

II.F.3 Nano-Bio Systems for Light-Driven Hydrogen Production

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Objectives

Our group is developing new approaches to storing light energy in the form of hydrogen (H_2). This collaborative project draws on synthetic chemistry, nanoscience, and biochemistry to engineer integrated systems for reducing aqueous protons to H_2 . Broad goals for this work are to enhance system performance by increasing turnover number (TON) and quantum yield. We also aim to understand the fundamental reaction steps of light absorption, charge transfer, and the assembly of protons and electrons into H_2 . Finally, development of externally sensitized photocathodes is being pursued as an alternative to sacrificial electron donors.

Technical Barriers

- Preparing water-soluble semiconductor nanocrystals (NCs) with improved light-induced charge separation
- Developing robust water-soluble synthetic and biomolecular catalysts for proton reduction
- Integrating NC photosensitizers and molecular catalysts for light-driven hydrogen production
- Characterizing the fundamental charge-transfer and chemical steps in hydrogen production

Abstract

Systems performing the reductive side of light-driven water splitting have been prepared using semiconductor quantum dots (QDs) or other NCs as photosensitizers and molecular catalysts for proton reduction. To improve charge separation, CdTe/CdSe/CdTe nanobarbells have been developed; pairing these NCs with nickel or cobalt catalysts yields improved TONs attributed to enhanced charge separation relative to CdSe QD-based systems. Ongoing work on new photocathodes employs layers of NCs for improved charge separation and removal of the sacrificial donor. The

analysis of molecular catalysts with redox-active ligands for charge storage adds to fundamental knowledge of reaction mechanism. Biomolecular catalysts have been prepared that have high longevity in photochemical systems and yield extremely high (>100,000) TONs when paired with QDs.

Progress Report

Systems performing the reductive side of water splitting to produce H_2 require a photosensitizer and a compatible proton-reducing catalyst, as well as a source of electrons (Figure 1). Our work on semiconductor NCs is toward developing robust and tunable photosensitizers. Earlier work in our labs demonstrated that dihydrolipoic acid (DHLA)-capped CdSe QDs paired with a simple Ni(II) catalyst produce H_2 in the presence of visible light with a TON > 600,000 with respect to catalyst.

To improve the performance of these systems we are engineering QD heterostructures with enhanced internal charge separation. CdTe/CdSe/CdTe nanobarbells are promising candidates because the staggered band alignment forces spatial separation of the photoexcited electron and hole, while still allowing for facile charge transfer. Pairing a Ni-DHLA catalyst with the nanobarbell photosensitizer and ascorbic acid as the sacrificial electron donor yields H_2 from water with a TON increased ten-fold relative to QDs of similar diameter.

A second approach involves the development of photocathodes with CdSe NCs arranged in layers according to NC size on NiO deposited on ITO/NiO. Photocathodes yield H_2 from aqueous media without the need for a sacrificial donor. A system designed to improve charge separation by having the smallest NCs close to the electrode and large NCs further away shows positive results in terms of rectification and H_2 production.

Synthetic molecular catalysts in development include Ni, Co, and Fe bis(dithiolene) complexes with redox-active ligands for charge storage. When pairing these catalysts with QD photosensitizers, we found that dissociation of

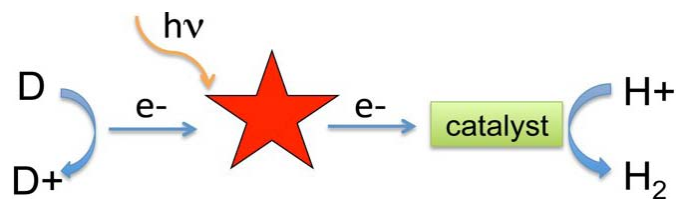


FIGURE 1. Schematic showing light-driven hydrogen generation using a photosensitizer (red star), sacrificial electron donor, and catalyst.

the water-solubilizing bidentate DHLA QD capping agent led to DHLA substitution on the catalyst. To eliminate this problem, tridentate capping agents are being employed to allow assessment of light-driven H_2 production by different coordination complexes, keeping the catalyst intact.

The development of catalysts for proton reduction has also made use of biomolecules (Figure 2). These catalysts have a number of advantages including the provision of a microenvironment for the catalytic site that can be engineered to alter second-sphere interactions. We have found that CoMP11 catalyst (left structure in Figure 2) paired with glutathione-capped CdSe QDs as electron donors yields high TON values ($>100,000$) for light-induced H_2 production. Unlike solid-state catalysts and molecular catalysts that are formed in situ, these catalysts are structurally defined, making this system promising for detailed mechanistic study and optimization.

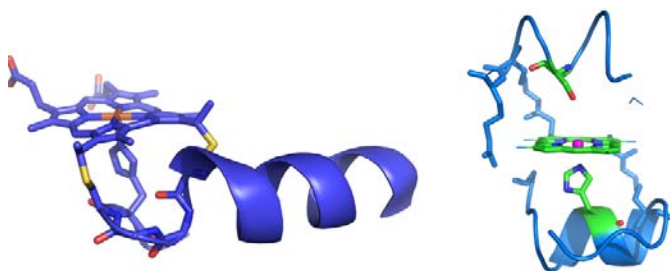


FIGURE 2. Models of biomolecular hydrogen evolution catalysts developed in this project.

Upcoming Activities

We will continue our development of systems pairing new NC photosensitizers with engineered biomolecular catalysts. In catalyst development, the polypeptide structure can be engineered to tune the level of solvent exposure and second-sphere interactions. We also will work toward the goal of eliminating sacrificial electron donors using photocathodes constructed from NC light absorbers to yield a photoelectrochemical H_2 -generating assembly. Finally, we plan systematic studies of these H_2 -generating systems using time-resolved spectroscopy to gain a fundamental understanding of charge transfer steps essential in catalysis.

Selected Publications

1. Kandemir, B.; Chakraborty, S.; Guo, Yi; Bren, K.L., Semisynthetic and Biomolecular Hydrogen Evolution Catalysts. *Inorg. Chem.* **2016**, *55*, 467–477.
2. Qiu, F.; Han, Z.; Peterson, J.J.; Odoi, M.Y.; Sowers, K.L.; Krauss, T.D., Photocatalytic Hydrogen Generation by CdSe/CdS Nanoparticles, *Nano Lett.* 2016, *16*, 5347–5352.
3. Lv, H.; Ruberu, T.P.; Fleischauer, V.; Brennessel, W; Neidig, M.; Eisenberg, R., Catalytic Light-driven Generation of Hydrogen from Water By Iron Dithiolene Complexes, *JACS*, **2016**, *138*, 11654–11663.