A laser focus on finding better ways to make renewable fuels

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Jay Winkler and his team are zapping metals to create new solar-fuel catalysts. Credit: California Institute of Technology

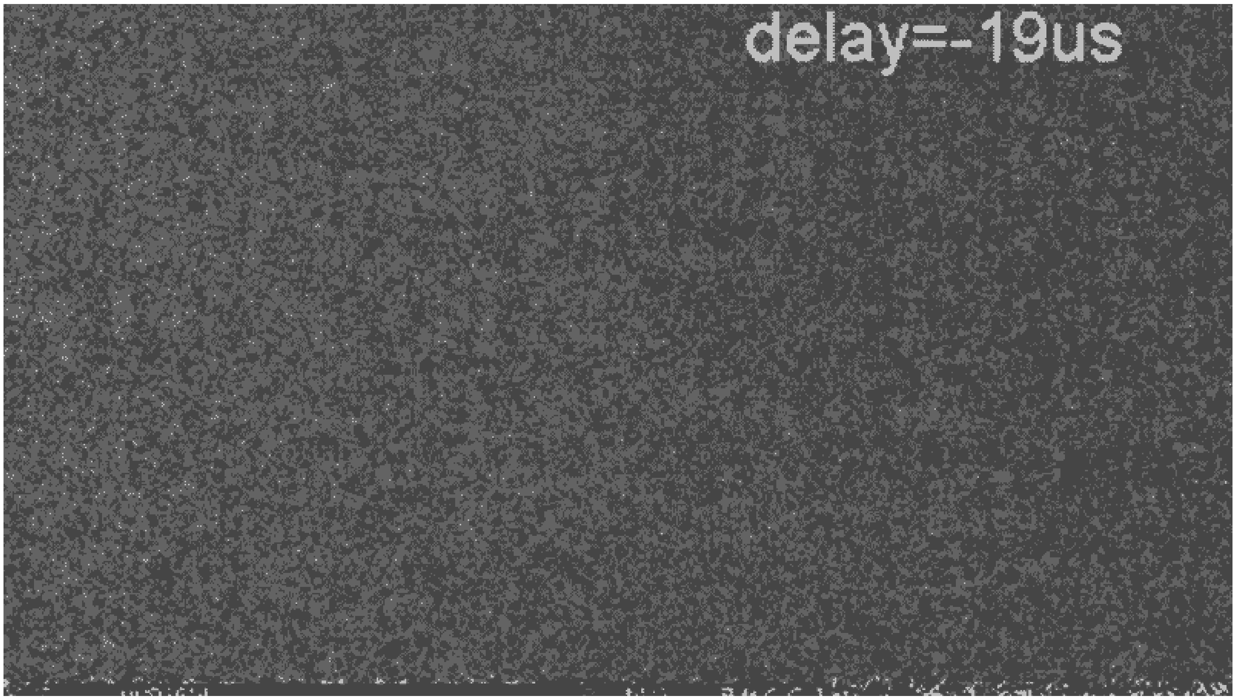
In the search for alternatives to oil-based fuels, one of the most promising, and challenging, strategies involves splitting water. Researchers have for decades made strides in using sunlight to split water molecules into oxygen and hydrogen, wherein the resulting hydrogen gas can be used as stored fuel. But the method is still too expensive. Materials called catalysts are needed to run the reaction, and the catalyst that works best, platinum, is rare and pricey. The hunt is on for good catalysts made of Earth-abundant, inexpensive materials.

"People were talking about splitting water back when I was a graduate student, during the energy crisis of the late 1970s. In fact, you can find papers in the literature where people talk about this as far back as the early part of the 20th century," says Jay Winkler (Ph.D. '84), a faculty associate and lecturer in chemistry at Caltech and a member of the Beckman Institute. "Platinum works very well as the catalyst, but it's not a practical material for large-scale energy generation because there's just not enough of it. Some other materials run the reaction well but are also very rare."

Winkler and his colleagues, led by Harry Gray, the Arnold O. Beckman Professor of Chemistry and former graduate advisor to Winkler, have been busy developing new types of catalysts based on environmentally friendly materials like iron and nickel. Their goal is not only to find new catalysts made of Earth-abundant materials, but also to find ways to make those catalysts drive the water-splitting reaction as efficiently as possible. Doing so would reduce the overall cost of the reaction enough to compete with natural resources like oil. This research is associated with the Center for Chemical Innovation in Solar Fuels (CCI Solar), a National Science Foundation-center based at Caltech.

Winkler's focus is on zapping metals with lasers. About five years ago, he and Astrid Müller, then a Caltech staff scientist and now a professor at the University of Rochester, fine-tuned a technique in which a high-energy pulsed laser is focused on a metal in a liquid (such as iron in water), generating a very high temperature and pressure. The process creates a bubble that collapses and re-expands a few times within milliseconds, releasing iron-based nanoparticles, which are the candidates for catalyzing the water-splitting reaction.

"The laser reactions create a bright flash of light and a loud bang," says Winkler. "We had to install a soundproof box around it because you could hear it out in the hall."



A laser-based method for generating new solar fuel catalysts is shown in this X-ray radiography video, which has been slowed down. The images are recorded using a wide broadband X-ray beam oriented parallel to the target and detected using a high-speed X-ray camera. After a 10-nanosecond laser pulse hits a silver metal target, a bubble is seen expanding, contracting and then expanding again. Solid nanoparticles that make up candidate solar fuel catalysts trickle out at the end. Credit: Karlsruhe Institute of Technology, Anton Plech (Source: Ibrahimkutty et al. Sci. Rep. 2015)

Splitting water is, in general, a somewhat simple reaction. The idea is to use the energy of sunlight to split two water molecules ($2H_2O$) into oxygen (O^2) and hydrogen ($2H_2$) molecules. The oxygen can be released into the atmosphere and the hydrogen stored as fuel. Running the reaction backward, with the help of a fuel cell, generates electricity.

"Running this reaction requires energy, and then we store that energy. We want to find catalysts that will make oxygen faster and with as little extra energy as possible."

Winker and his team are focusing on the first half of the water-splitting reaction; creating the oxygen. In their experiments, as a stand-in for sunlight, they use an electrode powered by electricity. Once they have made their potential catalysts using the laser technique, they coat the electrode with the catalysts and run the reaction, to see how fast oxygen is generated.

So far, the researchers have a few good candidates, such as a type of iron-based nanoparticle material known as a nickel iron-layered double hydroxide nanosheet. The team has been trying to figure out exactly why this catalyst works well. In one set of experiments, they developed an electrochemical method to trap and characterize molecular states generated during the reaction in order to find out which ones are key to its efficiency. They found that a highly oxidized iron site on the edge of a nanosheet was an essential element in the catalysis. This work, which was led by Harvard University's Bryan Hunter while he was a graduate student at Caltech in the Gray Lab (Ph.D. '17), will help other researchers tweak the catalyst and make it even better.

In the future, the team will continue to explore new catalysts for making hydrogen fuel. For example, they are experimenting with liquids other than water to use in their laser-zapping trials.

"Hydrogen fuels are not in wide use now," says Winkler. "But I think we'll get to a point where we can make these fuels more efficiently—and then they will become more competitive economically."

Provided by California Institute of Technology