

Enhancement of the Efficiency of Photocatalytic Reduction of Protons to Hydrogen via Molecular Assembly

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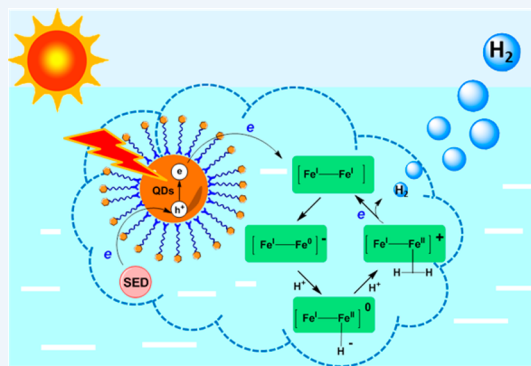
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CONSPECTUS: One of the best solutions for meeting future energy demands is the conversion of water into hydrogen fuel using solar energy. The splitting of water into molecular hydrogen (H_2) and oxygen (O_2) using light involves two half-reactions: the oxidation of water to O_2 and the reduction of protons to H_2 . To take advantage of the full range of the solar spectrum, researchers have extensively investigated artificial photosynthesis systems consisting of two photosensitizers and two catalysts with a Z-configuration: one photosensitizer-catalyst pair for H_2 evolution and the other for O_2 evolution.

This type of complete artificial photosynthesis system is difficult to build and optimize; therefore, researchers typically study the reductive half-reaction and the oxidative half-reaction separately. To study the two half-reactions, researchers use a sacrificial electron donor to provide electrons for the reductive half-reaction, and a sacrificial electron acceptor to capture electrons for the oxidative half-reaction. After optimization, they can eliminate the added donors and acceptors as the two half reactions are coupled to a complete photocatalytic water splitting system.

Most photocatalytic systems for the H_2 evolution half-reaction consist of a photosensitizer, a catalyst, and a sacrificial electron donor. To promote photoinduced electron transfer and photocatalytic H_2 production, these three components should be assembled together in a controlled manner. Researchers have struggled to design a photocatalytic system for H_2 evolution that uses earth-abundant materials and is both efficient and durable.

This Account reviews advances our laboratory has made in the development of new systems for photocatalytic H_2 evolution that uses earth-abundant materials and is both efficient and durable. We used organometallic complexes and quantum-confined semiconductor nanocrystals (QDs) as photosensitizers, and $[FeFe]-H_2ase$ mimics and inorganic transition metal salts as catalysts to construct photocatalytic systems with sacrificial electron donors. Covalently linked Re(I) complex- $[FeFe]-H_2ase$ mimic dyads and ferrocene-Re(I) complex- $[FeFe]-H_2ase$ mimic triads could photocatalyze H_2 production in organic solutions, but these photocatalytic systems tended to decompose. We also constructed several assemblies of CdTe and CdSe QDs as photosensitizers with $[FeFe]-H_2ase$ mimics as catalysts. These assemblies produced H_2 in aqueous solutions photocatalytically and efficiently, with turnover numbers (TONs) up to tens of thousands. Assemblies of 3-mercaptopropionic acid (MPA)-capped CdTe QDs with Co^{2+} ions formed Co_h -CdTe hollow nanospheres, and MPA capped-CdSe QDs with Ni^+ ions produced Ni_h -CdSe/CdS core/shell hybrids in situ in aqueous solutions upon irradiation. The resulting photocatalytic systems proved robust for H_2 evolution. These systems showed excellent activity and impressive durability in the photocatalytic reaction, suggesting that they can serve as a valuable part of an overall water splitting system.



■ INTRODUCTION

The dominating energy at present comes from burning fossil fuels that were produced in the earth through natural photosynthesis in the past 2.5 billion years. The global annual energy consumption is approaching about 14 TW in the present time and will reach 20 TW by 2030. This consumed energy requires one million years for the earth to accumulate in the form of fossil fuels.^{1,2} Thus, the fossil fuels are not a sustainable resource, and we must break our reliance on them. Furthermore, the heavy use of fossil fuels leads to large pollution problems and fast growing CO_2 emissions. Obviously, development of renewable, nonpolluting, sustainable energy resources is vital. In this context, solar power is among the most

promising alternatives. The sun provides more energy to the earth in an hour than the world consumes in a year.

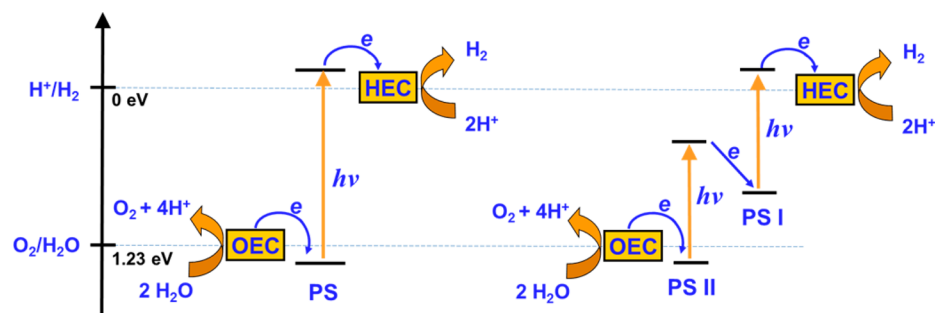
Conversion of solar energy into chemical fuel, particularly solar driven splitting of water into molecular hydrogen (H_2) and oxygen (O_2), represents one of the important approaches to the use of solar energy, since H_2 is an ideal solar fuel with its high specific enthalpy of combustion and benign combustion product (water).¹⁻⁴ As a redox reaction, water splitting can be divided into two half-reactions: the oxidation of water to O_2

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Scheme 1. Schematic Representation for Photocatalytic Water Splitting with One (left) and Two Photosensitizers (right)



and the reduction of protons to H_2 . Inspired by natural photosynthesis, many systems have been developed that involve photosensitizer(s) (PS) to capture solar photons and produce charge-separated species (Scheme 1).^{5–8} The positive charges thus generated are coupled to a catalyst (O_2 evolution catalyst, OEC) to oxidize water into O_2 and protons, and the electrons are transferred to another catalyst (H_2 evolution catalyst, HEC) to reduce protons into H_2 . The overall energetic requirement at pH 0 is 1.23 eV to produce one mole of H_2 from one mole of water, which corresponds to the energy of one molar of photons with wavelength at ca. 800 nm. However, the excited-state energy levels of the photosensitizer have to match the redox potentials of water. The energy level of the lowest unoccupied molecular orbital (LUMO) of the PS has to be above the water reduction potential level, and that of the highest occupied orbital (HOMO) should be below the water oxidation potential. Evidently, it is easy to make a photosensitizer with low excitation energy (thereby absorbing visible light), but it is very difficult to design a system with single photosensitizer that can absorb visible light and its excited-state energy levels also can match the redox potentials of water. To overcome this problem, one can utilize two photosensitizers (PS I and PS II) with a Z-scheme configuration as shown in Scheme 1 (right), that is, one as the photosensitizer for H_2 evolution and the other for O_2 evolution.⁸ In such a system, shuttling one electron from the oxidative side of the system to the reductive side requires two photons; that is, PS II and PS I each absorbs one photon. This system closely mimics natural photosynthesis. In the two photosensitizer concept, one only requires the LUMO level of PS I above water reduction potential, and the HOMO level of PS II below water oxidation potential. Thus, it is easy to find two such photosensitizers that utilize visible light to drive each half-reaction. Because of the complexity in building and optimizing such a complete artificial photosynthesis system, it is common to divide this system into reductive half-reaction and oxidative half-reaction and to study them separately. When studying the reductive half-reaction, a sacrificial electron donor is used to provide electrons.^{9–16} Similarly, in the study of the oxidative half-reaction, a sacrificial electron acceptor is used to capture electrons.¹⁷ After optimization, the two half-reactions can be coupled with each other to constitute an overall water splitting system without use of any sacrificial electron donor and acceptor.

