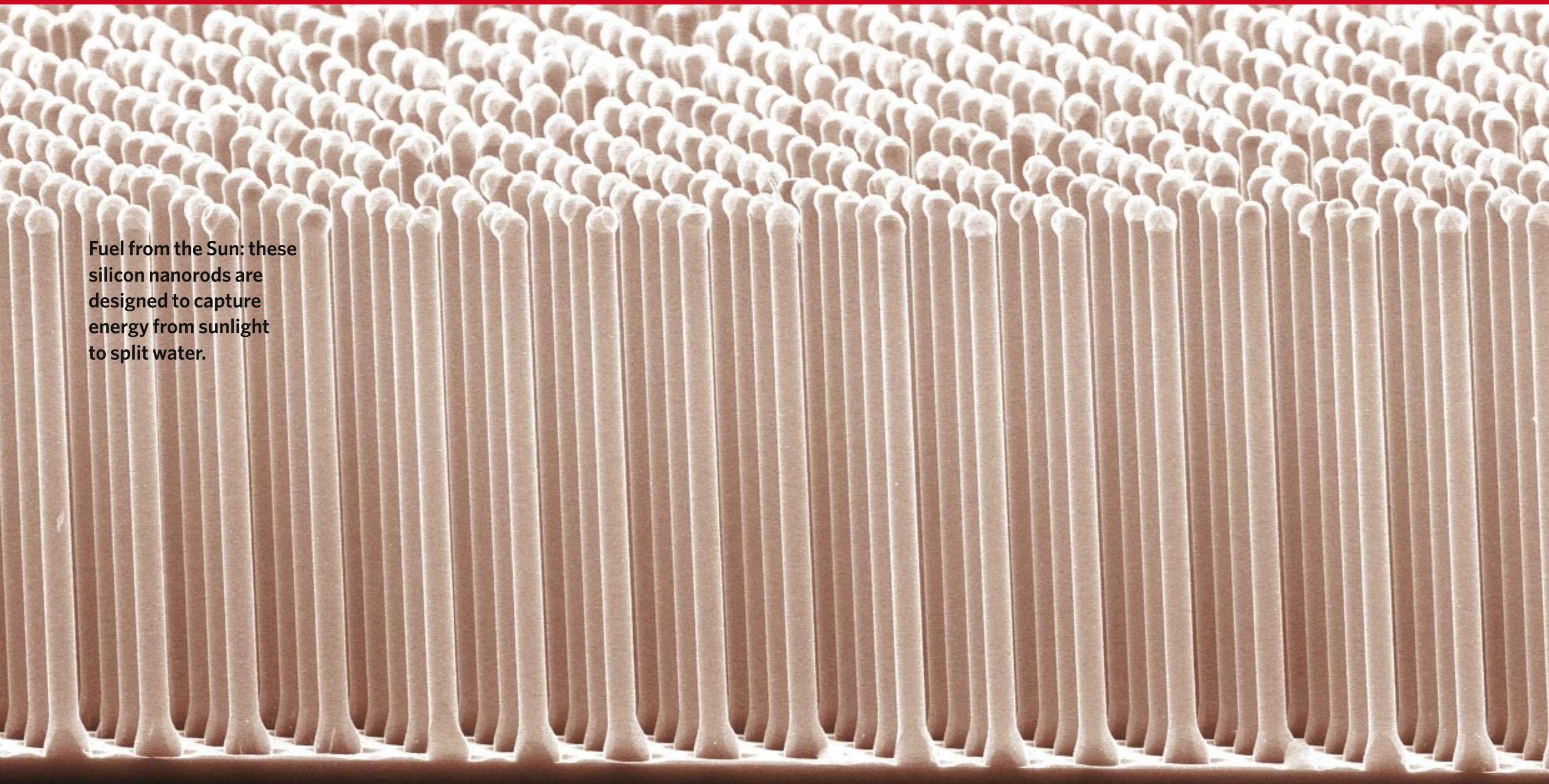

Fuel from the Sun: these silicon nanorods are designed to capture energy from sunlight to split water.

