Supporting Information

Spectacular photocatalytic hydrogen evolution using metal-

phosphide/CdS hybrid catalysts under sunlight irradiation

Experimental Methods

1. Chemicals and Materials. All materials were of analytical grade and used as received without further purification. $Cd(OAc)_2 \cdot 2H_2O$, Na_2S , $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, sodium citrate, $H_2PtCl_6 \cdot 6H_2O$, $NH_3 \cdot H_2O$ and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NaH₂PO₂, ascorbic acid and L(+)-lactic acid were obtained from Aladdin Industrial Inc.

2. Material Synthesis

2.1 Synthesis of CdS

A solution of Na₂S (200 mL, 0.14 M) was added slowly to the Cd(OAc)₂·2H₂O solution (250 mL, 0.14 M) under vigorous stirring to furnish a yellow precipitate. The mixture was stirred for 24 h and kept for an additional 24 h at room temperature. After filtered, the yellow solid was dispersed into 2×80 mL double distilled water. The mixture was kept at 473 K for 72 h in 2×100 mL Teflon-lined stainless steel autoclave. After cooled to room temperature, the yellow solid was filtered, washed subsequently with water and ethanol at least three times and dried under vacuum oven.

2.2 Synthesis of CoP nanoparticles

CoP nanoparticles were prepared via a thermal phosphidation reaction using $Co(OH)_2$ as precursor. In a typical process, 200 mg of $Co(NO_3)_2 \cdot 6H_2O$ was added to a 100 mL aqueous solution containing 50 mg sodium citrate and stirred for 15 min. Then excess NaOH solution (0.5 M) was added to the mixture dropwise. The formed suspension was separated by centrifugation and dried at vacuum oven. Afterwards, 50 mg of the obtained $Co(OH)_2$ and 250 mg of NaH₂PO₂ solid were ground in a mortar to form a uniform distribution and put in a quartz boat of the tube furnace. Subsequently the samples were maintained at 300 °C for 1 h with a heating rate of 2 °C ·min⁻¹ in a flowing 30 mL/min Ar atmosphere. Following cooling to room temperature in continued

Ar flow, the obtained black solid was washed subsequently by water and ethanol three times and dried at vacuum oven.

2.3 Synthesis of Ni₂P nanoparticles

 Ni_2P nanoparticles were prepared according to the same procedure as that for CoP, except that $Ni(NO_3)_2 \cdot 6H_2O$ was used instead of $Co(NO_3)_2 \cdot 6H_2O$.

2.4 Synthesis of Cu₃P nanoparticles

Cu₃P nanoparticles were prepared by using Cu(OH)₂ as precursor. In a typical synthesis, moderate $NH_3 \cdot H_2O$ was added dropwise to a 100 mL aqueous solution containing Cu(NO₃)₂·3H₂O (200 mg) and sodium citrate (50 mg) until the solution turned into clear from muddy. Then, excess 0.5 M NaOH solution was added to the above mixture to form a suspension, which was separated by centrifugation and dried at vacuum oven to obtain Cu(OH)₂ solid. After that, 50 mg Cu(OH)₂ and 250 mg NaH₂PO₂ solid were ground in a mortar and heated to 300 °C for 1 h in a flowing 30 mL/min Ar. Following cooling to room temperature in continued Ar flow, the obtained solid was washed subsequently by water and ethanol three times and dried at vacuum oven.

2.5 Synthesis of Pt nanoparticles

200 mg $H_2PtCl_6 \cdot 6H_2O$ and 50 mg sodium citrate was added to 100 mL aqueous solution containing 200 mg ascorbic acid and the reaction solution was refluxed for 5 h. The produced black precipitate was separated by centrifugation, washed by water and ethanol and dried at vacuum oven.

