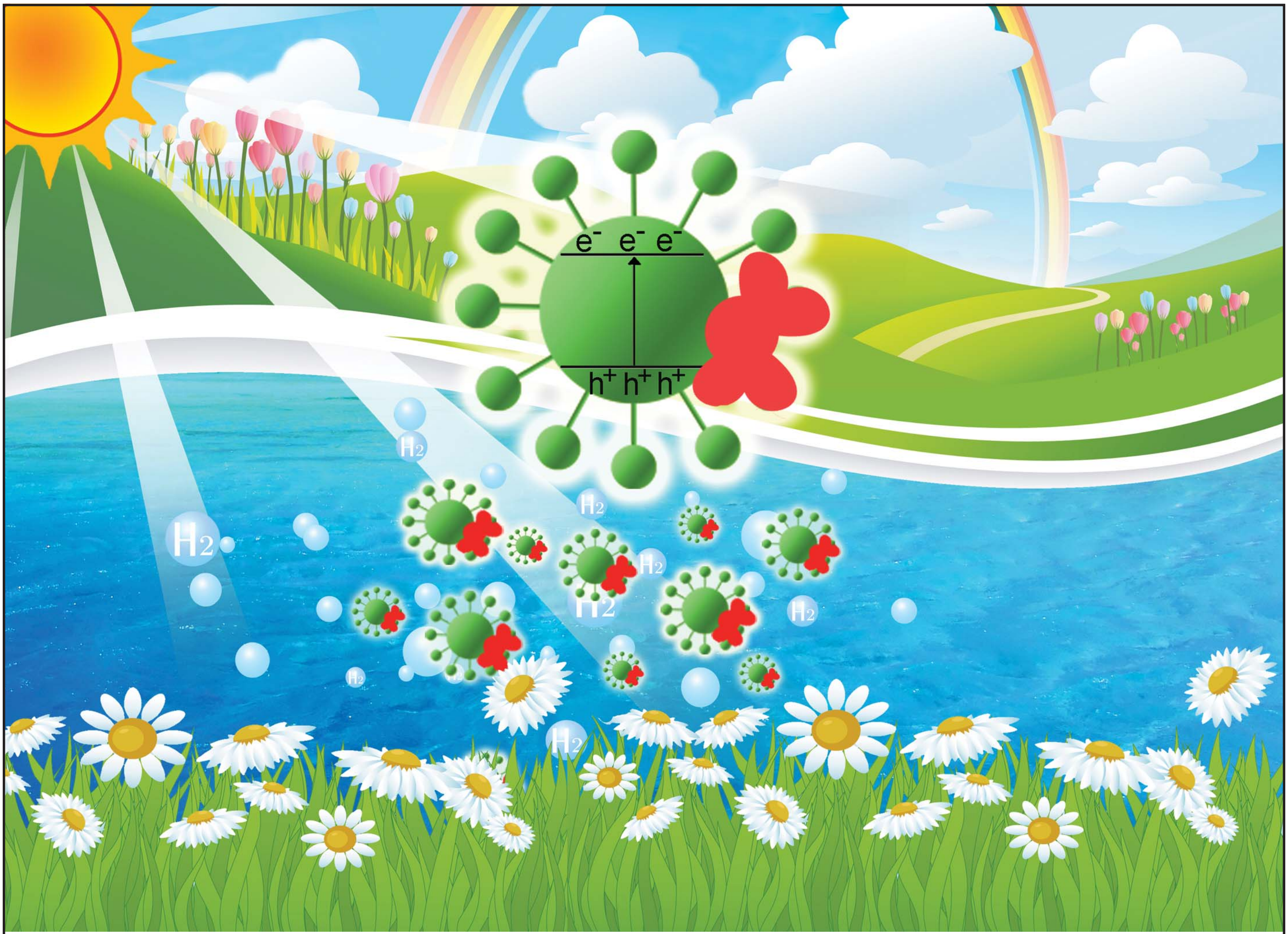

Showcasing research from Professor Li-Zhu Wu's group at Technical Institute of Physics and Chemistry, the Chinese Academy of Sciences, Beijing, P. R. China.

Title: Interface-directed assembly of a simple precursor of [FeFe]-H_2ase mimics on CdSe QDs for photosynthetic hydrogen evolution in water

Solar energy conversion of water into clean fuel hydrogen (H_2) offers one of the best solutions for meeting future energy demands. Natural [FeFe]-hydrogenase ([FeFe]-H_2ase) is known to catalyze the reversible reduction of protons to H_2 with remarkable activity under mild conditions. In an effort to develop efficient catalysts for H_2 evolution, interface-directed assembling approach is introduced to construct artificial photocatalyst, CdSe/$Fe_2S_2(CO)_6$ assembly that shows the highest efficiency known to date for H_2 evolution under visible light irradiation in water.

