# Electronic Supplementary Information

# Noble-metal-free $Cu_2S$-modified photocatalysts for enhanced photocatalytic hydrogen production by forming nanoscale p-n junction structure

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**Synthesis of $ZnIn_2S_4$ and $Cu_2S/ZnIn_2S_4$ photocatalysts**

Zinc sulphate heptahydrate ($ZnSO_4·7H_2O$), Indium nitrate tetrahydrate ($In(NO_3)_3·4H_2O$), cetyltrimethylammonium bromide (CTAB), thioacetamide ($C_2H_5NS$), and ethanol ($C_2H_6O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as purchased without further purification.

$ZnIn_2S_4$ photocatalysts were synthesized by a reported hydrothermal method.[1] Briefly, 0.735 g of $ZnSO_4·7H_2O$, 1.615 g of $In(NO_3)_3·4H_2O$, 0.65 g of CTAB, and a double excess of TAA were respectively dissolved in 50 mL of distilled water. The mixed solution was transferred into a 70-mL Teflon-lined autoclave, which was then sealed and kept at 160 °C for 12 h. After the autoclave cooled naturally in air, the produced $ZnIn_2S_4$ photocatalysts were washed with ethanol and deionized water several times and dried in vacuum at 80℃ for 5 h. $Cu_2S/ZnIn_2S_4$

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photocatalysts were prepared by an in-situ deposition of $Cu_2S$ onto $ZnIn_2S_4$. The preparation process is the same as that for $Cu_2S$/CdS. The Cu/Zn molar ratio of $Cu_2S/ZnIn_2S_4$ was controlled to be 0.05.

**Synthesis of $Cu_2S/TiO_2$ photocatalysts**

$TiO_2$ photocatalysts used in the present study were commercial P25 $TiO_2$ (Sigma Aldrich). $Cu_2S/TiO_2$ photocatalysts were prepared according to the following process. Typically, appropriate amounts of $Cu(NO_3)_2$ solution were added into 190 mL of 0.25 M $Na_2SO_3$/0.35 M $Na_2S$ aqueous solution containing 1.0 g of $TiO_2$ powders. The suspension was stirred for 0.5 h with nitrogen purged. The obtained $Cu_2S/TiO_2$ photocatalysts were washed with ethanol and deionized water several times and dried in vacuum at 80℃ for 5 h. The Cu/Ti molar ratio of $Cu_2S/TiO_2$ was controlled to be 0.05.

**Photocatalytic hydrogen production over $ZnIn_2S_4$, $Cu_2S/ZnIn_2S_4$, $TiO_2$ and $Cu_2S/TiO_2$ photocatalysts**

The reaction conditions for photocatalytic hydrogen production over $ZnIn_2S_4$ and $Cu_2S/ZnIn_2S_4$ photocatalysts were the same as those for CdS and $Cu_2S$/CdS photocatalyts. Photocatalytic reaction conditions for $TiO_2$ and $Cu_2S/TiO_2$ photocatalysts were a little different. The hydrogen production was tested with stirring under white light irradiation in a side irradiation Pyrex cell. 0.2 g of photocatalysts were added into 190 mL of aqueous solution containing 38 mL of methanol as sacrificial reagents. Nitrogen was purged through the cell before reaction to remove oxygen. A 300 W Xe lamp was used as the light source, and the temperature was kept at 35 ± 0.2 °C for the photocatalytic reaction.

**References**

1 S. Shen, L. Zhao, Z. Zhou and L. Guo, *J. Phys. Chem. C*, 2008, **112**, 16148.

The number of incident photons for the apparent quantum yield test can be calculated by the following equation.

$$n_i = \frac{PSt\lambda}{hc}$$

$n_i$ —— the number of incident photons;

$P$ —— light intensity / $W \cdot m^{-2}$;

$S$ —— irradiation area / $m^2$;

$\lambda$ —— wavelength / nm;

$h$ —— Planck constant / $J \cdot s$;

$c$ —— speed of light / $m \cdot s^{-1}$;

$t$ —— reaction time / s.

**Table S1.** The Cu/Cd molar ratios determined by EDX of different $Cu_2S$/CdS samples.

| Sample | the Cu/Cd molar ratio determined by EDX |
|---|---|
| $Cu_2S$/CdS-0.01 | 0.015 |
| $Cu_2S$/CdS-0.02 | 0.028 |
| $Cu_2S$/CdS-0.05 | 0.056 |
| $Cu_2S$/CdS-0.1 | 0.114 |
| $Cu_2S$/CdS-0.2 | 0.248 |

