

Electronic Supplementary Information for

**Self-assembled inorganic clusters of semiconducting quantum dots for effective solar hydrogen evolution**

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## 1. Chemicals

3-Mercaptopropionic acid (Alfa aesar, 99%), selenium powder (Aldrich, about 200 mesh), Ascorbic acid (Alfa aesar, 99%), glutathione (Acros, 98%),  $\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$  (99%),  $\text{Zn}(\text{OAc})_2$  (99%),  $\text{Zn}(\text{NO}_3)_2$  (99%),  $\text{Na}_2\text{SO}_3$  (99%) and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  were purchased from Sigma-Aldrich. Other chemicals are of analytical grade and used without further purification unless otherwise noted. Ultrapure water with 18.2 M $\Omega$  cm (Mettler Toledo, FE20, China) was used thorough.

## 2. Experiments

**Synthesis of water-soluble CdSe QDs:** <sup>1-3</sup> briefly, 40 mg selenium powder was transferred to 100 mL of  $\text{Na}_2\text{SO}_3$  (189.0 mg) aqueous solution. The resulting mixture was then refluxed until the selenium powder dissolved completely to obtain transparent  $\text{Na}_2\text{SeSO}_3$  solution. Aqueous colloidal water-soluble CdSe QDs were prepared by mixing a solution of  $\text{CdCl}_2 \cdot 5/2\text{H}_2\text{O}$  and stabilizer, 3-mercaptopropionic acid (MPA), then adjusting the pH to 11.0 with 1.0 M NaOH, and finally adding a measured volume of the above synthesized  $\text{Na}_2\text{SeSO}_3$  solution; the typical molar ratio of Cd:MPA:Se was 1.0:1.5:0.25. This mixture was placed in a three-necked flask and deaerated with  $\text{N}_2$  bubbling for 30 min. Finally, the bright-yellow, transparent solution was heated and refluxed for about 3.0 h to promote the growth of CdSe nanocrystals. The concentration of CdSe QDs in stock solution was about  $2.0 \times 10^{-5}$  mol/L.

**Synthesis of water-soluble ZnSe QDs:** <sup>4, 5</sup> briefly, a volume of 190 mL aqueous solution of 46 mg (0.2 mmol) of  $\text{Zn}(\text{OAc})_2$  and 92 mg (0.3 mmol) glutathione (GSH) was adjusted to pH 11.0 with 1.0 M NaOH. The solution was placed in a three-necked flask and was deaerated with  $\text{N}_2$  bubbling for 30 min to remove the residual  $\text{O}_2$ . Under vigorous stirring, 10 mL (0.05 mmol) freshly prepared  $\text{Na}_2\text{SeSO}_3$  aqueous solution was injected immediately, the mixture was deaerated for another 20 min. Then, the transparent solution was refluxed for about 2.0-3.0 h to promote the growth of glutathione stabilized ZnSe QDs. The obtained QDs were characterized by spectroscopic studies and high resolution TEM. The concentration of ZnSe QDs in stock solution was about  $1.5 \times 10^{-5}$  mol/L.

**Synthesis of water-soluble ZnS QDs:** <sup>6</sup> in a typical experiment, 57  $\mu\text{L}$  MPA was added to 36 mL demineralized water at room temperature, and vigorously stirred for 5.0 min. Water-soluble ZnS QDs were prepared by adding 2.0 mL (0.04 mol/L)  $\text{Zn}(\text{NO}_3)_2$  dropwise slowly, then adjusting the pH to 12.0, stirring for 10 min, another 4.0 mL (0.04 mol/L)  $\text{Zn}(\text{NO}_3)_2$  solution was added immediately. Stop stirring, 6.0 mL (0.04 mol/L)  $\text{Na}_2\text{S}$  solution was added into the solution, then adjusted the pH to 12.0 again. Stirring for few minutes at room

temperature to promote the growth of the MPA stabilized ZnS QDs. The obtained all kinds of water-soluble QDs are characterized before further utilization.

**Constructing the assembled clusters:** first of all, a desired ratio of CdSe QDs and ZnSe QDs was mixed together to give a mixture of aqueous solution. Then, the pH value of the solution was adjusted by adding HCl. During this process, the solution turned from transparent to turbid (pH=3.0), which was caused by the detach of surface ligands from QDs to cause the formation of assembled clusters. The pH value was precisely controlled to obtain a certain degree of aggregation. Finally, the assembled clusters were precipitated and rinsed by ultra-pure water for three times.

