Hydrogenases

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A Highly Efficient Photocatalytic System for Hydrogen Production by a Robust Hydrogenase Mimic in an Aqueous Solution**

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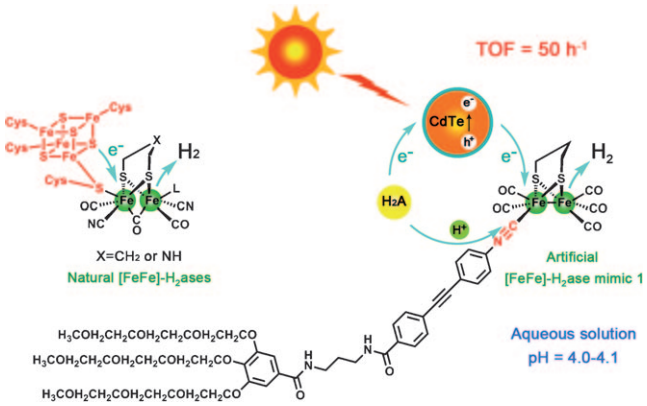
Utilization of sunlight to make solar fuels represents a promising solution to the looming energy crisis and climate change. Hydrogen (H_2), with high specific enthalpy of combustion and benign combustion product (water), is envisaged to be the ideal fuel for reducing mankind's dependence on fossil fuels and subsequent emissions of greenhouse gases.[1,2] Long ago, nature figured out how to use a photosynthetic complex to capture sunlight, and then to store its energy in a chemical form, H_2, in which hydrogenases (H_2ases) can catalyze the reversible reduction of protons to H_2 with remarkable activity.[3] With the structural elucidation of [FeFe]-H_2ases (Scheme 1),[4,5] scientists are working hard to develop artificial photosynthetic systems using [FeFe]-H_2ases mimics for H_2 generation,[6–10] multicomponent systems,[11–13] covalently linked dyads,[14–19] and supramolecular assemblies.[20–22] However, in comparison to the efficient [FeFe]-H_2ases in nature, these systems thus far give rise to none or a small amount of H_2 upon irradiation, and finally finish their photochemical H_2 production in organic solutions or a mixture of organic solvents and water. More strikingly, these synthetic [FeFe]-H_2ases mimics are not stable and would decompose generally within 1 hour of irradiation. Thus the creation of an artificial [FeFe]-H_2ase system that can produce H_2 by visible light with high catalytic activity and stability in an aqueous solution remains a significant basic science challenge.



Scheme 1. The structure of natural [FeFe]-H_2ases and artificial [FeFe]-H_2ase mimic **1**.

Herein, we report a highly efficient photocatalytic system that is comprised of an artificial water-soluble [FeFe]-H_2ase mimic **1**, photosensitizer, and ascorbic acid (H_2A) for H_2 production in pure water at room temperature (Scheme 1). Here, a cyanide (CN) group was incorporated to anchor three hydrophilic ether chains to the active site of the [FeFe]-H_2ase mimic to enhance the solubility of catalyst **1** in water. Nanocrystal quantum dots, CdTe, stabilized by 3-mercaptopropionic acid (MPA–CdTe) was selected as the photosensitizer owing to its broad visible-light absorption, aqueous dispersion, and economical advantage over precious metal photosensitizers.[22,23] The H_2A served as a proton source and a sacrificial electron donor is water-soluble and thus allows for the incorporation of a large amount of H_2A in the reaction vessel. With this system, we are able to achieve the production of 786 μmol (17.6 mL) H_2 after 10 hours of irradiation ($\lambda >$ 400 nm) in pure water with turnover number (TON) and turnover frequency values (TOF) of up to 505 and 50 h^{-1} under optimized conditions, which is, to the best of our knowledge, the highest photocatalytic efficiency and stability of artificial [FeFe]-H_2ase catalysts obtained so far. Spectroscopic study and a light-driven H_2 evolution experiment indicate that photoinduced electron transfer takes place from the MPA–CdTe species to [FeFe]-H_2ase catalyst **1**. The H_2A is not only a proton source for H_2 production but also an effective sacrificial electron donor for the hole formed in the MPA–CdTe after electron transfer. As a result a robust, efficient, and inexpensive system for the photocatalytic production of H_2 based on an artificial [FeFe]-H_2ase mimic in an aqueous solution is established.