Light-driven water splitting processes require the transfer of multiple electrons, that is, reduction of two protons into H_2 needs PS I to transfer two electrons to the HEC, while for oxidation of water the OEC has to accumulate four positive charges. On the other hand, a single photon absorption event results in the excitation and transfer of only one electron. Both the oxidative and the reductive half-reactions are kinetically

demanding processes. For example, in the reductive half-reaction, following accepting one electron the HEC produces an intermediate that may undergo charge recombination and/or decomposition. For efficient proton reduction, the second photoinduced electron transfer step to the HEC intermediate must occur on the time scale of the intermediate lifetime. The approach to promoting the electron transfer is to assemble the photosensitizer, the catalyst, and/or the sacrificial electron donor into a supramolecular system, thereby affecting their relative orientations, distances, and electron coupling. Ideally, the component molecules should be assembled in a controlled manner, as in the assembly of the photosynthesis apparatus.

There have been a large number of publications on the subject of converting solar energy into chemical fuel, particularly the reductive half-reaction in the artificial photosynthesis by using various photosensitizers and catalysts since the past years.^{9–18} This account is mainly limited to the recent progress of our laboratory in photocatalytic reduction of protons to hydrogen.^{18–29}

■ COMPONENTS OF THE PHOTOCATALYTIC SYSTEM FOR PROTON REDUCTION

To perform the reductive half-reaction of the light-driven water splitting, photocatalytic systems typically consist of a catalyst (Cat), a photosensitizer (PS), and a sacrificial electron donor (SED). In the interest of long-term sustainability, an ideal photocatalytic system should be one where both the catalyst and the photosensitizer are composed exclusively of earth-abundant elements and the resulting composition exhibits long-term stability and high efficiency for H_2 production. With the great efforts of multiple disciplines, significant progress has been achieved over the last 5 years in the design and synthesis of the new components and in the study of their combination into robust systems.^{9–29}

Photosensitizer

The photosensitizer in the photocatalytic reduction of proton functions as light absorber and electron deliverer to the catalyst. Ideal photosensitizers should have large extinction coefficient over a broad spectral range, long excited state lifetime, and superior photostability. Various photosensitizers involving organic and organometallic chromophores as well as quantum-confined semiconductor nanocrystals (QDs) have been developed.^{9–16,18–29} For most organic chromophores with few exceptions, their excited states undergo reductive quenching thus resulting in unstable radical anions that easily decompose. The commonly used organometallic chromophores are Pt, Pd, Ru, Ir, or Rh complexes, which consist of precious metals and have complicated structures. QDs have many characteristics that are ideal for light-harvesting and

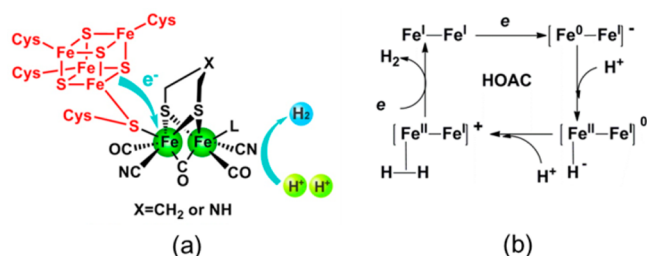
electron delivery. Compared with organic and organometallic chromophores, these QDs offer unique size-dependent absorption properties, large absorption cross sections over a broad spectral range, long exciton lifetimes, and superior photostability. QDs can simultaneously absorb multiple photons, or continuously absorb multiple photons even after electrons or holes are accumulated, thus enabling the coupling of single-photon/electron events with multiple-electron redox reactions necessary for photocatalytic H₂ production. The surface of QDs can be readily modified for specific functional targets and/or reaction environments, therefore can form molecular assemblies with the catalysts and/or SED. These characteristics make QDs superb candidates for photocatalytic generation of hydrogen.^{9–13,15,16,21–26}

Catalyst

The catalyst for the reductive half-reaction in artificial photosynthesis accepts electrons from the excited state photosensitizer (oxidative quenching) or from the photosensitizer radical anion generated from reductive quenching by SED, and catalyzes protons into H₂. While metallic colloidal Pt or Pt-complexes show excellent activity for H₂ production, they are scarce and expensive.^{16,29} Catalysts relying on noble-metal-free materials are therefore desirable. In this regard, complexes of cobalt, nickel, and iron have been found to function as catalysts for H₂ generation. For example, the complexes of Co having diglyoxime-type ligands exhibited significant activity for making H₂. The functionalized cobaloxime may stepwisely accept two electrons from the excited state of photosensitizer,^{12,13,25} resulting in the desired Co^I species that reduces two protons into H₂. Similarly, the assemblies from Ni^{II} salt and 2-mercaptoethanol or its derivatives also can efficiently catalyze proton reduction.^{9–11,26}

The most extensively investigated catalysts for proton reduction are [FeFe] hydrogenase ([FeFe]-H₂ase) and its mimics.^{14,15,18–24,27,28} Scheme 2a shows the structure of

Scheme 2. Active Site of Natural [FeFe]-H₂ase (a) and Plausible Mechanism for Proton Reduction (b)



[FeFe]-H₂ase active center revealed by X-ray crystallographic analysis.³⁰ The Fe₂S₂ subunit serves as the catalyst center for proton reduction, and the Fe₄S₄ cluster mediates transfer of electron to the active site. The turnover frequency (TOF) for the catalyzing proton reduction can reach up to 6000–9000 s⁻¹ under mild conditions. Inspired by the ideal characteristics of

the natural [FeFe]-H₂ase, a variety of its mimics have been developed.^{14,15,18–24,27,28} The two step electron transfer processes for reduction of protons to H₂ by use [FeFe]-H₂ase mimics as catalyst are shown in Scheme 2b.³⁰ It should be noted that [FeFe]-H₂ase and its mimics catalyze proton reduction in a way different from platinum catalysts.³¹ Typically platinum catalysts add one electron to each proton making two neutral hydrogen atoms that then join together to produce H₂. In contrast, in the catalysis of [FeFe]-H₂ase and its mimics, two electrons on the same proton forming a negatively charged hydride that then reacts with a proton to make molecular hydrogen.

