

*Supporting Information*

**Copper Phosphide Modified Cadmium Sulfide Nanorods for  
Highly Efficient Visible-Light-Driven Hydrogen Production  
in Water**

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## Experimental details

**Materials.** All the chemicals, including copper chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), cadmium chloride hemipentahydrate ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ), thiourea ( $\text{NH}_2\text{CSNH}_2$ ), ethylenediamine ( $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ), sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ), and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_3$ ), were obtained from Aldrich and used without further purification.

Preparation of the CdS NRs: CdS NRs were synthesized using a modified method according to the reported literature.<sup>1</sup> 20.25 mmol  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and 60.75 mmol  $\text{NH}_2\text{CSNH}_2$  were dispersed in 60 mL ethylenediamine and then transferred to a 100 mL Teflon-lined, stainless-steel autoclave, which was then maintained at 160 °C for more than 48 h and then cooled to room temperature. The yellow precipitates were collected and washed with absolute ethanol and distilled water three times each to remove the residues of organic solvent.

Preparation of the  $\text{Cu}_3\text{P}/\text{CdS}$  NRs and pure  $\text{Cu}_3\text{P}$ : To synthesize  $\text{Cu}_3\text{P}/\text{CdS}$  NRs, 50 mg CdS NRs, a calculated amount of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.2 mg, 0.4 mg, 0.8 mg, and 1.6 mg for four samples CP1 to CP4 respectively), and five-fold yellow phosphorus were dispersed in ethylenediamine under stirring. Subsequently, the mixture was transferred to a 50 mL Teflon-lined autoclave and was maintained at 140 °C for 12 h. After the autoclave was cooled to room temperature, the precipitates were collected and washed with benzene, ethanol, and distilled water three times each. The final products were dried in vacuum at 60 °C overnight. The weight percentages of  $\text{Cu}_3\text{P}$  were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). For comparison,

pure Cu<sub>3</sub>P was synthesized by a similar solvothermal method in the absence of CdS NRs.

**Characterization.** The powder X-ray diffraction (XRD) was measured by X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu K $\alpha$  radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min<sup>-1</sup> in 2 $\theta$ . Transmission electron microscopy (TEM) images and energy-dispersive X-ray analysis (EDX) were obtained with a JEM-2011 electron microscope equipped with a Rontec EDX system. The scanning electron microscopy (SEM) measurements were conducted using a JSM-6700F. The morphologies of the samples were also determined by a high-resolution transmission electron microscope (HR-TEM, JEM-2010) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data and the valence states of metal elements were obtained with an ESCALAB 250 instrument. The UV-vis absorption was performed on a SOLID 3700 UV-vis-NIR spectrophotometer. ICP-AES results were measured by an Optima 7300 DV. The photoluminescence (PL) spectra for solid samples were investigated through Acton Sp2500 (Princeton Instruments) with Liquid nitrogen cooled CCD.

**Photoelectrochemical measurements.** Photocurrent measurements were performed on a CHI 602E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system 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 ( $\lambda > 420$  nm) was used as the light source.

A 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte. The working electrodes were prepared by dropping a suspension (30 μL) made of Cu<sub>3</sub>P/CdS and CdS (Cu<sub>3</sub>P/CdS and CdS, 20 mg/mL) onto the surface of a FTO plate. The working electrodes were dried at room temperature. The photoresponsive signals of the samples were measured as light on and off at 0.0 V.