**Solar H<sub>2</sub> evolution:** typically, the above prepared assembled clusters of CdSe QDs and ZnSe QDs ( $1.6 \times 10^{-5}$  mol/L) was re-dispersed in 10 mL ascorbic acid aqueous solution (0.2 M) at pH = 4.0. The reaction mixture was degassed through bubbling nitrogen for 30 min to remove the residual oxygen gas, and then irradiated with a 500 W high-pressure mercury lamp (ZhongRuiDa Electric Light Factory, Beijing, China) with a cutoff filter to remove light below 400 nm ( $\sim 100$  mW $\cdot$ cm<sup>-2</sup> at flask surface) at room temperature. The molecular H<sub>2</sub> evolved was determined by Gas chromatography (GC) taking CH<sub>4</sub> as internal standard. Solar H<sub>2</sub> evolution of bare CdSe QDs and other QDs/Hole-relay assemblies was performed in a similar procedure.

**Preparation of QDs electrodes:** the pre-prepared CdSe QDs and assembled clusters of CdSe QDs and ZnSe QDs were re-dispersed in a certain volume of acetone. The solution was vigorously stirred and sonicated to form a concentrated and viscous suspension. At the same time, a FTO substrate was washed with ultrapure water and ethanol for three times. Then, the above prepared QDs suspensions were drop-casting on the surface of FTO and dried in air. The obtained sample electrodes were cut into same area before photoelectrochemical measurements.

**Photoelectrochemical measurement:** the experiment was performed in a three-electrode setup by taking the QDs based electrodes as the working electrode, platinum sheet as counter electrode, Ag/AgCl (3.0 M KCl) as reference electrode, and 0.1 M aqueous solution of Na<sub>2</sub>SO<sub>4</sub> as electrolyte under inert atmosphere. 300 W Xe-lamp ( $\sim 100$  mW cm<sup>-2</sup>) with a UV filter was employed as the light source. The transient photocurrent response to on-off illumination was performed when the sample electrode was applied a constant potential (-0.1 V vs. NHE).

### 3. Characterization

UV-Vis absorption spectra were recorded with a Shimadzu 1601PC spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature using a Hitachi 4500 fluorescence spectrophotometer. All optical measurements were performed at room temperature under ambient conditions. Attenuated total reflectance Fourier transform infrared (FT-IR) spectra were taken on Excalibur 3100 system (Varian, USA). High-resolution transmission electron microscopy (HRTEM) was performed on a JEM 2100F (Japan) electron microscope operated at an accelerating voltage of 200 kV. All pH measurements were made with a Model pHs-3C meter (Mettler Toledo FE20, China). Gas chromatography (GC) was performed on a TIAN MEI 7890 II GC using a 5 Å molecular sieve column and a thermal conductivity detector. PL decay measurements were performed with a FLSP 920 (Edinburgh Instruments Ltd., UK) apparatus with 406 nm laser excitation (pulse width ca.100 ps). Photoelectrochemical measurement was performed on a Zennium electrochemical workstation (Germany, Zahner Company). The X-ray photoelectron spectra (XPS) measurements were performed on an ESCALAB 250 spectrophotometer with Al-K $\alpha$  radiation. The binding energy scale was using the C 1s peak at 284.6 eV.

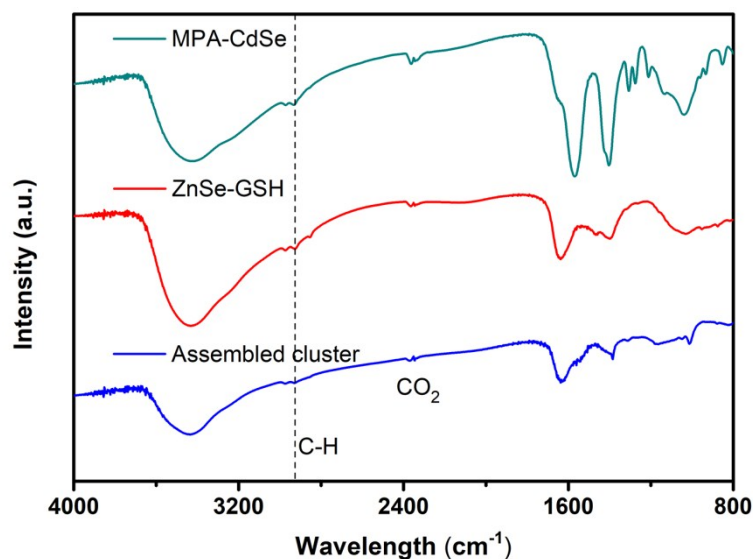
### 4. The calculation of the turnover frequency (TOF)