Sacrificial Electron Donor

The SED provides electrons for the reductive half-reaction of the artificial photosynthesis. The frequently used SED involve tertiary amines, alcohols, and ascorbic acid (H₂A). Generally, SED undergo decomposition following one electron oxidation, and such degradation produces proton(s). Thus, SED is not only the source of electrons but also the source of protons. For example, each molecule of H₂A can provide two electrons and two protons as described in Scheme 3.

■ PHOTOCATALYTIC HYDROGEN EVOLUTION BY DYADS AND TRIADS BASED ON ORGANOMETALLIC COMPLEXES AND [FeFe]-H₂ase MIMICS IN ORGANIC OR MIXED ORGANIC-AQUEOUS SOLUTIONS

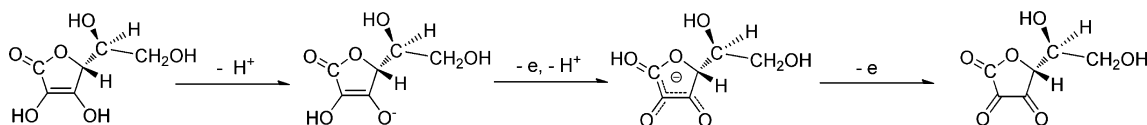
As mentioned above, in an efficient photocatalytic proton reduction system, the components should be organized in space to have specific orientation and distance for fast electron transfer and for preventing the yielded charge separation state from recombination. One approach to organizing the component molecules is to covalently link the photosensitizer and catalyst into a dyad or triad.

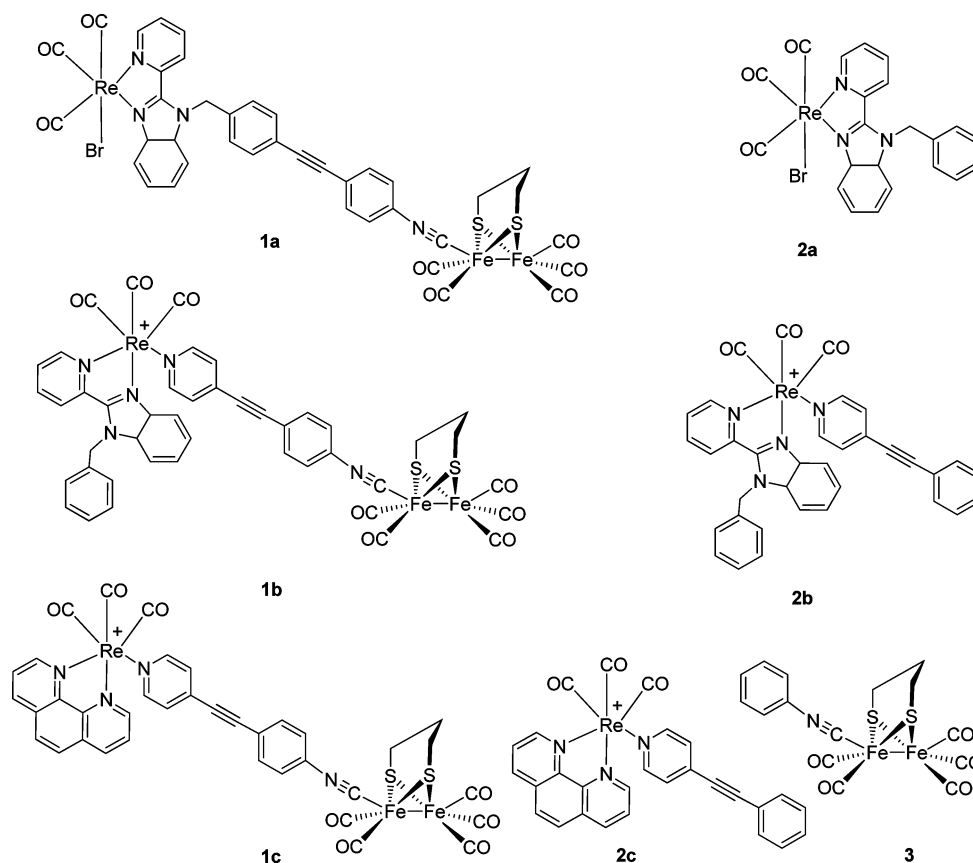
Re(I) Complex-[FeFe]-H₂ase Mimic Dyads (PS-Cat)^{18,19}

We synthesized three dyads **1a–1c** shown in Scheme 4. Rhenium(I) complexes were selected as the photosensitizer, and the typical active site model of [FeFe]-H₂ase, [μ -S₂(CH₂)₃]Fe₂(CO)₅CN, was used as the catalyst. We expected that, in these dyads, the linear, rigid, and conjugated bridge would satisfy the precise control over the spatial separation between the photosensitizer and the catalyst to achieve efficient intramolecular electron transfer from the excited state sensitizer to the catalytic site, and to avoid the fast back electron transfer in their charge separated state.

The photocatalytic H₂ evolution was carried out in degassed solutions of the dyads in CH₃CN/CH₃OH/H₂O mixture. CH₃OH served as SED and the source of proton. A great amount of H₂ was detected, although the H₂ evolution was not yet a catalytic light-driven reaction. The yield of H₂ production for **1a** was slightly lower than those of **1b** and **1c**. We also investigated the H₂ production with **3** as the catalyst, and **2a–2c** (Scheme 4) as the photosensitizer under the identical

Scheme 3. Oxidation of Ascorbic Acid



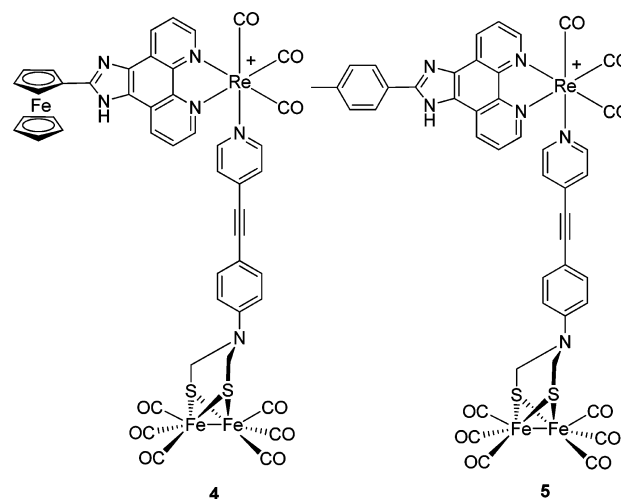
Scheme 4. Dyads of Re(I) Complex-[FeFe]-H₂ase Mimic for Photocatalytic H₂ Production and Their Reference Compounds

conditions. Such intermolecular multicomponent systems only yielded small amount of H₂.