**Photocatalytic hydrogen evolution.** The reactor for photocatalytic hydrogen evolution reaction is shown in scheme S1.<sup>2</sup> Generally, the photocatalytic hydrogen evolution experiments were carried out in a flask with gentle stirring at ambient temperature using a 300 W Xe lamp equipped with a UV cut-off filter ( $\lambda > 420$  nm). Photocatalyst was dispersed in an aqueous solution containing Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagents, 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.<sup>2</sup> Hydrogen gas was measured by gas chromatography (SP-6890, nitrogen as a carrier gas) using a thermal conductivity detector (TCD). The amount of H<sub>2</sub> was quantified by a calibration plot to the internal CH<sub>4</sub> standard.<sup>3-5</sup> The hydrogen evolution rate was calculated based on the Cu<sub>3</sub>P/CdS NRs photocatalyst. To compare the photocatalytic activity of different Cu<sub>3</sub>P/CdS NRs samples with different amount of Cu<sub>3</sub>P, the hydrogen production reactions were carried out in a 20 mL aqueous solution containing 1 mg photocatalyst, 15 mmol Na<sub>2</sub>S (0.75 M), and 21 mmol Na<sub>2</sub>SO<sub>3</sub> (1.05 M). The sample of simply mixed Cu<sub>3</sub>P-CdS NRs (0.44 wt % Cu<sub>3</sub>P) was also used for comparison. The cycling experiment was carried out in a 20 mL aqueous solution of a 50 mL flask containing 1 mg CP2 photocatalyst, 25

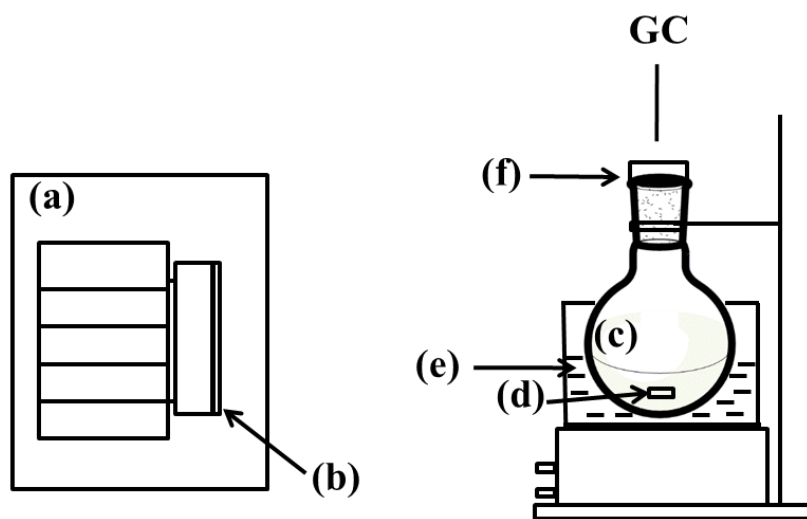
mmol Na<sub>2</sub>S (1.25 M), and 35 mmol Na<sub>2</sub>SO<sub>3</sub> (1.75 M). For long-term photocatalysis, a 250 mL flask was used instead, and 1 mg CP2 photocatalyst was dispersed in a 50 mL aqueous solution containing 62.5 mmol Na<sub>2</sub>S (1.25 M) and 87.5 mmol Na<sub>2</sub>SO<sub>3</sub> (1.75 M) as sacrificial reagents.

Apparent quantum yields (A.Q.Y.,  $\phi$ ) defined by the following equation were measured using a 450 nm ( $\pm 5$  nm) band-pass filter and an irradiatometer. The reaction was carried out in a 50 mL flask and 1 mg CP2 photocatalyst was dispersed in a 20 mL aqueous solution containing 25 mmol Na<sub>2</sub>S (1.25 M) and 35 mmol Na<sub>2</sub>SO<sub>3</sub> (1.75 M) as sacrificial reagents.

$$\begin{aligned} A. Q. Y. (\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\% \end{aligned}$$

