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 (CdCl₂·2.5H₂O, 99.0%), thiourea (NH₂CSNH₂, 99.0%), ethylenediamine (C₂H₄(NH₂)₂, 99.0%), iron chloride hexahydrate (FeCl₃·6H₂O, 99.0%), sodium sulfate (Na₂SO₄, 99.0%), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, 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 Fe₂P: 0.8 g FeCl₃·6H₂O and 0.48 g Na₂SO₄ 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 °C 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 NaH₂PO₂·H₂O were mixed together and annealed at 300 °C for 2 h in Ar flow to obtain the final Fe₂P sample.

Preparation of the Fe₂P/CdS NRs photocatalyst: the Fe₂P and CdS NRs were mixed by grinding and then annealed at 200 °C for 2 h in Ar flow. The weight ratio of Fe₂P in Fe₂P/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 Na₂SO₄ solution was used as the electrolyte. The working electrodes were prepared by dropping a suspension (20 μL) made of Fe₃P/CdS and CdS (the concentration of Fe₂P/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 CH₄ standard.³ The hydrogen evolution rate was calculated based on the Fe₂P/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:

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A.Q.Y. (\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% = \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%
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References

Figure S1. Powder XRD patterns of (a) CdS and (b) Fe$_2$P.
Figure S2. Photocatalytic H$_2$ production rate of CdS and 30 wt% Fe$_2$P/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$_2$S/0.35 M Na$_2$SO$_3$. 
**Figure S3.** SEM image of Fe$_2$P/CdS (30 wt%) after photocatalytic H$_2$ production.