The luminescence characteristic of ³MLCT state of the Re(I) complex in **2a** was slightly quenched by **3**. However, the luminescence of the Re(I) complex in **1a** was 20% quenched by the intramolecular catalyst. More strikingly, the luminescence of **1b** and **1c** was completely quenched by the corresponding intramolecular catalyst. Upon laser excitation with 355 nm light, **1a–1c** displayed intense absorption of [Fe¹Fe⁰] species.³² The luminescence quenching and the [Fe¹Fe⁰] formation evidenced the electron transfer from the excited photosensitizer to the catalyst site [Fe¹Fe¹], yielding the charge separation state PS^{•+}-Cat^{-•} that further reacted with SED and protons and underwent the second electron transfer process to complete the catalytic cycle (Scheme 2b).

Ferrocene-Re(I) Complex-[FeFe]-H₂ase Mimic Triad (D-PS-Cat)^{19,20,34}

We made a rigid triad **4** by using a ferrocene as a potential electron donor, a Re(I) complex as a photosensitizer, and a [FeFe]-H₂ase mimic as a catalyst (Scheme 5). The excited state of the Re(I) chromophore in **4** could be quenched with unity quantum efficiency either by the ferrocene or by the [FeFe]-H₂ase mimic.²⁰ We also synthesized dyad **5** as a reference of **4**, and performed a comparative study. Upon laser excitation, both **4** and **5** show strong transient absorption of [Fe¹Fe⁰] species,³² suggesting formation of D^{•+}-Ps-Cat^{-•} in **4** and Ps^{•+}-Cat^{-•} in **5**. Irradiation of the degassed solution of **4** or **5** in CH₃CN with Hantzsch 1,4-dihydropyridine as the SED and proton source resulted in H₂ evolution.³³ The turnover number (TON) reached 34 for **5** and 47 for **4**. Indeed, assembly of an electron donor into the dyad to build up a multistep photoinduced

Scheme 5. Triad of Ferrocene-Re(I) Complex-[FeFe]-H₂ase Mimic for Photocatalytic H₂ Production and Its Reference Dyad

electron transfer chain is a promising strategy for efficient H₂ evolution.

■ PHOTOCATALYTIC HYDROGEN EVOLUTION BY MOLECULAR ASSEMBLIES WITH QDs AS PHOTOSENSITIZER AND [FeFe]-H₂ase MIMICS AS CATALYST IN AQUEOUS SOLUTIONS

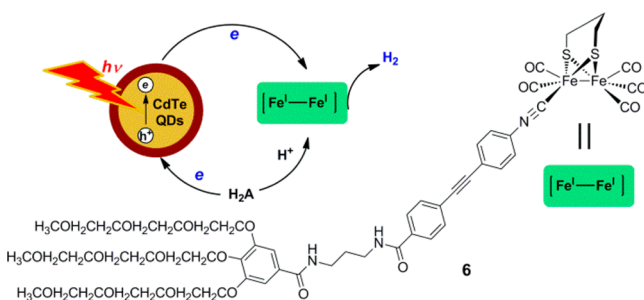
As previously mentioned, compared with traditional organic or organometallic photosensitizers, nanocrystal quantum dots

have superior properties for photocatalytic proton reduction. As reaction medium, water is an ideal solvent owing to its environment benign, low cost, and allowance of good proton mobility. We have developed several photocatalytic systems for photon reduction by using QDs as photosensitizer, [FeFe]-H₂ase mimics as catalyst in aqueous solutions.

Photocatalytic Assembly Constituted with CdTe QDs and Water-Soluble [FeFe]-H₂ase Mimic²¹

We constructed a catalyst (6) for photocatalytic H₂ evolution (Scheme 6), where three hydrophilic ether chains were linked

Scheme 6. Photocatalytic System with MPA-CdTe QDs as Photosensitizer and a Water-Soluble [FeFe]-H₂ase Mimic as Catalyst



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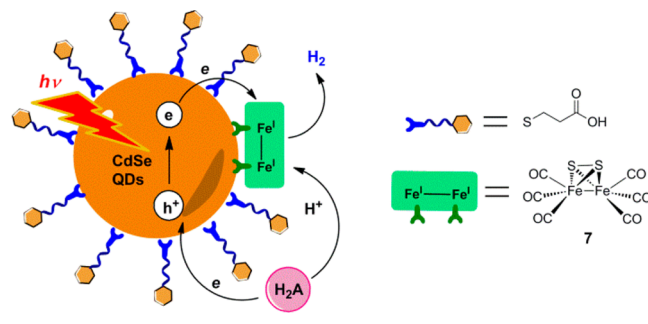
to the active site of the [FeFe]-H₂ase mimic so as to make the catalyst water-soluble. CdTe QDs stabilized by 3-mercaptopropionic acid (MPA-CdTe) was selected as the photosensitizer. In view of the rich surface binding properties and high surface-to-volume ratio, MPA-CdTe was expected to combine the [FeFe]-H₂ase mimic 6 to make a molecular assembly. In aqueous solution with H₂A as the proton source and SED, we were able to achieve H₂ production with a TON of up to 505. The photoinduced electron transfer from MPA-CdTe to the [FeFe]-H₂ase mimic was confirmed by the luminescence quenching and time-resolved experiments. The luminescence intensity of MPA-CdTe QDs was dramatically quenched by 6, while the luminescence lifetime did not change. The static quenching of the luminescence further supports the proposal that the QDs and the catalyst form assembly, thereby the intra-assembly electron transfer from excited QDs to the [FeFe]-H₂ase mimic is efficient. Flash photolysis of the aqueous solution of the QDs with 6 immediately gave characteristic transient absorption of [Fe^IFe⁰] species. All the observations evidenced the oxidative quenching of the excited state of the MPA-CdTe QDs by 6. We found that the excited MPA-CdTe also underwent reductive quenching by SED H₂A. However, under the experiment conditions the quenching rate was smaller by two orders in magnitude than that of the oxidative quenching. Thus, the oxidative quenching by catalyst 6 dominated the electron transfer processes. The [Fe^IFe⁰] species could further react with a proton. The formed hole remaining in the MPA-CdTe subsequently accepted an electron from H₂A, regenerating the photosensitizer.

