Correction

NEWS FEATURE

The editors note that on page 4547, right column, last paragraph, line 1, “Another of Cui’s designs” mistakenly appeared. The text should have read “Another of Yang’s designs.” The online version has been corrected. We regret the error.

www.pnas.org/cgi/doi/10.1073/pnas.1606805113
On a bench in a laboratory at Berkeley sits a device designed to make the ultimate green fuel. The stainless steel chamber, festooned with gaskets, nuts and bolts, and glass windows, looks like some kind of steam-punk aquarium. Inside, arrays of nanowire electrodes and bacterial colonies are using the light to turn water and carbon dioxide into methane, the main component in natural gas. This is one of the best attempts yet to realize the simple equation: sun + water + carbon dioxide = sustainable fuel.

Solar power is already a success story, but the electricity generated by photovoltaic panels can’t do every job. It is not much use in the tank of an airplane, for example. Three-quarters of the energy people use today is in the form of liquid and gaseous fuels, so the renewable energy portfolio needs fuels too.

That is why chemists are trying to copy plants. Through photosynthesis, plants take in carbon dioxide, water, and sunlight, and turn it into the chemicals they need, with oxygen as the only byproduct. For decades, scientists have wondered: Can we take a leaf out of the plant’s playbook, and grow our fuels and chemicals?

Last year brought cause for optimism, as researchers made three advances toward practical solar fuels. “When people see what we’ve done, they will realize it’s not pie-in-the-sky anymore,” says Daniel Nocera, a professor of chemistry at Harvard University. Now with the implications of climate change looming, competing researchers are advancing their prototypes and racing to not only prove technological success but also show marketplace viability.

Planting the Seeds

The first step in the complex chemistry performed by plants is to split water into hydrogen and oxygen. Chlorophyll and other pigments absorb light, which excites electrons. These electrons are passed along a chain of molecules, which use them to pry water molecules apart.

Splitting water is also central to artificial photosynthesis. This can be an end in itself, because hydrogen can be used as a fuel or it can be a first step toward more energy-dense hydrocarbon fuels, such as methane and ethanol.

Researchers have been working to make solar fuels since the 1970s. The inspiration came in 1972, when Akira Fujishima at Kanagawa University and Kenichi Honda at the University of Tokyo showed that two electrodes—one titanium dioxide and the other platinum—would catalyze the splitting of water when illuminated with visible light (1).

In Fujishima and Honda’s system, photons hit the titanium dioxide and create pairs of negative and positive charges: electrons and holes. The electrons flow through a wire to the platinum electrode, whereas the holes grab fresh electrons from water molecules at the surface of the titanium electrode, splitting the
molecules into hydrogen ions and oxygen. The hydrogen ions migrate through the liquid to the platinum site, where they complete the circuit and recombine with electrons to form molecules of \( \text{H}_2 \). 

Along with the oil crisis of 1973, this work inspired many young scientists to work on artificial photosynthesis. Arthur Nozik was among them. “I saw that paper and I got interested in solar power,” he recalls. Nozik was one of the founding researchers at what would become the National Renewable Energy Laboratory in Boulder, Colorado, where he began working on new electrode designs for water splitting.

**Hydrogen Hopes**

This first wave of enthusiasm soon passed as the price of oil came down and the budget for renewable energy research was cut during the Reagan administration. But Nozik and a few others kept the flame alight.

Then in 1998, John Turner at the National Renewable Energy Laboratory provided a sign that this work was paying off, with an electrode system that could split water with 12.4% efficiency (2). This was another turning point, and as the risks of climate change became clearer in the early 2000s, more researchers jumped back in.

One of the first aims was to find an alternative to expensive platinum electrodes. So researchers have been working to squeeze higher efficiency out of more abundant materials, including nickel and molybdenum sulfides. The Joint Center for Artificial Photosynthesis (JCAP), a Department of Energy program housed at the California Institute of Technology (Caltech), has tested hundreds of thousands of new catalysts, and their results are promising. Some of their discoveries match the performance of platinum; one of the best is a compound of cobalt and molybdenum (3).