As featured in:

Energy &
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See Wu *et al.*,
Energy Environ. Sci., 2013, **6**, 2597.

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Registered Charity Number 207890

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Cite this: *Energy Environ. Sci.*, 2013, **6**, 2597

Received 23rd March 2013
Accepted 4th July 2013

DOI: 10.1039/c3ee40992a

www.rsc.org/ees

Interface-directed assembly of a simple precursor of [FeFe]–H_2ase mimics on CdSe QDs for photosynthetic hydrogen evolution in water†

Cheng-Bo Li,‡ Zhi-Jun Li,‡ Shan Yu, Ge-Xia Wang, Feng Wang, Qing-Yuan Meng, Bin Chen, Ke Feng, Chen-Ho Tung and Li-Zhu Wu*

To prepare a water-soluble catalyst for photocatalytic hydrogen (H_2) evolution, a simple hydrophobic precursor of [FeFe]–H_2ase mimics, $Fe_2S_2(CO)_6$, has been successfully assembled on the surface of CdSe QDs using an interface-directed approach in aqueous/organic solution. The resulting photocatalyst shows the highest efficiency known to date for H_2 evolution with a turnover number (TON) of 8781 *vs.* $Fe_2S_2(CO)_6$ and an initial turnover frequency (TOF) of 596 h^{-1} under visible light irradiation in water.

Broader context

Solar energy conversion of water into clean fuel hydrogen (H_2) offers one of the best solutions for meeting future energy demands. Natural hydrogenases (H_2ases) bearing unique organometallic clusters with earth-abundant elements (Fe, Ni) can catalyze the reversible reduction of protons to H_2 with remarkable activity. With the structural elucidation of [FeFe]–H_2ase, scientists have been working hard to develop systems using [FeFe]–H_2ase mimics for photocatalytic H_2 generation. However, most of the photocatalysts function only in organic solvents and therefore are not applicable for coupling with water splitting technology. Over the past five years, two different approaches have been put forward to make water-soluble photocatalytic [FeFe]–H_2ase systems. Herein, we report the third way, *i.e.* interface-directed assembly for photocatalytic H_2 evolution in water. Benefiting from the unique characteristics of quantum dots (QDs), the precursor of [FeFe]–H_2ase mimics, $Fe_2S_2(CO)_6$, without any further chemical modification, can interact with CdSe QDs intimately to afford water-soluble CdSe/$Fe_2S_2(CO)_6$ assembly. Upon irradiation by LEDs (λ = 410 nm) with visible light for 82 h, the interface-directed assembly enables H_2 production with a TON of 8781 based on $Fe_2S_2(CO)_6$ and an initial TOF of 596 h^{-1} in the first 4 h. The stability and activity are the highest known to date for photocatalytic H_2 evolution from [FeFe]–H_2ase mimics.

Developing efficient and low-cost photocatalysts for H_2 production, particularly from water splitting using solar energy, holds great potential to meet future energy requirements.[1–7] Natural hydrogenases (H_2ases), bearing unique organometallic clusters with earth-abundant elements (Fe, Ni), can catalyze the reversible reduction of protons to H_2 with remarkable activity.[8,9] Since the structural elucidation of [FeFe]–H_2ases ($[(\mu\text{-SR})_2\{Fe(CO)_2L\}_2]$),[10–13] a great deal of effort has been made to develop photocatalytic systems using [FeFe]–H_2ase mimics for H_2 generation.[14–20] However, most of these photocatalysts function only in organic solvents and therefore are not applicable for coupling with water splitting technology.

In the course of making water-soluble photocatalytic [FeFe]–H_2ase systems, only a few examples of water-soluble catalysts have been reported so far.[21–31] Generally speaking, two different approaches have been put forward. In one way, a water-soluble substituent is directly connected to a Fe_2S_2 active site of the [FeFe]–H_2ase.[21–28] 1,3,5-Triaza-7-phospha-adamantane and 3,7-diacetyl-1,3,7-triaza-5-phospha-bicyclo-[3.3.1]nonane were employed by Darensbourg[21] and Sun,[22] respectively, to modulate water solubility of [FeFe]–H_2ase mimics. Our group introduced a hydrophilic isocyanide ligand[25] and a simple sulfonate group[27] to the Fe_2S_2 active site. The water-soluble [FeFe]–H_2ase mimics containing the isocyanide ligand in combination with CdTe QDs as photosensitizers catalyzed the reduction of proton to H_2 with a TON of up to 505.[25] The second approach is to incorporate [FeFe]–H_2ase mimics into self-assembling systems in water.[29–31] In 2010, we reported that hydrophobic [FeFe]–H_2ase mimics and rhenium(I) complexes could be incorporated into an aqueous sodium dodecyl sulfate (SDS) micellar solution.[29] Darensbourg found that with the help of cyclodextrin, a structural [FeFe]–H_2ase model could be dissolved in water.[30] With this system, Sun and Wang studied the H_2 photoproduction in water *via* the host–guest complexation of [FeFe]–H_2ase mimics and organic dyes (Eosin Y and Rose Bengal), and achieved 190 (TON) under optimized conditions.[31]

