Electronic Supplementary Information for

Interface-directed assembly of a simple precursor of [FeFe]-H$_2$ase mimic on CdSe QDs for photosynthetic hydrogen evolution in water

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1. Instruments and materials

Materials All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted.

Instruments UV/Vis spectra were measured with a Shimadzu UV-1601 PC spectrophotometer. Emission spectra were recorded on a Hitachi 4500 fluorescence spectrophotometer. Attenuated total reflectance FTIR spectra were taken on Excalibur 3100 system (Varian, USA). The composition of $CdSe/Fe_2S_2(CO)_6$ was determined by inductively coupled plasma mass spectroscopy (ICP, Varian 710-ES, USA). The XPS measurements were performed on an ESCALAB 250 spectrophotometer with Al-Kα radiation. In the flash photolysis experiments, the samples were purged with argon for 30 min. For the nanosecond transient absorption, excitation was provided by using an OPO laser at 410 nm with Edingburge LP920. The apparatus with femtosecond transient absorption of ~160 fs is briefly described below. An optical parametric amplifier (OPA-800CF-1, Spectra Physics) pumped by a regenerative amplifier (SPTF-100F-1KHPR, Spectra Physics) provided the actinic laser pulses at desired wavelengths (~120 fs, full width at half-maximum). A white light continuum probe (430-1400 nm) was generated from a 3 mm thick sapphire plate and was detected after interrogating the excited sample by a CCD detector (Spec-10:400B/LN) for the visible region. To ensure that each laser shot excites the sample relaxed fully from the previous excitation, the laser system was run at a repetition rate of 100 Hz. A mechanical chopper (model 75158, Newport) was set in the pump beam to regulate pump "on" and "off" for a pair of sequential actinic pulses. To improve the signal-to-noise ratio, each transient spectrum was obtained by averaging 98 individual measurements. All measurements were carried out at room temperature. Hydrogen (H_2) evolution experiments relative to the pH and concentration effect and control experiments were carried out under a high-pressure Hanovia mercury lamp equipped with a glass filter ($\lambda > 400$ nm, 120 ± 10 mW/ cm^2). The best TON of 8781 was determined by using 410 nm LED light (160 mW/cm^2).

2. Synthesis of CdSe QDs and purification

The CdSe QDs was synthesized according to the literature.[1] Firstly, the Se precursor Na_2SSeO_3 was synthesized: 40 mg (0.5 mmol) Se powder and 189 mg (1.5 mmol) Na_2SO_3 was added into 100 mL H_2O, and then the system was refluxed under anaerobic condition until Se powders were all dissolved. Secondly, 46 mg (0.2 mmol) $CdCl_2$ $2.5H_2O$ was added to 190 mL H_2O, then 26 μL (0.3 mmol) MPA was injected into the solution. After adjusting the pH value of the solution to 11 with 1 M NaOH, the solution was deoxygenated with argon for 30 minutes; then, 10 mL deoxygenated Na_2SSeO_3 was injected to the solution, with the ratio of [Cd]:[MPA]:[Se] as 1:1.5:0.25. After deoxygenated process with argon for 20 min, the system was refluxed for the growth of CdSe QDs. The size of QDs was monitored by UV-vis spectroscopy during reaction. Generally, refluxing of 3.5 h is necessary for the growth of QDs.

Purification: the prepared CdSe QDs solution was concentrated to be less than 1/4 volume of stock solution. Then addition of isopropanol by 4 times volume of CdSe QDs solution resulted in the precipitation. After centrifugation at a rate of 8000 r/min and decantation of the supernatant, the remaining precipitates were dissolved into water for further purification; such operation was repeated for 3 times.

3. The size, extinction coefficient (ε) and concentration (c) of the CdSe QDs

According to the equations suggested by Peng and coworkers,[2] the diameter (**D**), extinction coefficient (**ε**) and concentration (c) of the CdSe QDs can be determined as follows:

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - 0.4277\lambda + 41.57 \quad (1)$$

$$\varepsilon = 5857(D)^{2.65} \quad (2)$$

$$Abs = \varepsilon c L \quad (3)$$

Herein, **D** (nm) is the diameter or size of a given nanocrystals sample. **λ** is the wavelength of the first excitonic absorption peak (from low energy) of the corresponding sample. **ε** is the extinction coefficient of the corresponding sample. **Abs** is the absorbance of sample, **L** (1 cm) is the length of cuvette in the direction of irradiation and **c** is concentration of the corresponding sample.

In our experiments, the diameter (**D**) of the CdSe QDs was determined as 1.9 nm due to the absorption peak at 440 nm (Fig. S1), which is consistent with that determined by HRTEM. The extinction coefficient **ε** was 3.2×10^4 (L^{-1} mol cm^{-1}). Based on **Abs** = 0.20, the concentration **c** was calculated as 6.3×10^{-6} M in a 10 mL system containing 1 mg CdSe QDs.
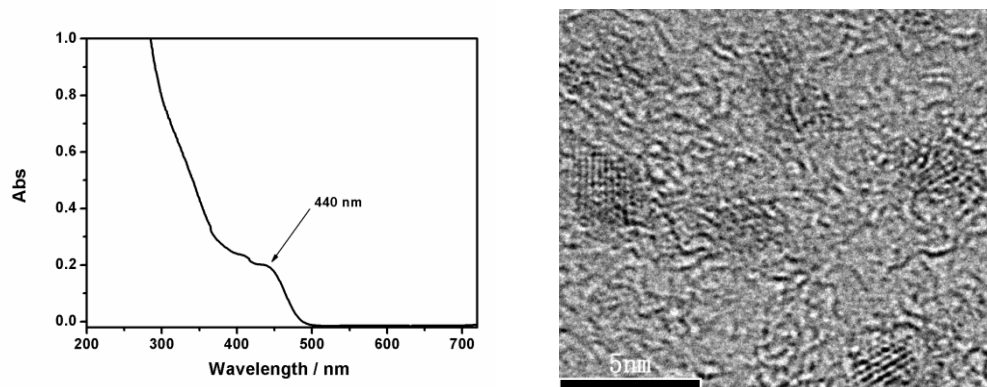
Fig. S1 (Left) UV/Vis absorption spectrum of CdSe QDs (6.3×10^{-6} M). The first excitonic absorption peak is centered at 440 nm and (right) the HRTEM picture of CdSe QDs.

