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Electronic Supplementary Material

A Cocatalyst-Free Eosin Y-Sensitized P-type Co_3O_4 Quantum Dots for Highly Efficient and Stable Visible-Light-Driven Water Reduction and Hydrogen Production†

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Experimental Section

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Fig. S4 TEM and HRTEM images of (a) Co_3O_4 QDs and (b) Co_3O_4 QDs/EY.

Fig. S5 FTIR spectra of Eosin Y, Co_3O_4 QDs/EY, dodecanol and Co_3O_4 QDs. (C: Co_3O_4, D: dodecanol, E: EY) .

Fig. S6 Comparison of the PL decay curves for Eosin Y, Co_3O_4 QDs/EY.

Experimental Section

Materials: The reagents, including dodecanol, n-butanol, ethanol, cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Eosin Y, triethanolamine (TEOA), hydrochloric acid (HCl) and sodium hydroxide (NaOH), were commercially available (Sinopharm Chemical Reagent Co., Ltd., analytical grade) and used without further purification. P25 TiO_2 was purchased from Degussa Pacific Ltd. (Shanghai Office) and used without further purification.

Synthesis of the photocatalysts: Co_3O_4 QDs were prepared via a facile reverse micelle method with microwave-assisted solvothermal process according to ref[1]. As-prepared Co_3O_4 QDs were washed with ethanol in an ultrasonic bath and separated out by centrifugation for three cycles and then dried in vacuum at 80^oC for 3 h. The mechanism of coating process of EY on Co_3O_4 QDs is illustrated in Fig. S1. Because the surface of the solid product was coated by a little dodecanol, the solid product performed hydrophobic. To remove dodecanol and coat EY on the surface of Co_3O_4 QDs, 5 mg solid product was mixed into 100 mL EY/TEOA/water solution under vigorous stirring and then ultrasonic dispersed for 30 min. In this process, dodecanol molecules coating on the surface of QDs would be replaced by EY molecules. After that, a separatory funnel was used to remove dodecanol floating on the top of solution, and the remained liquid was our liquid product which was used for photocatalysis directly. For comparison, Co_3O_4 QDs and commercial P25 TiO_2 with the weight of 5 mg were dispersed in EY/water solution and EY/TEOA/water solution according to the same method above, respectively, which was all used for photocatalysis directly.

Characterization of samples: Crystal structures and phase composition of the samples were determined by using a powder X-ray diffractometer (X'Pert PRO MPD, PANalytical, the Netherlands) with (θ/2θ) Bragg–Brentano geometry. The powder X-ray diffraction (PXRD) patterns were collected in the range $2\theta=20–70^o$ (40 kV, 40 mA; Cu Kα radiation, $\lambda=1.541874$Å; Ni filter; realtime multiple strip (RTMS) detector, X'Celerator). Before PXRD test, the EY-sensitized Co_3O_4 QDs sample was washed using water and dried at 80°C in vacuum (this sample was also used for X-ray photoelectron spectroscopy and transmission electron microscopy). Surface chemical components and states of the products were studied using an X-ray photoelectron spectrometer (AXIS Ultra DLD, Shimadzu/Kratos Analytical, Japan) with monochromatic Al Kα radiation (150 W, 15 kV, 1486.6 eV) and with pressure under high vacuum ($< 3\times10^{-9}$ Torr). Binding energies of X-ray photoelectron spectroscopy (XPS) were calibrated relative to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of samples. Particle size and morphology were confirmed by a transmission electron microscope that was operated at 300 kV (Tecnai G2 F30, FEI, USA). Samples for transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were ultrasonically dispersed in water, and then, by dipping and drying process, were deposited on copper grids, which were coated with holey or lacey amorphous carbon support films. The microstructures of samples were investigated by using a Fourier transform infrared spectrometer (FTIR: Vextex 70, Bruker, Germany) under transmittance mode. UV-Vis spectra of the photocatalysts were measured on a spectrophotometer (UV4100, HITACHI, Japan) employing a labsphere diffuse reflectance accessory. The analysis of photoluminescence (PL) spectra were carried out at room temperature using a fluorescence spectrophotometer (QuantaMaster 40, PTI, Canada). The excitation wavelength was 420 nm.

