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Supporting Information for

A Robust Hollow-structured "Artificial Catalyst" *in situ* Formed from CdTe QDs and Inorganic Cobalt Salts for Photocatalytic H_2 Evolution

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1. Chemicals

3-Mercaptopropionic acid (MPA, 99%), tellurium powder (Aldrich, about 200 mesh), $CdCl_2{\cdot}2.5H_2O$ (99%) and $NaBH_4$ (99%) were purchased from Sigma-Aldrich. Other chemicals are of analytical grade without further purification unless otherwise noted. The ultrapure water with 18.2 MΩ cm (Mettler Toledo, FE20, China) was used throughout the experiment.

2. Preparation of sodium hydrogen telluride

On the basis of the method for preparation of sodium hydrogen telluride (NaHTe),[S1] we made some modification. Briefly, 80 mg of sodium borohydride was transferred to a small flask; then 1 mL of ultrapure water was added. After 127.5 mg of tellurium powder was added in the flask, the reacting system was cooled by ice. A small outlet connected to the flask was kept open to discharge the pressure from the resulting hydrogen during the reaction. Generally in 3-5 h, the black tellurium powder disappeared and sodium tetraborate white precipitation appeared on the bottom of the flask instead. The resulting NaHTe in supernatant was separated for the preparation of CdTe particles.

3. Synthesis of water-soluble MPA-CdTe QDs

An aqueous colloidal MPA-CdTe QDs solution was prepared using the reaction between Cd^{2+} and NaHTe solution according to the literature.[S1] Cd^{2+} precursor solutions were prepared by mixing the solutions of $CdCl_2{\cdot}2.5H_2O$ and stabilizer (MPA), followed by pH adjustment to 11 with 1 M NaOH. The typical molar ratio of Cd : MPA : Te was kept as 1:1.2:0.2 in our experiment. This solution was placed in a three-necked flask, fitted and de-aerated with N_2 bubbling for 30 min. The resulting solution was then heated to 99-100°C and refluxed in different reaction time to control the size of MPA-CdTe QDs. Aliquots of the reaction solution were taken out at regular intervals for UV-vis absorption and luminescent characterization.

4. The size and extinction coefficient (ε) of MPA-CdTe QDs.

According to the work of Peng and coworkers,[S2] the diameter (**D**) and extinction coefficient (**ε**) of the MPA-CdTe QDs can be determined by the equations as follows:

$$\boxed{D=(9.8127\times10^{-7})\lambda^{3}-(1.7147\times10^{-3})\lambda^{2}+1.0064\lambda-194.84} \qquad (1)$$

$$\boxed{\varepsilon=10043(D)^{2.12}} \qquad (2)$$

wherein **D** (nm) is the diameter or size of a given nanocrystals sample, **λ** is the wavelength of the first absorption peak (from low energy) of the corresponding sample and **ε** is the extinction coefficient of the corresponding sample. In our experiments, the diameter (**D**) of the MPA-CdTe

QDs was determined as 3.4 nm and the extinction coefficient **ε** was 1.37×10^{5} ($L\cdot mol^{-1}\cdot cm^{-1}$) according to equation (1) and (2) respectively. The concentration the MPA-CdTe QDs was determined as 1.2×10^{-6} M (0.2 $mg\cdot mL^{-1}$) using the Beer–Lambert law.

5. Characterization of the MPA-CdTe QDs and "artificial catalyst"

UV-vis absorption spectra were recorded with a Shimadzu 1601PC spectrophotometer. Photoluminescence (PL) measurements were performed using a Hitachi 4500 fluorescence spectrophotometer. All optical measurements were performed under ambient conditions. The UV-vis diffuse reflectance spectra (UV-Vis-DRS) were recorded by Cary 5000 UV-visible-NIR spectrophotometer employed with a lab-sphere diffuse reflectance accessory in the range 200-800 nm. High-resolution transmission electron microscopy (HRTEM) was performed by JEM 2100F (operated at an accelerating voltage of 200 kV). X-ray powder diffraction (XRD) spectra were taken on a Bruker D8 Focus under Cu-$K\alpha$ radiation at (λ = 1.54056 Å). All pH measurements were made with a Model pHS-3C meter (Mettler Toledo FE20, China). Gas chromatography (GC) was performed with TIAN MEI 7890 II gas chromatograph using a 5 Å molecular sieve column and a thermal conductivity detector. The composition of Co-doped CdTe hollow nanospheres was determined by inductively coupled plasma mass spectroscopy (ICP, Varian 710-ES, USA).

