

II.G.7 Photobiohybrid Solar Fuels

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Objectives

The long-term objective of this project is to understand energy transduction in photochemical systems that combine the light harvesting, charge-separation of nanoparticles (NP) with catalytic H₂ activation by hydrogenases as models for solar energy conversion. Light-driven production of H₂ occurs naturally in photosynthetic microbes, where hydrogenases couple to low potential reductant pools and help to maintain electron flow under anaerobic-aerobic transitions. The ubiquitous role of H₂ as an energy carrier in microbial systems is underscored by significant structural-functional diversity among the different hydrogenase enzyme classes. Structural properties including active site coordination, substrate transfer pathways and cofactor compositions of hydrogenases are being investigated towards developing a broad understanding of the determinants that control enzymatic function.

Technical Barriers

The efficiencies of coupling natural or artificial photosynthesis to production of reduced chemical and fuels require a more fundamental understanding of the factors controlling energy transduction reactions, how this process couples to downstream enzymatic reactions, and the catalytic mechanisms. These aims of this project are to investigate the physical, thermodynamic and kinetic parameters of light-harvesting, charge-transfer and catalysis in molecular systems for solar hydrogen production.

Abstract

Photosynthetic light-capture and conversion efficiencies in plant-type systems are constrained at ~12.5% photon-to-fuel due to narrow spectral bandwidth, low-light saturation kinetics and thermodynamic losses during energy transduction. Together these limitations can constrain enzymatic rates to levels that are below full turnover capacities. Semiconducting nanomaterials exhibit a wider spectral response and higher saturation intensities and are promising for use in next generation photovoltaics and for solar harvesting in artificial photosynthetic schemes. To create and control the essential charge-transfer interactions between synthetic chromophores and biocatalysts requires developing a broader understanding of energy transduction processes at molecular junctions. This project integrates fundamental research on structure-function mechanisms of enzymatic H₂ activation, with steady-state and ultrafast measurements of photochemical conversion in enzyme-NP hybrids. The knowledge will be used to help elucidate the physical, thermodynamic and kinetic control of light-harvesting, charge-transfer and catalysis in molecular systems for solar hydrogen production.

Progress Report

Biophysical analysis of [FeFe]-hydrogenase and modeling of the catalytic mechanism

The [FeFe]-hydrogenase from the green alga *Chlamydomonas reinhardtii*, consisting of only the catalytic H-cluster, was analyzed using EPR and FTIR spectroscopy of enzymes poised under reducing and oxidizing conditions. The spectra revealed new paramagnetic signals and IR bands under various reductive treatments. Collectively these results have provided new insights on the electronic structure of the H-cluster, and the basis for a revised catalytic scheme (summarized in Figure 1) for [FeFe]-hydrogenases. The model incorporates electron exchange steps between the two H-cluster ([4Fe-4S]_H and 2Fe_H) sub-sites during enzymatic turnover. It has been proposed that oxidation of the 2Fe_H sub-site is concomitant with H₂ binding and activation, and necessary for intermolecular electron-transfer reactions to soluble electron carriers.

Solar energy conversion and catalysis in photobiohybrid complexes

We have shown that clostridial [FeFe]-hydrogenase can self-assemble with mercaptopropionic acid (MPA) capped CdS/CdTe quantum dots into photocatalytic complexes (Figure 2). Under illumination, NP light adsorption and charge-separation leads to interfacial electron-transfer into the bound hydrogenase via the ferredoxin-binding site

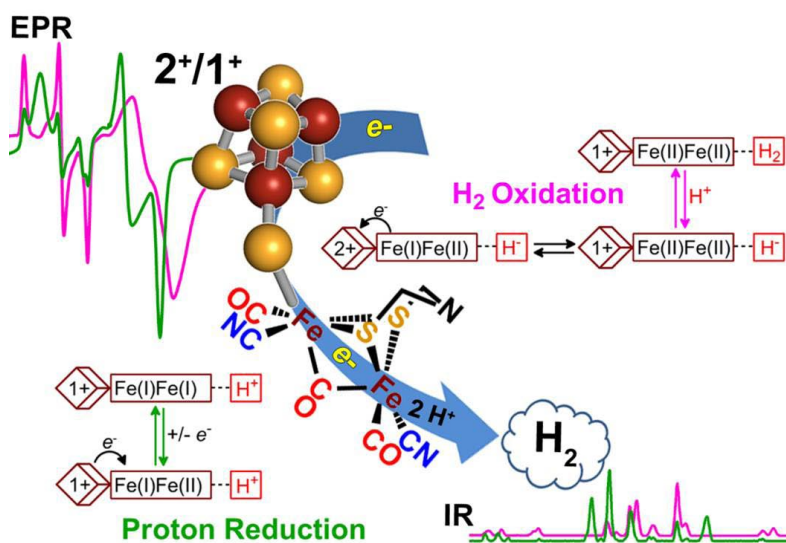


FIGURE 1. EPR (top-left) and IR (bottom-right) spectra of the reduced (green) and H-activated (magenta) H-cluster (center) of [FeFe]-hydrogenases are shown along with the proposed models for reversible H_2 catalysis (bottom-left, top-right).

