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Nature-Driven Photochemistry for Catalytic Solar Hydrogen Production: A Photosystem I−Transition Metal Catalyst Hybrid

Lisa M. Utschig,* Sunshine C. Silver, Karen L. Mulfort, and David M. Tiede*

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

S Supporting Information

ABSTRACT: Solar energy conversion of water into the environmentally clean fuel hydrogen offers one of the best long-term solutions for meeting future energy demands. Nature provides highly evolved, finely tuned molecular machinery for solar energy conversion that exquisitely manages photon capture and conversion processes to drive oxygenic water-splitting and carbon fixation. Herein, we use one of Nature's specialized energy-converters, the Photosystem I (PSI) protein, to drive hydrogen production from a synthetic molecular catalyst comprised of inexpensive, earth-abundant materials. PSI and a cobaloxime catalyst self-assemble, and the resultant complex rapidly produces hydrogen in aqueous solution upon exposure to visible light. This work establishes a strategy for enhancing photosynthetic efficiency for solar fuel production by augmenting natural photosynthetic systems with synthetically tunable abiotic catalysts.

For over 2 billion years, Nature's photosynthetic machinery has stored energy converted from sunlight and water in the chemical bonds of oxygen and carbohydrates. Inspired by photosynthesis, current solar fuel research involves developing systems to capture and convert the sun's energy, storing it in the energy-rich bonds of molecules such as hydrogen.[1−3] A number of solar fuel production strategies attempt to replicate Nature by employing synthetic chemical systems to create a fuel from sunlight and water.[4,5] Other approaches introduce photocatalytic hydrogen production capabilities into photosynthetic protein frameworks, including the creation of photosynthetic hybrids with hydrogenase[6,7] and platinum nanoparticle catalysts.[8,9] Herein, we present a new approach that links Nature's inherent photosynthetic chemistry with a synthetic molecular catalyst to create an inexpensive, totally earth-abundant hybrid complex that uses light to rapidly produce hydrogen directly from water.

In higher plants, green algae, and cyanobacteria, photosynthetic energy conversion reactions take place in integral membrane reaction center (RC) proteins, namely, Photosystem I (PSI)[10] and Photosystem II (PSII).[11] Key RC-based photochemical energy conversion reactions involve rapid, sequential electron transfers that result in stabilized charge separation across the membrane, establishing a favorable electrochemical potential. PSI and PSII function together, using the energy of absorbed photons to transfer electrons derived from water via PSII to reduce NADP$^+$ via PSI, producing both oxygen and ATP.[12]

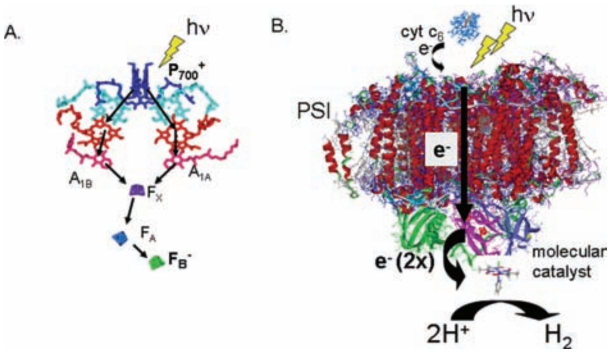

Figure 1. (A) Schematic representation of the cofactors of PSI. Light-excitation initiates a series of rapid, sequential electron transfer steps between the cofactors, resulting in formation of the charge-separated state $P_{700}{}^{+}F_B{}^{-}$. (B) Photocatalytic scheme of H_2 production from a PSI−cobaloxime hybrid complex wherein a photogenerated electron from PSI is transferred to the bound molecular catalyst. The catalyst must accept two successive photogenerated electrons from PSI to generate one H_2 molecule. Electron donors (sodium ascorbate ($C_6H_7O_6Na$) and cytochrome c_6) to reduce photon oxidized PSI ($P_{700}{}^{+}$) are necessary for rapid turnovers of PSI that enable multielectron transfer to the catalyst for H_2 production.