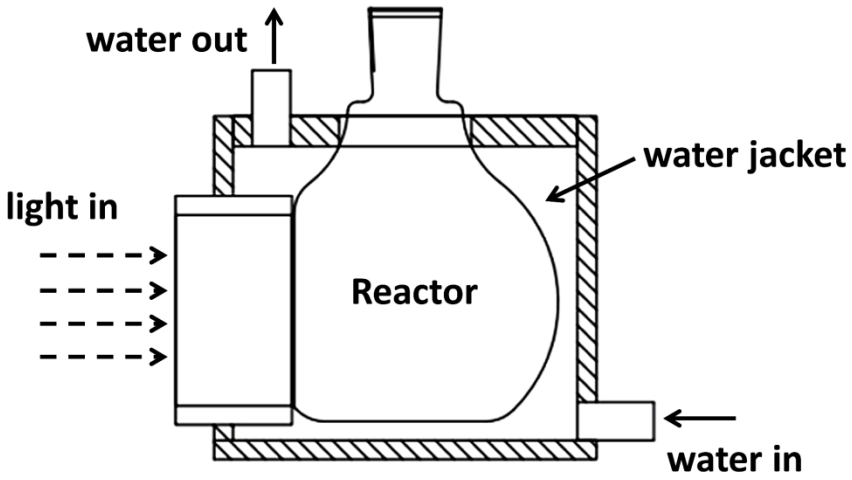


**Fig. S1.** The schematic diagram of the photocatalytic reactor for hydrogen production.

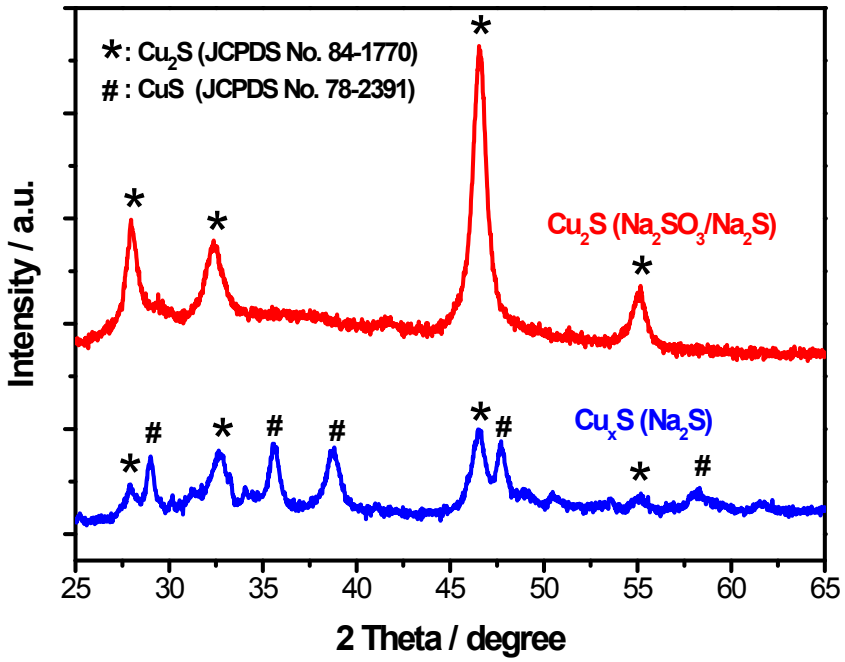


**Fig. S2.** XRD patterns of $Cu_xS$ ($Na_2S$) sample and $Cu_2S$ ($Na_2SO_3/Na_2S$) sample ($Cu_2S$ achieved by adding $Cu^{2+}$ into $Na_2SO_3/Na_2S$ solution).

