

## **A solid-state approach to fabricate CdS/CuS nano-heterojunction with promoted visible-light photocatalytic H<sub>2</sub>-evolution activity**

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### **Experimental**

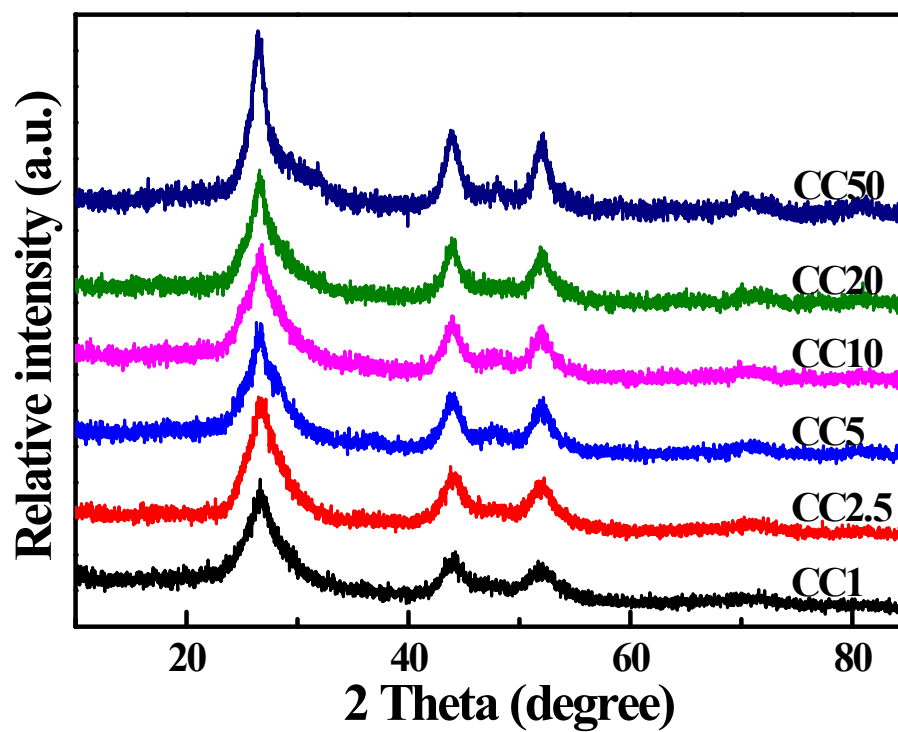
**Preparation of CdS/CuS samples.** All the reagents (purchased from Shanghai Chemical Industrial Company) used in the study were analytical-grade and without further purification. The CdS/CuS<sub>x</sub> samples were synthesized by a one-pot low-temperature solid-state method reported elsewhere. [S1-S3] No solvent was used in the synthesis process of CC<sub>x</sub>, and thioacetamide (TAA) was served as sulfur source, cadmium acetate and copper acetate was the cadmium source and copper source, respectively. In a typical synthesis, 1.066 g of Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O and 0.04 g of Cu(Ac)<sub>2</sub>·H<sub>2</sub>O were ground into homogeneous fine powder, then 0.316 g of TAA was added into the as prepared mixture and ground for 20 min. The products after grind were gathered and baked at 100 °C for 60 min. A series of CdS/CuS<sub>x</sub> (where x = 1, 2.5, 5, 10, 20, 50, represent the different percentage of CuS vs CdS, and these samples were labeled as CC<sub>x</sub>) composites were fabricated. For comparison, pure CdS and CuS samples were synthesized by the same method without copper source and cadmium source, respectively.