The sequential electron-transfer steps in PSI begin after photon excitation, where oxidation of the primary electron donor P_{700} (a dimer of chlorophyll molecules) proceeds with concurrent sequential electron transfers through a series of protein-embedded donor/acceptor molecules, terminating with electron transfer to the [4Fe-4S] cluster F_B. (Figure 1A) The inherent light-harvesting and electron-transfer machinery embedded within PSI make it amenable for abiotic H_2 production. PSI sustains an exceptionally long-lived charge-separated state $P_{700}{}^{+}F_B{}^{-}$ (∼60 ms) and a −580 mV (vs NHE) redox potential associated with the F_B cluster that provides sufficient driving force to reduce protons to H_2 at neutral pH.[13] For these reasons, there is significant interest in utilizing the isolated PSI protein for direct generation of solar fuels.[14]

Here we report a new strategy for solar fuel production that involves the insertion of sustainable first-row transition metal *molecular* catalysts into PSI (Figure 1B). A benefit of this design is that the molecular catalyst can be tuned through known chemical modifications, and this will enable future modular creation of multiple hybrid systems with different functions. As a first endeavor at the incorporation of molecular abiotic cofactors into RC

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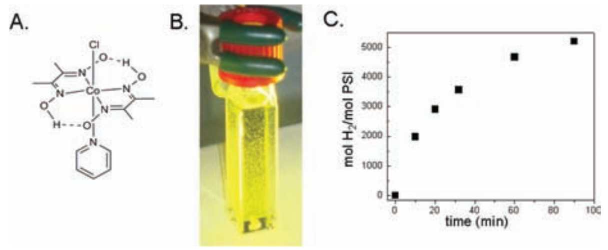

Figure 2. (A) Co(dmgH)$_2$pyCl (where dmgH = dimethylglyoximate, py = pyridine), the molecular catalyst used in this study. (B) Photograph of H_2 bubbles produced during illumination of an anaerobic aqueous solution containing 80 nM PSI—cobaloxime hybrid complex (see video in the Supporting Information). (C) Time profile of H_2 production following illumination of a PSI—cobaloxime hybrid complex.

proteins, we have chosen to target the well-known cobaloxime proton reduction electrocatalysts. Cobaloximes are pseudo-macrocyclic bis(dimethylglyoxamato)cobalt complexes that were originally developed as vitamin B_{12} mimics and found to catalyze electrochemical proton reduction.[15,16] Unlike hydrogenase active-site models, cobaloximes in general are tolerant to oxygen,[17] readily synthesized,[18,19] and catalytic for H_2 production with low overpotential.[16,20,21]

In aqueous solution, we find that cobaloxime readily self-assembles with PSI. Specifically, Co(dmgH)$_2$pyCl[18] (where dmgH = dimethylglyoximate, py = pyridine; Figure 2A) was added to native PSI (isolated from the cyanobacteria *Synechococcus leoploliensis* or *Synechococcus lividus*) in approximate ratios of 2.0—12.0 mol equiv of Co(dmgH)$_2$pyCl to PSI monomer in a buffer containing 20 mM Hepes (pH 6.9) and 0.03% *n*-dodecyl β-D-maltopyranoside. The mixture was tumbled in the dark at room temperature for 2 h to self-assemble the hybrid photocatalysts; unbound cobaloxime was removed from protein-bound complex by microfiltration. Metal analysis of the resultant complexes indicates that PSI binds Co(dmgH)$_2$pyCl in ratios dependent on the initial amount of Co(dmgH)$_2$pyCl added to the protein. Samples containing 2—4 Co per PSI monomer were found to be the most photocatalytically active.