Evaluation of photocatalytic activities: The photocatalytic hydrogen production experiments were performed in a 130 mL Pyrex glass cell, which had a flat, round side-window for external light incidence. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Technology Co., Ltd, China) with a UV cut-off filter ($\lambda \geq 420$ nm) was used as the light source. Temperature of the system during photocatalytic reaction was maintained by thermostatic circulating water at around 30°C. Hydrogen gas was detected with a gas chromatograph (GC, SP-2100, Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd, China), which was equipped with a thermal conductivity detector (TCD), TDX-01 column, and Ar carrier gas. The average intensity of incident light was measured with a spectroradiometer (AvaSpec-2048-USB2, Avantes, Netherland) and equal to 300 mW cm^{-2}, and the irradiated area was 3.14 cm^2. The reaction solution was prepared by the method above. The pH values of the reaction solution were adjusted by addition of 1 M HCl or NaOH. Before each experiment, the suspension was purged with nitrogen for 15 min to remove air.

The method for measuring apparent quantum yield (A.Q.Y.) was the same as those described in ref[2]. The A.Q.Y. was calculated with the following equation.

$$\begin{aligned} \text{A.Q.Y.}(\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved } \mathrm{H_2} \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \end{aligned}$$

The conversion efficiency of solar energy to hydrogen energy was measured in air at room temperature and under 100 mW/cm^2 illumination in a solar simulator with an AM1.5 global filter. The conversion efficiency of solar energy to hydrogen energy was calculated with the following equation.

$$\eta_{\mathrm{c}} = \frac{\Delta G^0_{H_2} R_{H_2}}{w_s A} \times 100\%$$

Where η_c is the conversion efficiency of solar energy to hydrogen energy, $\Delta G^0_{H_2}$ is the Gibbs free energy of hydrogen, which equal to 237.20 kJ/mol in standard condition, R_{H_2} is the rate of H_2 production, w_s is the irradiation intensity of incoming light, and A is the irradiation area.

Electrochemical Measurements: Electrochemical measurements were carried out on a potentiostat (273A, Princeton Applied Research Company, USA) in a three electrodes cell system with a large area platinum plate as counter electrode and a Ag/AgCl electrode as reference electrode. The films as work electrodes were prepared by the drying and calcination method. A clean FTO was put into a beaker contained colloidal solution of Co_3O_4 QDs or TiO_2, and then solvent was dried at 80^{o}C in air. The as-prepared Co_3O_4 QDs or TiO_2-coated FTO was calcined at 400^{o}C for 5 min, and then used for electrochemical measurements. An aqueous solution of 0.1 M Na_2SO_4 was used as electrolyte. The area of the work electrodes was fixed at 0.785 cm^2.

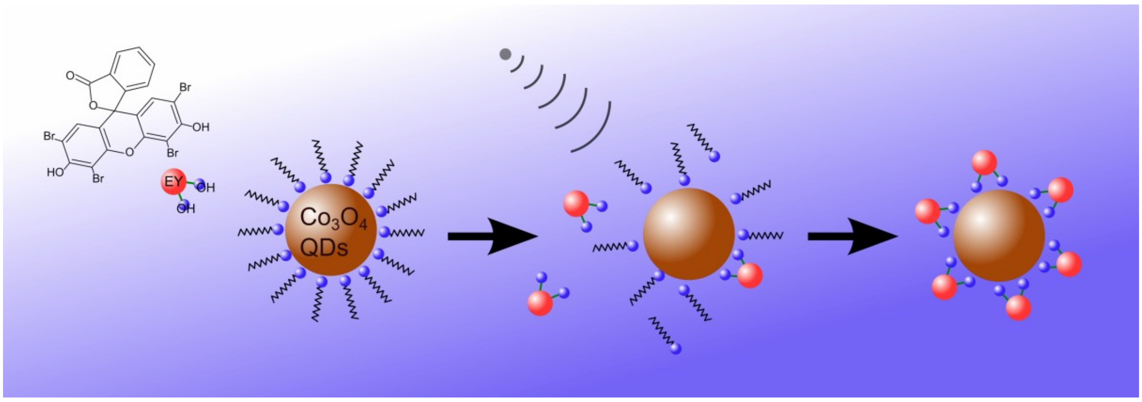


Fig. S1 The process of EY sensitization.