In this inorganic-cluster system, the surface cadmium ions serve as the active sites of proton reduction. Herein, we firstly quantify the number of surface cadmium ions on per QD particle. Our previous work has demonstrated that the ratio of surface Cd to inner Cd is 0.316 in per CdSe QD.<sup>3</sup> As a result, the surface Cd atoms account for ~24% of the total Cd atoms. According to the concentration of obtained CdSe QDs ( $2.0 \times 10^{-5}$  mol/L) and total amount of Cd precursor (0.4 mmol in 400 mL aqueous solution), it can be calculated that there are about 50 Cd atoms in per CdSe QD on average. Thus, the number of surface cadmium for proton reduction can be estimated to ~12. Under the optimal conditions, the highest turnover number of H<sub>2</sub> evolution based on per QD is ~5000. Accordingly, the turnover frequency (TOF) per surface catalytic site can be determined by following equation:

$$TOF = \frac{TON}{N_{[cat.]} * t_{(h)}} = \frac{5000}{12 * 12h} \approx 35 h^{-1}$$

in which  $N_{[cat.]}$  is the number of surface active sites per QD, and  $t$  is the time of light irradiation.

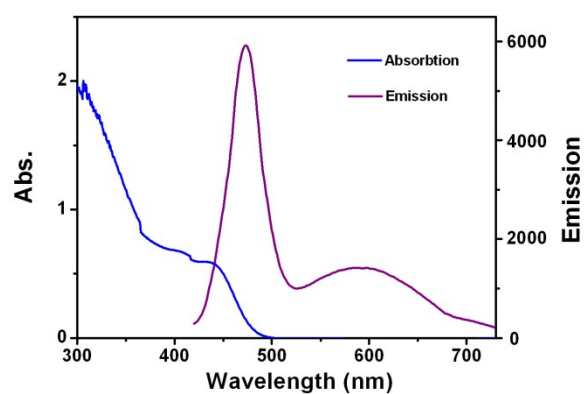
## 5. Fourier transform infrared (FT-IR) spectra



**Fig. S1** The FT-IR spectra of MPA-capped CdSe QDs, GSH-capped ZnSe QDs and the assembled clusters of CdSe and ZnSe QDs.

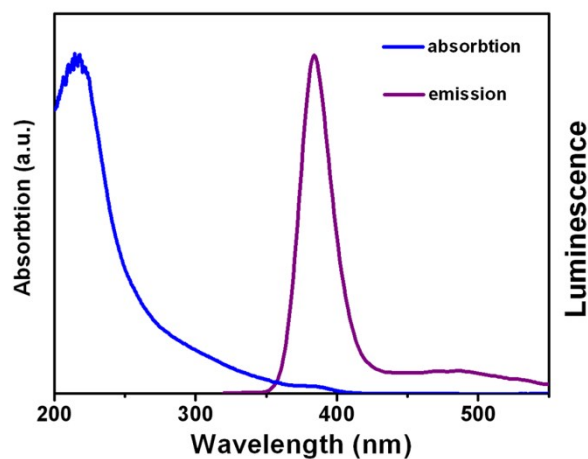
The featuring peak of the C-H stretching vibrations at  $\sim 2930\text{ cm}^{-1}$  indicated the presence of MPA and GSH on the surface of CdSe QDs and ZnSe QDs, respectively. However, the peak of C-H stretching vibrations were found dramatically declined in the assembled cluster, which implied the removal of organic ligands (MPA and GSH) on the surface of QDs.<sup>7, 8</sup>