6. Stern-Volmer equation

The luminescence quenching of the MPA-CdTe QDs was described by the Stern-Volmer equation (3),

$$\frac{I_0}{I}=\frac{\tau_0}{\tau}=1+k_q\tau_0C \qquad (3)$$

where I_0 and I are the luminescence intensity of the MPA-CdTe QDs in the absence and presence of $CoCl_2\cdot6H_2O$ in water; τ_0 and τ are the luminescence lifetime of the MPA-CdTe QDs in the absence and presence of $CoCl_2\cdot6H_2O$; k_q is the Stern-Volmer quenching constant and C is the concentration of $CoCl_2\cdot6H_2O$; k_q was subsequently determined as 2.1×10^{11} $mol^{-1}\cdot s^{-1}$ (see Figure S6c).

7. Langmuir binding isotherm

Chen and Rosenzweig[S3] suggested the following relationship (equation 4) between luminescence intensity and the concentration of quencher,

$$\frac{C}{I}=\left(\frac{1}{BI_0}\right)+\left(\frac{1}{I_0}\right)C \qquad (4)$$

Where I_0 and I are the luminescence intensity in the absence and presence of quencher, respectively; *C* is the concentration of quencher, and *B* is the binding constant (see Figure S6d).

8. General procedure for photocatalytic H_2 evolution

Aqueous colloidal MPA-CdTe solution (4.8×10^{-7} M, 0.8 mg/10 mL), ascorbic acid (H_2A, 2.84×10^{-2} M, 50 mg/10 mL), and $CoCl_2 \cdot 6H_2O$ (2.1×10^{-4} M, 0.5 mg/10 mL) were added to a Pyrex tube. The total volume of every sample was 10 mL. Prior to irradiation, the pH value of the solution was adjusted by the aqueous 1.0 M NaOH or 1.0 M HCl solution and determined by a pH meter. The sample was deaerated by bubbling nitrogen for 30 min. Then CH_4 (500 μL to ensure enough CH_4 was extracted from the samples in all H_2 evolution experiments) was injected as the internal standard for quantitative GC analysis. The sample was then irradiated under a high-pressure Hanovia mercury lamp (500 W) with light wavelength longer than 400 nm. The amount of photo-generated H_2 was characterized by GC analysis (TIAN MEI 7890-II) using nitrogen as the carrier gas with a molecular sieve column (5 Å) and a thermal conductivity detector. 500 μL of mixed gas was extracted from the sample tube and injected into the gas chromatograph immediately. The response factor for H_2/CH_4 was about 4.86 under the experimental conditions, which was established by calibration with known amounts of H_2 and CH_4, and determined before and after a series of measurements. The desired concentration of the reaction system was achieved by dissolving different amount of H_2A, MPA-CdTe QDs and $CoCl_2 \cdot 6H_2O$ into 10 mL of the mixed aqueous solution.

