Supporting Information

Enhanced Photocatalytic Hydrogen Production in Water under Visible Light Using Noble-Metal-Free Ferrous Phosphide as an Active Cocatalyst

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Experimental details

Materials. All the chemicals, including cadmium chloride hemipentahydrate ($CdCl_2 \cdot 2.5H_2O$, 99.0%), thiourea (NH_2CSNH_2, 99.0%), ethylenediamine ($C_2H_4(NH_2)_2$, 99.0%), iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.0%), sodium sulfate (Na_2SO_4, 99.0%), sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, 98.0%), and ascorbic acid (AA, 99.7%), were obtained from Aldrich or Acros and used without further purification.

Preparation of the CdS NRs: CdS NRs were synthesized according to the reported literature described elsewhere.[1-2]

Preparation of Fe_2P: 0.8 g $FeCl_3 \cdot 6H_2O$ and 0.48 g Na_2SO_4 were dissolved in 70 mL distilled water and the solution was then transferred to a 100 mL Teflon-lined, stainless-steel autoclave, which was maintained at 120 ºC for 6 h. After cooling down to room temperature, the as-synthesized material in the autoclave was collected and washed by absolute ethanol and distilled water five times each and dried under vacuum at room temperature overnight. After that, 0.3 g as-synthesized material and 3.0 g $NaH_2PO_2 \cdot H_2O$ were mixed together and annealed at 300 ºC for 2 h in Ar flow to obtain the final Fe_2P sample.

Preparation of the Fe_2P/CdS NRs photocatalyst: the Fe_2P and CdS NRs were mixed by grinding and then annealed at 200 ºC for 2 h in Ar flow. The weight ratio of Fe_2P in Fe_2P/CdS NRs is 2%, 5%, 10%, 20%, 30%, 50%, 80%.

Characterization. The powder X-ray diffraction (XRD) was measured by X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu Kα radiation

of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min^{-1} in 2θ. The scanning electron microscopy (SEM) measurements were conducted using a JSM-6700F. High-resolution transmission electron microscopy (HRTEM) images and energy-dispersive X-ray analysis (EDX) were obtained with a JEM-2010 electron microscope equipped with a Rontec EDX system. The UV-Vis absorption was performed on a SOLID 3700 UV-Vis-NIR spectrophotometer. The photoluminescence (PL) spectra for solid samples were investigated through JY Fluorolog-3-Tou.

Photoelectrochemical Measurements. Photocurrent measurements were performed on a CHI 602E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode with the photocatalyst-coated FTO as the working electrode, an Ag/AgCl as a reference electrode, and Pt wire as the counter electrode. 300 W Xenon lamp with a UV cut-off filter (λ > 420 nm) was used as the light source. A 0.5 M Na_2SO_4 solution was used as the electrolyte. The working electrodes were prepared by dropping a suspension (20 μL) made of Fe_2P/CdS and CdS (the concentration of Fe_2P/CdS and CdS being 20 mg/mL) onto the surface of a FTO plate. The working electrodes were dried at room temperature. The photoresponses of the samples as light on and off were measured at 0.0 V.

Photocatalytic hydrogen evolution. The photocatalytic hydrogen evolution experiments were carried out in a 50 mL flask with stirring at ambient temperature. A 300 W Xenon arc lamp through a UV cut-off filter (λ> 420 nm), which was positioned at 15 cm away from the reactor, was used as a visible light source for the photocatalytic reaction. The total intensity on the flask was *ca.* 1400 mw. 1.0 mg of the photocatalyst

was dispersed in 20 mL of aqueous solution containing 0.5 M ascorbic acid as sacrificial reagents, and pH adjust to 4.2 by NaOH. And then the suspension was stirred and purged with nitrogen for 30 min to remove air. Then, 5 mL of nitrogen was removed from the flask, followed by injecting 5 mL of methane (760 Torr) to serve as the internal standard. Hydrogen gas was measured by gas chromatography (SP-6890, nitrogen as a carrier gas) using a thermal conductivity detector (TCD). For each evaluation of hydrogen generation, 100 μL of the headspace was injected into the GC and was quantified by a calibration plot to the internal CH_4 standard.[3] The hydrogen evolution rate was calculated based on the Fe_2P/CdS NRs photocatalyst.

Apparent quantum yields (*A.Q.Y.*, ϕ) defined by the following equation were measured using a 450 nm (± 5 nm) band-pass filter and an irradiatometer:

$$A.Q.Y.(\%) = \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\%$$

$$= \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100\%$$

References

(1) Jang, J. S.; Joshi, U. A.; Lee, J. S. *J. Phys. Chem. C* **2007**, *111*, 13280-13287.

(2) Sun, Z.; Yue, Q.; Li, J.; Xu, J.; Zheng, H.; Du, P. *J. Mater. Chem. A* **2015**, *3*, 10243-10247.