## References

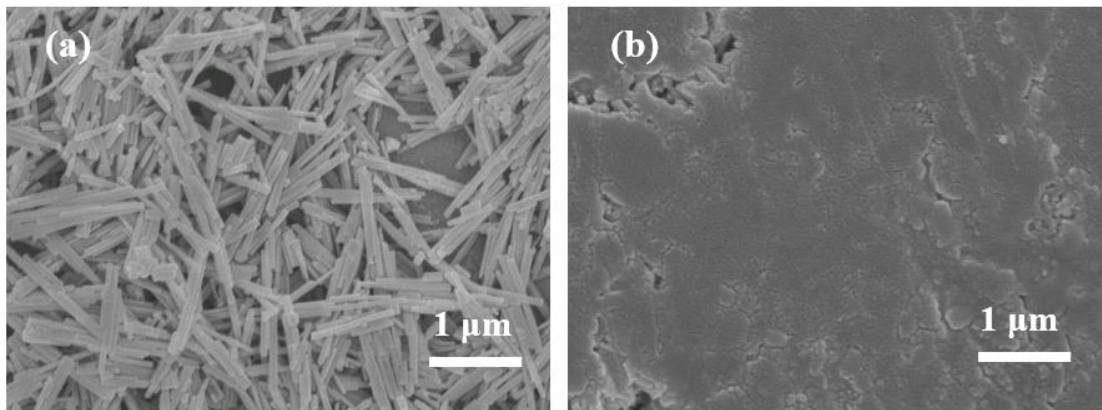
- (1) Jang, J. S.; Joshi, U. A.; Lee, J. S. *J. Phys. Chem. C* **2007**, *111*, 13280-13287.
- (2) Yan, Z. P.; Yu, X. X.; Han, A. L.; Xu, P.; Du, P. W. *J. Phys. Chem. C* **2014**, *118*, 22896-22903.
- (3) Du, P. W.; Knowles, K.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 12576-12577.
- (4) Han, Z. J.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. *Science* **2012**, *338*, 1321-1324.
- (5) Li, Z.-J.; Li, X.-B.; Wang, J.-J.; Yu, S.; Li, C.-B.; Tung, C.-H.; Wu, L.-Z. *Energy Environ. Sci.* **2013**, *6*, 465-469.



**Scheme S1.** Reactor of the present photocatalytic reaction system: (a) light source of 300 W Xe lamp; (b) UV cut off filter ( $\lambda > 420$  nm); (c) reaction solution; (d) magnetic stirring bar; (e) water jacket; (f) septum.

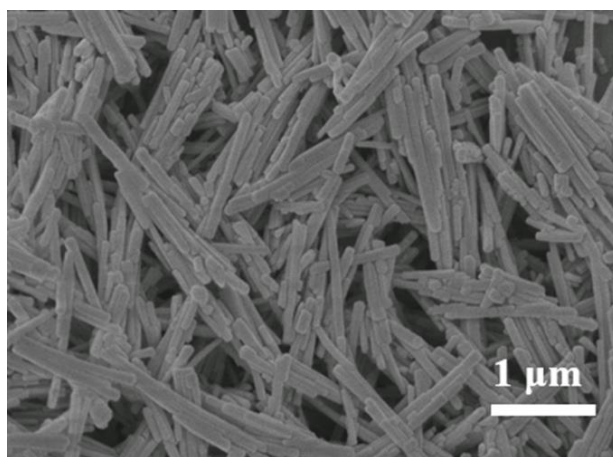
<b>Sample</b>	<b>Cu (wt%)/ ICP-AES data</b>	<b>Cu<sub>3</sub>P (wt%)/ Calculated based on Cu</b>
CP1	0.026	0.03
CP2	0.38	0.44
CP3	0.67	0.78
CP4	2.49	2.90

**Table S1.** Copper and Cu<sub>3</sub>P contents in Cu<sub>3</sub>P/CdS photocatalyst samples.



**Figure S1.** SEM images of (a) CdS NRs and (b) Cu<sub>3</sub>P.





**Figure S2.** SEM image of CP2 sample after photocatalytic H<sub>2</sub> production for 5 hours under visible light irradiation ( $\lambda >420$  nm). The reaction system contains 1 mg CP2 photocatalyst, 0.75 M Na<sub>2</sub>S, and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.