9. Figure S1

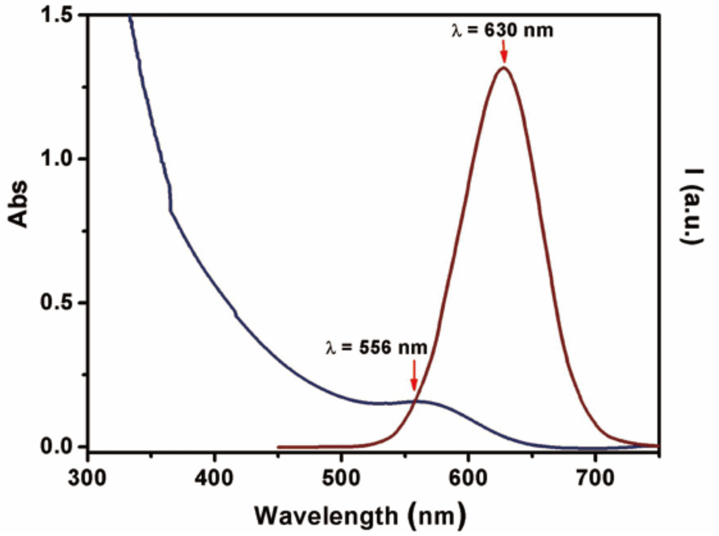

Figure S1. UV-vis absorption and luminescent spectra of MPA-CdTe QDs (0.2 mg·mL^{-1}, 1.2 × 10^{-6} M) in water (excitation wavelength: 406 nm).

10. Figure S2

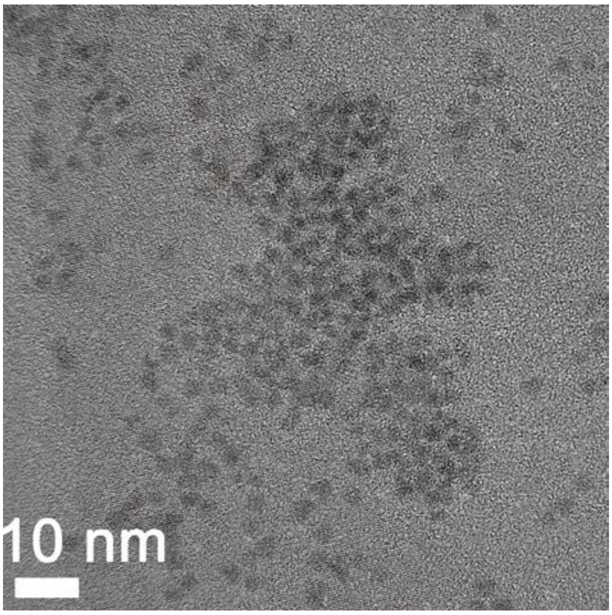

Figure S2. High-resolution transmission electron microscopy of MPA-CdTe QDs

11. Figure S3

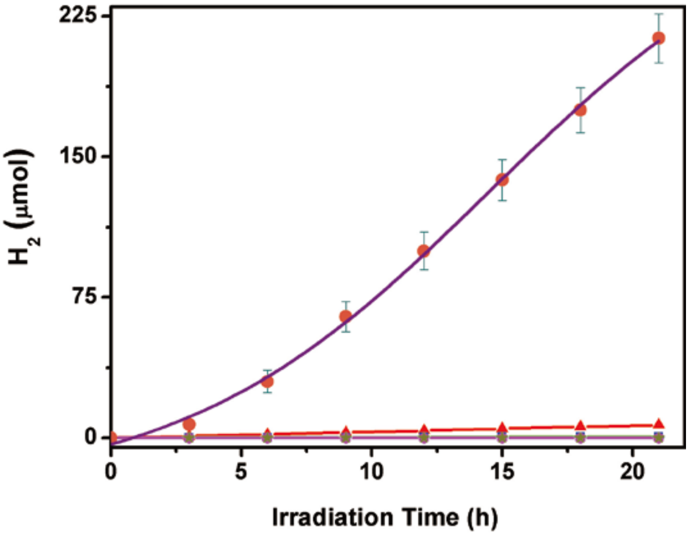

Figure S3 Photocatalytic H_2 evolution in 10 mL aqueous solution (pH = 4.65) with visible light irradiation for 21 h (λ > 400 nm). Reaction condition: $CoCl_2 \cdot 6H_2O$ (2.1×10^{-4} M, 0.5 mg/10 mL), MPA-CdTe QDs (4.8×10^{-7} M, 8.0×10^{-2} mg·mL^{-1}, 0.8 mg/10 mL), and H_2A (2.84×10^{-2} M, 50 mg/10 mL) (circle); control experiments were operated at the same concentration and condition with one component absent or replaced; (triangle: the sample without $CoCl_2 \cdot 6H_2O$; cubic: the sample without the MPA-CdTe QDs; pentagon: the sample without H_2A; hexagon: the sample without light irradiation; star: the sample with the commercial CdTe powder for replacement of MPA-CdTe QDs). Error bars represent mean ± s.d. of three independent experiments.

