Supporting Information

Diethylenetriamine-Functionalized CdS Nanoparticles Decorated on Cu_2S Snowflake Microparticles for Photocatalytic Hydrogen Production

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Experimental

1.1 Materials

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), ethylenediamine (EDA), thiourea (CH_4N_2S), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3) and diethylenetriamine (DETA) was obtained from Shanghai Chemical Reagent Corp. (P.R. China).

1.2 Preparation of Cu_2S snowflakes

Cu_2S snowflakes were prepared at a low temperature according to the precipitation method of Zhang et al[1].

1.3 Preparation of CU/CD composite.

Firstly, $CdCl_2 \cdot 2.5H_2O$ (1 mmol) and thiourea (3 mmol) were dissolved into 36mL of a mixed solution of diethylenetriamine and deionized water at a ratio of 2: 1. The mixed solution was fully stirred. Then, a certain amount of Cu_2S is added to the uniformly mixed solution, and the theoretical mass ratio of Cu_2S to CD is controlled to 0, 3, 10, and 20 wt%, respectively. Followed that, it was transferred to an autoclave and heated at 373K for 8 h. The precipitate formed was filtered and washed several times with deionized water. Then, the washed precipitate was dried in an oven at 333 K for 8h. The CU/CD composites were named as CU/CD-1, CU/CD-2, and CU/CD-3 according to different qualities of Cu_2S investment.

1.4 Preparation of CdS nanoroads (CdS NRs)

1 mmol of $CdCl_2 \cdot 2.5H_2O$ and 2 mmol of thiourea were added to 30ml of ethylenediamine, and then stirred for 1 hour. After stirring, the solution was

transferred to the autoclave. Heat at 180°C for 24h. After cooling to room temperature, the yellow precipitate in the autoclave was repeatedly washed with water several times, and then finally placed in a 333K oven to dry for 8h to obtain CdS nanorods.

1.5 Characterization

Analysis of catalyst structure by X-ray diffraction (XRD Rigaku D/MAX 24000) pattern. Scanning electron microscope (SEM Hitachi Regulus8220) and Transmission electron microscope (TEM JEOL JEM-2010) were obtained on the topographic features and element mapping images of the photocatalyst. The specific surface area used the BET method to obtain nitrogen adsorption data by using a surface analyzer (ASAP2010). The Fluorescence spectrometer (FLS920) and the ultraviolet-visible spectrophotometer (DRS Hitachi UV-3600) were used to measure the diffuse reflection absorption spectrum (DRS) and photoluminescence (PL) of the sample. The surface structure of the catalyst was analyzed by X-ray photoelectron spectra (XPS Thermo ESCALAB 250) and Fourier transform infrared (FT-IR Nicolet 6700). The Brunauer-Emmett-Teller (BET) specific surface area values were subject to nitrogen adsorption data at 77 K obtained by a Micromeritics ASAP 2010 system with a multipoint BET method. The electrochemical measurement was recorded by the Shanghai Chenhua CHI-660D workstation in a three-electrode cell system. The electrolyte solution is 1.0 M Na_2SO_4.

1.6 Photocatalytic activity evaluation

Typically, 20 mg of catalyst was dispersed in 50 mL of a mixed solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3. Pt (0.6 wt%) was directly photodeposited on the

photocatalysts by dissolving $H_2PtCl_6 \cdot 6H_2O$ into the reactant suspension. N_2 was passed through the reactor for more than 30 min to remove air. The light source used a 300 W xenon lamp (CEL-HXF300, Ceaulight, China) equipped with a 420 nm filter. The distance from light source to catalyst surface is 20 cm. The light intensity at 420 nm is 3.74 mW/cm^2. An online gas chromatograph (GC-7900) with 1 mL of gas was extracted after 1 hour of light exposure to test the hydrogen production. In order to investigate the reusability performance of the samples, the used photocatalyst was washed via DW after each light for 3 h to eliminate any possible adsorbed species from the previous cycle, and then dried at 333 K. The recovered photocatalyst was used for the next H_2 evolution under the same conditions. The apparent quantum efficiency (QE) of hydrogen produced at 420 nm was estimated by the following formula:

$$QE(\%) = \frac{number\ of\ racted\ electrons}{number\ of\ incident\ photons} \times 100 = \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100 \quad (1)$$

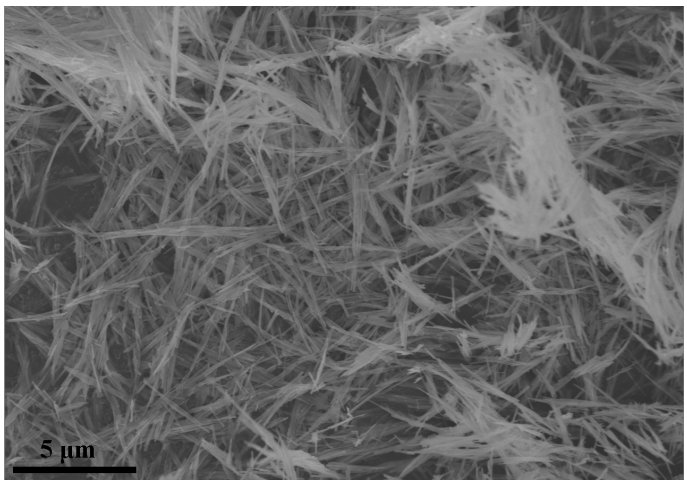


Figure S1. SEM images of CdS NRs.