These self-assembled PSI—cobaloxime complexes produce H_2 upon illumination with visible light. H_2 photocatalysis experiments were performed in a N_2-purged, sealed 5.3 mL spectrophotometer cell with a path length of 1.0 cm. PSI—cobaloxime complex was diluted to a final concentration of 60—80 nM PSI monomer in 20 mM MES (pH 6.3) buffer with 0.03% *n*-dodecyl β-D-maltopyranoside. The final reaction mixture contained 100 mM sodium ascorbate as the sacrificial electron donor and 4—8 μM *S. lividus* cytochrome c_6 (cyt c_6) as the mediator to reduce $P_{700}{}^+$. The samples were illuminated with a 300 W xenon lamp (Perkin-Elmer). The light was extensively filtered using a 500 nm long-pass filter, a 29 cm water filter, and a low-pass heat cut filter (KG-1, Schott). Samples (100 μL) were taken from the headspace every 10—30 min and analyzed for H_2 by gas chromatography (Varian CP-4900).

Immediately upon illumination, rapid bubbling can be observed that gas chromatography analysis shows is associated with H_2 formation from the PSI—cobaloxime hybrid (Figure 2B). The maximum rate for the photoreduction of water by this hybrid was measured to be 170 mol H_2 (mol PSI)$^{-1}$ min^{-1} (turnover frequency), observed within 10 min of illumination. H_2 production from the PSI-cobaloxime hybrid leveled off after 1.5 h, with a total turnover number of 5200 mol H_2/mol PSI (Figure 2C).

Table 1. Comparison of Rates for Light-Induced Hydrogen Production from Photosystem I—Catalyst Hybrid Systems

Photosystem I—catalyst system	rate of H_2 production [mol H_2 (mol PSI)$^{-1}$ min^{-1}]^a
PSI—cobaloxime[a,b]	170
PSI—Pt nanoparticle[a,9]	350
PSI—molecular wire—Pt nanoparticle[a,8]	70
PSI—hydrogenase[6,7]	0.8—43

[a] Soluble cytochrome c_6 as the mediator [b] This work

Thus, self-assembly of the Co(dmgH)$_2$pyCl molecular electrocatalyst with isolated PSI results in an active H_2-forming hybrid complex that works in water at near-neutral pH.

The efficiency of H_2 production suggests that Co(dmgH)$_2$-pyCl is binding near the protein surface on the acceptor end of PSI, possibly tucked in hydrophobic pockets or coordinated to histidine residues. Research efforts aimed at locating the catalyst binding sites are ongoing. Metal analysis of PSI after photocatalysis indicates that >90% of the cobaloxime has dissociated from the protein. This could explain the relatively short duration of the PSI—cobaloxime-catalyzed H_2 production reaction. We have not determined if the cobaloxime released from the protein has degraded following photocatalysis, and efforts to "self-repair" the system by the addition of excess Co(dmgH)$_2$pyCl to the reaction mixture did not restore photochemical H_2 production. Synthetic and biochemical improvements that stabilize the protein—catalyst interaction in aqueous environments are underway and are expected to increase the total turnovers of the PSI—cobaloxime hybrid.

Potential strategies to stabilize the PSI—catalyst complex during photocatalysis include covalently linking[8] or electrostatically targeting[9] the molecular catalyst to sites on PSI—two successful strategies for coupling Pt nanoparticles to PSI. Table 1 highlights the H_2 production rates for PSI—catalyst hybrid systems. In addition to the Pt-based systems, PSI has been coupled with hydrogenase (H_2ase), an enzyme that catalyzes reversible H_2/H^+ interconversion.[6,7] Note that the hydrogen generation turnover frequency for the PSI—cobaloxime hybrid nears that of the best-reported PSI—Pt nanoparticle hybrid (cyt c_6) system, 350 mol H_2 (mol PSI)$^{-1}$ min^{-1} (or 21 034 mol H_2 (mol PSI)$^{-1}$ h^{-1}),[9] recorded under equivalent illumination conditions.