The MPA–CdTe species were prepared according to the reported procedures and used directly.[24–26] On the basis of the low-energy absorption band centered at 571 nm, the particle size of the MPA–CdTe species was determined to be 3.4 nm using the equation developed by Peng and co-workers (see the Supporting Information).[27] For the [FeFe]-H_2ase mimic **1**, the diiron core tethered to 4-(4-alkynyl-benzoic

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acid)phenylisocyanide was firstly synthesized by the Sonogashira reaction of a [FeFe]-H_2ase complex with 4-iodophenylisocyanide and 4-ethynylbenzoic acid in a yield of 75%. This species was condensed with an amine bearing three hydrophilic ether chains to afford the desired catalyst **1** (52%), which was well-characterized by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information). Of particular importance is that the [FeFe]-H_2ase mimic **1** is quite soluble in pure water as expected.

The photochemical H_2 evolution experiments were carried out in 10 mL of water in the presence of the [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M), MPA–CdTe (5.00×10^{-4} M) (here and elsewhere, referring to the concentration of Cd^{2+}), and H_2A (8.52×10^{-3} M, 15 mg) at room temperature under visible light ($\lambda > 400$ nm). Because the MPA-capped CdTe species is very sensitive to the pH value of the solution,[28,29] we kept the initial concentration of H_2A at 15 mg/10 mL with a pH value approximately equal to its pK_a value of 4.03.[30] The reaction solution was placed in a Pyrex tube and then irradiated by a high-pressure Hanovia mercury lamp (500 W). A glass filter was used to cut off light below 400 nm to guarantee the irradiation by visible light. The generated photoproduct of H_2 was characterized by GC analysis using a molecular sieve column (5 Å), thermal conductivity detector, and nitrogen carrier gas with methane as the internal standard. The response factor of 2.76 for H_2/CH_4 was determined by calibration with known amounts of H_2 and CH_4 under the experimental conditions. Figure 1a (triangle) shows the H_2 production over time from the mixture under irradiation. The rate of H_2 production was noted as linear during the first 6 hours, and then gradually declined over the next 2 hours. Irrespective of H_2 dissolution in the solvent, the amount of H_2 reached 58 μmol (1.3 mL) within 8 hours of irradiation. Control experiments indicated that the MPA–CdTe species, [FeFe]-H_2ase mimic **1**, H_2A, and light are all essential for H_2 generation; the absence of any of them yielded unobservable to insignificant amount of H_2 (Figure S1 in the Supporting Information).

The rate of light-driven H_2 production was found to depend on the pH value of the solution, the concentration of H_2A, and the MPA-CdTe species. As a proton source, the amount of H_2A affects the pH value of the aqueous solution. To ensure the same concentration of H_2A throughout the experiment, we adjusted the pH value with HCl and NaOH prior to irradiation. As shown in Figure 1b, a sharp maximal rate for H_2 generation was observed at pH 4.0, while significant amounts of H_2 were also obtained at either lower or higher pH values. This pH-dependent effect is related to a number of factors, including the equilibrium of $H_2A \leftrightarrow H^+ + HA^-$, a change in the H^+/H_2 reduction potential of the [FeFe]-H_2ase mimic **1** and stability of the MPA–CdTe species. At higher pH, for example, the decrease in the rate of H_2 generation is likely a result of unfavorable protonation of the reduced [FeFe]-H_2ase mimic **1**, whereas at lower pH values, the MPA ligands would dissociate from the CdTe surface causing precipitation and defects that can capture the excited electrons on the surface of the MPA–CdTe species.[28,29] Simultaneously, the equilibrium of H_2A to HA^- and H^+ is suppressed, thus lowering the ability of H_2A to function as a sacrificial electron donor. This behavior is well manifested by the fact that at the optimal pH value of 4.0, a significant improvement in H_2 production was observed when the concentration of H_2A was increased from 15 mg/10 mL to 75 mg/10 mL (Figure 1c). Further increasing the concentration of H_2A to 150 mg/10 mL led to no further increase in H_2 production. Clearly, H_2A is crucial for photocatalytic H_2 production. The concentration of the MPA–CdTe also affects the rate of light-driven H_2 production. When the concentration of the MPA–CdTe species was increased from 1.60×10^{-4} M to 5.00×10^{-4} M in the solution at pH 4.0, where H_2A is 15 mg/10 mL, the rate of H_2 production was much improved