## 6. Steady-state spectra of CdSe QDs



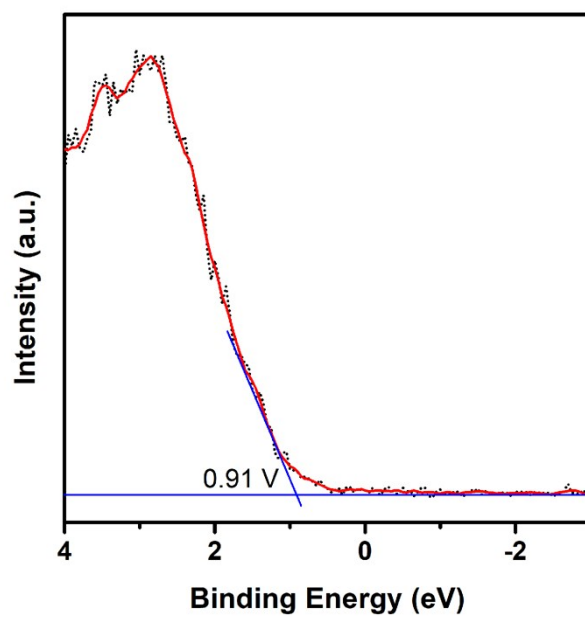
**Fig. S2** Steady-state spectra of the as-synthesized CdSe QDs, demonstrating that the first excitonic absorption peak of CdSe QDs is at 445 nm and the emission is around 474 nm (400 nm excitation).

## 7. The steady-state spectra of ZnSe QDs



**Fig. S3** Steady-state spectra of the as-synthesized ZnSe QDs, indicating that the absorption of ZnSe QDs is below 400 nm and the emission is around 390 nm (300 nm excitation).

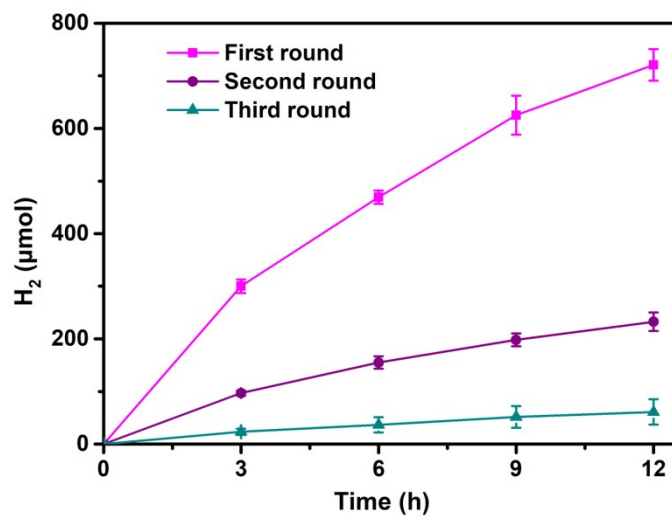
## 8. Valence band XPS spectrum of ZnSe QDs



**Fig. S4** The valence band XPS spectrum of ZnSe QDs, indicating that the valence band position of ZnSe QDs is about +0.91 V.

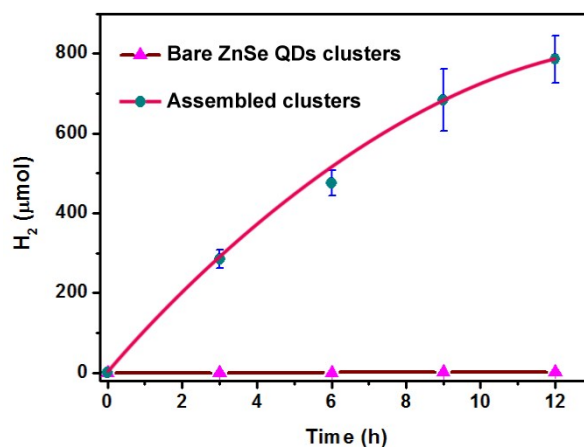


## 9. Photocatalytic H<sub>2</sub> evolution with multiple catalytic rounds



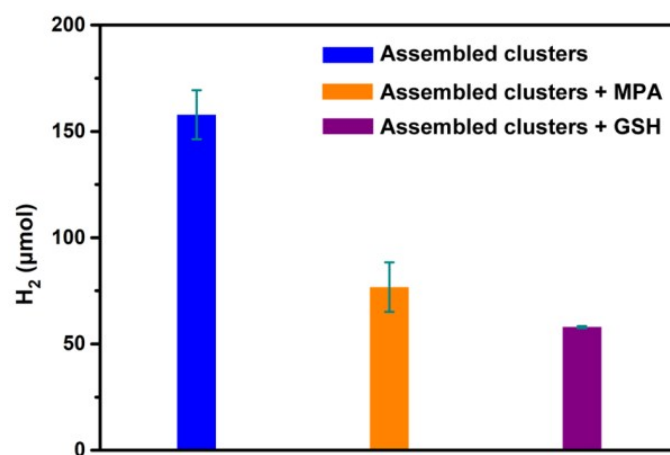
**Fig. S5** Photocatalytic H<sub>2</sub> evolution experiments of the assembled clusters with multiple catalytic rounds. The assembled clusters of CdSe QDs and ZnSe QDs were repurified and then dispersed fresh ascorbic acid aqueous solution every rounds.