12. Figure S4

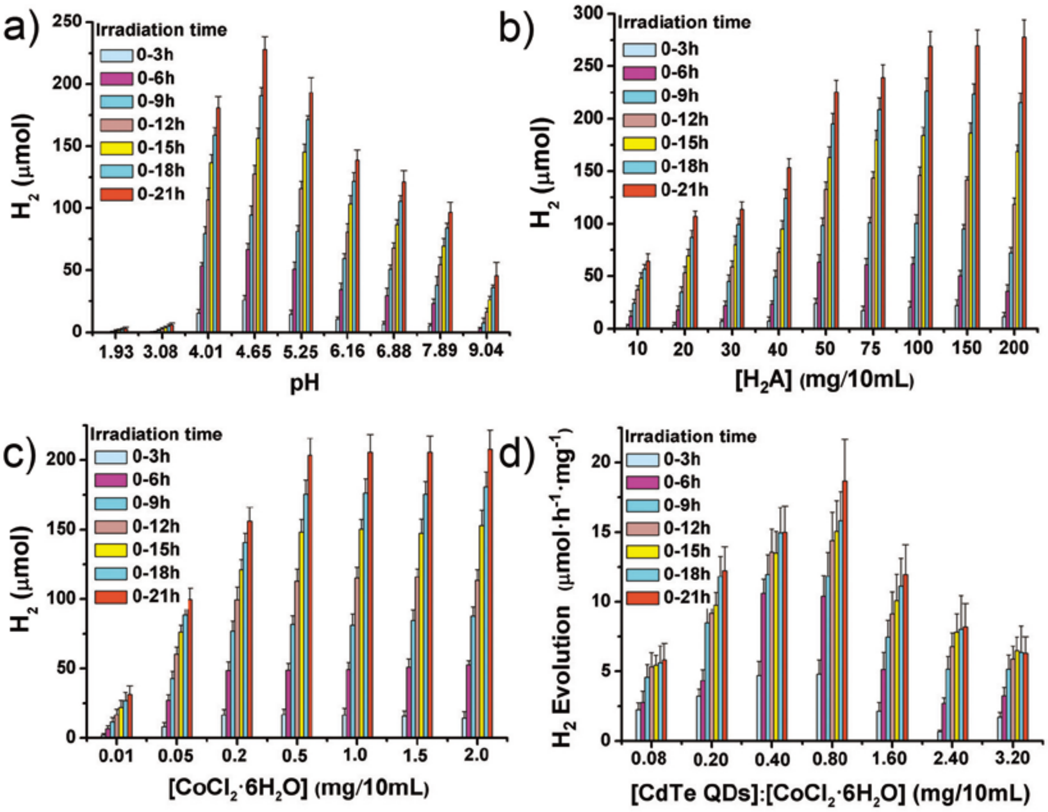

Figure S4. Optimization of experimental conditionsfor the photocatalytic H_2 evolution ($\lambda > 400$ nm) in an aqueous solution; the parameters of each factors are fixed as follows excepted for the one to be studied: $CoCl_2{\cdot}6H_2O$ (2.1×10^{-4} M, 0.5 mg/10 mL), MPA-CdTe QDs (4.8×10^{-7} M, 8.0×10^{-2} mg·mL^{-1}, 0.8 mg/10 mL), H_2A (2.84×10^{-2} M, 50 mg/10 mL), and pH = 4.65. (a) pH effect; (b) concentration effect of H_2A; (c) concentration effect of $CoCl_2{\cdot}6H_2O$; (d) concentration effect of the MPA-CdTe QDs. Error bars represent mean ± s.d. of three independent experiments.