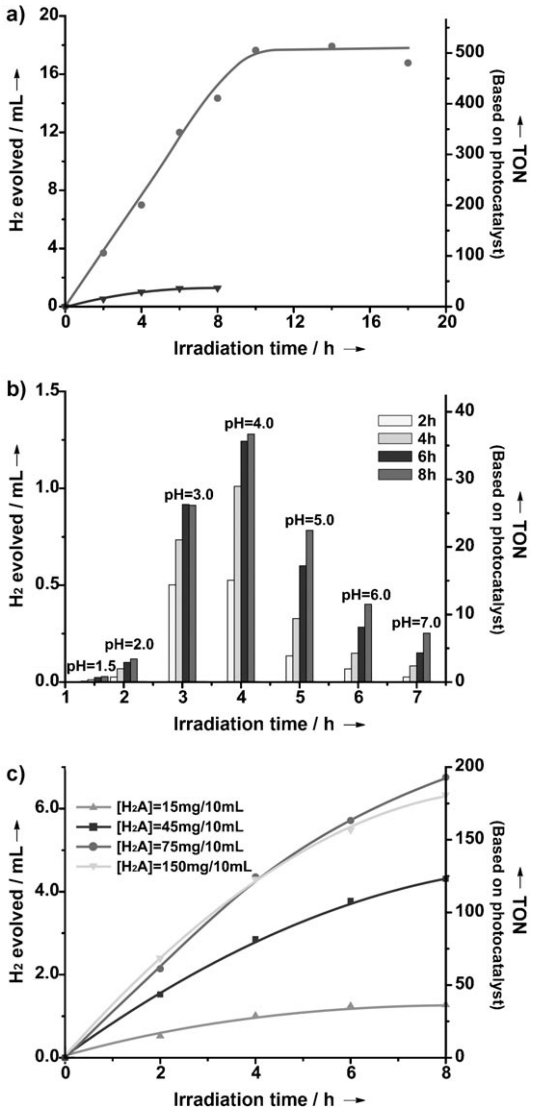

Figure 1. a) Photocatalytic H_2 evolution at pH 4.0–4.1 in H_2O; sample concentration: [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M), H_2A (8.52×10^{-3} M), MPA–CdTe (5.00×10^{-4} M; triangle); [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M), H_2A (8.52×10^{-2} M), MPA–CdTe (1.00×10^{-3} M; circle); b) Photocatalytic H_2 evolution in H_2O at different pH values; [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M), MPA–CdTe (5.00×10^{-4} M), H_2A (8.52×10^{-3} M); c) Photocatalytic H_2 evolution at pH 4.0–4.1 in H_2O as a function of H_2A concentration; [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M), MPA–CdTe (5.00×10^{-4} M), H_2A (8.52×10^{-3} M–8.52×10^{-2} M), respectively.

(Figure S2). Taken together, we carried out the experiment under optimized conditions. A total of 786 μmol (17.6 mL) H_2 was produced from an aqueous solution containing [FeFe]-H_2ase catalyst **1** (1.56×10^{-4} M), MPA–CdTe (1.00×10^{-3} M), and H_2A (8.52×10^{-2} M, 150 mg/10 mL) at pH 4.0. As shown in Figure 1a (circle), the production of more than 500 equivalents of H_2 per [FeFe]-H_2ase mimic **1** was achieved during 10 hours of irradiation with a maximum TOF of 50 H_2 per catalyst per hour. The result implies that both catalyst **1** and the MPA–CdTe species are regenerated and the whole reaction is photocatalytic in nature. The catalytic activity and stability are the highest known to date for iron catalytic reduction system for H_2 production.[31]

To gain an insight into the photocatalytic H_2 production from the aqueous solution, we studied the photophysical properties of the MPA–CdTe species with the addition of [FeFe]-H_2ase catalyst **1**. The MPA–CdTe species exhibits broad absorption bands in a range of 350–670 nm (Figure S3). Excitation of the characteristic absorption of the MPA–CdTe species at 365 nm results in a maximal luminescence at 625 nm with a quantum yield of 0.458 based on quinine in 0.5 M H_2SO_4 aqueous solution as the reference ($\Phi = 0.546$).[32] The luminescence is very sensitive to the pH value of the solution. When the pH value of an aqueous solution of the MPA–CdTe was adjusted to 4.0–4.1 by HCl, the maximum of the luminescence shifted to lower energy at 675 nm with an accompanying decrease in luminescence intensity, lifetime, and quantum yield (Figure S4); these observations are consistent with those reported in the literature.[28,29] Progressive addition of [FeFe]-H_2ase catalyst **1** into the solution of MPA–CdTe at pH 4.0 dramatically quenched the luminescence with a rate constant of $1.43\times10^{4}\,M^{-1}$ (Figure 2 and Figure S5). Because of the small spectroscopic overlap of the absorption of [FeFe]-H_2ase catalyst **1** and the emission of the MPA–CdTe species (Figure 2), the energy-transfer process from the excited MPA–CdTe species to [FeFe]-H_2ase catalyst **1** would be negligible if it occurs. Therefore, the luminescence quenching of MPA–CdTe may be attributed to electron transfer from the excited MPA–CdTe species to [FeFe]-H_2ase mimic **1**. To confirm this is indeed the case, we also estimated

