

***Supporting Information***

**Core-shell Amorphous Cobalt Phosphide/Cadmium Sulfide  
Semiconductor Nanorods for Exceptional Photocatalytic  
Hydrogen Production under Visible Light**

Zijun Sun,<sup>a</sup> Bihu Lv,<sup>b</sup> Jingshi Li,<sup>a</sup> Min Xiao,<sup>b</sup> Xiaoyong Wang,<sup>\*b</sup> and Pingwu Du<sup>\*a</sup>

<sup>a</sup> CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, and the Collaborative Innovation Center of Chemistry for Energy Materials (*iChEM*), University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui Province, 230026, P. R. China

<sup>b</sup> National Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing, Jiangsu Province, 210093, P. R. China

\*To whom correspondence should be addressed

E-mail: [dupingwu@ustc.edu.cn](mailto:dupingwu@ustc.edu.cn); [wxiaoyong@nju.edu.cn](mailto:wxiaoyong@nju.edu.cn)

Tel/Fax: 86-551-63606207

## Materials and Methods

**Materials.** All the chemicals, including cadmium chloride hemipentahydrate ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ), thiourea ( $\text{NH}_2\text{CSNH}_2$ ), ethylenediamine ( $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ), cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 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 fabricated by a modified solvothermal method.<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 later maintained at 160 °C for 48 h and then allowed to cool down to room temperature. The yellow precipitate was collected and washed with ethanol and distilled water three times each to remove the residue of any organic solvent.

Preparation of core-shell  $\text{CoP}_x/\text{CdS}$  NRs photocatalyst and pure  $\text{CoP}_x$ : To synthesize core-shell  $\text{CoP}_x/\text{CdS}$  NRs, 200 mg CdS NRs, a specified amount of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (4 mg, 16 mg, 32 mg, 64 mg, and 108 mg for five samples SC1 to SC5 respectively), and five-fold yellow phosphorus were dispersed in ethylenediamine under stirring and ultrasonication. Subsequently, the mixture was transferred to a 50 mL Teflon-lined stainless autoclave and was solvothermally treated 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. For comparison, pure  $\text{CoP}_x$  was also synthesized by a similar solvothermal method in the absence of CdS NRs.

Preparation of Pt/CdS NRs: 0.5 wt% Pt was loaded on CdS in-situ by photoreduction method using  $\text{H}_2\text{PtCl}_6$ .

**Photocatalytic hydrogen evolution.** The photocatalytic hydrogen evolution experiments were carried out in a 50 mL flask at ambient temperature using a 300 W Xe lamp equipped with a UV cut-off filter ( $\lambda > 420$  nm). 1.0 mg of the photocatalyst was dispersed in 20 mL of aqueous solution containing  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  as the electron donor, and then the suspension was stirred and purged with nitrogen for 20 min to remove air. To compare the photocatalytic activity of different  $\text{CoP}_x/\text{CdS}$  NRs samples with different amount of  $\text{CoP}_x$ , the hydrogen production reactions were carried out in a 20 mL aqueous solution containing 1 mg photocatalyst, 15 mmol  $\text{Na}_2\text{S}$  (0.75 M), and 21 mmol  $\text{Na}_2\text{SO}_3$  (1.05 M). For long-term photocatalysis, a 250 mL flask was used instead, and 1 mg SC2 photocatalyst was dispersed in a 50 mL aqueous solution containing 75 mmol  $\text{Na}_2\text{S}$  (1.5 M) and 105 mmol  $\text{Na}_2\text{SO}_3$  (2.1 M) as sacrificial reagents. 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  $\mu\text{L}$  of the headspace was injected into the GC and was quantified by a calibration plot to the internal  $\text{CH}_4$  standard.<sup>[2-5]</sup>

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 SC2 photocatalyst was dispersed in a 20 mL aqueous solution containing 25 mmol  $\text{Na}_2\text{S}$  (1.25 M) and 35 mmol  $\text{Na}_2\text{SO}_3$  (1.75 M) as sacrificial reagents.

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

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

The turnover numbers (TONs) and turnover frequency (TOF) was calculated by using the follow equation:

$$TON = \frac{\text{moles of } H_2 \text{ evolved}}{\text{moles of cobalt on photocatalyst}}$$

$$TOF = \frac{\text{moles of } H_2 \text{ evolved per hour}}{\text{moles of cobalt on photocatalyst}}$$

Organic electron acceptors (methyl viologen dication ( $MV^{2+}$ ) and N,N'-(1,3-propylene)-5,5'-dimethylbipyridine ( $DQ^{2+}$ )) were used to detect the reducing power. A 3 mL aqueous solution containing sample SC2 ( $8.3 \mu\text{g}\cdot\text{mL}^{-1}$ ), 0.625 M  $\text{Na}_2\text{S}$  and 0.875 M  $\text{Na}_2\text{SO}_3$  and  $3 \times 10^{-5}$  M  $MV^{2+}$  (or  $DQ^{2+}$ ) were irradiated under visible light ( $\lambda > 420$  nm). And UV-vis absorption spectra was used to detect the change of Organic electron acceptors.