13. Figure S5

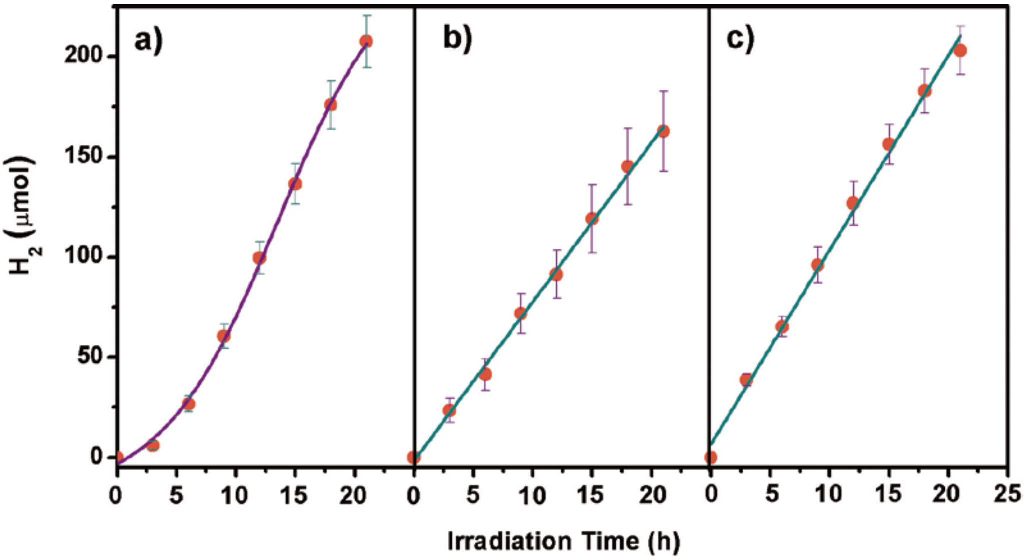

Figure S5. Photocatalytic performance of Co_h-CdTe hollow nanospheres under visible light irradiation (λ > 400 nm): (a) H_2 evolution from the 10 mL aqueous system, containing $CoCl_2 \cdot 6H_2O$ (2.1×10^{-4} M, 0.5 mg/10 mL), the MPA-CdTe QDs (2.4×10^{-7} M, 4.0×10^{-2} mg·mL^{-1}, 0.4 mg/10 mL), and H_2A (1.14×10^{-1} M, 200 mg/10 mL) at pH = 4.65. (b) H_2 production using Co_h-CdTe hollow nanospheres formed from system (a) in 10 mL of 1.14×10^{-1} M (200 mg/10 mL) H_2A aqueous solution at pH = 4.65. (c) H_2 production using Co_h-CdTe hollow nanospheres formed from system (a) in 10 mL aqueous solution at pH = 4.65; the aqueous solution containing 1.14×10^{-1} M (200 mg/10 mL) H_2A and $CoCl_2 \cdot 6H_2O$ (2.1×10^{-4} M, 0.5 mg/10 mL). Error bars represent mean ± s.d. of three independent experiments.