4. The band gap (ΔE_g) of CdSe QDs

The band gap (ΔE_g) of QDs could be calculated from the band-gap emission (λ_{peak}) of emission spectrum of the corresponding sample using equation (4); the other way to calculate the band gap (ΔE_g) is based on the diameter of the corresponding sample using equation (5).[3]

$$\Delta E_g = \frac{1240}{\lambda_{peak}} \tag{4}$$

$$\Delta E_g = \Delta E_g^b + \frac{h}{8D^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) \tag{5}$$

Herein, ΔE_g (eV) is the band gap of QDs, λ_{peak} (nm) the band-edge emission of emission spectrum of corresponding sample, ΔE_g^b (for CdSe, $\Delta E_g^b = 1.74$ eV) is the band gap of the bulk of corresponding sample, h is Planck's constant, D is the diameter of QDs, and m_e (0.13 m_0, $m_0 = 9.1 \times 10^{-31}$ kg) and m_h (0.4 m_0) are the effective masses of electrons and holes, respectively. m_0 is the mass of free electrons.

In our experiments, the band-edge emission (λ_{peak}) of the CdSe QDs was 465 nm, ΔE_g was determined as 2.7 eV from equation (4). Alternatively, based on the diameter (D) of the CdSe QDs (1.9 nm), the corresponding ΔE_g was determined as 2.7 eV from equation (5), quite consistent with the result from equation (4).
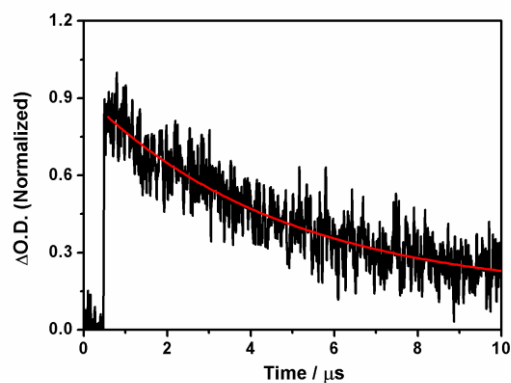
5. Femtosecond transient absorption and kinetics recovery of the characteristic absorption bleaching of CdSe QDs.
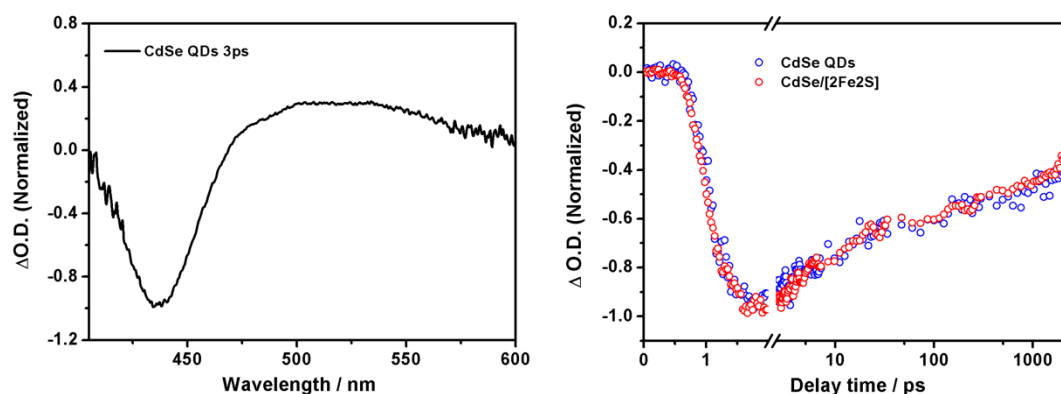
Fig. S2 left: Femtosecond transient absorption of CdSe QDs (3 ps) upon laser excitation at 400 nm; right: bleaching recovery kinetics of the lowest energy exciton bands in CdSe QDs monitored at 440 nm for only CdSe QDs and CdSe/Fe$_2$S$_2$(CO)$_6$ assembly, respectively.

The femtosecond transient absorption of CdSe QDs shows strong bleaching centred at 440 nm, which can be explained by excitonic absorption from lowest lying electron level (1S) in the conduction band. Above 470 nm, a broad transient absorption band attributed to deep levels usually associated with surface defects was observed with longer lifetime in microsecond range.

6. Kinetic decay of CdSe QDs monitored at 530 nm with nanosecond transient absorption spectroscopy

Fig. S3 Kinetic decay of CdSe QDs with a lifetime of 4.7 µs monitored with nanosecond transient absorption spectroscopy at 530 nm.

7. References

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3. M. N. Kalasad, M. K. Rabinal and B. G. Mulimani, *Langmuir*, 2009, **25**, 12729.