In this communication, we wish to report the third approach to a water-soluble artificial photosynthetic [FeFe]–H_2ase system,

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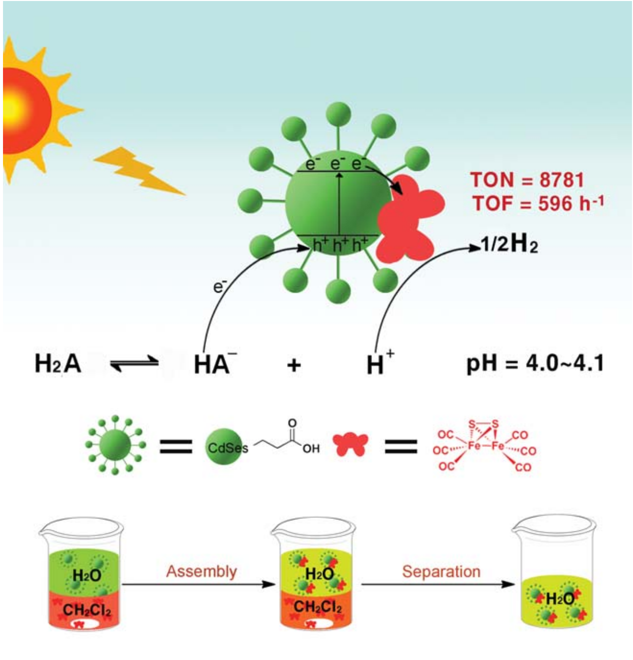
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, The Chinese Academy of Sciences, Beijing 100190, P. R. China. E-mail: lzwu@mail.ipc.ac.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ee40992a

‡ The two authors contributed equally to this work.

i.e. interface-directed assembly of a simple [FeFe]–H_2ase mimic onto CdSe QDs for H_2 evolution in water. Herein, water-soluble QDs[25,32,33] were used as the photosensitizer owing to their unique characteristics ideal for light-harvesting and charge separation. The quantum confinement effect, rich surface binding properties and high surface-to-volume ratio make QDs promising in the combination with molecular catalysts. Pickett *et al.* in 2010, for example, firstly introduced $Fe_2S_2(CO)_6$ onto InP nanocrystals to construct a photoelectrochemical cell for H_2 evolution.[34] Very recently, Chen *et al.* anchored cobaloxime catalyst molecules to the surface of CdSe/ZnS QDs *via* a phosphonate linkage,[35] and Li *et al.* added ZnS nanoparticles into the dimethylformamide (DMF) solution of $[(\mu\text{-SPh-4-NH}_2)_2Fe_2(CO)_6]$ to construct a hybrid catalyst $[(\mu\text{-SPh-4-NH}_2)_2Fe_2(CO)_6]$/ZnS.[36] Nevertheless, the photocatalytic experiments for H_2 evolution were carried out in toluene or DMF–H_2O mixed solution. Most recently, Eisenberg, Holland and Krauss *et al.* used CdSe nanocrystals capped with dihydrolipoic acid (DHLA) as the light absorber and a soluble Ni^{2+}–DHLA catalyst for the light-driven generation of H_2 in water.[32] We envision herein that the surface affinity of water-soluble QDs could allow for the interaction of the sulfide atoms on a water-insoluble [FeFe]–H_2ase mimic in aqueous solution by interface-directed surface binding. This expectation was found indeed to be the case. The precursor of [FeFe]–H_2ase mimics, $Fe_2S_2(CO)_6$, without any further chemical modification, can interact with CdSe QDs intimately to afford a water-soluble CdSe/$Fe_2S_2(CO)_6$ assembly (Scheme 1). Upon irradiation with visible light by LEDs ($\lambda = 410$ nm) for 82 h, the assembly enables H_2 production with a TON of 8781 based on $Fe_2S_2(CO)_6$ and an initial TOF of 596 h^{-1} in the first 4 h. The stability and activity are the highest known to date for photocatalytic H_2 evolution from [FeFe]–H_2ase mimics.