Interface-Directed Assembly of a Simple Precursor of [FeFe]-H₂ase Mimics on the Surface of CdSe QDs²²

The surface affinity of water-soluble QDs could allow for the interaction of the sulfur atoms in a water-insoluble [FeFe]-H₂ase mimic in aqueous solution by interface-directed surface

binding. Thus, we utilized the [FeFe]-H₂ase mimic, Fe₂S₂(CO)₆ (7), as the catalyst and MPA-CdSe QDs as the photosensitizer to make water-soluble CdSe/Fe₂S₂(CO)₆ assembly for photocatalytic H₂ evolution (Scheme 7). This

Scheme 7. Interface-Directed Assembly of CdSe/Fe₂S₂(CO)₆ and its H₂ Photogeneration

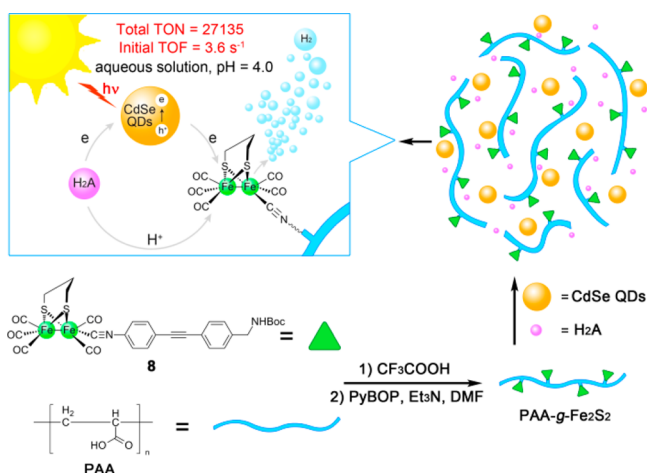


assembly was produced at the interface of the MPA-CdSe QDs aqueous solution and the 7 dichloromethane solution. On average each QD contained one-third of Fe₂S₂(CO)₆. The photocatalytic H₂ evolution was performed in the aqueous solution of the assembly in the presence of H₂A. This system was able to produce H₂ with a TON of 8781 based on Fe₂S₂(CO)₆ and an initial TOF of 596 h⁻¹ in the first 4 h. The high efficient hydrogen evolution was obviously attributed to the fast electron transfer from the excited MPA-CdSe QDs to catalyst unit 7 owing to their intimate contact in the assembly. Indeed, the luminescence of the CdSe QDs was quenched dramatically upon binding Fe₂S₂(CO)₆. Flash photolysis of the MPA-CdSe QDs resulted in exciton bleaching. In the absence of Fe₂S₂(CO)₆, the characteristic bleaching of CdSe QDs at 440 nm is long-lived. For the CdSe/Fe₂S₂(CO)₆ assembly, this bleaching underwent fast and complete recovery. In the later case, after the bleaching recovery, the transient absorption spectrum is consistent with the characteristic absorption of the [Fe^IFe⁰] species.

Photocatalytic Assembly with Poly(acrylic acid)-Based [FeFe]-H₂ase Mimic As Catalyst and MPA-CdSe QDs as Photosensitizer²³

The carboxyl groups in poly(acrylic acid) (PAA) chain provide modification sites for functionalization. Hence, we anchored [FeFe]-H₂ase mimic (8) on the polymer chain to make grafted polymer PAA-g-Fe₂S₂ as water-soluble catalyst (Scheme 8). With MPA-CdSe QDs as the photosensitizer, H₂A as the proton source and SED, we constructed the first set of polymer-based [FeFe]-H₂ase mimics for photocatalytic H₂ production. It has been established³⁴ that the carboxyl groups of PAA can coordinate the cadmium ions on the surface of the CdSe (or CdTe) QDs. In our case, the grafted polymer PAA-g-Fe₂S₂ chain might also wrap round the QD nanoparticles by coordination between the carboxyl groups of the polymer and cadmium ions of CdSe QDs to form photosensitizer-catalyst assembly. This will narrow the distance between the photosensitizer and the grafted catalyst, thus promoting the photoinduced electron transfer from the QDs to the [FeFe]-H₂ase mimic and the photocatalytic H₂ production. This system showed exceptional TON of 27000 (based on the [Fe^IFe^I] unit), and quantum yield (QY) up to 5% for photocatalytic H₂ evolution. The efficient photoinduced electron transfer was supported by the emission quenching

Scheme 8. Synthetic Route to PAA-g-Fe₂S₂ for the Photocatalytic H₂ Production



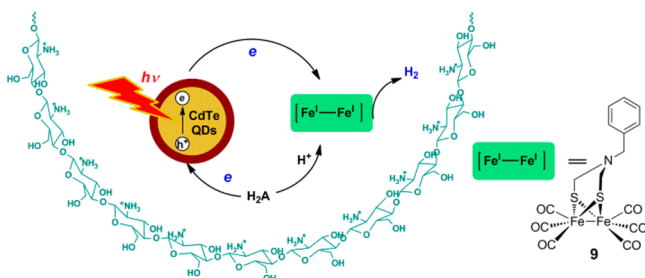
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and flash photolysis experiments. The emission of the MPA-CdSe QDs in aqueous solution was quenched with efficiency up to 81% by PAA-g-Fe₂S₂. The solution of MPA-CdSe QDs and PAA-g-Fe₂S₂ gave the transient absorption of the [Fe^IFe⁰] species after excitation by laser light. This [Fe^IFe⁰] species was quenched by adjusting the pH due to the formation of the protonated [Fe^IFe^{II}·H⁻] species in acidic solution.

Chitosan-Confined [FeFe]-H₂ase Mimic and CdTe QDs²⁴

Chitosan contains a significant amount of primary amines and hydroxyl groups. When the amines are protonated, chitosan bears a polycationic character. In view of the hydrophobic and electrostatic interactions, chitosan might incorporate [FeFe]-H₂ase mimics, as in the case of [FeFe]-H₂ase buried deeply within the protein matrix in nature. Hence, we selected the structurally simplest [FeFe]-H₂ase mimic **9** (Scheme 9) as the

Scheme 9. Chitosan-Confined H₂ Photogeneration



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catalyst, MPA-CdTe QDs as the photosensitizer, and H₂A as the proton source and SED to construct a photocatalytic system for H₂ production. The MPA-stabilized CdTe QDs have negatively charged surface, and can interact with cationic chitosan. Therefore, chitosan, **9**, and MPA-CdTe QDs would form the assembly. The strong interaction and close contact between the photosensitizer and the catalyst in the assembly would enhance the efficiency of the photoinduced electron transfer and the photocatalytic H₂ production. We carried out the hydrogen evolution with this photocatalytic system

containing chitosan (1.0 g L⁻¹) in methanol/water (1:3, v/v) at pH 4.5. This assembly was capable of producing H₂ with TON up to 5.28 × 10⁴ under visible light irradiation. The catalytic stability was enhanced from 8 to 60 h, and the catalytic activity is over 4.16 × 10³-fold higher than that of the same system without chitosan.

The catalyst confined in the chitosan environment in the present artificial photosynthesis is reminiscent of the [Fe₂S₂] subcluster of natural [FeFe]-H₂ase buried in heterogeneous protein matrix. The excellent performance of the present system suggests that the environment surrounding the catalytic center plays a crucial role on the photocatalytic H₂ production. Thus, to create an active H₂ evolution system based on artificial [FeFe]-H₂ase, one should need to mimic not only the structure of the active center but also the biological environment surrounding the center in the natural [FeFe]-H₂ase.