(3) Du, P., J.; Jarosz, P.; Zhang, J.; Brennessel, W. W.; Eisenberg, R. *J. Phys. Chem. B*. **2007**, *111*, 6887-6894.

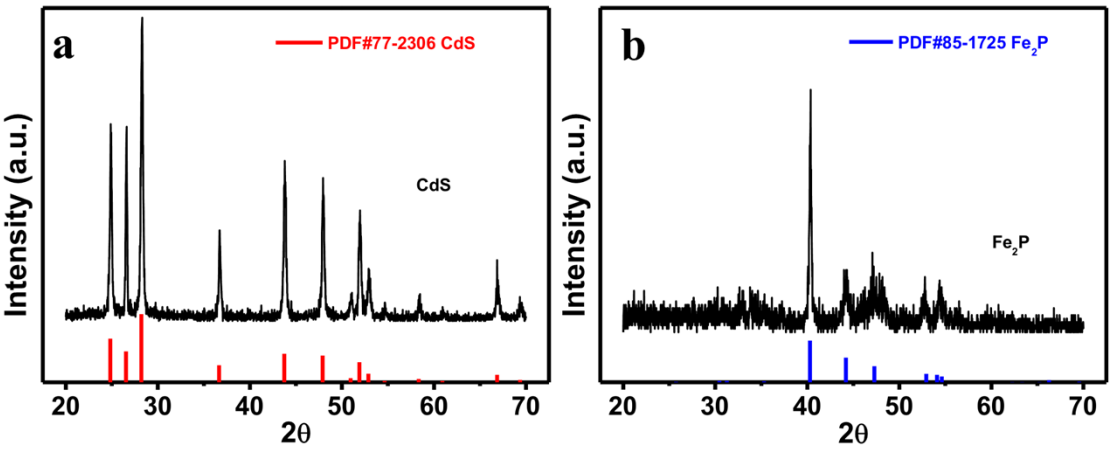

Figure S1. Powder XRD patterns of **(a)** CdS and **(b)** Fe_2P.

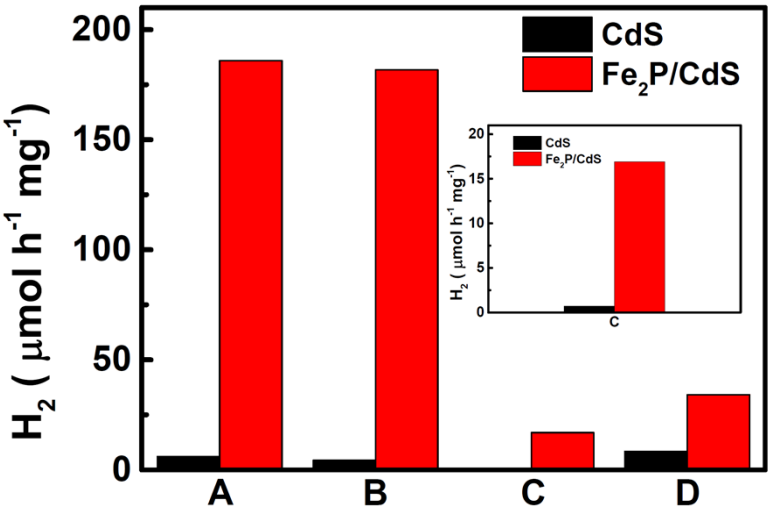

Figure S2. Photocatalytic H_2 production rate of CdS and 30 wt% Fe_2P/CdS in the presence of different electron donors: (A) 0.5 M ascorbic acid, pH=4.2; (B) 10% lactic acid; (C) 10% TEOA; (D) 0.25 M Na_2S/0.35 M Na_2SO_3.

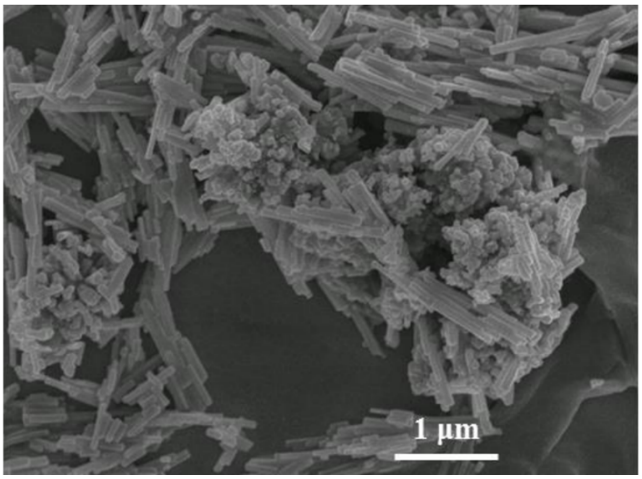

Figure S3. SEM image of Fe_2P/CdS (30 wt%) after photocatalytic H_2 production.