Scheme 1 The interface-directed assembly of CdSe/$Fe_2S_2(CO)_6$ and its H_2 photogeneration.

The water-soluble CdSe QDs were synthesized according to the method described in the literature,[37] where $CdCl_2 \cdot 2.5H_2O$ was selected as a Cd precursor, Na_2SeSO_3 as a Se precursor and 3-mercapto-propionic acid (MPA) as a stabilizing ligand. Firstly, Na_2SSeO_3 was prepared by adding 40 mg (0.5 mmol) Se powder and 189 mg (1.5 mmol) Na_2SO_3 into 100 mL H_2O followed by refluxing under anaerobic conditions until Se powder was dissolved completely. And then 46 mg (0.2 mmol) $CdCl_2 \cdot 2.5H_2O$ was dissolved into 190 mL H_2O, with 26 μL (0.3 mmol) MPA injected into the solution; after adjusting the pH value of the solution to 11 with 1 M NaOH, the solution was deoxygenated with Ar for 30 minutes. Next, 10 mL oxygen-free Na_2SeSO_3 solution was injected. The system was refluxed under anaerobic conditions for 3.5 h. The resulting CdSe QDs were further purified with alcohols[38] to remove the free ions and ligands remaining in the system (see ESI†). The diameter of MPA–CdSe QDs was determined as 1.9 nm by the transmission electron microscopy (TEM) images as well as the equation developed by Peng[39] (see ESI†).

Inspired by the work of Pickett, who discovered the interaction ability of $Fe_2S_2(CO)_6$ with InP nanocrystals to make a photoelectrochemical electrode,[34] we selected $Fe_2S_2(CO)_6$, the precursor of [FeFe]–H_2ase mimics, as the catalyst to interact with the surface of CdSe QDs. Indeed, the hydrophobic $Fe_2S_2(CO)_6$ was able to bind CdSe QDs at the aqueous–organic interface. Typically, an aqueous solution of MPA–CdSe QDs (1.2×10^{-4} M, calculated from the low-energy absorption band, see ESI†) was mixed with a dichloromethane solution of $Fe_2S_2(CO)_6$ (1.0×10^{-2} M), and vigorously stirred for 12 h at room temperature. During this process, the color of the water phase was changed from green to yellowish green, indicating the formation of CdSe/$Fe_2S_2(CO)_6$ assembly. The water phase was then precipitated with isopropanol to obtain the assembly.

Fourier transform infrared (FTIR) spectroscopy of the assembly (Fig. 1a) shows apparent peaks in the carbonyl stretching region (2081 cm^{-1}, 2038 cm^{-1}, 1997 cm^{-1}), similar to the free $Fe_2S_2(CO)_6$ species (2083 cm^{-1}, 2040 cm^{-1}, 2000 cm^{-1}). The slight broadening and small high field shift of the peaks suggest that $Fe_2S_2(CO)_6$ chemisorbs on the surface of CdSe QDs.[34] X-ray photoelectron spectroscopy (XPS) displays signals of Fe($2p_{1/2}$) at 723 eV and Fe($2p_{3/2}$) at 710 eV with satellite signals (Sat.) for both the assembly and $Fe_2S_2(CO)_6$ (Fig. 1b). The results imply that the valence state of the iron core remains unchanged in the assembly. Inductively coupled plasma-mass spectroscopy (ICP-MS) was also used to determine the amount of $Fe_2S_2(CO)_6$, which is 0.78% (w/w) in the assembly. This means that the concentrations of $Fe_2S_2(CO)_6$ and CdSe QDs are 2.3×10^{-6} M and 6.3×10^{-6} M, respectively (1 mg CdSe/$Fe_2S_2(CO)_6$ assembly in 10 mL H_2O).

The visible light driven H_2 evolution was performed at room temperature. CdSe/$Fe_2S_2(CO)_6$ assembly and ascorbic acid (H_2A) were added into 10 mL water in a Pyrex tube to construct the H_2 evolution systems. Generally, the reaction was carried out under irradiation by a high-pressure Hanovia mercury lamp. A glass filter was used to cut off light with wavelength shorter than 400 nm. Bubbles coming out from the solution could be directly observed soon after turning on the light. The generated 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. Condition experiments show that several factors could affect the efficiency of H_2 production. Particularly, the pH value of the system, the concentration of the sacrificial donor and proton source H_2A, and the concentration of the CdSe/$Fe_2S_2(CO)_6$ assembly were crucial in our system.