## 10. Photocatalytic H<sub>2</sub> evolution of bare ZnSe QDs clusters



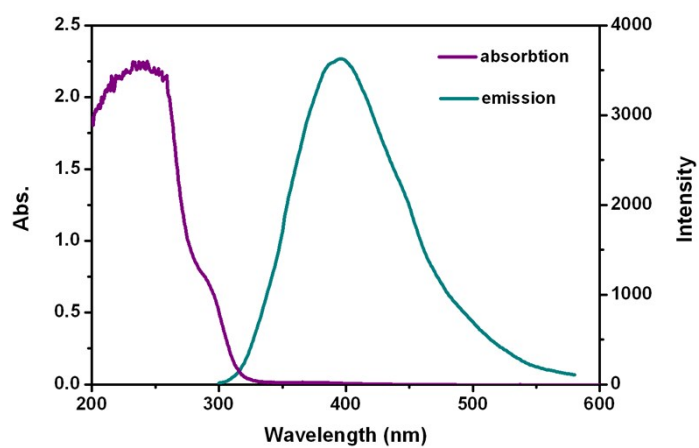
**Fig. S6** The profiles of H<sub>2</sub> evolution for bare ZnSe QDs clusters and assembled clusters of CdSe QDs and ZnSe QDs (the concentration of ZnSe QDs is  $8 \times 10^{-6}$  mol/L for both of the systems) under the same condition by taking 10 mL ascorbic acid (0.2 M) aqueous solution (pH = 4.0) as a sacrificial reagent under visible light irradiation during 12.0 h. Error bars represent mean  $\pm$ s.d. of three independent experiments.

## 11. The influence of ligands on photocatalytic H<sub>2</sub> evolution activity



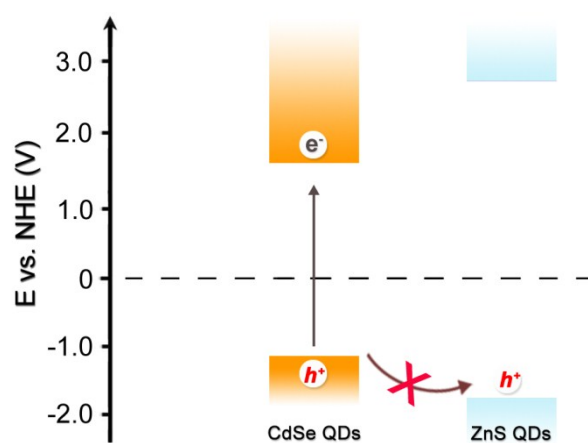
**Fig. S7** Photocatalytic H<sub>2</sub> evolution of assembled clusters of CdSe QDs and ZnSe QDs as well as the influences of thiol ligands, MPA and GSH in 2.0 h visible-light irradiation.

## 12. UV-vis absorption spectrum of ZnS QDs



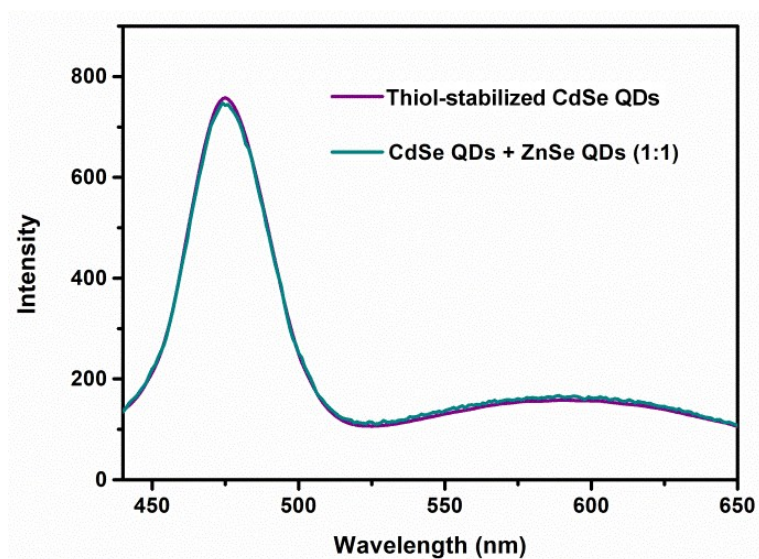
**Fig. S8** Steady-state spectra of the as-synthesized ZnS QDs, indicating that the absorption of ZnS QDs is below 330 nm and the emission is around 390 nm (300 nm excitation).