B. KAYES, M. FILLER

The photon trap

Chemists have long wanted to recreate photosynthesis in the lab — and to improve on its efficiency at converting sunlight into fuel. **Katharine Sanderson** reports on their latest efforts.

Solar cells can take sunlight and produce a current, giving instant power. But as soon as the Sun goes down, the lights go dim. If you could turn sunlight into fuel — to use for transportation or simply to store for later — you'd be on to a good thing.

Nature can already do this thanks to photosynthesis. Green plants take water, sunlight and carbon dioxide to make sugars and starches. This provides all the fuel they need, and most of the fuel we need too, in the form of food or oil.

The problem is that plants aren't very efficient at fuel making — only about 3% of the Sun's energy ends up as a useable fuel. And the fuel that works for plants doesn't necessarily work for us — the sugars and starches have to be further processed if our needs are more sophisticated than simply eating or burning.

But where plants excel is in getting electrons out of water to produce a fuel. A photovoltaic system, or solar cell, is simply a means of shifting electrons from one place to another. To make a fuel, the electrons are siphoned off, and stored in chemical bonds.

Plants get their electron supply from water. Chemists worldwide are trying to design synthetic systems that do the same. And the design they have to beat, or at least mimic, not only works at room temperature, it does so without the need for expensive metal catalysts. Making something cheap and similar to the machinery used by plants, the photosystem-II protein complex (PSII), remains a fundamental challenge.

Some US chemists taking on the challenge are part of a collaborative effort called Powering the Planet, backed by the National Science Foundation. Three basic chemistry problems, each tackled by a different research team, form the crux of the project. One is to design an affordable material to collect energy from the Sun and convert it into current (led by Nate Lewis at the California Institute of Technology, or Caltech). Another is to perfect a catalyst at one end of the material to split water and produce oxygen (led by Dan Nocera at the Massachusetts Institute of Technology). And, the third is to design another catalyst at the other end to produce hydrogen, to be used as a fuel (led by Harry Gray, also at Caltech).

"We've made dramatic advances," says Gray, who can be seen as the father of the project, having supervised both Nocera and Lewis as students in the 1980s. "We're not close to assembling the full device yet."

To start the fuel-making process, sunlight hits a photo-active material. In plants this is chlorophyll, but in the lab it can be a silicon semiconductor, which has its electrons whacked out of position by the incoming photons. The dislodged electrons start to flow in one direction, creating a current. Left behind are positive charges, known as holes, and they drift in the opposite direction. This is a basic solar cell, which requires silicon of high purity, otherwise material defects cause the electrons and holes to recombine, reducing its performance.

Plant power

In the Powering the Planet design[1], catalysts at either end of the semiconductor are used to drag the electrons and holes out of the system, preventing them from recombining with each other (see graphic). And water is added to provide the raw material for making the fuel.

One catalyst uses the holes in the semiconductor to drag further electrons from water. This process splits water, releasing oxygen and positively charged hydrogen ions (protons). These protons flow to the other catalyst, which combines them with the electrons in the semiconductor ultimately to make hydrogen molecules.

As well as providing hydrogen fuel for combustion, both the hydrogen and oxygen gases can be fed into a fuel cell — a means of reacting hydrogen with oxygen to produce water and electricity for powering an electric vehicle.

There are other ways to split water artificially. In 1975, Nobel prizewinning physicist Jack Kilby invented an electrolysis system that

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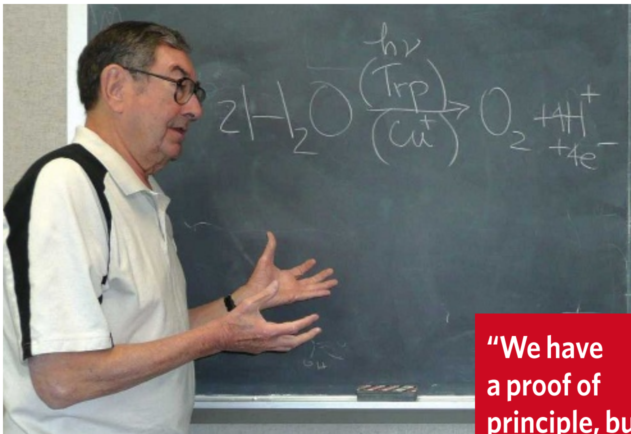


Harry Gray uses sunlight to make hydrogen fuel.

used power from a solar cell to drive electric current through a water-based solution (an electrolyte). This process produced protons and hydroxide ions, which reacted at the electrodes to make hydrogen and oxygen.

