

II.G.14 Photobiohybrid Solar Fuels – Nanoparticle-Hydrogenase Complexes

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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. By coupling hydrogenase catalysis to semiconductor nanoparticles, light driven H₂ production can be achieved by transfer of the nanoparticle exciton electron into the electron transport network of the enzyme. 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. Integration of a nanoparticle with hydrogenase catalysis allows for control over reductant potential, and will contribute to 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. The aims of this project are to investigate the physical, thermodynamic and kinetic parameters of light-harvesting, charge-transfer and catalysis in nanoparticle-hydrogenase systems for solar hydrogen production. Investigation of the assembly, charge transfer and

catalytic properties are providing mechanistic insights into both nanoparticle and enzyme behavior, as well as design principles for optimizing artificial photosynthetic systems

Abstract

We have developed complexes of CdS and CdTe nanorods capped with 3-mercaptopropionic acid (MPA) coupled to *Clostridium acetobutylicum* [FeFe]-hydrogenase I (CaI) that photocatalyze reduction of H⁺ to H₂ at photon conversion efficiencies of up to 20% under illumination at 405 nm. Characterization has focused the compositional and mechanistic aspects of complexes that control photochemical conversion of solar energy into H₂. Complexes self-assemble by an electrostatically driven association between nanoparticle ligands and the CaI surface. Production of H₂ by the complexes was observed only under illumination, and only in the presence of a sacrificial donor. Nanoparticle-to-CaI molar ratio, sacrificial donor concentration and light intensity each have a pronounced effect on photocatalytic H₂ production. Photocatalytic activity appears to depend on contributions from electron and hole transfer, exciton recombination, and photon absorption rate. Recent investigations have focused on electron transfer rate and the effect of exciton electron potential. Kinetics of electron transfer play a critical role in the overall photochemical reactivity, as the quantum efficiency of electron transfer defines the upper limit on the quantum yield of H₂ generation. We investigated the competitiveness of ET with the electron relaxation pathways in CdS nanoparticles by directly measuring the rate and quantum efficiency of ET from photoexcited CdS nanoparticles to CaI using transient absorption spectroscopy. We found that the electron transfer rate constant (k_{ET}) and the electron relaxation rate constant in CdS (k_{CdS}) were comparable, with values of 10^7 s⁻¹, resulting in a quantum efficiency of ET of 42% for complexes with the average CaI:CdS molar ratio of 1:1. Given the direct competition between the two processes that occur with similar rates, we propose that gains in efficiencies of H₂ production could be achieved by increasing k_{ET} and/or decreasing k_{CdS} through structural modifications of the nanocrystals (i.e., core-shell particles). We have also investigated the effect of exciton electron potential on electron transfer and H₂ production. By varying nanoparticle diameter, the band-gap and the conduction band potential can be controlled. The electron transfer rate into CaI from CdTe nanoparticles with diameters between 2.0 and 3.5 nm was measured using time-resolved photoluminescence. The k_{ET} values were constant across the diameter range, despite a decrease in the electron overpotential from 250 to 30 mV between 2.0 and 3.5 nm diameter nanoparticles. Photocatalytic H₂ production and photon conversion

efficiencies increased with increasing diameter despite lower overpotentials. Given the inverse trend in H_2 production and the insensitivity of k_{ET} to electron overpotential, we conclude that ΔG_{ET} is not a determining factor in photocatalysis by CdTe-CaI complexes, and contributions from other factors, including nanoparticle recombination rates, enzyme coverage, and exciton lifetimes, dominate photocatalytic behavior. Future studies will focus on further elucidation of the interdependent factors which contribute to photocatalysis in these systems.