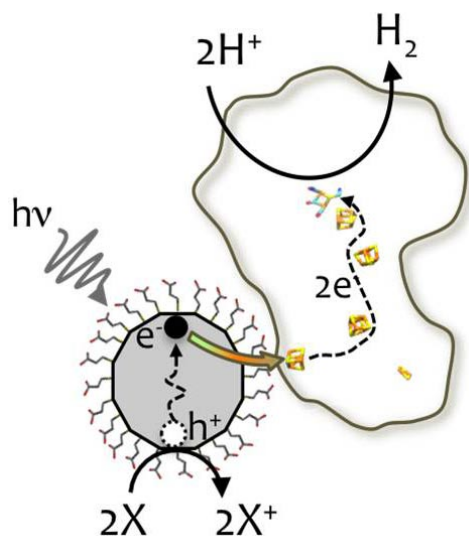


FIGURE 2. NP-hydrogenase complex. Photoexcited electrons from the nanoparticle are injected into hydrogenase to drive H_2 production.

adjacent to a surface localized [4Fe-4S]-cluster. Ultrafast measurements showed photoexcited, interfacial electron-transfer from NPs leads to injection of electrons into the [4Fe-4S] cluster at a rate of $\sim 10^7 \text{ s}^{-1}$. We are currently investigating how altering the kinetics of competing reactions (e.g., NP charge recombination), and the free-energy of the electron-transfer step, affect the quantum yields of H_2 production. Changing NP dimension (e.g., diameter) provides a means to control these properties. The interplay of kinetic/

thermodynamic effects are complex, and are further complicated by the inherent heterogeneity of molecular compositions. Resolving the details of each of these effects will help to understand the mechanisms that control energy transduction in nanoparticle-based complexes.

Computational modeling of proton-transfer in [FeFe]-hydrogenase

The free energies along proton-transfer (PT) pathways in [FeFe]-hydrogenase were investigated using QM/MM and umbrella sampling techniques. Key residues were identified along with pK_a estimations from a thermodynamics integration method and used to model PT profiles to the H-cluster.

Single-molecule resolution measurements of enzyme turnover

In collaboration with the Moore and Gust group at ASU, clostridial [FeFe]-hydrogenase was studied on Au electrodes bearing self-assembled thiol monolayers (SAMs). Binding was mediated between positively charged patches on the hydrogenase and carboxylate groups on the SAM. Single-molecule images were obtained in an electrochemical STM and showed the tunneling currents increased under an applied bias, which led to an estimated lower limit k_{cat} value of $20,000 \text{ s}^{-1}$, in combination by macroscopic voltammetry.

Future Directions

- Theoretical calculations on QM/MM H-cluster models poised under different protonation and redox states are being completed towards identifying candidate structures for discrete catalytic intermediates and the relevant vibrational spectra.
- Investigate algal [FeFe]-hydrogenase proton-transfer mutants using FTIR, Mossbauer, HYSCORE and EPR spectroscopy. Current FTIR results indicate disruption of proton-transfer results in the selective enrichment of catalytic site intermediates under reduction. Future work will aim to resolve assignments of IR bands, Fe oxidation levels, H-cluster spin-states in the context of reduction and H_2 oxidation.
- We have been characterizing the electron-transfer and photocatalytic properties of complexes between [FeFe]-hydrogenase and CdS, CdSe and CdTe nanoparticles. These efforts will be aimed at revealing how the physical compositions and dimensions of NPs control electron-transfer rates using ultrafast time-resolved spectroscopy, and measurement of H_2 production quantum yields, towards understanding the thermodynamic and kinetic control of solar conversion in these systems.

- Collaborative studies with Prof Dukovic's group at CU-Boulder are aimed towards developing a comprehensive NP-hydrogenase charge-transfer framework model, and the effects of interfacial ligands (i.e., chain length, head-group chemistry) on k_{ET} dynamics.

Publication list (including patents) acknowledging the DOE grant or contract

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