■ ASSEMBLY WITH QDs AS PHOTOSENSITIZER AND TRANSITION METAL SALT AS CATALYST FOR PHOTOCATALYTIC HYDROGEN EVOLUTION IN AQUEOUS SOLUTION

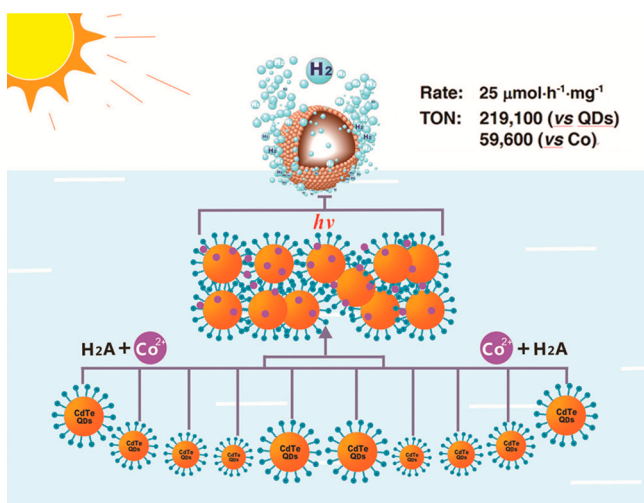
The organic frameworks of the [FeFe]-H₂ase and its mimic are readily degraded by light irradiation, oxidative, or other chemical processes that greatly limit their working lifetime. In the present section, we used inorganic transition metal salts as the catalyst and MPA-CdTe or MPA-CdSe QDs as photosensitizer to construct efficient, durable, and earth-abundant artificial photocatalytic systems for H₂ evolution in aqueous solutions. Such photocatalytic systems can work at least 100 h without noticeable decrease in efficiency.

Hollow Nanospheres Formed in Situ Around Hydrogen Bubbles from CdTe and Inorganic Cobalt Salt²⁵

Although cobalt-based molecular catalyst have emerged in the past few years as one of the most versatile non-notable catalysts coupled with photosensitizers for H₂ evolution,¹⁵ direct incorporation of inorganic cobalt salts into the photocatalytic system is scarcely reported. We used cobalt chloride as catalyst, MPA-CdTe QDs as photosensitizer, and H₂A as the source of proton and SED to construct a robust photocatalytic system for H₂ evolution (Scheme 10). Upon irradiation of this photocatalytic system in aqueous solution with visible light, the H₂ production rate was almost linear even after 21 h in addition to a subtle induction period at the very early stage (Figure 1). When the light was turned off, the H₂ evolution immediately stopped. After rerunning the experiment, the activity was maintained without a noticeable decrease in the second as well as the subsequent runs. The system was able to produce H₂ with TON of ca. 2.2 × 10⁵ or 6.0 × 10⁴ with respect to the MPA-CdTe QDs or cobalt ions after 70 h irradiation.

During irradiation, the photocatalytic solution became turbid and formed precipitate. Examination of the precipitates revealed that the system produced hollow-structured nanospheres in situ in the induction period of the early stage irradiation. Upon irradiation of the photocatalytic solution, the photogenerated holes on CdTe QDs were capable of oxidizing MPA on the QDs, yielding CdS on the surface of the CdTe QDs. The negative surface dangling bonds (Te²⁻, S²⁻) of the QDs would interact with positively charged Co²⁺ ions to form Co_n-CdTe QD photocatalyst in situ.^{25,35} Such photocatalyst could generate H₂ bubbles upon irradiation. Driven by the minimization of the interface energy and further photodecomposition of the stabilizing agent MPA, the Co_n-CdTe

Scheme 10. Schematic Representation of the Formation of $\text{Co}_h\text{-CdTe}$ Hollow Nanosphere and Its Photocatalysis



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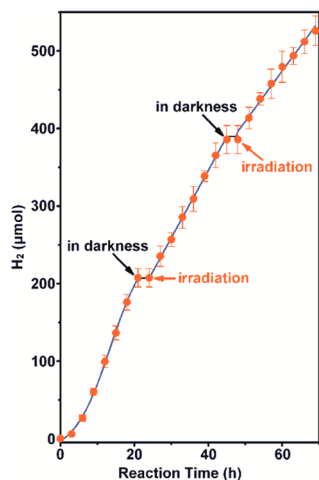


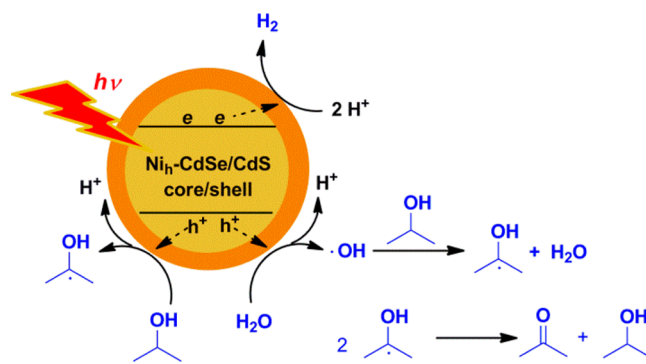
Figure 1. Time course of H_2 evolution at optimal condition: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.1×10^{-4} M), MPA-CdTe QDs (2.4×10^{-7} M), and H_2A (1.14×10^{-1} M) in water under visible light irradiation. Reproduced from ref 25 with permission from The Royal Society of Chemistry.

QDs would aggregate and were organized around the gas–liquid interface of the H_2 bubbles to form hollow-structured nanospheres of $\text{Co}_h\text{-CdTe}$ QDs. The diameter of the hollow nanospheres was in the range of 10–20 nm and the shell thickness was 3–6 nm. This shell thickness corresponded to monolayer to bilayer CdTe QDs (the diameter is 3.4 nm). The number of $\text{Co}_h\text{-CdTe}$ QDs in one hollow nanosphere was calculated to be 95–286. The content of Co ions in the hollow nanospheres was identified to be 0.13% (wt %). The intimate interaction between the photosensitizer and the catalyst would promote photoinduced electron transfer and photocatalytic H_2 production. Indeed, the luminescence of the CdTe QDs was efficiently quenched by the cobalt ions. Compared with the $[\text{FeFe}]\text{-H}_2\text{ase}$ mimics, the inorganic metal salt as catalyst establishes a new paradigm for creating H_2 production photocatalysts.

$\text{Ni}_h\text{-CdSe/CdS}$ Core/Shell Photocatalyst Formed in Situ from MPA-CdSe QDs and Nickel Salt²⁶

We also used MPA-CdSe QDs as photosensitizer, NiCl_2 as catalyst, and 2-propanol as proton source and SED to make photocatalytic system for H_2 evolution (Scheme 11).