Fig. 2a shows that the photocatalytic H_2 production is very dependent on the pH value of the system, where the optimal pH value for H_2 evolution is 4.0, while lower 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 changes of surface charge of CdSe QDs and the equilibrium of $H_2A \leftrightarrow H^+ + HA^-$ ($pK_a = 4.03$ and 3.90 for H_2A and HA^-, respectively[40]). Increasing the concentration of H_2A from 1.7×10^{-2} M to 8.5×10^{-2} M greatly improved the efficiency of H_2 production (Fig. 2b). Further increasing the concentration of H_2A to 1.1×10^{-1} M, however, led to no obvious increase in the amount of H_2 production. In addition, when the concentration of the assembly was increased from 8.0×10^{-7} M to 2.3×10^{-6} M (based on $Fe_2S_2(CO)_6$) at pH 4.0 (Fig. 2c), where the concentration of H_2A was fixed at 8.5×10^{-2} M, the amount of H_2 evolution was significantly increased from 16.1 μmol to 87.6 μmol for 20 h irradiation. With further increase of the assembly concentration to 4.6×10^{-6} M, the rate of H_2 evolution was increased but the TON declined. As a result, an

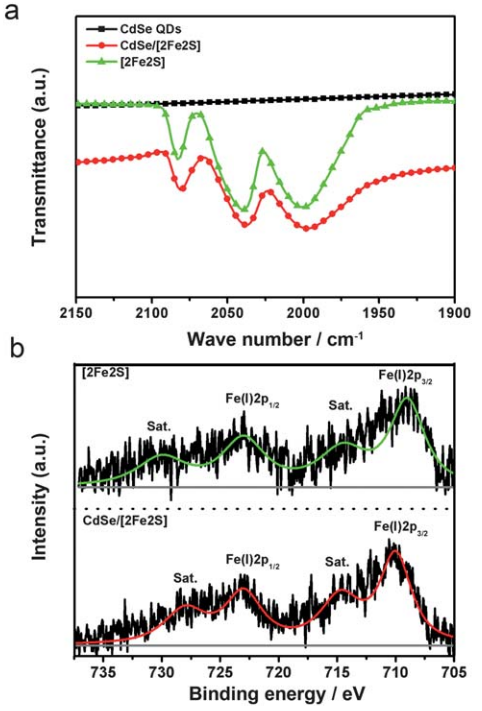


Fig. 1 (a) FTIR spectra of the carbonyl stretching region of the CdSe QDs (black squares), $Fe_2S_2(CO)_6$ (green triangles) and CdSe/$Fe_2S_2(CO)_6$ assembly (red dots) in solid state; (b) XPS data of $Fe_2S_2(CO)_6$ (above) and CdSe/$Fe_2S_2(CO)_6$ assembly (below). "Sat." means satellite peaks.

