

## Supplementary information

# Microwave-assisted synthesis of nanocrystalline Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalyst with twin structure: effect of SDBS and enhanced performance for H<sub>2</sub> evolution

Yao-Guang Yu,<sup>a</sup> Gang Chen,<sup>\*a</sup> Yan-Song Zhou,<sup>a</sup> Yu Wang<sup>a</sup> and Chong Wang<sup>b</sup>

<sup>a</sup> Department of Chemistry, Harbin Institute of Technology, Harbin 150001, P. R. China, E-mail: gchen@hit.edu.cn; ygyu@hit.edu.cn, Tel: +86-451-86403117

<sup>b</sup> School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, P. R. China

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## Characterization of photocatalysts

Crystal structures of as-prepared products were investigated by a Rigaku D/max-2000 diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm). The microstructure and composition analysis were conducted on a field emission scanning electron microscope (FESEM, FEI QUANTA 200F) working at 30 kV and a transmission electron microscope (TEM, FEI Tecnai G<sup>2</sup>) equipped with an energy-dispersive X-ray spectrometer (EDS) working at 300 kV. High angle annular dark field (HAADF) imaging was obtained in scanning TEM (STEM) mode. BET specific surface areas and pore volumes were calculated from nitrogen adsorption/desorption isotherms determined at 77 K using an AUTOSORB-1-MP surface analyzer (the sample was outgassed under vacuum at 150 °C). UV-vis diffuse reflectance spectra were acquired by a spectrophotometer (TU-1900) and were converted from reflection to absorbance by the standard Kubelka-Munk method.  $\text{BaSO}_4$  was used as the reflectance standard. Infrared analysis was identified by a FTIR spectrometer (Shi-madzu) in the range of 400–4000  $\text{cm}^{-1}$  with the samples milled in KBr wafers.

## Details of molecular dynamics simulation

MD simulations of the interaction between SDBS and the (111) surface of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  solid solution were carried out in a simulation box (1.58 nm  $\times$  3.15 nm  $\times$  7.85 nm) with periodic boundary conditions using Materials Studio 5.0 version (from Accelrys Inc). Due to the asymmetric structure between the top and the bottom of the supercell, a dipole correction was introduced to avoid any arbitrary boundary effect.<sup>1</sup> The box consisted of a (111) surface of cubic  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  solid solution, two liquid phases and a vacuum layer of 10 nm height. One liquid phase was near the (111) surface of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  solid solution containing a SDBS molecule and 200 methanol molecules with density of 0.9  $\text{g}\cdot\text{cm}^{-3}$ , while another one was fixed below the vacuum layer containing 50 methanol molecules with density of 0.8  $\text{g}\cdot\text{cm}^{-3}$  in order to prevent the dipole field effect. The MD simulation was performed at 339 K, NVT ensemble and COMPASS force field, with the time step of 1 fs and simulation time of 0.5 ns.

The interaction energy  $E_{(111)\text{-SDBS}}$  was calculated as:

$$E_{(111)\text{-SDBS}} = E_{\text{total}} - E_{(111)} - E_{\text{SDBS}}$$

Here,  $E_{\text{total}}$  is the total energy of (111) surface of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  solid solution together with the adsorbed SBDS molecule;  $E_{(111)}$  and  $E_{\text{SDBS}}$  are the total energy of the  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  crystal and free SBDS molecule, respectively.

### **Photocatalytic reactions**

The photocatalytic reaction was performed in a closed gas-circulation system with a side window. The photocatalyst powders (0.015 g) were dispersed by ultrasonication for 30 min in an aqueous solution (400 mL) containing  $\text{Na}_2\text{SO}_3$  ( $0.6 \text{ mol}\cdot\text{L}^{-1}$ ) and  $\text{Na}_2\text{S}$  ( $0.4 \text{ mol}\cdot\text{L}^{-1}$ ) as electron donors. Nitrogen was purged through the system for 30 min to remove oxygen before reaction. The reaction was carried out by irradiating the suspension with light from a 300 W Xe lamp which was equipped with an optical filter ( $\lambda \geq 400 \text{ nm}$ ) to cut off the light in the ultraviolet region. The amount of produced  $\text{H}_2$  was measured by gas chromatography (Agilent 6820) with a thermal conductivity detector (TCD) and Ar was used as the carrier gas.