**Characterization.** Powder X-ray diffraction (XRD) results were measured by X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized  $\text{Cu K}\alpha$  radiation of  $1.54178 \text{ \AA}$ , operating at 40 kV and 200 mA. The scanning rate was  $5^\circ \text{ min}^{-1}$  in  $2\theta$ . The scanning electron microscopy (SEM) measurement was conducted using a JSM-6700F. The morphologies and energy-dispersive X-ray analysis (EDX) of the samples were 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 and a Rontec EDX system. X-ray photoelectron spectroscopy (XPS)

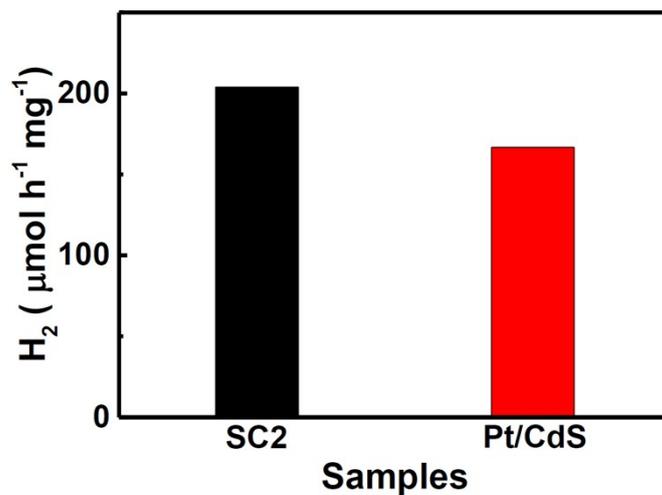
data and the valence states of metal elements were obtained with an ESCALAB 250 instrument. UV-Vis diffuse reflection spectroscopy (DRS) was performed on a SOLID 3700 UV-Vis spectrometer. The photoluminescence (PL) spectra for solid samples were investigated through an Acton Sp2500 (Princeton Instruments) with a liquid nitrogen cooled CCD. The time-resolved photoluminescence (TRPL) spectral analysis was performed on a PicoHarp 300 (PicoQuant). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) results were measured by an Optima 7300 DV.

## References.

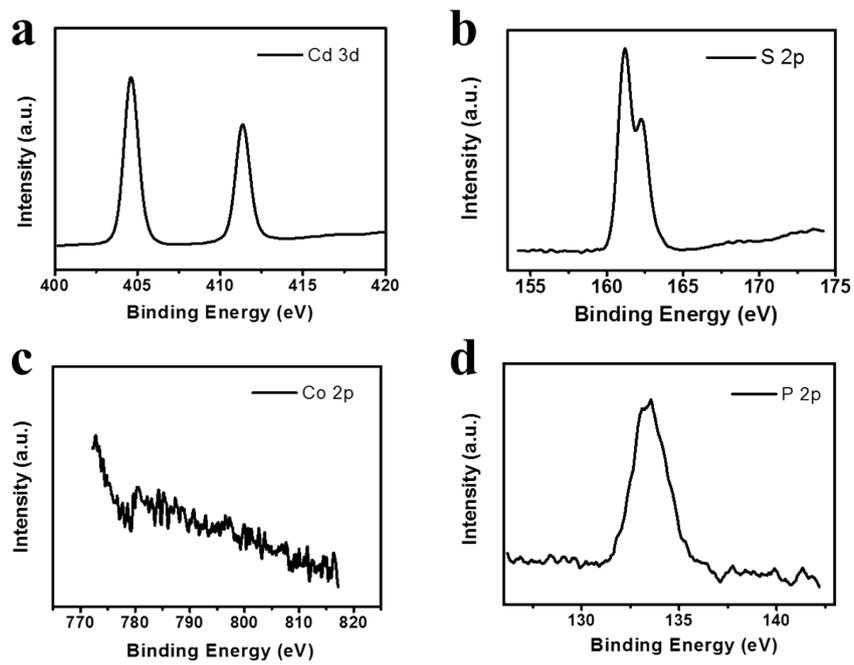
- [1] Jang JS, Joshi UA, Lee JS (2007) Solvothermal synthesis of CdS nanowires for photocatalytic hydrogen and electricity production. *J. Phys. Chem. C* 111(35): 13280-13287.
- [2] Du PW, Knowles K, Eisenberg R (2008) A homogeneous system for the photogeneration of hydrogen from water based on a platinum(II) terpyridyl acetylde chromophore and a molecular cobalt catalyst. *J. Am. Chem. Soc.* 130(38): 12576-12577.
- [3] Du P, Schneider J, Jarosz P, Zhang J, Brennessel WW, Eisenberg R (2007) Photoinduced electron transfer in platinum(II) terpyridyl acetylde chromophores: reductive and oxidative quenching and hydrogen production. *J. Phys. Chem. B.* 111(24): 6887-6894.