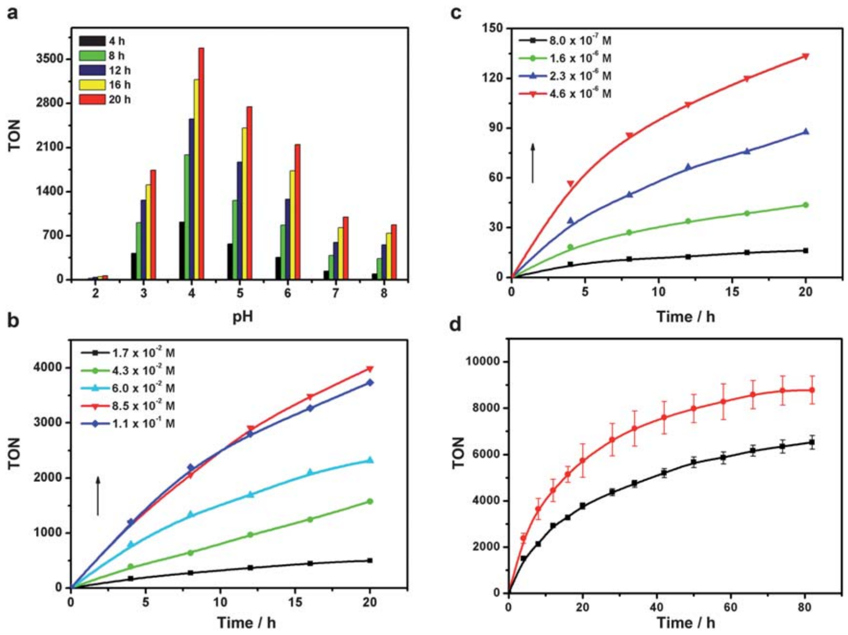


Fig. 2 (a) Photocatalytic H_2 evolution at different pH values in 10 mL H_2O; CdSe/$Fe_2S_2(CO)_6$ (6.3×10^{-6} M/2.3×10^{-6} M), H_2A (8.5×10^{-2} M); (b) the dependence of H_2 evolution on the concentration of H_2A from 1.7×10^{-2} M to 1.1×10^{-1} M; CdSe/$Fe_2S_2(CO)_6$ (6.3×10^{-6} M/2.3×10^{-6} M); (c) H_2 evolution as a function of concentration of the CdSe/$Fe_2S_2(CO)_6$ assembly from 8.0×10^{-7} M to 4.6×10^{-6} M (based on $Fe_2S_2(CO)_6$); (d) photocatalytic H_2 evolution under irradiation using a high-pressure Hanovia mercury lamp (black square) and 410 nm LED light (red dot), respectively, under optimized conditions: CdSe/$Fe_2S_2(CO)_6$ (6.3×10^{-6} M/2.3×10^{-6} M), H_2A (8.5×10^{-2} M), pH 4.0; error bars represent mean ± s.d. of two independent experiments. All H_2 evolution reactions were irradiated using a high-pressure Hanovia mercury lamp with a glass filter ($\lambda > 400$ nm) except for Fig. 2d.

optimized H_2 evolution system containing 8.5×10^{-2} M H_2A and 2.3×10^{-6} M CdSe/$Fe_2S_2(CO)_6$ assembly in 10 mL water at pH 4.0 was able to photocatalyze H_2 evolution for 82 h with a TON of 6530 (based on $Fe_2S_2(CO)_6$) by using a mercury lamp as the light source (Fig. 2d, black square line). An even better result could be achieved with the same system when the light source was changed to a LED lamp (410 nm, 160 mW cm^{-2}), with a TON of up to 8781 and an initial TOF of 596 h^{-1} in the first 4 h (Fig. 2d, red dot line). The better activity and stability of the CdSe/$Fe_2S_2(CO)_6$ assembly in H_2O compared to that of the reported hybrid in a mixture of organic solvent and H_2O[36] further prove the significance to establish a photocatalytic H_2 evolution system in H_2O.

Control experiments demonstrate the significantly higher activity of the CdSe/$Fe_2S_2(CO)_6$ assembly to that of either CdSe QDs only or a mixture of $Fe_2S_2(CO)_6$ and CdSe QDs (Table 1). The comparison was carried out in 10 mL solution ($H_2O/CH_3CN = 3/1$, v/v), due to the insolubility of $Fe_2S_2(CO)_6$ in water. For systematic comparison, all of the systems were kept at the same concentration of CdSe QDs (6.3×10^{-6} M) and H_2A (8.5×10^{-2} M) at pH 4.0. With visible light irradiation for 8 h, the CdSe/$Fe_2S_2(CO)_6$ assembly produced 34.7 μmol H_2, which is 3 times to that produced from the simple-mixed system of $Fe_2S_2(CO)_6$ and CdSe QDs, 11.1 μmol H_2 (Table 1). More encouragingly, when we replaced the H_2O/CH_3CN mixed solvent with H_2O for the assembled system, the efficiency of H_2 evolution was improved greatly, with the amount of H_2 increasing from 34.7 μmol to 49.7 μmol. In the absence of $Fe_2S_2(CO)_6$, however, the amount of H_2 generated from the CdSe QDs system (1.5 μmol) is far less than those from the assembly or the mixture systems. These results reveal the critical roles of not only the catalyst $Fe_2S_2(CO)_6$ but also the interface-directed interaction in the H_2 evolution system.

We speculated that efficient electron transfer from the excited CdSe QDs to $Fe_2S_2(CO)_6$ took place owing to their intimate contact in the CdSe/$Fe_2S_2(CO)_6$ assembly. To confirm the assumption, emission quenching and flash photolysis experiments were carried out (Fig. 4). As shown in Fig. 4a, the emission peaks of CdSe QDs generated from the band edge (the narrow emission centered at 465 nm) and trap state (the broad emission centered at about 650 nm) are quenched dramatically upon binding $Fe_2S_2(CO)_6$ on the surface of CdSe QDs, which might be attributed to electron transfer[41] from the excited CdSe QDs to $Fe_2S_2(CO)_6$. The small red shift probably results from the enhanced electronic coupling between CdSe QDs and $Fe_2S_2(CO)_6$. When the same concentration of $Fe_2S_2(CO)_6$ was added into H_2O–CH_3CN (3/1, v/v) solution of CdSe QDs, the emission was slightly quenched. The quenching efficiency estimated at 465 nm for the CdSe/$Fe_2S_2(CO)_6$ assembly and the mixture of CdSe QDs and $Fe_2S_2(CO)_6$ is 60% and 15%, respectively. In view of the small spectroscopic overlap of absorption of $Fe_2S_2(CO)_6$ and emission of CdSe QDs, the energy transfer between the excited CdSe QDs and $Fe_2S_2(CO)_6$ would be negligible; the emission quenching therefore originates from the photo-induced electron transfer (PET) from the CdSe QDs to $Fe_2S_2(CO)_6$. The larger quenching extent of CdSe/$Fe_2S_2(CO)_6$ assembly than that of the mixture of CdSe QDs and $Fe_2S_2(CO)_6$ (the concentration of $Fe_2S_2(CO)_6$ is identical to that in the assembly) further confirmed that the close contact between CdSe QDs and $Fe_2S_2(CO)_6$ is of significance for such an efficient electron transfer.