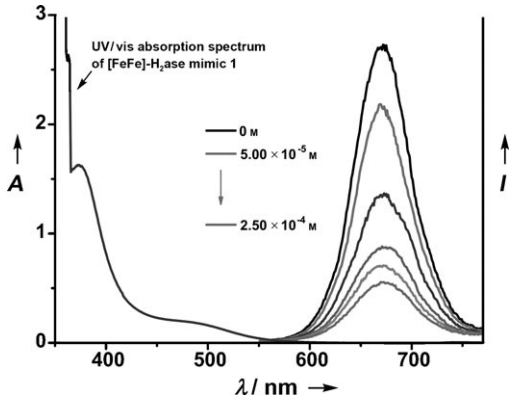

Figure 2. UV/Vis absorption spectrum of [FeFe]-H_2ase mimic **1** (1.56×10^{-4} M) in water and emission spectra of the MPA–CdTe (2.50×10^{-4} M) at pH 4.0–4.1 in the absence and presence of [FeFe]-H_2ase **1** (5.00×10^{-5} M–2.50×10^{-4} M), excited at 400 nm.

the free-energy change (ΔG^0) of this reaction. According to the valence-band energy level (E_{vb}) of the thio-capped CdTe quantum dots ($\approx$3.5 nm) which is 0.09 eV (all potentials discussed here are vs. NHE),[33] the reduction potential (E_{red}) of [FeFe]-H_2ase mimic **1** obtained from cyclic voltammograms is −0.88 eV (Figure S6), the excited-state energy (E_{00}) of the MPA–CdTe species is 1.98 eV at neutral pH and 1.84 eV at pH 4.0, respectively, the free-energy change (ΔG^0) was determined as −1.01 eV at neutral pH and −0.87 eV at pH 4.0. These findings indicate that the photoinduced electron-transfer process from the MPA–CdTe species to the catalytic centre **1** in this designed system is exothermic. Furthermore, the photoinduced electron-transfer process was evidenced by a flash photolysis study at room temperature. In the absence of [FeFe]-H_2ase mimic **1**, no signal could be detected upon exposure to laser-pulsed light at 355 nm because the transient absorption of CdTe is too fast to be recorded by the time resolution of the instrument.[34] However, when [FeFe]-H_2ase mimic **1** was introduced, three characteristic absorption bands at 420, 560, and 700 nm emerged immediately (Figure S7). These bands are quite similar to those of reported Fe^0Fe^I species generated by the reduction of a [FeFe]-H_2ase mimic.[12,35] The decay throughout the absorption region occurred on the same time scale and could be well described by a monoexponential function with a lifetime of 278 μs for the solution of the MPA–CdTe and [FeFe]-H_2ase mimic **1**. Prolonged irradiation of the solution led to no permanent change, thus indicating the Fe^0Fe^I species formed by the photoinduced electron transfer was quite stable.

On the basis of the above results, it could be speculated that the excited MPA–CdTe species is oxidatively quenched by the [FeFe]-H_2ase mimic **1** when irradiated by light, as simulated in Scheme 1. The reduced [FeFe]-H_2ase mimic **1** can further react with a proton to afford H_2 evolution.[36–39] On the other hand, the formed hole remaining in the MPA–CdTe species after electron transfer is subsequently regenerated by electron transfer from the sacrificial electron donor H_2A. It is known that the redox potential of H_2A is sufficiently negative to reduce the holes photogenerated in MPA–CdTe species,[23,40] but it is too positive to directly reduce [FeFe]-H_2ase catalyst **1**. While the excited MPA–CdTe species is capable of both oxidative and reductive quenching with [FeFe]-H_2ase catalyst **1** and H_2A, the relative extent of quenching and rate constants indicate that oxidative quenching with [FeFe]-H_2ase catalyst **1** dominates (Figure S4). As compared with those reported in the literature,[11–21] the durability of the present system is greatly increased; possibly as a result of the stabilization of a catalytic intermediate that may relate to competitively oxidative and reductive quenching by [FeFe]-H_2ase catalyst **1** and H_2A, respectively. Because two electrons are required to produce each molecule of H_2, the consecutive two-electron oxidation of H_2A is believed to be responsible for the regeneration of the MPA–CdTe species and [FeFe]-H_2ase catalyst **1**.

