

One step closer to artificial photosynthesis and 'solar fuels'

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Credit: Lance Hayashida/Caltech Marcomm

Caltech scientists, inspired by a chemical process found in leaves, have developed an electrically conductive film that could help pave the way



for devices capable of harnessing sunlight to split water into hydrogen fuel.

When applied to semiconducting materials such as silicon, the <u>nickel</u> <u>oxide</u> film prevents rust buildup and facilitates an important chemical process in the solar-driven production of fuels such as methane or hydrogen.

"We have developed a new type of protective coating that enables a key process in the solar-driven production of fuels to be performed with record efficiency, stability, and effectiveness, and in a system that is intrinsically safe and does not produce explosive mixtures of hydrogen and oxygen," says Nate Lewis, the George L. Argyros Professor and professor of chemistry at Caltech and a coauthor of a new study, published the week of March 9 in the online issue of the *Proceedings of the National Academy of Sciences (PNAS)*, that describes the film.

The development could help lead to safe, efficient artificial photosynthetic systems—also called solar-fuel generators or "artificial leaves"—that replicate the natural process of photosynthesis that plants use to convert sunlight, water, and carbon dioxide into oxygen and fuel in the form of carbohydrates, or sugars.

The artificial leaf that Lewis' team is developing in part at Caltech's Joint Center for Artificial Photosynthesis (JCAP) consists of three main components: two electrodes—a photoanode and a <u>photocathode</u>—and a membrane. The photoanode uses sunlight to oxidize water molecules to generate oxygen gas, protons, and electrons, while the photocathode recombines the protons and electrons to form hydrogen gas. The membrane, which is typically made of plastic, keeps the two gases separate in order to eliminate any possibility of an explosion, and lets the gas be collected under pressure to safely push it into a pipeline.





George L. Argyros Professor and Professor of Chemistry Nate Lewis and postdoc Ke Sun, who together have helped develop a protective film that is rustresistant, highly transparent, and highly catalytic. This new thin-film could help pave the way for devices capable of harnessing the sunlight to generate fuels. Credit: Lance Hayashida/Caltech Marcomm

Scientists have tried building the electrodes out of common semiconductors such as silicon or gallium arsenide—which absorb light and are also used in solar panels—but a major problem is that these materials develop an oxide layer (that is, rust) when exposed to water.



Lewis and other scientists have experimented with creating protective coatings for the electrodes, but all previous attempts have failed for various reasons. "You want the coating to be many things: chemically compatible with the semiconductor it's trying to protect, impermeable to water, electrically conductive, highly transparent to incoming light, and highly catalytic for the reaction to make oxygen and fuels," says Lewis, who is also JCAP's scientific director. "Creating a protective layer that displayed any one of these attributes would be a significant leap forward, but what we've now discovered is a material that can do all of these things at once."

The team has shown that its nickel oxide film is compatible with many different kinds of semiconductor materials, including silicon, indium phosphide, and cadmium telluride. When applied to photoanodes, the nickel oxide film far exceeded the performance of other similar films—including one that Lewis's group created just last year. That film was more complicated—it consisted of two layers versus one and used as its main ingredient titanium dioxide (TiO2, also known as titania), a naturally occurring compound that is also used to make sunscreens, toothpastes, and white paint.

"After watching the photoanodes run at record performance without any noticeable degradation for 24 hours, and then 100 hours, and then 500 hours, I knew we had done what scientists had failed to do before," says Ke Sun, a postdoc in Lewis's lab and the first author of the new study.

Lewis's team developed a technique for creating the nickel oxide film that involves smashing atoms of argon into a pellet of nickel atoms at high speeds, in an oxygen-rich environment. "The nickel fragments that sputter off of the pellet react with the oxygen atoms to produce an oxidized form of nickel that gets deposited onto the semiconductor," Lewis says.





Ke Sun, a Caltech postdoc in the lab of George L. Argyros Professor and Professor of Chemistry Nate Lewis, peers into a sample of a new, protective film that he has helped develop to aid in the process of harnessing sunlight to generate fuels. Credit: Lance Hayashida/Caltech Marcomm

Crucially, the team's nickel <u>oxide film</u> works well in conjunction with the membrane that separates the photoanode from the photocathode and staggers the production of hydrogen and oxygen gases.

"Without a membrane, the photoanode and photocathode are close enough to each other to conduct electricity, and if you also have bubbles



of highly reactive hydrogen and oxygen gases being produced in the same place at the same time, that is a recipe for disaster," Lewis says. "With our film, you can build a safe device that will not explode, and that lasts and is efficient, all at once."

Lewis cautions that scientists are still a long way off from developing a commercial product that can convert sunlight into fuel. Other components of the system, such as the photocathode, will also need to be perfected.

"Our team is also working on a photocathode," Lewis says. "What we have to do is combine both of these elements together and show that the entire system works. That will not be easy, but we now have one of the missing key pieces that has eluded the field for the past half-century."

More information: Stable solar-driven oxidation of water by semiconducting photoanodes protected by transparent catalytic nickel oxide films, *PNAS*, <u>www.pnas.org/cgi/doi/10.1073/pnas.1423034112</u>

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