innovation

The Spectrum of Clean Energy Innovation

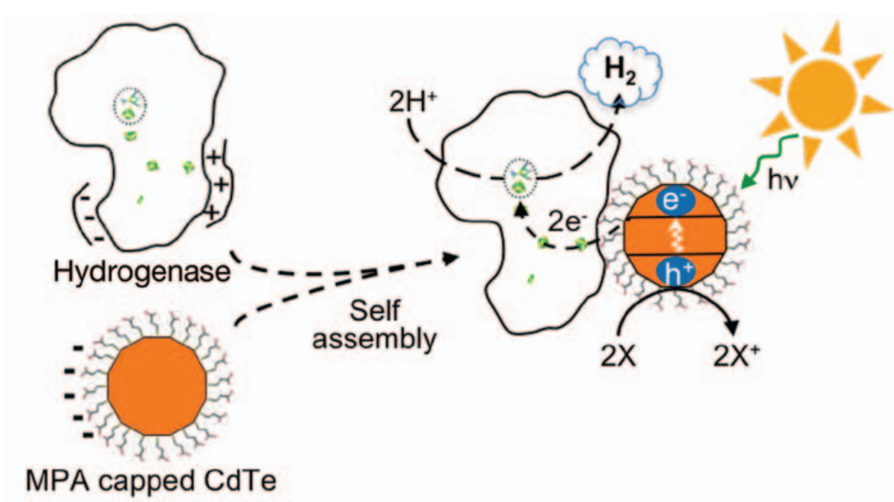
Fundamental Science
Market-Relevant Research
Systems Integration
Testing and Validation
Commercialization
Deployment

NREL Melds Nature with Nanotech for Solar-Powered Hydrogen Production

NREL researchers are finding ways to mimic photosynthesis by combining enzymes with nanoparticles—particles on the scale of a billionth of a meter—to produce hydrogen directly from water and sunlight.

This breakthrough project began in 2008 with scientists and researchers asking how they might learn from nature and develop a synthetic process that is more efficient than plants at converting sunlight to hydrogen. The goal was to find a new way to produce hydrogen that could then be commercialized inexpensively for fuel cells and other uses. Among the various approaches to making hydrogen, the NREL researchers wondered about a hybrid molecular assembly that might pair the best natural molecule with a synthesized nanoparticle.

Researchers looked at using hydrogenase enzymes as one part of the equation. These biological catalysts can convert electrons and protons into hydrogen gas, or convert hydrogen into electrons and protons. The choice seemed worthwhile because the hydrogenase enzyme has some intriguing properties: a high substrate selectivity, meaning a very high preference for catalyzing reactions with protons rather than with other atoms and molecules; and fast turnover, which enables it to produce a hydrogen molecule in milliseconds.



NREL researchers have found that a hydrogenase enzyme (upper left) and a cadmium telluride (CdTe) quantum dot capped with mercaptopropionic acid, or MPA (lower left), will self-assemble to form a biohybrid complex (right). When sunlight hits the quantum dot, it generates electrons (e-) and transfers them to the enzyme, which combines the electrons with protons (H^+) to produce hydrogen gas (H_2). *Illustration by Paul King, NREL*

Through deep technical expertise and an unmatched breadth of capabilities, NREL leads an integrated approach across the spectrum of renewable energy innovation. From scientific discovery to accelerating market deployment, NREL works in partnership with private industry to drive the transformation of our nation's energy systems.

This case study illustrates NREL's innovations in Fundamental Science through Market-Relevant Research

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

For the nanoparticles, NREL researchers began assessing quantum dots, which are nanoparticles of the same semiconductors used to make solar cells. Light hitting a quantum dot will free an electron—in a solar cell, the electrons would be collected to produce an electrical current. But because of their ultra-small size, quantum dots exhibit unusual characteristics resulting from quantum-mechanical effects. For example, the size of a quantum dot determines the frequency of light to which it will respond.

As NREL researchers progressed, they faced the basic challenge of how to test whether this biohybrid theory would work, because there was no ready-made recipe for this mixture. The reaction solutions had to be optimized; pH balances and salt concentrations needed to be monitored.

As with other experiments, the process involved many steps that had to work successfully in sequence. The first was using biochemical and optical techniques to observe whether the molecules would assemble into a hybrid complex when combined. Researchers found that quantum dots of cadmium telluride coated in carboxylic acids, such as mercaptopropionic acid, easily formed highly stable complexes with the hydrogenase.

Next, the team had to be certain that the quantum dots would continue to be functional and light-sensitive. This meant that electrons freed from their atoms by the energy of sunlight could transfer to the hydrogenase. During biological photosynthesis, ferredoxin, an iron-sulfur protein, helps to transfer electrons to hydrogenase, relying on surface interactions between the positive hydrogenase and the negative regions of the ferredoxin. In the new biohybrid, the negatively charged carboxylic acid-coated quantum dot interacted with the positively charged hydrogenase in a way that allowed it to replace ferredoxin as the electron source for the hydrogenase.

Then the team illuminated the biohybrids in solution and found that the efficiency of generating hydrogen from sunlight varied with the ratio of quantum dots to hydrogenase, and was best when the two components were present in equal proportions. The efficiency was also a direct function of how efficient the quantum dots were at generating electrons from sunlight.

In their findings, published in 2010 in the *Journal of the American Chemical Society*, the team noted that this breakthrough can help guide the development of more efficient, viable technologies to convert sunlight to hydrogen. Equally important is the fundamental science proof of concept for this process, which allows scientists to look at how hybrids are assembled and provides a template for the development of other hybrid assemblies.

Solar Hydrogen Production Draws on NREL's Experience with Quantum Dots

Research into quantum dots has a long history at NREL, and if that research could be considered a tree with many branches, the trunk would be the work of the lab's senior research fellow, Arthur Nozik, and his long-time collaborator, Olga Micic.

Nozik and Micic conducted some of the earliest research on quantum dots in the 1980s, and since then this scientific area that has grown enormously. Their work fostered some of the initial publications on semiconductor quantum dots. Nozik investigated how quantum dots might work for solar energy applications, expanding on earlier concepts and research.

For example, in 2000, Nozik and his research team found that quantum dots could increase the efficiency of solar cells through a process now termed "multiple exciton generation," or "MEG," and they confirmed MEG in various semiconductor quantum dots starting in 2005. In essence, MEG means that a single photon of light can generate more than one electron, potentially yielding solar cells that produce more electricity from the same amount of sunlight.

Micic, a principal scientist when she died in 2006, had an international reputation in the basic science of quantum dot synthesis and provided critical contributions to this new area. MEG now represents a broadly researched component of next-generation approaches to solar photon conversion to electricity and solar fuels.

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401
303-275-3000 • www.nrel.gov

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

NREL/FS-6A42-50990 • September 2011

Printed with a renewable-source ink on paper containing at least 50% wastepaper, including 10% post consumer waste.

innovation