In summary, a robust, inexpensive, and efficient photocatalytic system for H_2 production from an artificial [FeFe]-H_2ase mimic in an aqueous solution has been achieved. The TON (505) and TOF values (50 h^{-1}) obtained are competitive

with those from current state-of-the-art catalytic systems for H_2 production. Although natural H_2ases have been incorporated with some semiconducting materials,[23,41,42] this is the first example of a synthetic [FeFe]-H_2ase mimic combined with nanocrystal quantum dots for light-driven H_2 evolution without any external manipulation.[43] We have shown that a synthetic [FeFe]-H_2ase mimic, even the most popular one that would decompose generally on 1 hour irradiation, can be an effective catalyst for photochemical H_2 production. The catalytic efficiency and stability indicate that both catalyst **1** and the MPA–CdTe species can be regenerated effectively during the entire photocatalytic reaction. Further studies on the mechanism are in progress to understand how the MPA–CdTe species associates with [FeFe]-H_2ase mimc **1** and H_2A, and to improve the stability of [FeFe]-H_2ase mimic and efficiency for light-driven H_2 production.

Experimental Section

All the experimental details were described in the Supporting Information. Characterization for [FeFe]-H_2ase mimic **1**: ^{1}H NMR (400 MHz, CD_3CN): $\delta = 7.86$ (d, $J = 7.5$ Hz, 2H), 7.68 (s, 1H), 7.60 (d, $J = 7.4$ Hz, 4H), 7.40 (d, $J = 7.3$ Hz, 2H), 7.16 (s, 2H), 4.16 (d, $J = 18.2$ Hz, 6H), 3.80 (s, 4H), 3.71 (s, 2H), 3.63 (s, 6H), 3.54 (s, 12H), 3.45 (s, 10H), 3.27 (s, 9H), 2.11 (s, 2H), 1.81 (s, 4H), 1.27 ppm (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 211.03$, 209.57, 170.78, 168.09, 166.88, 152.59, 141.62, 134.48, 132.86, 131.93, 129.58, 128.28, 127.40, 126.26, 125.74, 123.61, 107.70, 91.59, 90.10, 72.48, 72.03, 70.74, 70.62, 70.54, 69.88, 69.24, 59.10, 36.54, 36.26, 32.04, 30.64, 29.82, 29.48, 23.63, 22.82, 14.23 ppm; elemental analysis calcd for $C_{55}H_{69}Fe_2N_3O_{19}S_2 \cdot 0.35\,CH_2Cl_2$: C, 51.88; H, 5.48; N, 3.28; found: C, 51.88; H, 5.40; N, 3.38; IR (CH_2Cl_2): $\tilde{\nu} = \nu$(CO) 2039, 1998, 1970; ν(C≡N) 2284; ν(C≡C) 2123 cm^{-1}; ESIMS for **1**: two fragment peaks of **1**: m/z 659.4 for [M1−H] and m/z 663.4 for [M2] (Scheme S2).

A typical procedure for H_2 production is as follows. Aqueous solution of [FeFe]-H_2ase mimic **1** (3.12×10^{-4} M) and aqueous colloidal MPA-CdTe solution (5 mL, 1.00×10^{-3} M) were added to a Schlenk tube. Different amount of ascorbic acid was dissolved in the mixed solution to obtain the desired concentration. The total volume of every sample was 10 mL. The pH value of the mixed solution was determined by a pH meter and was adjusted by the addition of aqueous NaOH or HCl solution. The sample was saturated by nitrogen gas to eliminate oxygen. Then CH_4 (150 μL in concentration effect and control experiments; 300 μL in optimized concentration experiments to ensure enough CH_4 was extracted from the samples) was injected as the internal standard for quantitative GC analysis. The sample was irradiated under a high-pressure Hanovia mercury lamp (500 W) with light wavelength longer than 400 nm. The generated photoproduct of H_2 was characterized by GC analysis (14B Shimadzu) using nitrogen as the carrier gas with a molecular sieve column (5 Å; 30 m × 0.53 mm) and a thermal conductivity detector. Then 200 μL of mixed gas was extracted from the sample tube and injected into the GC. The response factor for H_2/CH_4 was about 2.76 under the experimental conditions, which was established by calibration with known amounts of H_2 and CH_4, and determined before and after a series of measurements.

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