These catalysts are now being used in a slightly different approach from Fujishima and Honda’s. Instead of using light directly, water can be split by plugging electrodes into a source of electrical power. The current then drives the same reactions that were set off by the charge-splitting effect of the photons. And if you generate that electrical power using a solar cell, you have a renewable source of fuel.

In August, chemist Leone Spiccia at Monash University in Victoria, Australia, demonstrated such a two-part system that could possibly compete in a tough market; it also broke efficiency records. Spiccia used high-performance triple-junction solar cells to generate electricity. The electricity passes through nickel-foam electrodes to catalyze water splitting. The system converts solar energy into hydrogen fuel with an efficiency of 22%. Spiccia is now working on reducing inefficiencies in the connections between the parts, and he believes that an overall efficiency of 28% or 30% is possible.

But being green is only one argument for a technology; it also has to make economic sense. Triple-junction solar cells are expensive, so Spiccia’s system might need subsidies to compete with dirtier sources of hydrogen.

Today, hydrogen is primarily made by steam reforming of methane, an energy-intensive but inexpensive process. Hydrogen made this way costs about $2 per kilogram, says Nathan Lewis, a chemist at Caltech and the former director of JCAP at Caltech. Making hydrogen using electrolysis fed by conventional solar cells would come in at around $5 to $7 per kilo, he estimates. Spiccia hasn’t done a full cost analysis but readily admits hydrogen made using his prototype would be more expensive than what is on the market today. There’s much room for improvement in his first demo system.

Lewis favors a design that eliminates the need for a separate solar cell. As part of JCAP, he developed a water-splitting system with electrodes that are something like submerged photovoltaic panels. His system looks like a sealed reactor full of water, illuminated from the outside, shiny photodiodes within. As in an ordinary solar cell, light strikes a semiconductor, generating electrons and positively charged “holes.” But rather than funnel these off to an electrical grid or a battery, the JCAP device passes them directly to catalysts to split water.
One of Lewis’s main challenges has been making a solar cell that will not break down underwater. The key to this was a thin protective layer of titanium dioxide a few nanometers thick. In August, the group published the results of their reactor design, which can produce hydrogen fuel with 10% efficiency (5).

Lewis explains his long-term vision for hydrogen production: a system that would use printable materials to make large-area, flexible reactors that can be deployed cheaply. “We want to make something simple enough to spray onto your house,” he says. That ultimate goal is still a big basic materials science and research problem.

In the meantime, Lewis is motivated by trying to get something realistic to market as soon as possible, he says. For him, that’s a solar fuel system that makes hydrogen.

Hydrogen isn’t the ideal fuel, as almost all our existing infrastructure is built for more energy-dense options, like gasoline and methane. One immediate benefit of having a clean source of hydrogen would be for sustainable production of ammonia for fertilizer, which is made by combining nitrogen and hydrogen. Hydrogen can also power fuel cells, and above all, it can be used as a starting point for other reactions. “I think of hydrogen as a way to upgrade things,” says Jens Norskov, professor of photon science at Stanford University.

Green Gas
Still, it would be more efficient if an artificial leaf could produce more energy-dense fuels directly, by using carbon dioxide as a feedstock. Carbon dioxide can be captured from power plants, and the aim of many projects is to then store the gas. It would be much more useful to convert the stuff into a transportation fuel or a high-value chemical.

Harry Atwater, now director of JCAP, says methanol or ethanol would be good options. Ethanol is already blended into fuel, and there are efficient ways to convert methanol into gasoline. But generating even these relatively simple hydrocarbons is much harder than splitting water.

That’s because the chemistry is much more complex. Splitting a molecule of water takes only two electrons, says Norskov. Making the simple hydrocarbon methanol is a reaction involving eight electrons, each with different energies, which have to be shuffled around through several steps to create the single-carbon molecule.

What chemists can’t easily do in the laboratory, leaves do with ease: making complex sugars and other organic molecules. Nature uses 3D enzymes to wrangle all of the ingredients, roping them together to make all of the intermediate reactions and electron transfers happen in order. These delicate natural catalysts are rapidly damaged by the energetic process, and are nearly continuously rebuilt and replaced by plant cells. Synthetic catalysts must either heal themselves somehow—an idea Nocera has been working on—or be incredibly durable, made out of hard materials. Designing a self-healing or durable catalyst that can pull off all this chemistry is tremendously challenging. “There’s nothing that works even close to well enough,” says Norskov.