### 13. Band-position of ZnS QDs



**Fig. S9** The illustration of Type-I band alignment between CdSe QDs and ZnS QDs. As a result, hole migration from CdSe QDs to ZnS QDs is thermodynamically unfeasible.

## 14. Emission quenching



**Fig. S10** Comparison of the emission of thiol-stabilized CdSe QDs and physical mixture of CdSe QDs and ZnSe QDs in aqueous solution. (420 excitation)

## 15. Summary of CdSe QDs-based artificial photosystems for H<sub>2</sub> evolution

**Table S1** Summary of CdSe QD-based artificial photosystem for H<sub>2</sub> evolution

Light source	QDs	H <sub>2</sub> Evolution Co-catalyst	Sacrificial reagent	Rate	Reference
$\lambda > 320$ nm (400 mW·cm <sup>-2</sup> )	MCE-CdSe QDs	none	Na <sub>2</sub> SO <sub>3</sub>	120 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (~5.7 $\mu\text{mol/h}$ )	<i>Chem. Commun.</i> <b>2012</b> , 48, 371 <sup>9</sup>
$\lambda > 420$ nm (300 W Xe-lamp)	CdSe nanorods	Pt	Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> S	36000 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (~90 $\mu\text{mol/h}$ )	<i>J. Phys. Chem. Lett.</i> <b>2012</b> , 3, 3781 <sup>10</sup>
$\lambda > 400$ nm (150 mW·cm <sup>-2</sup> )	MPA-CdSe QDs	Ni <sup>2+</sup>	2-propanol	153000 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (~76 $\mu\text{mol/h}$ )	<i>Adv. Mater.</i> <b>2013</b> , 25, 6613 <sup>3</sup>
LEDs (520 nm) (13 mW·cm <sup>-2</sup> )	DHLA-CdSe QDs	Ni-DHLA	Ascorbic acid	~8.0 $\mu\text{mol/h}$	<i>Science</i> <b>2012</b> , 338, 1321 <sup>11</sup>
LEDs (520 nm) (13 mW·cm <sup>-2</sup> )	TDL-CdSe QDs	Ni-TDL	Ascorbic acid	~18 $\mu\text{mol/h}$	<i>Proc. Nat. Acad. Sci. U.S.A.</i> <b>2013</b> , 110, 16716 <sup>12</sup>
$\lambda > 400$ nm (150 mW·cm <sup>-2</sup> )	MPA-CdSe QDs	Fe <sub>2</sub> S <sub>2</sub> (CO) <sub>6</sub>	Ascorbic acid	~6.2 $\mu\text{mol/h}$	<i>Energy Environ. Sci.</i> <b>2013</b> , 6, 2597 <sup>13</sup>
$\lambda > 400$ nm (150 mW·cm <sup>-2</sup> )	MPA-CdSe QDs	Ni(OH) <sub>2</sub>	2-propanol	~10000 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (~55 $\mu\text{mol/h}$ )	<i>ChemSusChem</i> <b>2015</b> , 8, 642 <sup>14</sup>
$\lambda > 420$ nm (200 mW·cm <sup>-2</sup> )	OA-CdSe QDs	Au nanoparticles	Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> S	~73000 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (73 $\mu\text{mol/h}$ )	<i>Adv. Mater.</i> <b>2017</b> , 29, 1700803 <sup>15</sup>
$\lambda > 400$ nm (100 mW·cm <sup>-2</sup> )	Self-assembled cluster of CdSe and ZnSe QDs	none	Ascorbic acid	~30000 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (~66 $\mu\text{mol/h}$ )	This work

MCE: 2-Mercaptoethanol; MPA: 3-Mercaptopropionic acid; DHLA: Dihydrolipoic acid; TDL: 2-(3-Mercapto-2,2-bis(mercaptomethyl)propoxy)acetic Acid or 2-(3-Thiocyanato-2,2-bis(thiocyanatomethyl)propoxy)acetic Acid; OA: oleic acid.

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