Photosynthesis reimagined

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Argonne scientists in collaboration with researchers from Arizona State University have found a way to imitate Photosystem II, the first protein complex in the long chain of reactions that use energy from the sun to create usable fuel.

(Phys.org) —Using water as fuel has been a recurrent theme of science fiction since the days of Jules Verne. A recent discovery, however, may bring it one step closer to science fact by mimicking the very first steps of the photosynthetic water-splitting pathway.

Scientists at the U.S. Department of Energy's Argonne National Laboratory in collaboration with researchers from Arizona State

University have found a way to imitate Photosystem II, the first protein complex in the long chain of reactions that use energy from the sun to create usable fuel. The result was reported in the journal *Nature Chemistry*.

Photosystem II uses energized electrons to split water into oxygen, protons and the electrons that are necessary to complete the photosynthetic process.

Once light strikes an electron in a chlorophyll molecule at the heart of photosystem II, the excited electron moves to a higher energy state, leaving behind a positively charged region called a "hole," which is in then filled by other electrons that are stripped from water by a special enzyme. The excited electron then travels through a number of "electron carrier" proteins like a baton being passed among relay racers.

However, the motion of an electron brings with it a negative charge. The protein compensates for this by transferring a positively-charged proton as well. When both steps happen, the "baton exchange" is complete and charge separation happens successfully.

"The problem is that even though we know exactly how these reactions occur in nature, it's extremely difficult to replicate them in the laboratory because the protein environment is so hard to imitate," said Argonne nanoscientist Tijana Rajh.

In this experiment, Rajh and her colleagues used facilities at Argonne's Center for Nanoscale Materials to create an organic/inorganic hybrid based around a titanium dioxide nanoparticle. This hybrid performed the same elementary steps of charge separation as in the natural system, including the transfer of both electrons and protons facilitated by the protein environment.

The researchers were able to follow and compare these first steps by using electron paramagnetic resonance (EPR) spectroscopy, which is similar to the techniques used in MRI machines in doctors' offices – however, it looks at electron spins instead of those of atomic nuclei.

"There are three parts to doing this kind of research: synthesizing the material, performing EPR experiments and making theoretical calculations," Rajh said.

"EPR is the optimal technique for studying photochemical reactions because it's the only technique that lets us see both the electrons and the holes," said Argonne chemist Oleg Poluektov.

In the future, Rajh and Poluektov hope to generate a more perfect imitation of the biological system. "We're trying to mimic a natural solution that's cheap, stable, and efficient. Right now, we can only do two out of three," Rajh said.

More information: "A bioinspired redox relay that mimics radical interactions of the Tyr–His pairs of photosystem II." Jackson D. Megiatto Jr, et al. *Nature Chemistry* (2014) DOI: 10.1038/nchem.1862. Received 11 July 2013. Accepted 20 December 2013 Published online 09 February 2014

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