3. Photocatalytic activity measurement

The photocatalytic hydrogen-production experiments were performed in a 60 mL quartz tube sealed with a silicone rubber septum. In a typical photocatalytic experiment, 1 mg CoP/CdS photocatalyst and 3 mL L(+)-lactic acid were added into the tube. Then the total volume of the mixed solution was adjusted to 15 mL with distilled water. The system was deoxygenated with argon for 30 min before irradiation to remove the air. Gas (0.6 mL) was sampled from the tube through the septum intermittently and the amount of produced hydrogen was measured by a gas chromatograph (GC-2014C, Shimadzu, with argon as a carrier gas), which was equipped with a 5 Å molecular sieve column (3 m × 2 mm) and a thermal-conductivity detector. The H₂-production rate was calculated according to the mass of CoP/CdS. White LED light source (30 × 3 W, $\lambda > 420$ nm) were used as the irradiation light sources. The LEDs were positioned 2 cm away from the sample which was kept under continuous

stirring at room temperature. The focused intensity on the flask was about 16 mW cm⁻² and the emission spectrum is shown below. The number of incident photons was 3.35×10^{17} photons/s which was measured by using an irradiance meter. When using real sunlight as the irradiation source, the focused intensity and the number of incident photons are 16.1 mW cm⁻² and 3.38×10^{17} photons/s, respectively. The apparent QE was calculated according to the equation below:

 $QE = \frac{number \ of \ reacted \ electrons}{number \ of \ incident \ photons} \times 100\%$

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



The irradiation spectrum of the white LED light.

4. Materials characterization

The size and lattice fringes were analyzed on a transmission electron microscope (TEM) (JEM 2100F) with an accelerating voltage of 200 kV. Energy dispersive X-ray (EDX) measurements and scanning electron microscope (SEM) images were taken on a Hitachi S-4800 field emission scanning electron microscope operating at 5.0 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) and their corresponding Energy disperses X-ray (EDX) mapping were recorded on Tecnai G2 F20 U-TWIN with operating voltage at 300 kV. Powder X-ray diffraction (XRD) pattern was recorded on a Bruker AXS D8 X-ray diffractometer with Cu K_a ($\lambda = 1.54056$ Å). X-ray photoelectron spectroscopy (XPS) was measured in a PHI 5300 ESCA system. An Al K_a X-ray source with a power of 250 W was used. The charge effect was calibrated using the binding energy of C1s. UV-vis diffuse reflectance spectra were recorded on a spectrophotometer (Hitachi U-3010).



Figure S1. XRD pattern of the obtained CdS.



Figure S2. (a) TEM and (b) HRTEM images of the CdS.



Figure S3. UV-vis DRS spectra of the samples CoP/CdS(x) (x = 1, 3, 5, 8, and 15) and pure CdS.



Figure S4. XRD patterns of the samples CoP/CdS(x) (x = 1, 3, 5, 8, and 15), CdS and CoP.



Figure S5. Comparison of photo-generating hydrogen with different components after 10 h of irradiation in 15 mL aqueous solution. (CdS: 1 mg, CoP/CdS: 1 mg, L(+)-lactic acid 3 mL). LED light: $\lambda > 420$ nm, 30 × 3W. There was almost no H₂ generation when CH₃CN, MeOH or EtOH were used as solvents, which suggested that water was probably the real substrate in the photocatalytic reaction.

	I	1			I
Photocatalyst	Amount of catalyst	Activity (the value	Activity (×	QE	Reference
	(mg)	reported in	1000 µmol	(%)	
		literature)	h ⁻¹ g ⁻¹)		
CoP/CdS	1		251.5	25.1	This work
Ni ₂ P/CdS	1		143.6	14.3	This work
Cu ₃ P/CdS	1		77.6	7.7	This work
Pt/CdS/CdSe	4	162 μmol·h ⁻¹	40.5	20	35
Ni ²⁺ /CdS	0.36	74.6 μmol·h ⁻¹ ·mg ⁻	74.6	12.2	S1
		1			
MoS ₂ /CdS	100	540 μmol·h ⁻¹	5.4		13
WS ₂ /CdS	10	1984 μmol·h ⁻¹ ·g ⁻¹	1.984		S2
MoS ₂ /CdS	100	1315 μmol·h ⁻¹	13.15		S3
NiS/CdS	50	1131 μmol·h ⁻¹ ·g ⁻¹	1.131	6.1	29
Ni(OH) ₂ /CdS	50	5085 μmol·h ⁻¹ ·g ⁻¹	5.085	28	S4
Pt-PdS/CdS	300	8.77 mmol·h ⁻¹	29.233	93	23
Pt/ZnO/Cd _{0.8} Zn _{0.5} S	20	36.5 mmol·h ⁻¹ ·g ⁻¹	36.5	50.4	36
Au/ZnO/CdS	100	60.8 μmol·h ⁻¹	6.08		S5
Pt/WO ₃ /CdS	50	2900 μmol·h ⁻¹ ·g ⁻¹	2.9		37
PdS/CdS/ZnO	100	2075 μmol·h ⁻¹ ·g ⁻¹	2.075		S6
Ni/CdS		63 mmol·h ⁻¹ ·g ⁻¹	63	53	S7
Ni ²⁺ /CdSe	Ni ²⁺ (5.0×10 ⁻⁹ mol)	TON ^a 600,000;		36	S8
	CdSe (2.5×10 ⁻⁸ mol)	TOF ^{<i>b</i>} 7000			