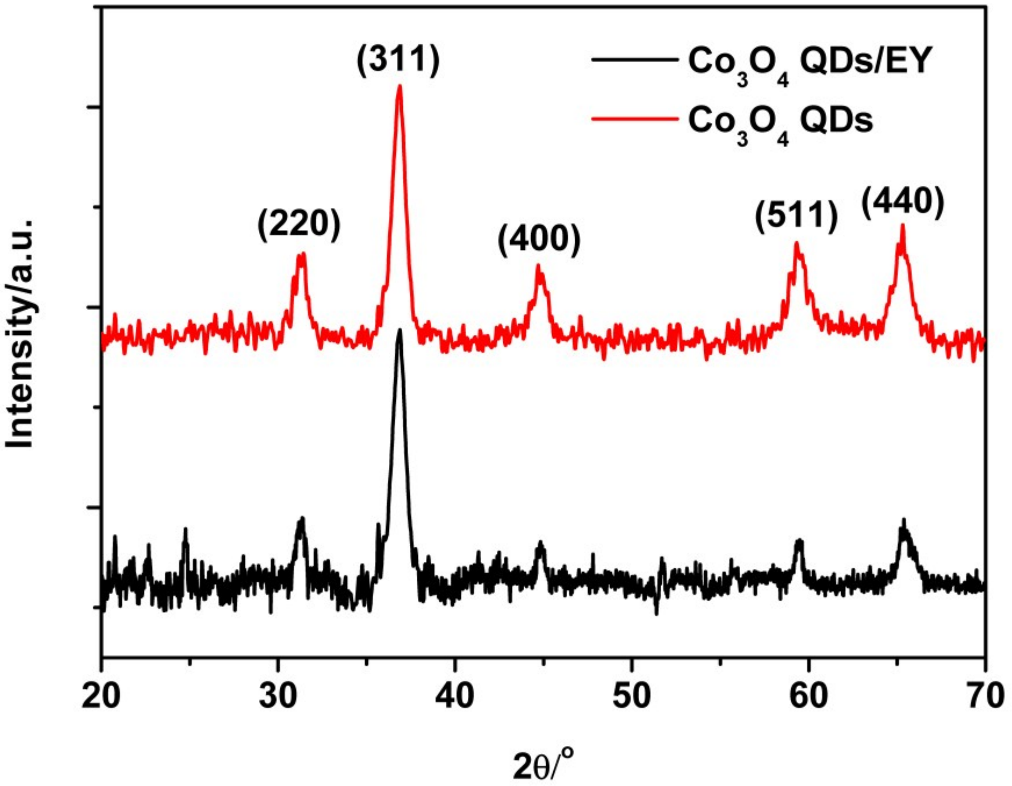
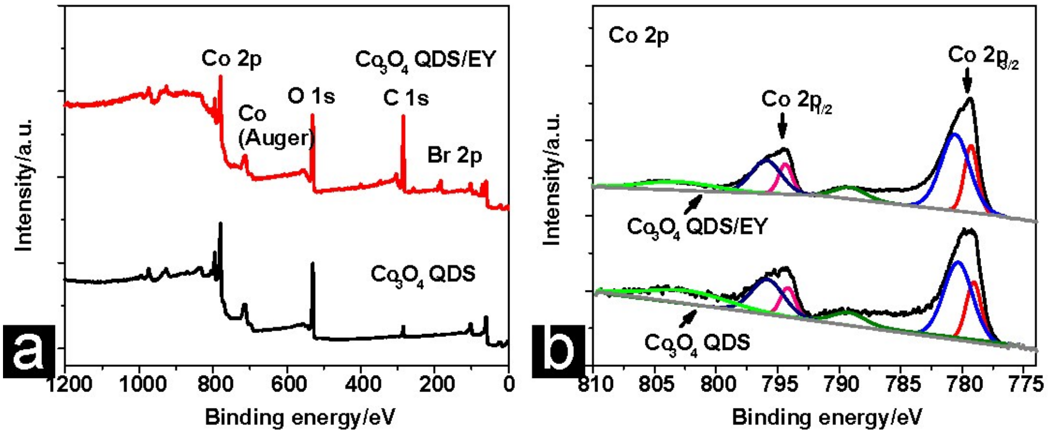


Fig. S2 PXRD spectra of Co_3O_4 QDs/EY and Co_3O_4 QDs.