**Table S1.** Cobalt content in CoP<sub>x</sub>/CdS photocatalyst samples.

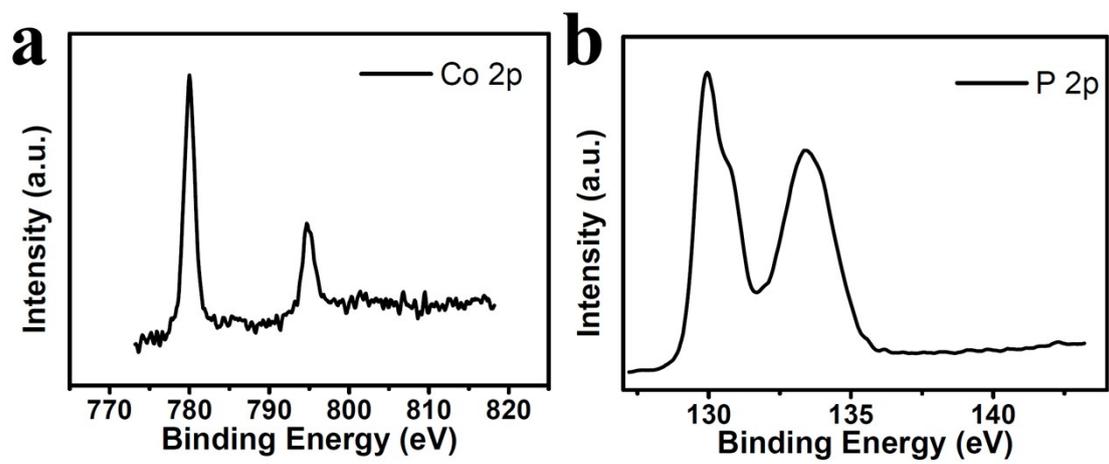
<b>Sample</b>	<b>Co (wt%)/ ICP-AES data</b>	<b>P (wt%)/ ICP-AES data</b>
SC1	0.08	0.25
SC2	0.32	0.92
SC3	0.98	2.62
SC4	2.15	5.10
SC5	3.50	13.19



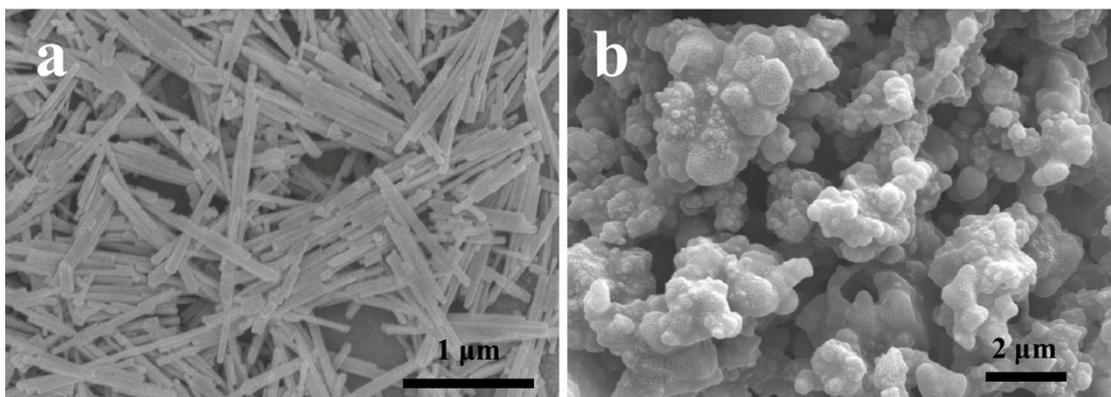
**Figure S1.** Comparison of photocatalytic hydrogen production rate of SC2 sample with 0.5 wt% Pt/CdS NRs under visible light ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M Na<sub>2</sub>S, and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.