Table 1 Comparison of photocatalytic H₂-production performance of CoP/CdS with other similar systems.

^a mole H₂/mole catalyst after 100 h; ^b mole H₂/mole catalyst/hour.



Figure S6. The photo of the photocatalytic experiment using sunlight as irradiation source for 1 mg CoP/CdS(5) in 15 mL aqueous solution containing 3 mL L(+)-lactic acid at room temperature. The irradiation started from10:00 am and it was sunny until 12:00 am and then became cloudy. Location: Beijing, China, Dec 6, 2014.



Figure S7. XRD patterns of the samples CoP/CdS(5) before and after 30 h, 50 h irradiation.



Figure S8. XPS spectra in the (a) Co $2p_{3/2}$ and (b) P 2p regions.



Figure S9. (a) XPS spectrum of the C (1s) region and (b) survey spectrum of the obtained CoP nanoparticles.



Figure S10. XRD pattern of the obtained Ni_2P nanoparticles.



Figure S11. (a) TEM and (b) HRTEM images of the Ni_2P nanoparticles.



Figure S12. (a) TEM and (b) HRTEM images of Ni_2P/CdS hybrid (Ni_2P 5 wt%).



Figure S13. XRD pattern of the obtained Cu₃P nanoparticles.



Figure S14. (a) TEM and (b) HRTEM images of the Cu₃P nanoparticles.



Figure S15. (a) TEM and (b) HRTEM images of the Cu_3P/CdS hybrid sample ($Cu_3P 5 \text{ wt\%}$).



Figure S16. XRD pattern of the obtained Pt nanoparticles.



Figure S17. TEM image of the Pt nanoparticles.



Figure S18. (a) TEM and (b) HRTEM images of the Pt/CdS hybrid sample (Pt 5 wt%).

References

S1. J. J. Wang, Z. J. Li, X. B. Li, X. B. Fan, Q. Y. Meng, S. Yu, C. B. Li, J. X. Li, C. H. Tung and L. Z. Wu, *ChemSusChem*, 2014, 7, 1468–1475.

S2 J. Chen, X. J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue and H. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, 1210–1214.

S3. G. Chen, D. Li, F. Li, Y. Fan, H. Zhao, Y. Luo, R. Yu and Q. Meng, *Appl. Catal. A: Gen.*, 2012, 443–444, 138–144.

S4. J. Ran, J. Yu and M. Jaroniec, Green Chem., 2011, 13, 2708-2713.

S5. Z. B. Yu, Y. P. Xie, G. Liu, G. Q. Lu, X. L. Ma and H. M. Cheng, *J. Mater. Chem. A*, 2013, **1**, 2773–2776.

S6. Y. P. Xie, Z. B. Yu, G. Liu, X. L. Ma and H. M. Cheng, *Energy Environ. Sci.*, 2014, 7, 1895–1901.

S7. T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrovic, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Susha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk and J. Feldmann, *Nature Mater.*, 2014, 13, 1013–1018.

S8. Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, Science, 2012, 338, 1321-1324.