**Characterization.** Powder X-ray diffraction (XRD) patterns were performed at a Bruker D8 Advance diffractometer with Ni-filtered Cu K $\alpha$  radiation at a scan rate (2 $\theta$ ) of 8° min<sup>-1</sup>. The accelerating voltage and applied current were 40 KV and 40 mA, respectively. The UV-vis diffuse reflectance spectrum (UV-vis DRS) were acquired from the dry-pressed disk samples by using a UV-vis spectrophotometer (Lambda 650) with Teflon as reflectance standard. X-ray photoelectron spectroscopy (XPS) of samples were obtained from the detection by a Leybold Heraeus-Shenyang SKL-12 X-ray photoelectron spectrometer and the spectra were excited by using Mg K $\alpha$  radiation at 10 kV and 15 mA. The transmission electron microscopy (TEM) images were obtained from a Hitachi H-7650 (HITACHI, Japan) transmission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM) images were tested by a JEM2100F transmission electron microscope at an acceleration voltage of 200 kV.

**Photocatalytic H<sub>2</sub> production activity.** The visible-light photocatalytic H<sub>2</sub> production activity was evaluated by experiments performed in a 100 mL Pyrex flask with three openings sealed with silicone rubber septum. The experiments were carried out at room temperature and atmospheric pressure. The visible light source was a 350 W Xe arc lamp with a  $\leq$ 420 nm UV-cutoff filter and the light source was placed 15 cm away from the photocatalytic reactor. The

focused light intensity (in the wavelength range from 420 nm to 1000 nm) on the reactor was measured by a visible-light radiometer (Model: FZ-A China) was ca.  $70 \text{ mW}\cdot\text{cm}^{-2}$ . In a typically reaction system, 50 mg of as-prepared photocatalyst was dispersed in 80mL of mixed aqueous solution containing 0.35 M  $\text{Na}_2\text{S}$  and 0.25 M  $\text{Na}_2\text{SO}_3$  with continuous stirring. In the previous of irradiation, the reaction system was bubbled with  $\text{N}_2$  for 30 min to insure the dissolved oxygen and residual air in the flask were removed. During the experiment, continuous magnetic stirring was used to maintain a suspension state of the photocatalyst particles. After a 60 min of visible light irradiation, 400  $\mu\text{L}$  gas was sampled immediately through the septum. The ratio of  $\text{H}_2$  in the sample was analyzed by gas chromatograph (GC-14C. Shimadzu, Japan; TCD,  $\text{N}_2$  as a carrier gas).

**Photoelectrochemical measurement.** The working electrodes were prepared as follow: 0.02 g as-prepared photocatalyst, 0.02 g polyethyleneglycol (molecular weight 20,000) and 0.5 mL ethanol were mixed and ground into a slurry. Then the slurry was coated onto a 2 cm $\times$ 1.2 cm F-doped  $\text{SnO}_2$ -coated (FTO) glass electrode by the doctor blade method. The coated area and the thickness of the film were limited to 1  $\text{cm}^2$  and 0.01 mm, respectively. Finally, the as-coated electrodes were dried in an oven at 100  $^\circ\text{C}$  for 120 min. The measurement of the photocurrent was performed on an electrochemical analyzer (CHI660E. Shanghai Chenhua Limited, China) in a standard three-electrode system. In the system, the prepared glass electrodes were used as the working electrodes, Pt wire as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode, the electrolyte was 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution. The light source is a 350 W Xe arc lamp with a  $\lambda\leq 420$  nm cutoff filter.