Aside from Kilby's simple system, more complex electrolysis cells have been built that use a photoactive semiconductor coated on one side with a platinum catalyst as one of the electrodes. When immersed in water, the semiconductor can both harvest light and generate the electrons and holes needed to split water into protons and oxygen. Hydrogen is released directly from the surface of the semiconductor, and oxygen is produced at a second platinum electrode.

This cell was built in 1998 by John Turner from the National Renewable Energy Laboratory in Golden, Colorado. His device converted water to hydrogen with 12.4% efficiency, four times as good as photosynthesis. But Turner had to use expensive materials such as platinum, the system had a lifetime of just 20 hours, and the hydrogen produced cost US$13 per kilogram[2]. "We can do better," says Turner.

The problem with all electrolysis systems is that the electrode materials degrade rapidly in solution, and need to be replaced, increasing costs and decreasing efficiency. The main difference between Turner's cell and future technologies will be the materials used, with the precious-metal catalyst and expensive single-crystal silicon superseded by cheaper materials. "If we're going to solve this problem we can't use materials that are toxic or expensive," says Gray. "This rules out standard catalysts."

Nate Lewis is leading Powering the Planet's light-harvesting effort. His team is refining a silicon material that he describes as "cheap and scaleable". Instead of expensive single-crystal silicon, Lewis's photoelectric material is a carpet of nanoscale silicon rods, all pointing upwards. He's done this work with Harry Atwater, director of the Caltech Center for Sustainable Energy Research.

The rods are each single crystals, but the method used to grow them is much simpler than the precision wafer-processing technology needed for conventional solar cells. Atwater claims that this makes the rod silicon only as expensive as the silicon feedstock, at between $40 and $70 per kilogram.

"We have a proof of principle, but we have a long way to go." — Harry Gray

The nanorods are also amazingly defect-free. "Once a nanowire begins to grow a little taller than it is wide, it expels defects," says Atwater. This means that the only place where the holes and electrons could recombine is at the tip of each tiny rod.

In the device imagined by the Powering the Planet team, Lewis and Atwater's silicon-rod carpet will be held inside a plastic membrane. The catalysts are coated on opposite sides of the membrane to prevent the oxygen and hydrogen reuniting, potentially explosively.

Catalysing success

Harry Gray is making good progress at the hydrogen-producing end of the system. His catalyst is a cobalt molecule. "It works really well, with quite reasonable efficiency," he says. This rather depends on your expectations. In catalysis, turnover rates are used to measure how many substrate molecules are converted to a product each second. Hydrogenase enzymes, which power the same reaction in plants, have turnovers of about 6,000 per second[2], but Gray's catalyst is still a factor of a thousand less efficient than the hydrogenase enzyme, he says. "We have a proof of principle, but we have a long way to go," says Gray.

Dan Nocera, at the Massachusetts Institute of Technology, Cambridge, is developing the oxygen-producing catalyst, which is proving to be the hardest part of the challenge. Nocera's team began by looking at expensive metals that are related to cheaper metals: a trick often used by chemists. Choose a target metal that could be potentially used, then look at its position in the periodic table and move down a row to a heavier, more expensive metal, where processes happen more slowly, and are more easily studied. Nocera has been using ruthenium, directly below iron. He hopes to transfer what he has learned to iron, copper or nickel, and is confident that this leap will happen soon, making a working system possible within five years, he says.