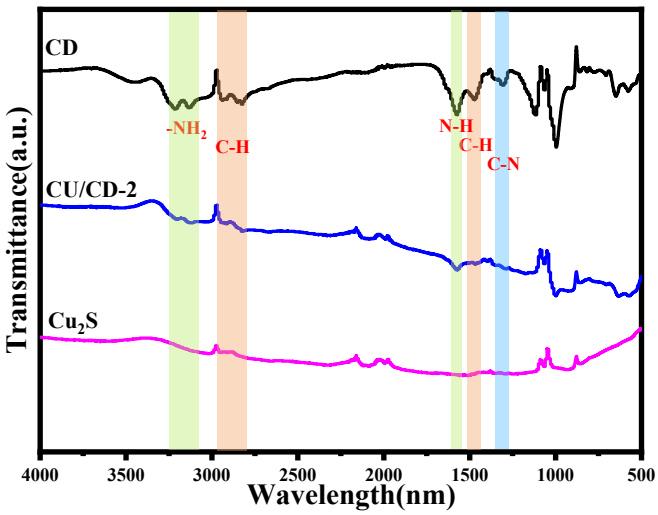


Figure S2. FT-IR spectra of different samples.

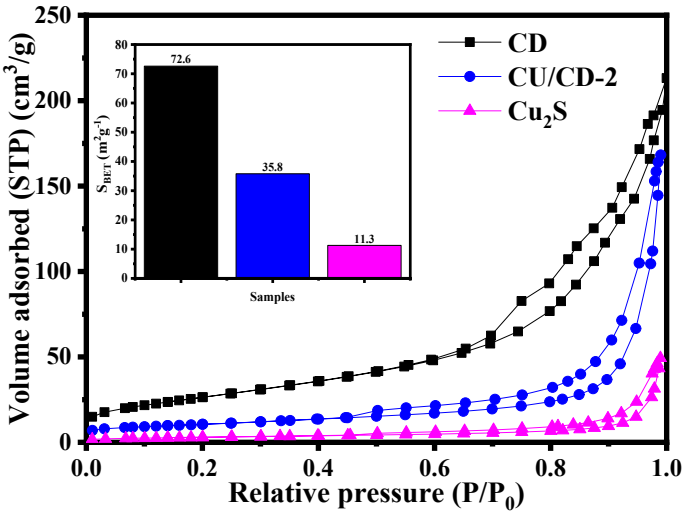


Figure S3. Nitrogen adsorption-desorption isotherms of different samples, inset: BET specific surface area (S_{BET}) of different samples.

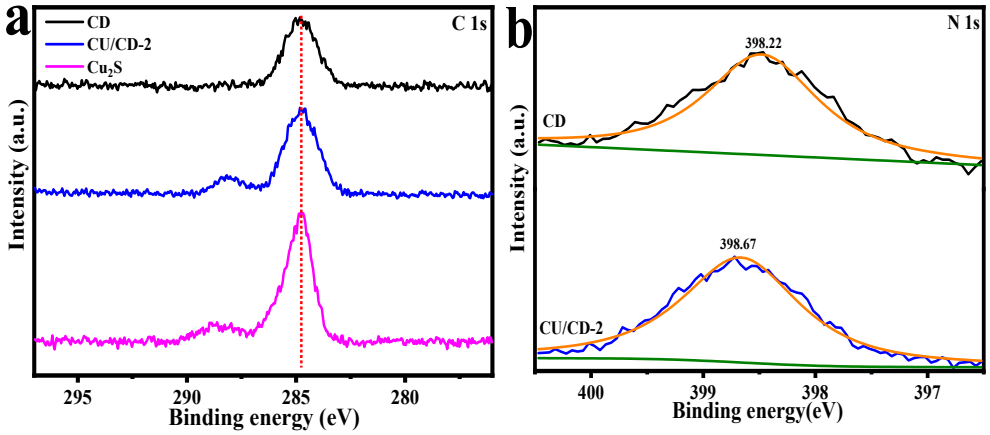
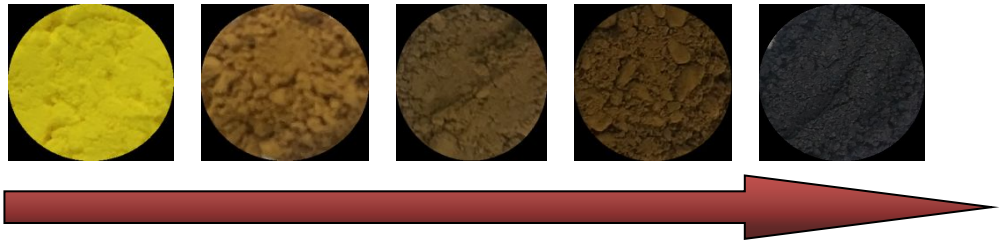


Figure S4. XPS spectra of (a) C 1s of different photocatalysts, and (b) N 1s of CU/CD-2 and CD.