Scheme 11. Schematic Representation of the Mechanism for Photocatalytic H_2 Evolution by $\text{Ni}_h\text{-CdSe/CdS}$ Core/Shell Photocatalyst



Irradiation of this photocatalytic system in 2-propanol–water (1:1 v/v) solution resulted in efficient H_2 evolution. With 10 h irradiation, the TON value reached 15 340 per CdSe QD and 18 000 with respect to nickel ion. The internal quantum yield with the irradiation light of 410 nm was up to 11.2%. Consecutive irradiation cycles showed that the reproducibility of the photocatalytic H_2 evolution was excellent. Examinations suggested that during irradiation the stabilizing agent (MPA) underwent oxidation to sulfide ions (S^{2-}) by the photoinduced hole on CdSe QDs, and a CdS ultrathin shell was formed in situ on the surface of CdSe core. Nickel ions would bind to the hanging bond (S^{2-}) on the QD surface to produce $\text{Ni}_h\text{-CdSe/CdS}$ core/shell architecture. The diameter of the $\text{Ni}_h\text{-CdSe/CdS}$ core/shell QDs was ca. 2.6 nm, and the thickness of the CdS shell was 0.35 nm, corresponding to one monolayer of CdS. The amount of nickel on the surface of the QDs was 0.5 wt %. Formation of such an assembly would enhance the photoinduced electron transfer from the QDs to nickel ions. Excitation of MPA-CdSe QDs at 406 nm resulted in typical emission of the QDs. For the $\text{Ni}_h\text{-CdSe/CdS}$ core/shell, this emission was remarkably quenched. Upon laser-pulsed at 410 nm, the $\text{Ni}_h\text{-CdSe/CdS}$ core/shell displayed a bleaching at 430 nm with shorter lifetime than that of MPA-CdSe QDs. The faster recovery of the exciton bleaching in the presence of Ni^{2+} ions suggested fast electron transfer from excited MPA-CdSe QDs to the Ni^{2+} active sites.

CONCLUSION

The design of an artificial photosynthesis system that can split water and is earth-abundant, efficient, and durable remains a fundamental challenge. Because of the complexity in building and optimizing such a complete water splitting system, it is common to divide the system into reductive and oxidative half-reactions for study. We have designed a variety of photosensitizers, catalysts, and sacrificial electron donors, and assembled them together for photocatalytic H_2 evolution. QDs as photosensitizer show superb performance over organic dyes and organometallic complexes in the photocatalytic proton reduction. Both $[\text{FeFe}]\text{-H}_2\text{ase}$ mimics and inorganic transition metal salts as catalyst may form assemblies with QDs

that can efficiently photocatalyze H₂ evolution in the presence of a SED in aqueous solutions. Particularly, the assemblies of MPA-CdTe QDs (or MPA-CdSe QDs) as inorganic cobalt (or nickel) salts in aqueous solutions are able to photocatalytically produce H₂ with exceptional activity and impressive durability under visible light irradiation, suggesting that these assemblies can serve as a valuable part in overall water splitting system. The study on photocatalytic O₂ evolution has not yet received great achievements as the H₂ evolution counterpart. The challenge for the next decade lies in designing robust photocatalytic systems for oxidizing water and coupling the reductive and oxidative half-reactions to constitute complete artificial photosynthetic water splitting systems for solar energy to chemical energy conversion.

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Notes

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REFERENCES

- (1) Armadori, N.; Balzani, V. The Future of Energy Supply: Challenges and Opportunities. *Angew. Chem., Int. Ed.* **2007**, *46*, 52–66.
- (2) Barber, J. Photosynthetic Energy Conversion: Natural and Artificial. *Chem. Soc. Rev.* **2009**, *38*, 185–196.
- (3) Gray, H. B. Powering the Planet with Solar Fuel. *Nat. Chem.* **2009**, *1*, 7.
- (4) Esswein, A. J.; Nocera, D. G. Hydrogen Production by Molecular Photocatalysis. *Chem. Rev.* **2007**, *107*, 4022–4047.
- (5) Ohno, T.; Bai, L.; Hisatomi, T.; Maeda, K.; Domen, K. Photocatalytic Water Splitting Using Modified GaN:ZnO Solid Solution under Visible Light: Long-Time Operation and Regeneration of Activity. *J. Am. Chem. Soc.* **2012**, *134*, 8254–8259.
- (6) Wang, D.; Hisatomi, T.; Takata, T.; Pan, C.; Katayama, M.; Kubota, J.; Domen, K. Core/Shell Photocatalyst with Spatially Separated Co-Catalysts for Efficient Reduction and Oxidation of Water. *Angew. Chem., Int. Ed.* **2013**, *52*, 11252–11256.
- (7) Wang, X.; Xu, Q.; Li, M.; Shen, S.; Wang, X.; Wang, Y.; Feng, Z.; Shi, J.; Han, H.; Li, C. Photocatalytic Overall Water Splitting Promoted by an α - β Phase Junction on Ga₂O₃. *Angew. Chem., Int. Ed.* **2012**, *51*, 13089–13092.
- (8) Abe, R.; Shinmei, K.; Koumura, N.; Hara, K.; Ohtani, B. Visible-Light-Induced Water Splitting Based on Two-Step Photoexcitation between Dye-Sensitized Layered Niobate and Tungsten Oxide Photocatalysts in the Presence of a Triiodide/Iodide Shuttle Redox Mediator. *J. Am. Chem. Soc.* **2013**, *135*, 16872–16884.
- (9) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. Robust Photogeneration of H₂ in Water Using Semiconductor Nanocrystals and a Nickel Catalyst. *Science* **2012**, *338*, 1321–1324.
- (10) Han, Z.; Shen, L.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Nickel Pyridinethiolate Complexes as Catalysts for the Light-Driven Production of Hydrogen from Aqueous Solutions in Noble-Metal-Free Systems. *J. Am. Chem. Soc.* **2013**, *135*, 14659–14669.
- (11) Zhang, W.; Hong, J.; Zheng, J.; Huang, Z.; Zhou, J.; Xu, R. Nickel–Thiolate Complex Catalyst Assembled in One Step in Water for Solar H₂ Production. *J. Am. Chem. Soc.* **2011**, *133*, 20680–20683.
- (12) Das, A.; Han, Z.; Haghghi, M. G.; Eisenberg, R. Photogeneration of Hydrogen from Water Using CdSe Nanocrystals Demonstrating the Importance of Surface Exchange. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 16716–16723.
- (13) Huang, J.; Mulfort, K. L.; Du, P.; Chen, L. X. Photodriven Charge Separation Dynamics in CdSe/ZnS Core/Shell Quantum Dot/Cobaloxime Hybrid for Efficient Hydrogen Production. *J. Am. Chem. Soc.* **2012**, *134*, 16472–16475.
- (14) Yu, T.; Zeng, Y.; Chen, J.; Li, Y.-Y.; Yang, G.; Li, Y. Exceptional Dendrimer-Based Mimics of Diiron Hydrogenase for the Photochemical Production of Hydrogen. *Angew. Chem., Int. Ed.* **2013**, *52*, 5631–5635.
- (15) Brown, K. A.; Wilker, M. B.; Boehm, M.; Dukovic, G.; King, P. W. Characterization of Photochemical Processes for H₂ Production by CdS Nanorod–[FeFe] Hydrogenase Complexes. *J. Am. Chem. Soc.* **2012**, *134*, 5627–5636.
- (16) Zhu, H.; Song, N.; Lv, H.; Hill, C. L.; Lian, T. Near Unity Quantum Yield of Light-Driven Redox Mediator Reduction and Efficient H₂ Generation Using Colloidal Nanorod Heterostructures. *J. Am. Chem. Soc.* **2012**, *134*, 11701–11708.
- (17) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. A Molecular Ruthenium Catalyst with Water-Oxidation Activity Comparable to that of Photosystem II. *Nat. Chem.* **2012**, *4*, 418–423.