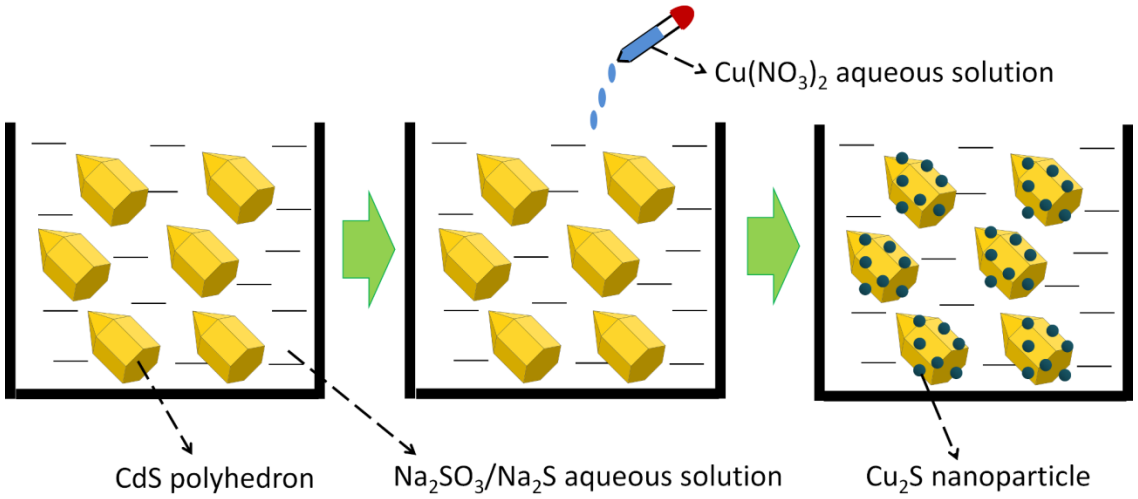


**Fig. S3.** Illustration of the deposition process of $Cu_2S$ nanoparticles on CdS polyhedrons.

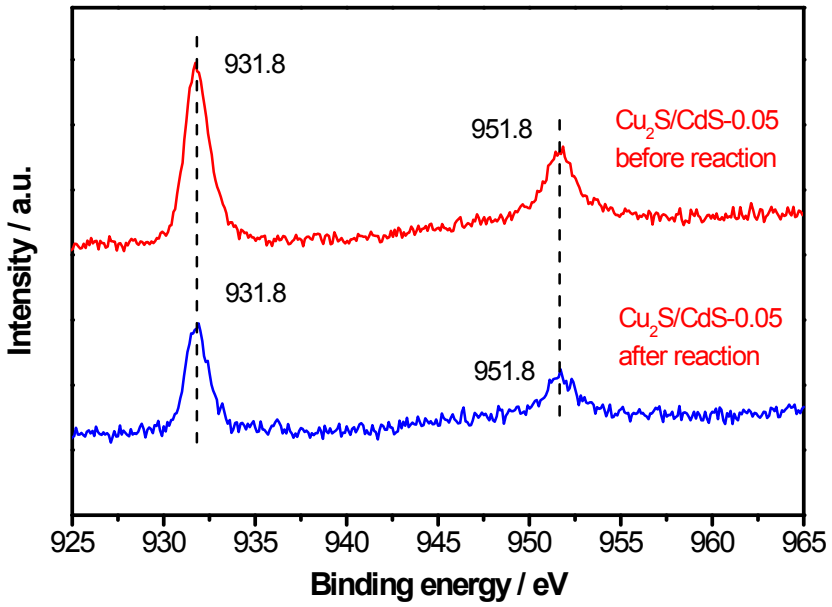


**Fig. S4.** Cu 2p XPS spectra of $Cu_2S$/CdS-0.05 sample before and after long-time photocatalytic reaction.

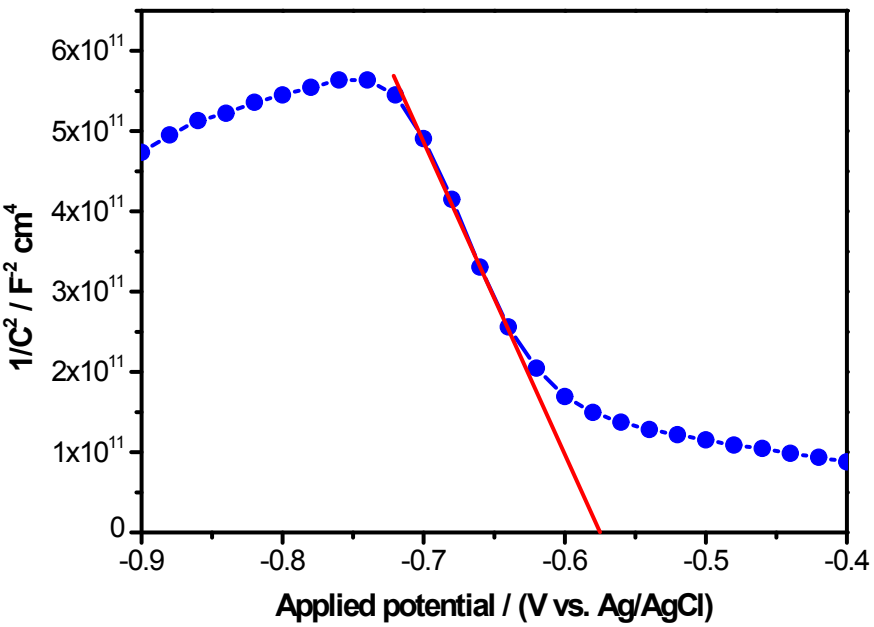


**Fig. S5.** Mott-Schottky plot of $Cu_2S$ film. The Mott-Schottky measurement was carried out at the frequency of 5 kHz in a conventional three-electrode cell with Ag/AgCl reference electrode and a platinum wire as the counter electrode. A 0.5 M aqueous solution of $Na_2SO_4$ was used as the electrolyte. The $Cu_2S$ film was prepared by dripping the suspension of 250 μL of water, 250 μL of ethanol, 10 μL of Nafion solution (DuPont), and 1.0 mg of $Cu_2S$ powders onto a platinized-carbon electrode and leaving the solvent evaporating in air.