Progress Report

Characterization of CdTe-CaI complexes [4]

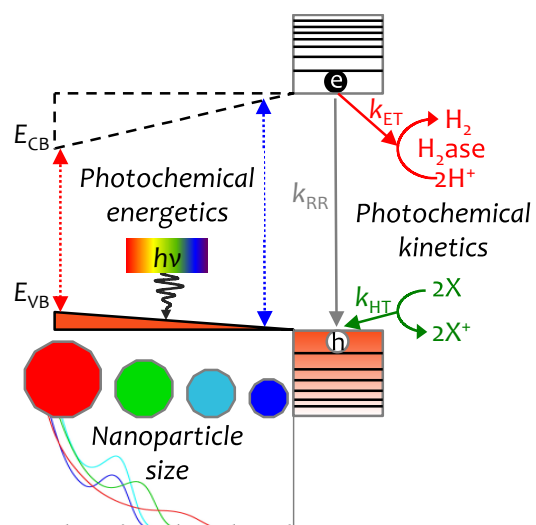
- Molecular assembly CdTe-CaI complexes was mediated by electrostatic interactions and resulted in stable, enzymatically active complexes. The assembly kinetics were monitored by CdTe photoluminescence (PL) spectroscopy and exhibited first-order Langmuir adsorption behavior.
- Photocatalytic H_2 production required the presence of a sacrificial donor (ascorbic acid), and was found to be highly dependent on donor concentration and CdTe-to-CaI molar ratio.
- Nanoparticle photoluminescence efficiency affected H_2 production, likely due to competition for available exciton electrons.

Characterization of CdS-CaI complexes [2]

- Complex self-assembly resulted in CdS binding to the *in vivo* electron donor (ferredoxin, Fd) binding site, as evidenced by the inhibition of Fd-driven H_2 production by CdS. Competition assays yielded a ΔG_{ABS} in the regime between electrostatic and covalent interactions.
- Photocatalytic H_2 production was dependent on molar ratio, and the results were interpreted using a Poisson distribution. H_2 production efficiency maximized in solutions favoring a single CaI per nanorod. Higher CaI coverage appears to lead to competition of electrons and loss in efficiency due to back-electron-transfer.
- H_2 production was limited by light intensities at fluxes up to approximately 3x solar flux.
- The quantum yield of H_2 production measured for monochromatic 405nm light was 20%.

Electron transfer in CdS-CaI complexes [1]

- Electron transfer rates of 10^7 were measured by transient absorption. These rates are on the same order as the recombination rate of the nanoparticle. Quantum efficiency of electron transfer was measured at 42% for 1-to-1 molar ratios, and the efficiency increased with increasing CaI concentration.



- It may be possible to enhance complex efficiency by manipulating the nanoparticle recombination rates such that ET is faster than recombination, improving the completion for exciton electrons.
- The electron transfer rate was unaffected by catalytic inhibition of CaI, indicating electron transfer occurs between the CdS and an accessory Fe-S cluster of the CaI, followed by transfer through the enzyme electron transfer pathway to the active site.

CdTe nanoparticle size manuscript in preparation)

- Electron transfer rates are insensitive to the nanoparticle size, despite increasing electron overpotential with decreasing nanoparticle diameter.
- Photocatalytic H_2 production rates and quantum efficiencies increasing with increasing diameter, with a maximum quantum efficiency for 3.5 nm CdTe of 12%.
- CdTe-CaI electron transfer and photocatalytic H_2 production rates are insensitive to electron overpotential and likely depend on combination of other factors, including nanoparticle recombination rates, enzyme coverage, and exciton lifetime.

Future Directions

- Investigate the photocatalytic properties of nanoparticle/ $Ni-N_2P_2$ complexes in collaboration with Dr. Wendy Shaw at PNNL.
- Continue collaborative studies with CU-Boulder on developing a nanoparticle/-hydrogenase charge-transfer framework model, effects of interfacial ligands on k_{ET} dynamics, and core-shell complexes.
- Integrate metallic nanoparticles into nanoparticle-hydrogenase complexes to investigate the impact

of surface plasmon enhancement on artificial photosynthesis in these systems.

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

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