According to the size of CdSe QDs (1.9 nm) or their band edge emission peak (465 nm, Fig. 4a), the band gap of CdSe QDs is about 2.7 eV (see ESI†). The valence band of CdSe locates close to 0.5 V *vs.* NHE,[42,43] which means that the conduction band position of the CdSe QDs is approximately −2.2 V *vs.* NHE. Considering that the reduction potential of $Fe_2S_2(CO)_6$ is −0.66 V *vs.* NHE,[32] which indicates that the electron transfer process from the conduction band of CdSe QDs to the catalytic centre of $Fe_2S_2(CO)_6$ is thermodynamically feasible (Fig. 3).

The photo-induced electron-transfer process is further verified by the flash photolysis study at room temperature. Similar to that observed by Wojdyla,[44] we did not detect the complete recovery of CdSe QD bleaching at 440 nm by using a femtosecond flash photolysis with the longest timescale of 2.5 ns (see ESI, Fig. S2†), and hence a nanosecond scale transient absorption measurement was carried out. As shown in Fig. 4b, the decay rate of the characteristic bleaching of CdSe QDs at 440 nm for the assembly was 8.8 ns (calculated as the signal decay to 1/*e* of the maximal value), shorter than that of the CdSe QDs alone ($\tau = 17.6$ ns), indicating the occurrence of the electron transfer process. However, in a longer timescale of microseconds, the strong bleaching signal of the assembly disappeared. Simultaneously, a set of new peaks centered at 430 nm, 520 nm, 600 nm

Table 1 Control experiments of the photocatalytic H_2 evolution[a]

Photocatalytic system	Solvents	H_2/μmol
CdSe QDs	$H_2O/CH_3CN = 3/1$, v/v	1.5
A mixture of CdSe QDs and $Fe_2S_2(CO)_6$	$H_2O/CH_3CN = 3/1$, v/v	11.1
CdSe/$Fe_2S_2(CO)_6$ assembly	$H_2O/CH_3CN = 3/1$, v/v	34.7
CdSe/$Fe_2S_2(CO)_6$ assembly	H_2O	49.7

[a] All the systems were kept under identical concentrations of H_2A (4.3×10^{-2} M) and CdSe QDs (6.3×10^{-6} M) in 10 mL solution at pH 4.0, and irradiated for 8 h by a high-pressure Hanovia mercury lamp; the concentration of $Fe_2S_2(CO)_6$ was fixed at 2.3×10^{-6} M.

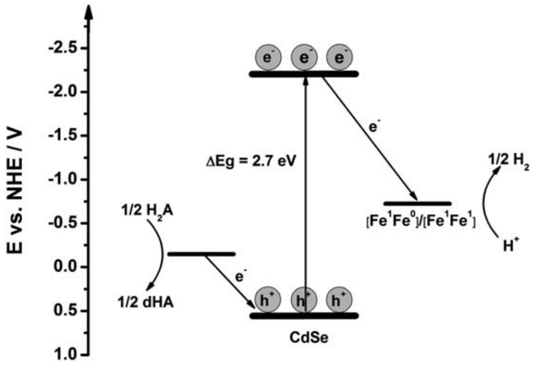


Fig. 3 The schematic electron transfer process in the present system.