CD **CU/CD-1** **CU/CD-2** **CU/CD-3** **Cu_2S**

Figure S5. The color transformation of the photocatalysts.

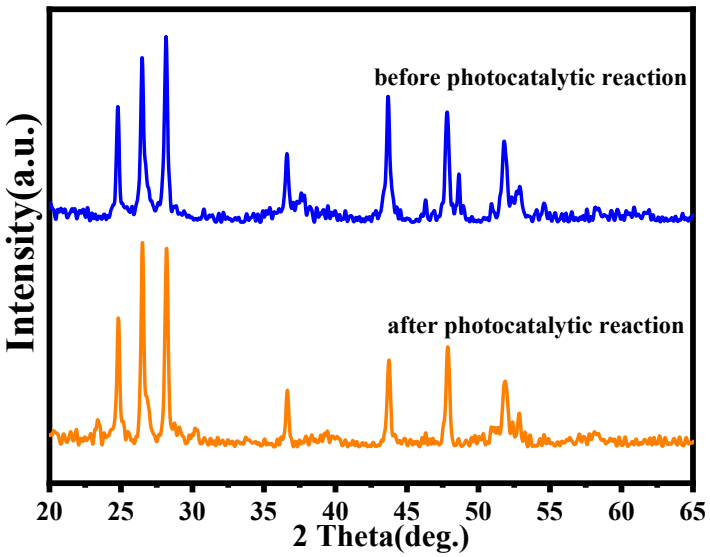


Figure S6. XRD patterns of CU/CD-2 before and after the photocatalytic reaction.

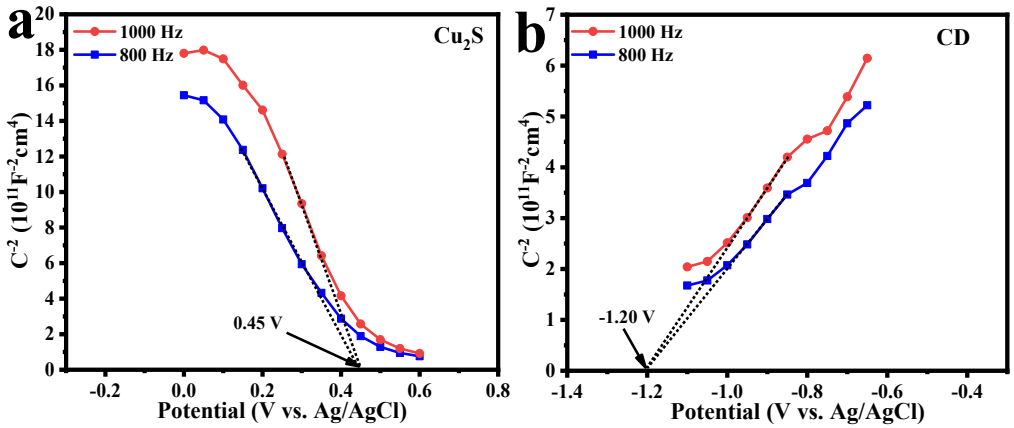


Figure S7. (a)Mott-Schottky plot of Cu_2S. (b) Mott-Schottky plot of CD.

Table S1 The atomic percentage of each element in CU/CD-2.

Elements in CU/CD-2 by XPS	Atomic %
C	21.12
Cd	28.36
N	8.04
O	9.44
S	30.63
Cu	2.41

Table S2 Comparisons of photocatalytic activities of different samples.

Photocatalyst	Light source	Sacrificial agent	H_2 production ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Ref.
Cu1.94/CdS	500W Xe-lamp	0.1 M Na_2S+0.3 M Na_2SO_3	71	[2]
CdS/ZnS/PdS	225W Xe-lamp $\lambda \geq 320$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	1021	[3]
CdS/Ti^{3+}/N-TiO_2	300W Xe-lamp $\lambda \geq 420$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	1119	[4]
S^{2-}-CdS/CdS	350W Xe-lamp $\lambda \geq 420$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	1789	[5]
NiS/CdS/TiO_2	300W Xe-lamp $\lambda \geq 420$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	2149	[6]
CdS/ZnS	300W Xe-lamp $\lambda > 422$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	820	[7]
CU/CD-2	300W Xe-lamp $\lambda \geq 420$ nm	0.35 M Na_2S+0.25 M Na_2SO_3	9000	This work

Reference

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