- (18) Wang, W.-G.; Wang, F.; Wang, H.-Y.; Si, G.; Tung, C.-H.; Wu, L.-Z. Photocatalytic Hydrogen Evolution by [FeFe] Hydrogenase Mimics in Homogeneous Solution. *Chem.—Asian J.* **2010**, *5*, 1796–1803.
- (19) Wang, F.; Wang, W.-G.; Wang, H.-Y.; Si, G.; Tung, C.-H.; Wu, L.-Z. Artificial Photosynthetic Systems Based on [FeFe]-Hydrogenase Mimics: the Road to High Efficiency for Light-Driven Hydrogen Evolution. *ACS Catal.* **2012**, *2*, 407–416.
- (20) Wang, H.-Y.; Si, G.; Cao, W.-N.; Wang, W.-G.; Li, Z.-J.; Wang, F.; Tung, C.-H.; Wu, L.-Z. A Triad [FeFe] Hydrogenase System for Light-Driven Hydrogen Evolution. *Chem. Commun.* **2011**, *47*, 8406–8408.
- (21) Wang, F.; Wang, W.-G.; Wang, X.-J.; Wang, H.-Y.; Tung, C.-H.; Wu, L.-Z. A Highly Efficient Photocatalytic System for Hydrogen Production by a Robust Hydrogenase Mimic in an Aqueous Solution. *Angew. Chem., Int. Ed.* **2011**, *50*, 3193–3197.
- (22) Li, C.-B.; Li, Z.-J.; Yu, S.; Wang, G.-X.; Wang, F.; Meng, Q.-Y.; Chen, B.; Feng, K.; Tung, C.-H.; Wu, L.-Z. Interface-Directed Assembly of a Simple Precursor of [FeFe]-H₂ase Mimics on CdSe QDs for Photosynthetic Hydrogen Evolution in Water. *Energy Environ. Sci.* **2013**, *6*, 2597–2602.
- (23) Wang, F.; Liang, W.-J.; Jian, J.-X.; Li, C.-B.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Exceptional Poly(acrylic acid)-Based Artificial [FeFe]-Hydrogenases for Photocatalytic H₂ Production in Water. *Angew. Chem., Int. Ed.* **2013**, *52*, 8134–8138.
- (24) Jian, J.-X.; Liu, Q.; Li, Z.-J.; Wang, F.; Li, X.-B.; Li, C.-B.; Liu, B.; Meng, Q.-Y.; Chen, B.; Feng, K.; Tung, C.-H.; Wu, L.-Z. Chitosan Confinement Enhances Hydrogen Photogeneration from a Mimic of the Diiron Subsite of [FeFe]-hydrogenase. *Nat. Commun.* **2013**, *4*, 2695.
- (25) Li, Z.-J.; Li, X.-B.; Wang, J.-J.; Yu, S.; Li, C.-B.; Tung, C.-H.; Wu, L.-Z. A Robust “Artificial Catalyst” in situ Formed from CdTe QDs and Inorganic Cobalt Salts for Photocatalytic Hydrogen Evolution. *Energy Environ. Sci.* **2013**, *6*, 465–469.
- (26) Li, Z.-J.; Wang, J.-J.; Li, X.-B.; Fan, X.-B.; Meng, Q.-Y.; Feng, K.; Chen, B.; Tung, C.-H.; Wu, L.-Z. An Exceptional Artificial Photocatalyst, Ni₄CdSe/CdS Core/Shell Hybrid, Made *in situ* from CdSe Quantum Dots and Nickel Salts for Efficient Hydrogen Evolution. *Adv. Mater.* **2013**, *25*, 6613–6618.
- (27) Cao, W.-N.; Wang, F.; Wang, H.-Y.; Chen, B.; Feng, K.; Tung, C.-H.; Wu, L.-Z. Photocatalytic Hydrogen Production from a Simple Water-Soluble [FeFe]-hydrogenase Model System. *Chem. Commun.* **2012**, *48*, 8081–8083.
- (28) Wang, H.-Y.; Wang, W.-G.; Si, G.; Wang, F.; Tung, C.-H.; Wu, L.-Z. Photocatalytic Hydrogen Evolution from Rhenium(I) Complexes to [FeFe] Hydrogenase Mimics in Aqueous SDS Micellar Systems: A Biomimetic Pathway. *Langmuir* **2010**, *26*, 9766–9771.
- (29) Zhang, H.-H.; Feng, K.; Chen, B.; Meng, Q.-Y.; Li, Z.-J.; Tung, C.-H.; Wu, L.-Z. Water-Soluble Sulfonated-Graphene-Platinum Nanocomposites: Facile Photochemical Preparation with Enhanced Catalytic Activity for Hydrogen Photogeneration. *Catal. Sci. Technol.* **2013**, *3*, 1815–1821.
- (30) Frey, M. Hydrogenases: Hydrogen-Activating Enzymes. *ChemBioChem* **2002**, *3*, 153–160.
- (31) Alper, J. Water Splitting Goes Au Naturel. *Science* **2003**, *299*, 1686–1687.
- (32) Na, Y.; Wang, M.; Pan, J.; Zhang, P.; Åkermark, B.; Sun, L. Visible Light-Driven Electron Transfer and Hydrogen Generation Catalyzed by Bioinspired [2Fe2S] Complexes. *Inorg. Chem.* **2008**, *47*, 2805–2810.
- (33) Wang, H.-Y. Bio-inspired Models of [FeFe] Hydrogenases Active Site for Catalyzing Hydrogen Production. Ph.D. Thesis, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 2011.
- (34) Zhang, H.; Zhou, Z.; Yang, B.; Gao, M. The Influence of Carboxyl Groups on the Photoluminescence of Mercaptocarboxylic Acid-Stabilized CdTe Nanoparticles. *J. Phys. Chem. B* **2003**, *107*, 8–13.
- (35) Li, Z.-J.; Fan, X.-B.; Li, X.-B.; Li, J.-X.; Ye, C.; Wang, J.-J.; Yu, S.; Li, C.-B.; Gao, Y.-J.; Meng, Q.-Y.; Tung, C.-H.; Wu, L.-Z. Visible Light