14. Figure S6

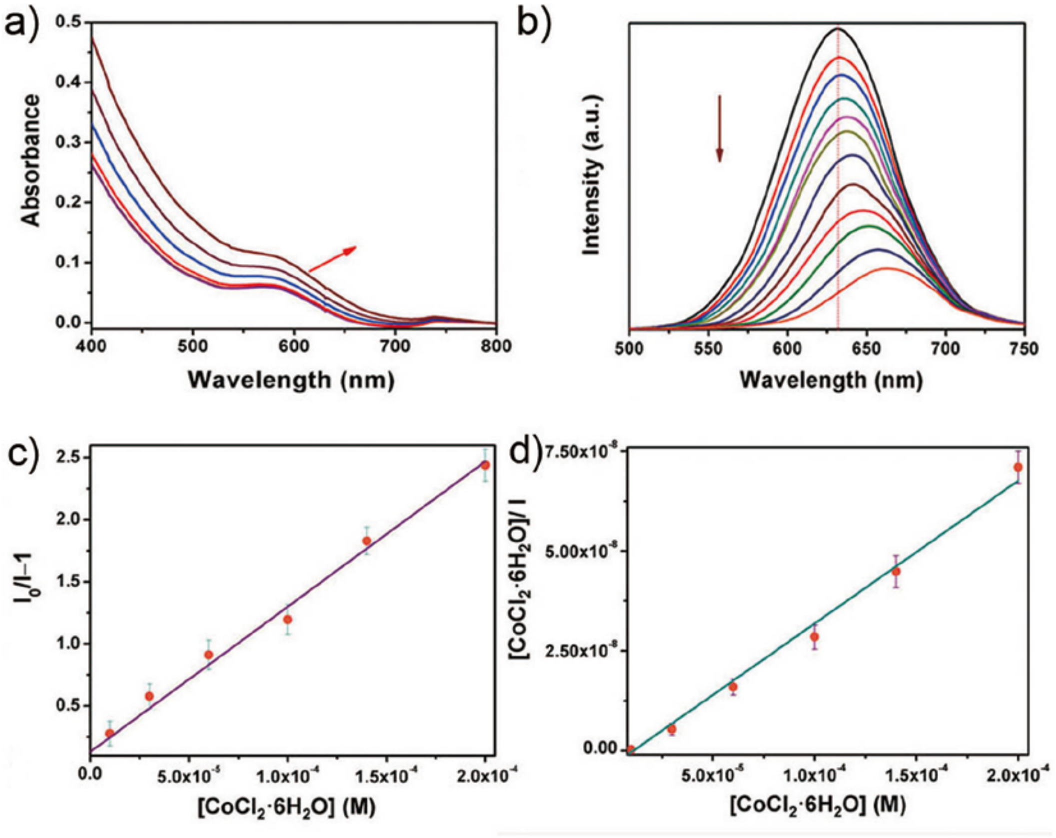

Figure S6. Spectroscopic properties: (a) UV-vis absorption spectra of MPA-CdTe QDs (4.8×10^{-7} M, 8.0×10^{-2} mg·mL^{-1}) with different concentration of $CoCl_2 \cdot 6H_2O$ (0 to 3.2×10^{-4} M) in water; (b) the luminescence spectra of MPA-CdTe QDs (4.8×10^{-7} M, 8.0×10^{-2} mg·•mL^{-1}) with different concentration of $CoCl_2 \cdot 6H_2O$ (0 to 2.6×10^{-4} M) in water (excitation wavelength: 406 nm); (c) Stern-Volmer plot for the luminescence quenching of MPA-CdTe QDs with $CoCl_2 \cdot 6H_2O$ in water; (d) Langmuir binding isotherm description of MPA-CdTe QDs with $CoCl_2 \cdot 6H_2O$ in water. Error bars represent mean ± s.d. of three independent experiments.

15. Figure S7

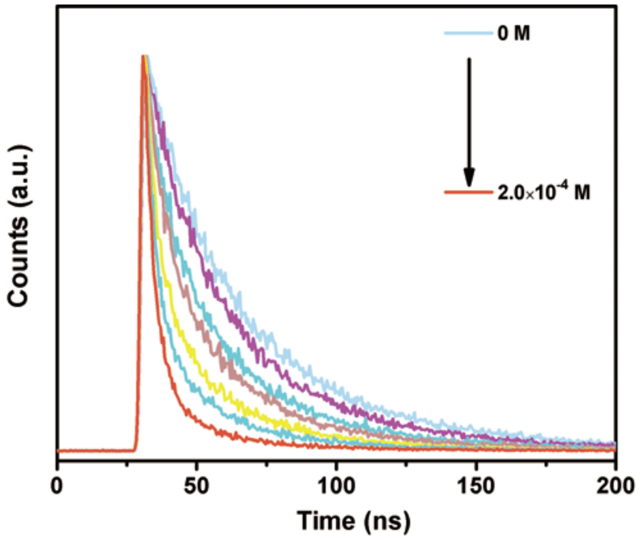

Figure S7. The luminescence decays (630-665 nm) of MPA-CdTe QDs (4.8 × 10^{-7} M, 8.0 × 10^{-2} mg·mL^{-1}) with various concentrations of $CoCl_2·6H_2O$ (0 to 2.0 × 10^{-4} M) in water (excitation wavelength: 406 nm).

16. References

(S1) Zhang, H.; Zhou, Z.; Yang, B.; Gao, M. *J. Phys. Chem. B* **2002**, *107*, 8.

(S2) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854.

(S3) Chen, Y.; Rosenzweig, Z. *Anal. Chem.* **2002**, *74*, 5132.