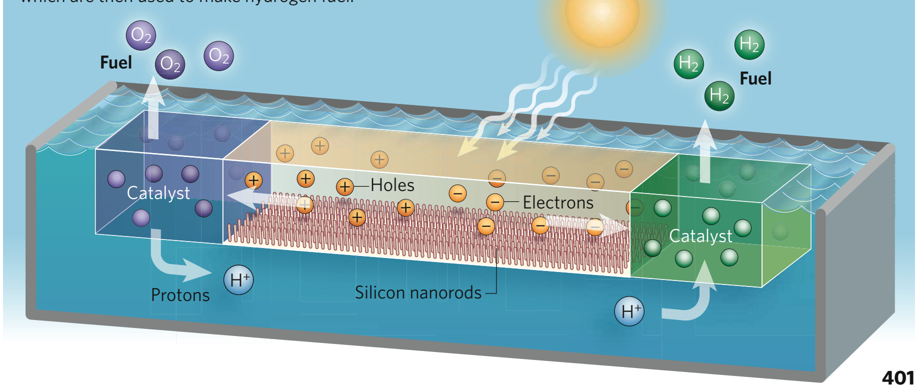
James Durrant, a chemist at Imperial College London, is also investigating water-splitting materials. He is well aware of the chemistry problems faced by Nocera in his quest for a cheaper catalyst. "Oxidizing water is vicious chemistry," he says. The catalytic reactions involve molecules undergoing multi-electron processes, which are poorly understood. "As bad as it is to transfer one electron, the molecule is even more reluctant to give up the second electron," explains Atwater.

This is because adding solar energy to water, and tying it up in molecules with higher energy bonds (oxygen and hydrogen) is what's known as a thermodynamically uphill process. And most of that uphill struggle happens at the oxygen-producing site. Making a single molecule of oxygen involves splitting two water molecules, and the whole process involves four electrons and four protons. "That's a lot of electrons and protons," says Nocera. For this reason, Nocera says he doesn't want to simply copy photosynthesis. "It took two billion years of evolution," he says. "I don't think I can do it in 20."

Other chemists are still trying to beat nature at its own game. A dozen European research partners, coordinated by Stenbjörn Styring

THE POWERING THE PLANT DESIGN

Solar energy is used to split water into oxygen and protons, which are then used to make hydrogen fuel.



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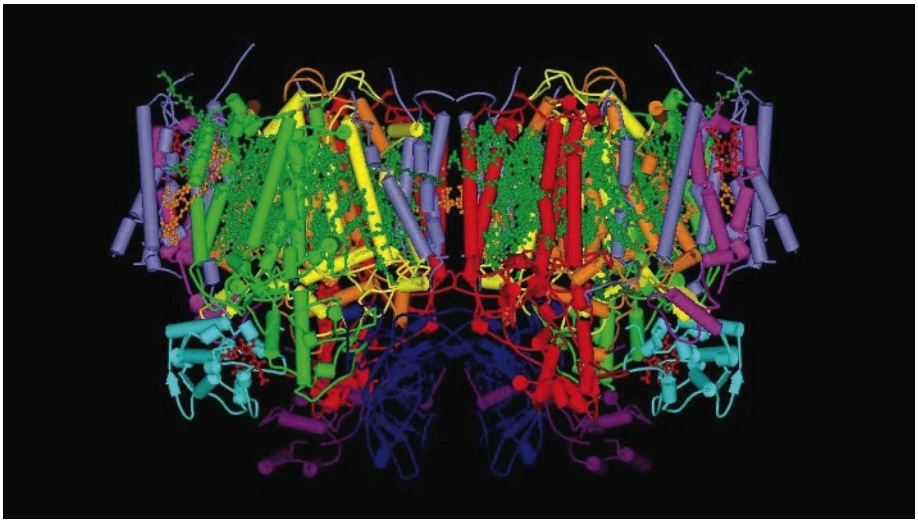

Chemists want to replicate photosystem II (modelled above), used by plants to convert light into fuel.

from Uppsala University, Sweden, form the Solar-H network, funded by the European Union. They are looking closely at natural photosynthesis for inspiration.

To harvest energy from sunlight, the Solar-H team uses a ruthenium-centred molecule that helpfully absorbs light at a similar wavelength to chlorophyll. For the hardest part of the problem — the oxygen catalyst — the Solar-H team turns to the heart of PSII, which contains a molecule with four manganese atoms known as the oxygen-evolving complex.

Styring has been working on this problem for 15 years, and he has shown that it isn't necessary to fully replicate the oxygen-evolving complex. Instead, he thinks that just two manganese atoms are sufficient. Styring says he has recently had a breakthrough: a molecule that can split water into oxygen and protons, although the system is powered electrochemically, not by light.

