earth's total continental crust to a depth of 1 kilometer,” Rappé says. Scale-up is problematic with the semiconductor system as well. Although Turner's devices convert 12% of sunlight to hydrogen, the materials would cost as much as \$50,000 per square meter, according to an estimate by Harry Gray, a chemist at the California Institute of Technology (Caltech) in Pasadena. To be viable on a large scale, “we need to build something this good for \$100 per square meter,” Gray says.

Wanted: the perfect catalyst

So more recently, much of the work in the water-splitting field has begun to shift to trying to make light collectors and catalysts from abundant and cheap materials. A prime exam-

ple is the quest for H₂-forming catalysts. Natural photosynthesis carries out the reaction using enzymes called hydrogenases, which are built from the abundant elements iron and nickel. The enzymes have evolved until they can knit roughly 9000 pairs of hydrogen atoms into molecular H₂ every second. Many early water-splitting systems performed the same reaction even faster using pure platinum as the catalyst. But platinum is too rare and expensive to be broadly useful.

Champaign, and colleagues devised catalysts with molecular arms that act like a bucket brigade to ferry protons to the catalytic core. In the 12 August 2011 issue of *Science* (p. 863), DuBois and his colleagues described how they had refined this strategy further by creating a nickel-based catalyst that stitches 106,000 H₂ molecules together every second (http://scim.ag/_DuBois).

The new H₂ makers still aren't ideal. They work only at high speed when researchers apply an electrical voltage of more than 1 volt to their system, a sizable energetic penalty. So DuBois's team is now working to tweak the catalysts to work at a lower added voltage. In a paper published online in *Science* on 29 September (<http://scim.ag/Nocera>), Dan Nocera, a chemist at the Massachusetts Institute of Technology in Cambridge, reported that he and his colleagues had come up with another H₂ catalyst that works with an extra voltage of only 35 thousandths of a volt (millivolts). It, too, is made from rela-

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tively cheap metals: molybdenum, nickel, and zinc. But Nocera's catalyst is slower than DuBois's, so the race is on to marry the best attributes of each.

Balancing speed and extra energy input has been an even tougher problem with the catalysts needed for other reactions in water splitting, which grabs oxygen atoms from two water molecules and links them together as O_2 . In 2008, Nocera and his team made headlines when they unveiled a cobalt-phosphate (Co-Pi) catalyst that works at 300 millivolts applied potential over the minimum 1.23 electron volts required to link two oxygen atoms. The group followed that up with a nickel-borate compound that does much the same thing. And in the 29 September online paper, the researchers described a triple-layer silicon wafer lined with their Co-Pi catalyst on one face and with their H_2 catalyst on the other. The silicon absorbed sunlight and passed charges to the two catalysts, which then split water. "I love the triple junction. It's pretty sexy," says Felix Castellano, a chemist at Bowling Green University in Ohio.

Turner cautions that the overall efficiency of the device—it converts just 5% of the energy in sunlight to hydrogen—is still too low, and the extra voltage input required is still too high, to be commercially useful. Nocera counters that this initial system was built using amorphous silicon wafers as the sunlight absorbers. Such wafers are only 8% efficient in converting light to electrical charges. An artificial leaf based on crystalline silicon solar cells, which are 20% efficient, could convert sunlight to chemical energy with an efficiency of 12%, he says. But Nocera's team has yet to demonstrate such a device.

Other related catalysts are also entering the picture. Charles Dismukes, a chemist at Rutgers University in Piscataway, New Jersey, and colleagues reported last year that they had made a series of O_2 -forming catalysts using lithium, manganese, and oxygen. And earlier this year, Dismukes's team reported in the *Journal of the American Chemical Society* that they had created another oxygen-forming complex with cobalt and oxygen. What's unique about all these new oxygen formers is that they share almost an identical cubic molecular structure, which is also at the heart of the natural O_2 -forming complex in photosystem II. "There is only one blueprint from biology that can be copied," Dismukes says.