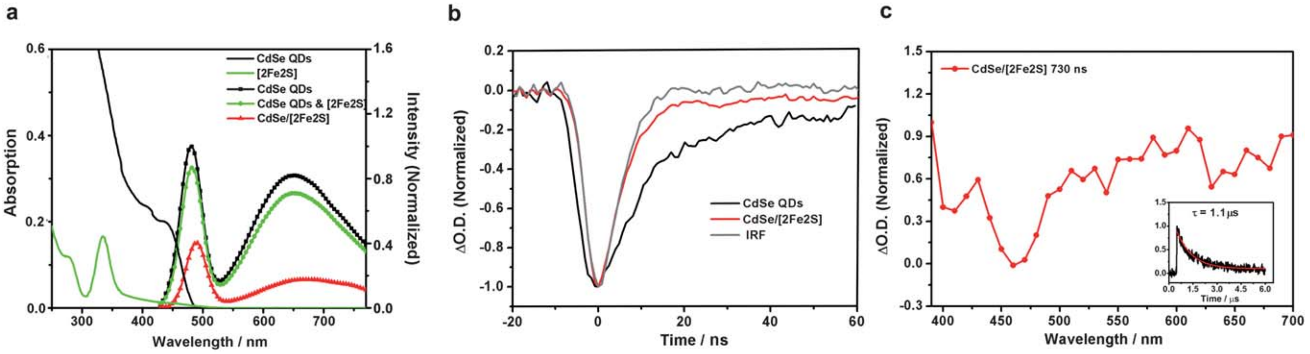


Fig. 4 (a) UV/vis absorption spectra of CdSe QDs (6.3×10^{-6} M, in H_2O, black line); UV/vis absorption spectra of $Fe_2S_2(CO)_6$ (2.3×10^{-6} M, in CH_3CN, green line) and emission spectra of CdSe QDs (6.3×10^{-6} M, black line + scatter), mixture of CdSe QDs and $Fe_2S_2(CO)_6$ (6.3×10^{-6} M and 2.3×10^{-6} M, respectively, green line + scatter), CdSe/$Fe_2S_2(CO)_6$ assembly (6.3×10^{-6} M/2.3×10^{-6} M, red line + scatter) in H_2O/CH_3CN (3/1, v/v); (b) the nanosecond recovery kinetics of transient bleaching recovery for CdSe QDs (black) and CdSe/$Fe_2S_2(CO)_6$ (red) monitored at 440 nm upon laser excitation at 410 nm, the signal of IRF (gray) is the response of the instrument; (c) nanosecond transient absorption spectra of the CdSe/$Fe_2S_2(CO)_6$ assembly upon laser excitation at 410 nm; the inset shows the kinetic decay monitored at 430 nm.

and 700 nm emerged with a lifetime of 1.1 μs at 430 nm (Fig. 4c). These absorptions are analogous to the reduced Fe^0Fe^I species generated by the reduction of [FeFe]–H_2ase mimics.[45,46] Since the CdSe QDs show broad transient absorption above 470 nm in a time scale of microseconds (Fig. S3†),[44] as well as that only partial CdSe QDs bind $Fe_2S_2(CO)_6$ in the assembling system (for the concentration of CdSe QDs and $Fe_2S_2(CO)_6$ being 6.3×10^{-6} M and 2.3×10^{-6} M, respectively), we proposed that the transient signals of the assembly may result from the spectral overlap of both Fe^0Fe^I species and CdSe QDs. As a result, the reduced $Fe_2S_2(CO)_6$ could further react with protons to evolve H_2,[21,47,48] and the holes left in CdSe QDs are consumed by the sacrificial electron donor H_2A.

In conclusion, we have developed an efficient and robust photocatalytic H_2 evolution system in water. The interface-directed CdSe/$Fe_2S_2(CO)_6$ assembly has been demonstrated to be the promising third way to construct a photocatalytic system of [FeFe]–H_2ase mimics in water. The resulting assembly not only facilitates the electron transfer from the excited CdSe QDs to the catalytic center $Fe_2S_2(CO)_6$ for efficient H_2 evolution, but also avoids complicated modification of the catalytic center for water-solubility. Under optimal conditions, this system[49] is able to produce H_2 with a TON of up to 8781 (based on $Fe_2S_2(CO)_6$) with visible light irradiation for 82 h. The efficiency and stability of [FeFe]–H_2ase mimics for light-driven H_2 production systems are the highest ones reported to date, although they are still far below the values of natural [FeFe]–H_2ase enzymes.[8,9,50–53] The present work demonstrates that the close contact and strong interaction are particularly important for improving the performance of photocatalytic H_2 evolution of artificial [FeFe]–H_2ase systems.

Acknowledgements

We are grateful for financial support from the Ministry of Science and Technology of China (2009CB22008, 2013CB834505 and 2013CB834804), the National Science Foundation of China (21090343, 91027041 and 50973125), Solar Energy Initiative of the Knowledge Innovation Program of the Chinese Academy of Sciences, and the Bureau for Basic Research of the Chinese Academy of Sciences. The authors would like to acknowledge Ms Yuejuan Ma for her help in preparation of the graphics.

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