Table S1 Cd<sub>x</sub>Zn<sub>1-x</sub>S photocatalysts synthesized through various synthetic methods for photocatalytic H<sub>2</sub> production

photocatalyst	synthetic method	mass (mg)	light source	incident light	activity (μmol·h <sup>-1</sup> ·g <sup>-1</sup> )	aqueous solution	ref
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S (with twins)	Precipitation	100	300W Xe lamp	λ <sub>≥</sub> 430 nm	17900	0.35 M	2
	-hydrothermal					Na <sub>2</sub> S and 0.25 M Na <sub>2</sub> SO <sub>3</sub>	
Cd <sub>0.6</sub> Zn <sub>0.4</sub> S: 2%La	Solvothermal	15	300W Xe lamp	AM1.5 and λ <sub>≥</sub> 400 nm	92700	0.6 M Na <sub>2</sub> S and 0.8 M Na <sub>2</sub> SO <sub>3</sub>	3
Cd <sub>0.7</sub> Zn <sub>0.3</sub> S	Coprecipitation	100	300W Xe lamp	visible light	ca. 350	0.05 M Na <sub>2</sub> S and 0.02 M Na <sub>2</sub> SO <sub>3</sub>	4
Cd <sub>0.8</sub> Zn <sub>0.2</sub> S	Cation exchange	50	350W Xe lamp	λ <sub>≥</sub> 400 nm	2128	0.1 M Na <sub>2</sub> S and 0.04 M Na <sub>2</sub> SO <sub>3</sub>	5
Cd <sub>0.5</sub> Zn <sub>0.5</sub> S	Thermolysis	50	350W Xe lamp	λ <sub>≥</sub> 400 nm	7420	0.44 M Na <sub>2</sub> S and 0.31 M Na <sub>2</sub> SO <sub>3</sub>	6
Cd <sub>0.6</sub> Zn <sub>0.4</sub> S-0.6	Microwave-assisted synthesis	15	300W Xe lamp	λ <sub>≥</sub> 400 nm	240000	0.4 M Na <sub>2</sub> S and 0.6 M Na <sub>2</sub> SO <sub>3</sub>	current work

Summarizing the information about the Cd<sub>x</sub>Zn<sub>1-x</sub>S photocatalysts synthesized through various synthetic methods, reaction condition plays a key role in controlling the photocatalytic performance. It can be seen that neither calcination in high temperature nor coprecipitation in room temperature is positive to the enhancement of photocatalytic performance, because calcination in high temperature would lead to the formation of sintering while coprecipitation in room temperature usually obtains products in poor crystallinity. Cd<sub>x</sub>Zn<sub>1-x</sub>S photocatalysts synthesized through hydro/solvothermal method usually exhibit good crystallinity, large specific surface

area and excellent photocatalytic performance. However, amount of products synthesized through hydro/solvothermal method is usually low because of the limitation of autoclave capacity. Compared with the other methods, microwave-assisted synthesis possesses many great advantages. The remarkable reaction rate could shorten the reaction time from hours to minutes and the amount of products could easily reach to gram-scale.

## Reference

1. L. Bengtsson, *Physical Review B*, 1999, **59**, 12301.
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Figure S1–S12

