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NATIONAL RENEWABLE ENERGY LABORATORY

Closer Look Reveals New Insights on Enzymatic Catalysts for H_2 Production

Highlights in Science

Researchers use spectroscopic tools to analyze H_2 activation by [FeFe]-Hydrogenase HydA1 from *Chlamydomonas reinhardtii*.

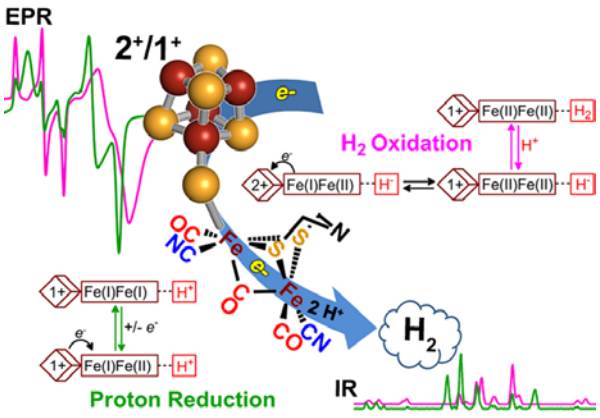
Hydrogenases are enzymes found in microbes that catalyze hydrogen production at fast rates (>10^4 s-1), and they are endowed with unique organometallic catalytic sites composed of earth-abundant metals (e.g., Fe, Ni). Investigations on the natural diversity of hydrogenases and how they operate deliver key principles for guiding the design of more efficient synthetic catalysts derived from nonprecious metals.

Researchers from the National Renewable Energy Laboratory (NREL) and their partners from Montana State University uncovered new, detailed information about how these enzymes function, making their mechanistic understanding for the H_2 activation process more complete. The potential to activate hydrogen at higher rates and efficiencies to produce H_2 is thereby advanced.

The researchers used electron paramagnetic resonance (EPR) and infrared (IR) spectroscopies to identify new electronic and vibrational information for the catalytic site H-cluster of [FeFe]-hydrogenases under turnover.

While a general model of H_2 activation exists for [FeFe]-hydrogenases, the structural and biophysical properties of the intermediates of the catalytic site H-cluster are poorly defined. The simplicity of algal [FeFe]-hydrogenases enables new access to catalytically relevant intermediates that were not detected in previous studies focused on more complex enzymes isolated from bacteria.

Uncovering the mechanistic details of how the unique active site of hydrogenases activate H_2 helps to provide the essential requirements for the design of efficient bio-inspired synthetic catalysts. The new spectral details are leading to a more complete model of how these extraordinary enzymes can function to activate H_2 at unparalleled rates and efficiencies.



EPR (top left) and IR (bottom right) spectra of the reduced (green) and H_2 activated (magenta) H-cluster (center) of [FeFe]-hydrogenases are shown along with the proposed models for reversible H_2 catalysis (bottom left, top right). Image by David Mulder, NREL

Technical Contact: Paul King, *paul.king@nrel.gov*

Reference: Mulder, D.W.; Ratzloff, M.W.; Shepard, E.M.; Byer, A.S.; Noone, S.M.; Peters, J.W.; Broderick, J.B.; King, P.W. (2013). "EPR and FTIR Analysis of the Mechanism of H_2 Activation by [FeFe]-Hydrogenase HydA1 from *Chlamydomonas reinhardtii*." *Journal of the American Chemical Society* 135; pp. 6921-6929. *dx.doi.org/10.1021/ja4000257*.

Key Research Results

Achievement

The researchers used electron paramagnetic resonance and infrared spectroscopies to reveal new mechanistic details during catalytic turnover of H_2.

Key Result

Findings indicate that the complete activation/oxidation of H_2 is a coupled two-electron/two-proton reaction, and it is possible that electronic transitions to a $[4Fe\text{-}4S]^{1+}$ cluster at the catalytic site are made during each successive turnover event, signifying its role to mediate electron transfer during H_2 catalysis.

Potential Impact

Developing a fundamental understanding of the mechanisms by which enzymes activate small molecules like H_2 and catalyze fuel-forming reactions may lead to more efficient synthetic catalysts for future development of renewable energy solutions.

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15013 Denver West Parkway
Golden, CO 80401
303-275-3000 | www.nrel.gov

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