**Fig. S1.** XRD patterns of CdS/CuS1, CdS/CuS2.5, CdS/CuS5, CdS/CuS10, CdS/CuS20 and CdS/CuS50 samples.

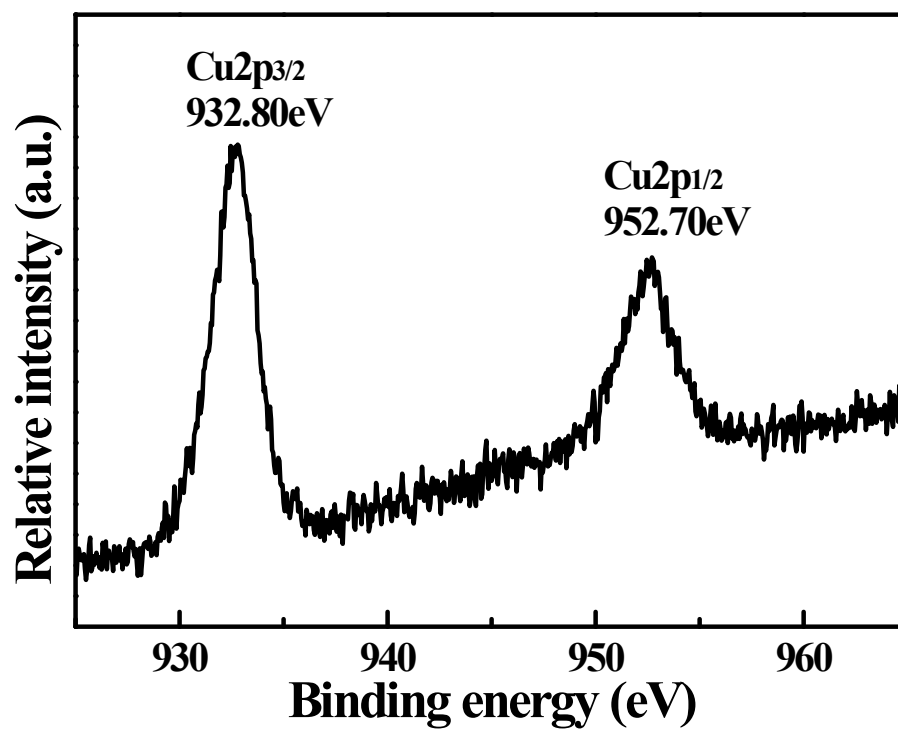


Fig. S2. High-resolution XPS spectra of Cu 2p of the CdS/CuS10 sample.