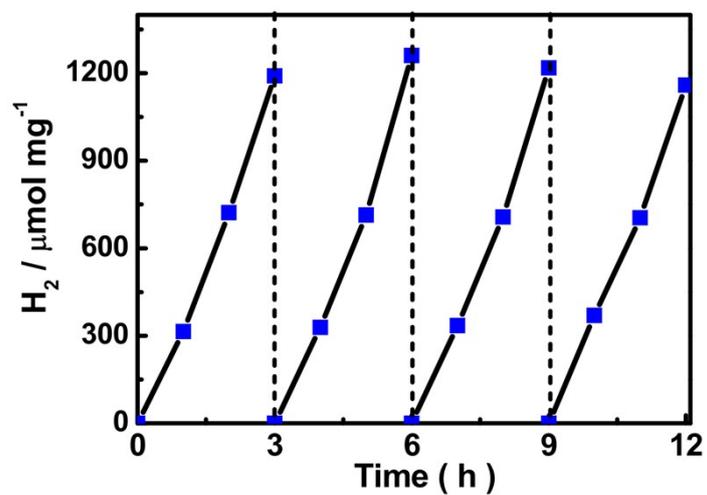
**Figure S2.** High-resolution XPS spectra of (a) Cd 3d, (b) S 2p, (c) Co 2p, and (d) P 2p.



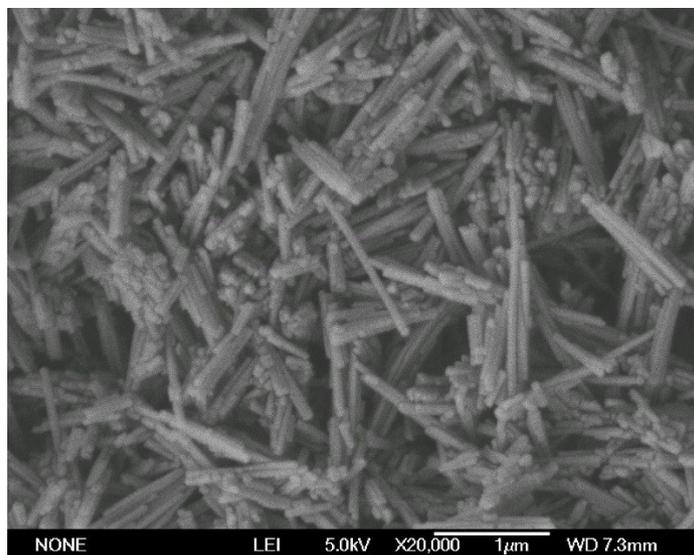
**Figure S3.** High-resolution XPS spectra of pure  $\text{CoP}_x$  of (a) Co 2p and (b) P 2p.



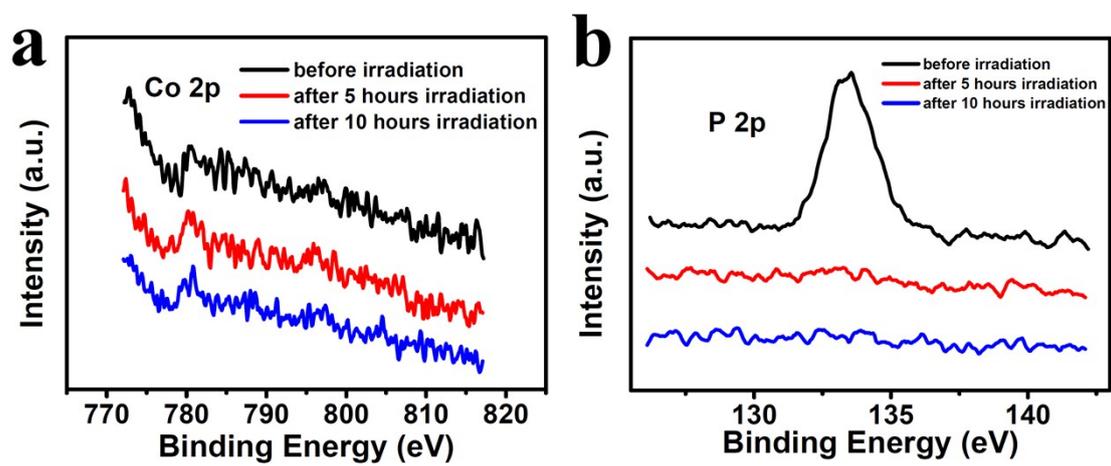
**Figure S4.** SEM images of (a) CdS NRs and (b) CoP<sub>x</sub>.



**Figure S5.** Cycling runs for photocatalytic hydrogen evolution in the presence of 1.0 mg SC2 samples in a 50 mL aqueous solution containing 1.25 M Na<sub>2</sub>S and 1.75 M Na<sub>2</sub>SO<sub>3</sub> at room temperature. After every 3 hours, the produced H<sub>2</sub> was evacuated.



**Figure S6.** SEM of the SC2 sample after visible light irradiation.



**Figure S7.** High-resolution XPS data of (a) Co 2p and (b) P 2p for sample SC2 before and after photocatalytic hydrogen production under visible light.