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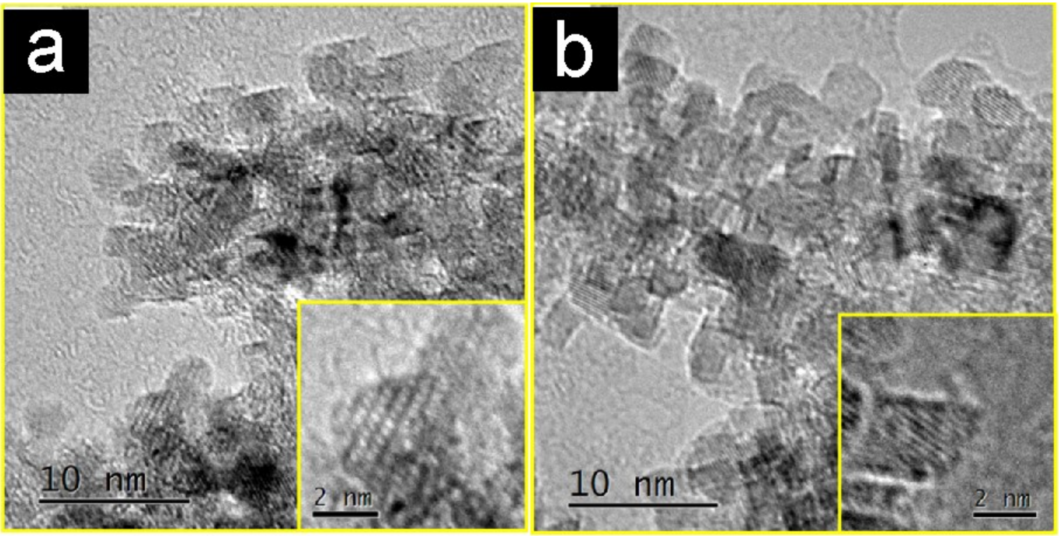

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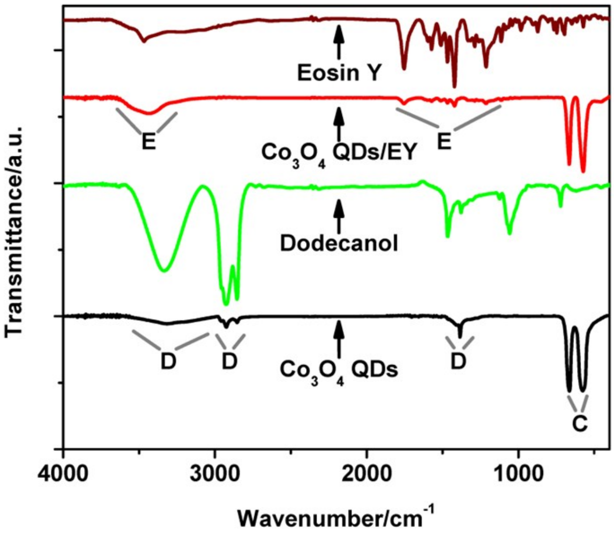

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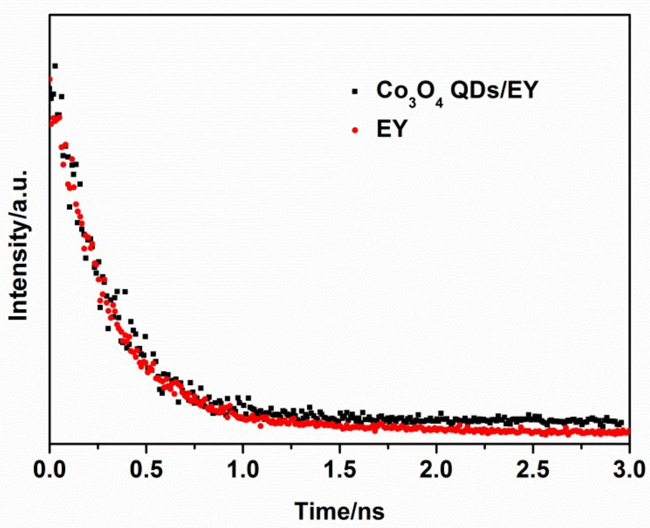

Fig. S6 Comparison of the PL decay curves for Eosin Y, Co_3O_4 QDs/EY.
Excitation wavelength was 337 nm. Test conditions: pH and the concentration of TEOA and EY in each system were 10.95, 0.29 M and 0.01 mM, respectively. The weight concentration of Co_3O_4 QDs was 0.01 mg mL^{-1} in Co_3O_4 QDs/EY system.

Notes and references

1. N. Zhang, J. Shi, S. S. Mao and L. Guo, *Chem. Commun.*, 2014, **50**, 2002-2004.
2. D. Jing and L. Guo, *Journal of Physical Chemistry B*, 2006, **110**, 11139-11145.