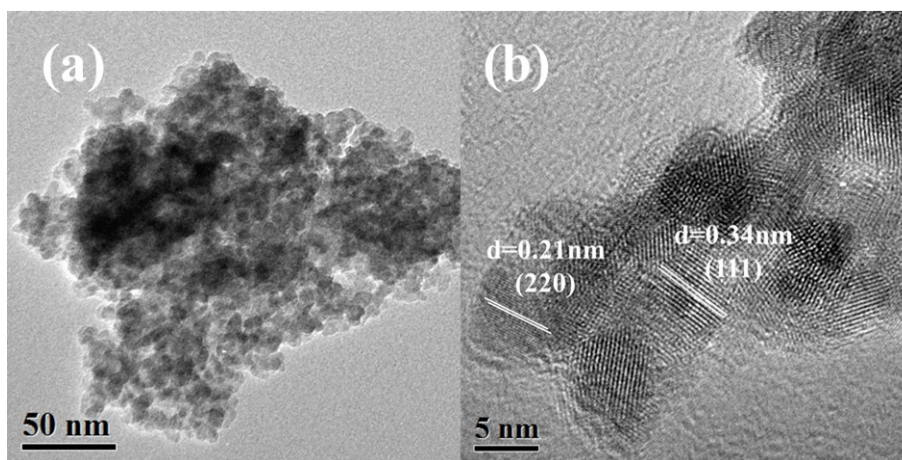
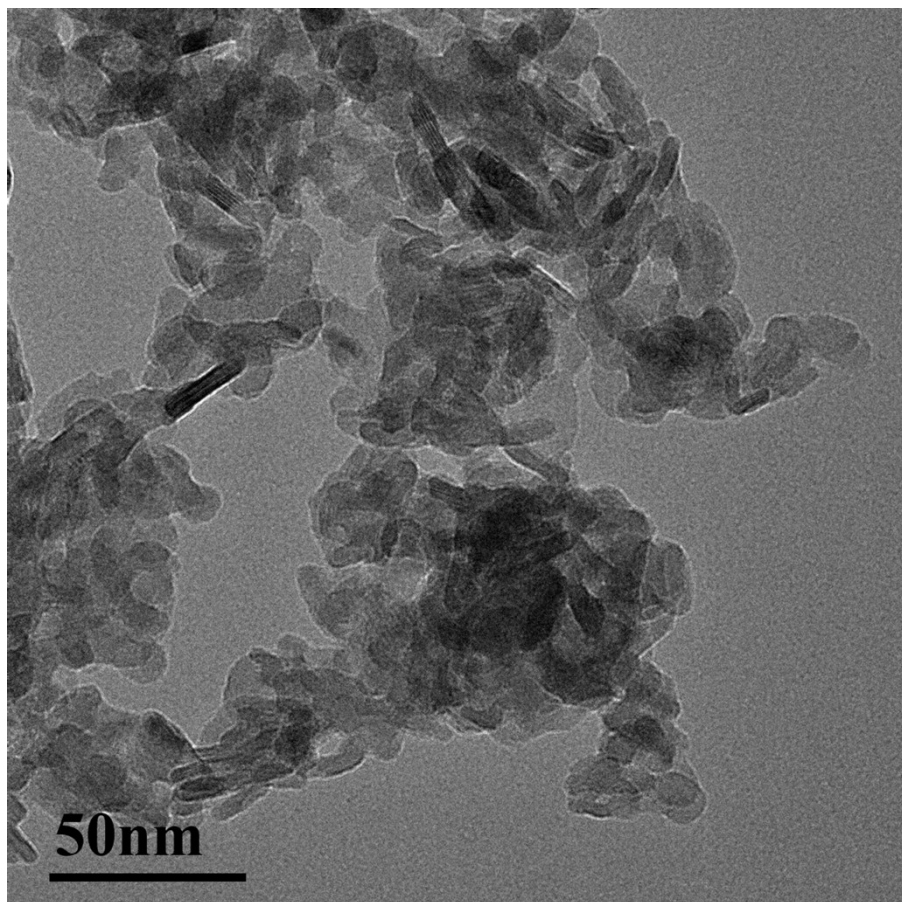
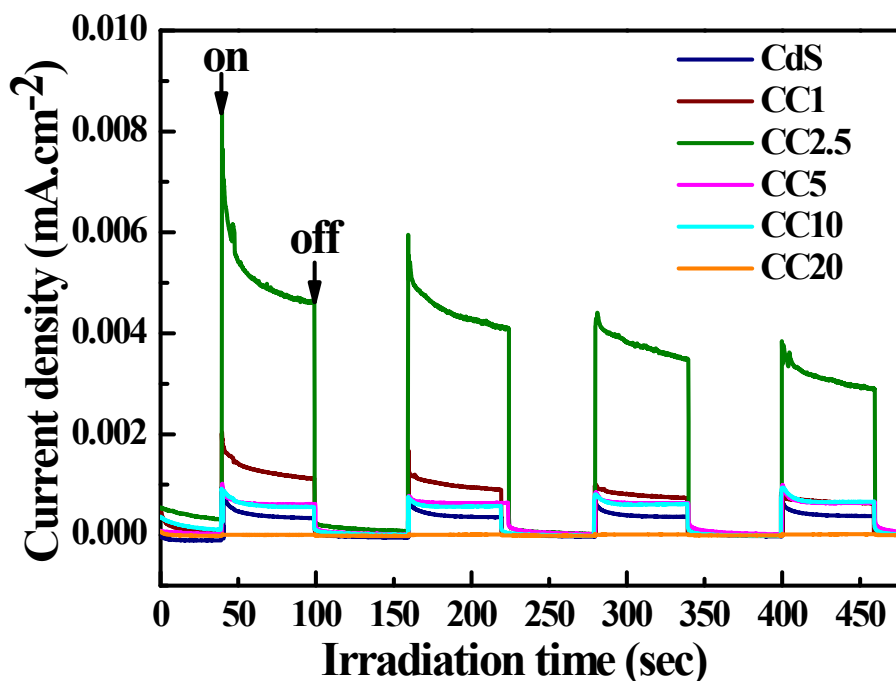


Fig. S3. (a) TEM and (b) high-resolution TEM images of pristine CdS sample.



**Fig. S4.** TEM image of pristine CuS sample.



**Fig. S5.** Transient photocurrent responses of CdS, CdS/CuS1, CdS/CuS2.5, CdS/CuS5, CdS/CuS10, CdS/CuS20 samples in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution under visible-light irradiation.

## References

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