The successful generation of H_2 from the PSI—cobaloxime hybrid is a clear demonstration of Nature's optimized RC photon capture and charge-separation chemistry driving photocatalysis by enabling the successful coupling of single-electron photoexcited states to multiple proton-coupled electron-transfer reactions at the transition metal catalyst sites. The total turnover number of 5200 mol H_2/mol PSI for the PSI—cobaloxime hybrid compares favorably to turnover numbers obtained for related synthetic photosensitizer—cobaloxime complexes that range from 38 to 9000.[22,23] For comparison, the total turnover number for the PSI—Pt nanoparticle hybrid is ~80 000 mol H_2/mol PSI in 5 h.[9] In biomolecular photocatalytic systems, synthetic photosensitizers act as light-harvesters and photoreductants, transferring an electron to the catalyst either directly or via an electron mediator through diffusion-regulated interaction.[22] However, limitations on excited-state lifetimes provide a challenge for effectively coupling the electron transfer between the photosensitizer and catalyst to create a charge-separated state which then initiates catalysis. Furthermore, supramolecular motifs which couple photosensitizers with cobaloxime catalysts were designed to overcome diffusional limitations associated with lackluster photocatalysis, but these appear to actually promote fast back-electron-transfer and charge recombination.[24,25] Notably, the PSI–cobaloxime hybrid is composed of totally earth-abundant materials, as opposed to employing photosensitizers that typically contain precious noble metals (i.e., Pt, Ir, Re, or Ru). Also, the hybrid operates in water, whereas many common synthetic designs only catalyze H_2 production in organic solvents with high proton concentrations, making them impractical solutions for water-splitting or future scale-up.

The Co(II/I) Co(dmgH)$_2$pyCl reduction potential necessary for hydrogen generation has a significant solvent dependence. For example, the Co(II/I) reduction potential has been reported to vary from −0.88 V (NHE) in CH_3CN to −0.74 V (NHE) in DMF.[19] We note that the reduction potentials for the catalyst in these solvents lie outside the range expected to support efficient electron transfer from the terminal electron acceptor, F_B, in PSI. Thus, we speculate on possible mechanisms to account for the efficient photocatalysis reported here. (1) The reduction potential of Co(dmgH)$_2$pyCl, when bound with the mixed-phase protein/aqueous environment in PSI, is different than the reduction potentials reported for free Co(dmgH)$_2$pyCl in homogeneous organic solvents. In support of this possibility, we have found anodic (positive) shifts in the redox potential of cobaloxime when bound in apomyoglobin heme pockets and to synthetic peptides,[26] suggesting a possible shift of Co(dmgH)$_2$pyCl when bound to PSI, especially if an axial ligand of Co(dmgH)$_2$pyCl is replaced with an amino acid residue. (2) Co(dmgH)$_2$pyCl is reduced by a cofactor other than F_B, such as A_1 or F_X, that has more reducing potential. (3) Electron transfer occurs via a slow, irreversible, thermodynamically uphill pathway. The finding that hydrogen generation by the PSI–catalyst hybrid is dependent upon cyt c_6 functioning as an efficient donor to P700+ may suggest a mechanism proceeding through trapped reduced acceptor states.[27,28] Ongoing work is investigating these possibilities.

In summary, we have prepared the first solar fuel hybrid that utilizes Nature's optimized photochemistry to drive H_2 production from a molecular complex. This new hybrid architecture was realized by simple self-assembly of the photosynthetic RC protein, PSI, with a well-known molecular H_2 electrocatalyst, Co(dmgH)$_2$pyCl. This system provides a benchmark for creation of future PSI–molecular catalyst hybrids, presenting new opportunities for solar fuel production that merge synthetic inorganic capabilities with classic bioinorganic approaches. A practical concern for using photosynthetic systems in a solar energy future is the low overall photosynthetic efficiency for solar energy conversion[14] that is limited in part by the kinetic constraints imposed by the "dark" Calvin cycle for CO_2 fixation.[29,30] The PSI–transition metal catalyst work establishes a strategy for enhancing photosynthetic efficiency for solar fuel production by augmenting natural photosynthetic systems with synthetically tunable abiotic catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete ref 14, experimental methods, metal binding, H_2 production data, and a video clip of light-induced H_2 production. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

utschig@anl.gov; tiede@anl.gov

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