Perhaps the greatest challenge for constructing the artificial leaf is matching the specificity of plant enzymes. The natural proteins can produce very specific products, such as pure methane, whereas synthetic catalysts tend to churn out an unpredictable medley of carbon-containing compounds.

Building with Bacteria
Instead of waiting for synthetic chemists to match nature’s wonders, some chemists have recruited bacteria to help do the job. Peidong Yang, at the University of California, Berkeley, has made a complete solar fuels system with what he calls living catalysts. His system uses nanowire electrodes, which are in principle similar to Fujishima and Honda’s work, and Turner’s as well. But because they have nanowire-carpeted surfaces rather than smooth ones, these electrodes can both absorb more light and hold more catalyst in a given area than earlier ones. That means they can better keep up with solar flux, and get the energy from more photons converted into more electrons that can split more water. One electrode has nanowires paired with a synthetic catalyst; another is seeded with bacteria.

A design published recently in PNAS makes methane (6). This set-up uses a double-chambered reactor. "I don’t know whether a synthetic catalyst or a bacterial one will win out.” —Peidong Yang

In one windowed chamber, the anode splits water to make oxygen gas and hydrogen ions, the same basic process other researchers have exploited. In a second chamber, a cathode coated with a nickel catalyst brokers a reaction between the hydrogen ions and electrons to make dissolved hydrogen gas. Methanosarcina barkeri bacteria, acting as living catalysts, take up that gas and combine it with CO₂ to make methane. The process is highly efficient: 86% of the electrons produced by splitting water are used in the methane-producing reaction. The methane bubbles out of the water and is then captured. It’s too early to make firm predictions about the commercial cost of a large-scale system of this kind, but bacteria are already routinely used to brew alcohol and even drugs in large vats. And there is a product that uses an analogous combination of human chemistry and bacterial smarts, the semisynthetic malaria drug artemisinin made by Sanofi (7).

Another of Yang’s designs uses a strain of bacteria that produces acetate. That acetate is then eaten by genetically engineered Escherichia coli that can convert it into plastics or butanol. Yang is collaborating with synthetic biologist Michelle C. Y. Chang, who is developing strains of bacteria that can both generate a greater variety of chemicals and live in the reactor. At Harvard, Nocera and synthetic biologist Pamela Bourzac...
Silver are also working on a design that uses microbes (8). Their efficiency is better; so far they’ve made isopropanol but they’re also working on more widely used fuels.

**The Price of Sustainable Fuel**

Norskov and others are excited to see these new ideas achieving success in prototypes. Just as researchers have had to move on from platinum catalysts, they may end up using microbial partners for complete artificial photosynthesis, if that turns out to work better.

“I don’t know whether a synthetic catalyst or a bacterial one will win out,” says Yang. A chemist at heart, he favors an all-inorganic system. Bacteria are sensitive to pH, temperature, and other environmental factors, all of which puts a certain strain on the design of the engineered components. But bacteria can do chemistry that synthetic catalysts can’t, so it’s worth babying them. Today bacteria are the best, he says. Maybe they’ll be a stepping stone to a fully synthetic system.

These three recent successes—Spiccia’s record-breaking electrolysis, JCAP’s integrated cell, and Yang and Nocera’s full photosynthesis systems—are cause for hope. Still, demonstrating a laboratory prototype is very different from confronting the complex economic realities of the energy markets. If and when solar fuels are first introduced, they are sure to be more expensive than fossil fuels, so researchers may need to show that costs can come down further before companies get involved.

Beyond the basic science, it will be a question of political will, as climate change policy remains contentious. “We’re going to need some help on the policy side,” says Atwater. A carbon tax would help, as would subsidies for companies interested in commercializing these technologies. “The science and the politics are mixed together,” says Nozik. “The question is: are we going to run out of time?”

---