Many other advances are also making their way out of the lab. Castellano and colleagues have recently created a family of cheap polymers capable of absorbing the energy from

Sunlight in Your Tank—Right Away

Using sunlight to split water and generate hydrogen doesn't make the most useful chemical fuel. To use hydrogen on a large scale, societies would have to develop a new infrastructure to store, transport, and distribute the energy carrier. With that limitation in mind, some researchers are looking to use artificial photosynthesis to generate hydrocarbon fuels like those we already burn.

Their goal is essentially to run combustion in reverse, starting with carbon dioxide (CO_2) and water and using the energy in sunlight to knit the chemical bonds needed to make hydrocarbons, such as gaseous methane and liquid methanol. "That's a technology that's going to come," says Harry Gray, a chemist at the California Institute of Technology in Pasadena. "But it is hard."

The difficulty is that CO_2 is a very stable molecule. In converting CO_2 to hydrocarbons, the first step is to strip off one of the oxygen atoms, leaving behind a molecule of carbon monoxide (CO), a more reactive combination of carbon and oxygen. CO can then be combined with molecular hydrogen and converted into liquid hydrocarbons using an industrial process known as Fischer-Tropsch synthesis.

That first step of converting CO_2 to CO is the energy hog. A minimum of 1.33 electron volts (eV) of energy must be applied to carry out the reaction. Over the past few decades, researchers have developed numerous catalysts that carry out the process. But virtually all of them require adding a lot of extra energy, typically another 1.5 eV. As a result, it would take far more energy to synthesize a hydrocarbon fuel than the fuel's molecules could store in their chemical bonds.

On 29 September, however, researchers led by Richard Masel of Dioxide Materials in Champaign, Illinois, and Paul Kenis of the University of Illinois, Urbana-Champaign, reported online in *Science* (http://scim.ag/_Masel) that they've come up with a less energy-intensive way to convert CO_2 to CO. By adding a type of solvent called an ionic liquid to the CO_2 in their setup, they reduced the added energy needed for splitting CO_2 by 90%. Ionic liquids are liquid salts that are adept at stabilizing negatively charged compounds. Adding a negative charge is the first step required to convert CO_2 to CO; the Illinois researchers suspect the increased stability reduces the voltage needed to do the job.

The Illinois catalysts are slow, and so far the researchers have not powered them with electrical charges from a solar cell. But other labs are taking an approach that looks more like full-fledged artificial photosynthesis. At Lawrence Berkeley National Laboratory in California, for example, chemist Heinz Frei and his colleagues reported in 2005 that for the first time they had used energy from visible light to convert CO_2 to CO using a porous catalyst made from silica and impregnated with zinc and copper. Frei's team has used related catalysts to split water to generate molecular hydrogen. Now the group is working to put the two pieces together to combine light-generated CO and H_2 to make methanol, one of the simplest hydrocarbons.

It's not ExxonMobil yet. But with further developments, the technology could lead to fuels made basically from air, water, and sunlight.

—R.F.S.

low-energy green photons and reemitting it as lower numbers of higher energy blue photons. They are now working on using this upconversion process to make use of more of the solar spectrum to split water. Researchers led by Steve Cronin of the University of Southern California in Los Angeles are adding metal nanoparticles to conventional solar absorbers as another way to convert low-energy photons to electrical charges that can then be harnessed to improve the efficiency of water-splitting setups. And Gray's group at Caltech has teamed up with students at 17 other universities to create a "solar army" that has already made progress in finding new water-splitting catalysts.

These and other advances will need to continue if artificial photosynthesis ever hopes

to contend with fossil fuels. With today's low natural gas prices, companies can use a mature technology called steam reforming to convert natural gas to hydrogen at a cost of about \$1 to \$1.50 per kilogram of H_2 generated, which contains about the same amount of energy as a gallon of gasoline. Yet a recent analysis by Turner and his colleagues showed that, even if researchers could create an artificial photosynthesis system that cost \$200 per square meter for the equipment and was 25% efficient at converting sunlight to H_2 , the H_2 would still cost \$2.55 per kilogram. That's not saying artificial photosynthesis isn't worth pursuing—only that fossil fuels are the leading energy source for a reason, and they won't be easy to dethrone.

—ROBERT F. SERVICE

Science

Turning Over a New Leaf

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