

# Solar cell directly splits water for hydrogen

February 18 2008

Plants trees and algae do it. Even some bacteria and moss do it, but scientists have had a difficult time developing methods to turn sunlight into useful fuel. Now, Penn State researchers have a proof-of-concept device that can split water and produce recoverable hydrogen.

"This is a proof-of-concept system that is very inefficient. But ultimately, catalytic systems with 10 to 15 percent solar conversion efficiency might be achievable," says Thomas E. Mallouk, the DuPont Professor of Materials Chemistry and Physics. "If this could be realized, water photolysis would provide a clean source of hydrogen fuel from water and sunlight."

Although solar cells can now produce electricity from visible light at efficiencies of greater than 10 percent, solar hydrogen cells – like those developed by Craig Grimes, professor of electrical engineering at Penn State – have been limited by the poor spectral response of the semiconductors used. In principle, molecular light absorbers can use more of the visible spectrum in a process that is mimetic of natural photosynthesis. Photosynthesis uses chlorophyll and other dye molecules to absorb visible light.

So far, experiments with natural and synthetic dye molecules have produced either hydrogen or oxygen-using chemicals consumed in the process, but have not yet created an ongoing, continuous process. Those processes also generally would cost more than splitting water with electricity. One reason for the difficulty is that once produced, hydrogen and oxygen easily recombine. The catalysts that have been used to study the oxygen and hydrogen half-reactions are also good catalysts for the recombination reaction.

Mallouk and W. Justin Youngblood, postdoctoral fellow in chemistry, together with collaborators at Arizona State University, developed a catalyst system that, combined with a dye, can mimic the electron transfer and water oxidation processes that occur in plants during photosynthesis. They

reported the results of their experiments at the annual meeting of the American Association for the Advancement of Science today in Boston.

The key to their process is a tiny complex of molecules with a center catalyst of iridium oxide molecules surrounded by orange-red dye molecules. These clusters are about 2 nanometers in diameter with the catalyst and dye components approximately the same size. The researchers chose orange-red dye because it absorbs sunlight in the blue range, which has the most energy. The dye used has also been thoroughly studied in previous artificial photosynthesis experiments.

They space the dye molecules around the center core leaving surface area on the catalyst for the reaction. When visible light strikes the dye, the energy excites electrons in the dye, which, with the help of the catalyst, can split the water molecule, creating free oxygen.

"Each surface iridium atom can cycle through the water oxidation reaction about 50 times per second," says Mallouk. "That is about three orders of magnitude faster than the next best synthetic catalysts, and comparable to the turnover rate of Photosystem II in green plant photosynthesis." Photosystem II is the protein complex in plants that oxidizes water and starts the photosynthetic process.

The researchers impregnated a titanium dioxide electrode with the catalyst complex for the anode and used a platinum cathode. They immersed the electrodes in a salt solution, but separated them from each other to avoid the problem of the hydrogen and oxygen recombining. Light need only shine on the dye-sensitized titanium dioxide anode for the system to work. This type of cell is similar to those that produce electricity, but the addition of the catalyst allows the reaction to split the water into its component gases.

The water splitting requires 1.23 volts, and the current experimental configuration cannot quite

achieve that level so the researchers add about 0.3 volts from an outside source. Their current system achieves an efficiency of about 0.3 percent.

"Nature is only 1 to 3 percent efficient with photosynthesis," says Mallouk. "Which is why you can not expect the clippings from your lawn to power your house and your car. We would like not to have to use all the land area that is used for agriculture to get the energy we need from solar cells."

The researchers have a variety of approaches to improve the process. They plan to investigate improving the efficiency of the dye, improving the catalyst and adjusting the general geometry of the system. Rather than spherical dye catalyst complexes, a different geometry that keeps more of the reacting area available to the sun and the reactants might be better. Improvements to the overall geometry may also help.

"At every branch in the process, there is a choice," says Mallouk. "The question is how to get the electrons to stay in the proper path and not, for example, release their energy and go down to ground state without doing any work."

The distance between molecules is important in controlling the rate of electron transfer and getting the electrons where they need to go. By shortening some of the distances and making others longer, more of the electrons would take the proper path and put their energy to work splitting water and producing hydrogen.

Source: Penn State

APA citation: Solar cell directly splits water for hydrogen (2008, February 18) retrieved 10 December 2022 from <https://phys.org/news/2008-02-solar-cell-hydrogen.html>

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