Even after this prolonged effort, Styring expects criticism when he publishes the work, partly because the oxygen-evolving molecule isn't fully catalytic — the molecule is changed by the reaction and so probably cannot be reused. "People will be very sceptical, and so are we," he says. "This is a very difficult field."

He will have a hard time convincing researchers such as Durrant. "The only molecular system known to perform thermodynamically efficient water oxidation is PSII," says Durrant. "We're a long way from having a molecular system that works as well," he says.

Other chemists say that simply mimicking photosynthesis is too short sighted. "Photosynthesis is basically a failure for energy conversion," says Tom Mallouk at Pennsylvania State University. To beat the world's energy problems, scientists have to be more ambitious than the 3% efficiency achieved by plants. "If that's all we want, the thing to do is grow corn," says Mallouk. He thinks the goal should be at least 10%, preferably 20% power conversion efficiency, using materials that do not cost much more per unit area than house paint, he says.

The Powering the Planet team is optimistic it can beat photosynthesis, even if it doesn't beat Turner's efficiency record. And they are determined to beat Turner on cost. "In the end, we want to be at 5–10% solar-to-fuels efficiency," says Lewis. "We know the materials that work. It's just a question of making it work faster, better, cheaper."

"People will be very sceptical, and so are we. This is a very difficult field."
— Stenbjörn Styring

Another materials approach to water splitting is being taken by Kazunari Domen at the University of Tokyo. In future, says Domen, if human beings use solar energy on a huge scale, we need to use technology that captures solar energy over much larger areas. To achieve this, he uses a photocatalyst particle that generates hydrogen and oxygen simultaneously on its own surface. The material is a solid solution, a mixture of metal oxides impregnated with nanoparticles of another mixed oxide. Domen is still developing these materials, which as yet don't work for all wavelengths of light.

Domen admits there is still lots of basic research to be done. Indeed, all of the groups defend their work as basic chemistry first — and applied research second. "We're doing fundamental chemistry, unashamedly," says Lewis. "There's lots of basic stuff to do to solve this."

To get a fully practical system may take years, although Atwater thinks that the silicon-rod carpets are already ripe for commercialization as light-capturing solar panels. A few small companies are investigating water-splitting, including Nanoptek, a start-up firm in Maynard, Massachusetts, which is building on the original Kilby approach by developing photoelectrodes that will harvest photons over a wider energy range.

Fueling the future

G24 Innovations (G24i) in Cardiff, Wales, is developing small-scale electricity generating systems based on organic dyes — again mimicking nature's use of chlorophyll in photosynthesis — for personal electronics, mobile phones and laptops, with the goal of bringing these mass communication devices to remote parts of the world. The company's first products — solar-powered chargers — rolled off the production line in February.

The approach is based on technology pioneered by Michael Grätzel at the Swiss Federal Institute of Technology in Lausanne. In his photoelectrochemical cells, the amount of silicon needed is greatly reduced, because the expensive semiconductor is used purely to ferry electrons and holes around, and sunlight is captured by an organic dye. But G24i's products only generate electricity, rather than convert sunlight to fuel.

There are different opinions in the field about when a commercial fuel-generating device will become reality. Where Atwater sees immediate commercial opportunities for his part of the project, Durrant can't see there being anything practical working for at least ten years. Gray thinks the problem requires at least another three or four years' work, and can see good motivation for pushing ahead. "This is a big deal in terms of competitiveness and innovation," says Gray. "When solar energy comes in big time this is a trillion-dollar business."

Turner wants to see a longer-term approach to pay for this kind of research. For the past 30 years, he says, funding has been "spotty and not focused". This is a mistake, he thinks, if the future energy needs of the world are to be met. "Sunlight is truly our largest energy resource by far — it outshines everything else." ■

Katharine Sanderson is a reporter for *Nature* based in London.

1. Lewis, N. S. & Nocera, D. G. *PNAS* **103,** 15729–15735 (2006).
2. Khaselev, O. & Turner, J. *Science* **280,** 425–427 (1998).