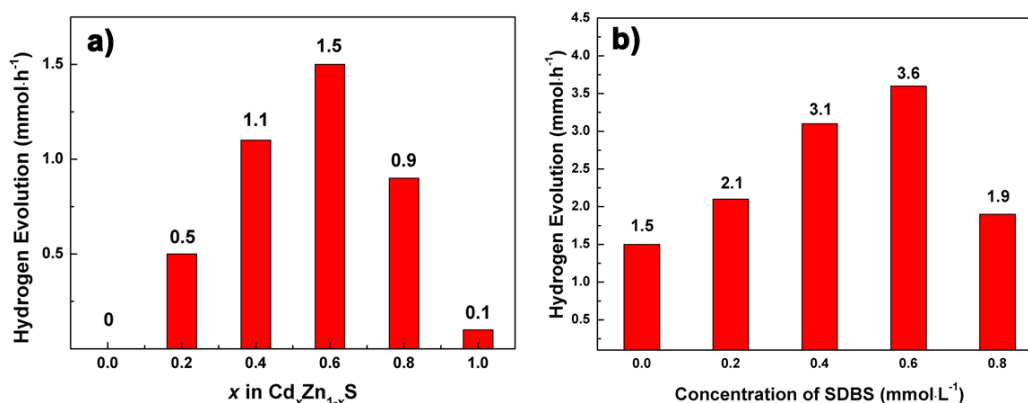


Fig. S1 H<sub>2</sub> evolution from an aqueous solution containing 0.6 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> and 0.4 mol·L<sup>-1</sup> Na<sub>2</sub>S catalyzed by a) Cd<sub>*x*</sub>Zn<sub>1-*x*</sub>S photocatalysts ( $x=0-1$ ) and b) Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalysts synthesized with variable concentration of SDBS.

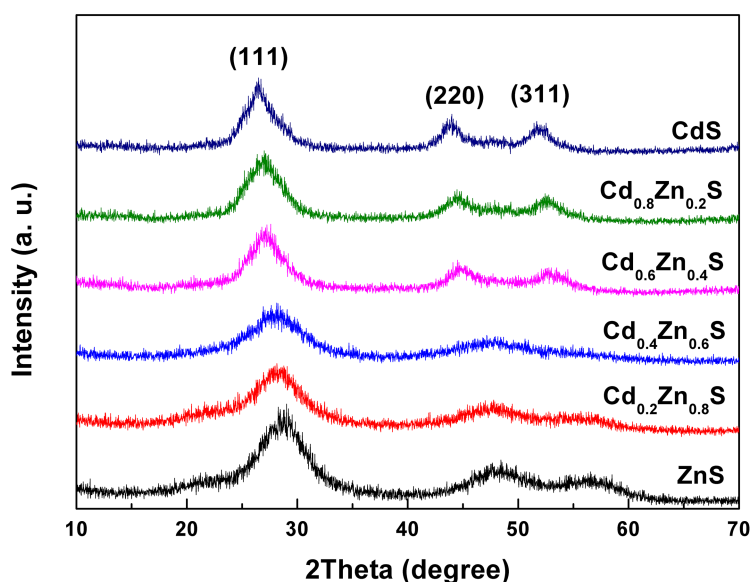


Fig. S2 XRD patterns of Cd<sub>*x*</sub>Zn<sub>1-*x*</sub>S solid solution ( $x=0-1$ ). Diffraction peaks of pure CdS and ZnS can be indexed to CdS (JCPDS No. 65-2887) and ZnS (JCPDS No. 65-0309) indicating both of CdS and ZnS synthesized through this route are cubic sphalerite structure.

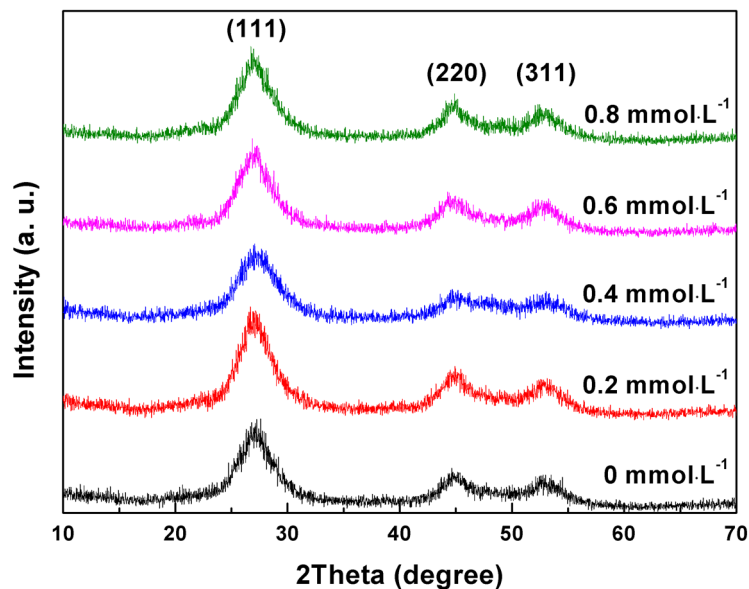


Fig. S3 XRD patterns of Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalysts synthesized with variable concentration of SDBS.

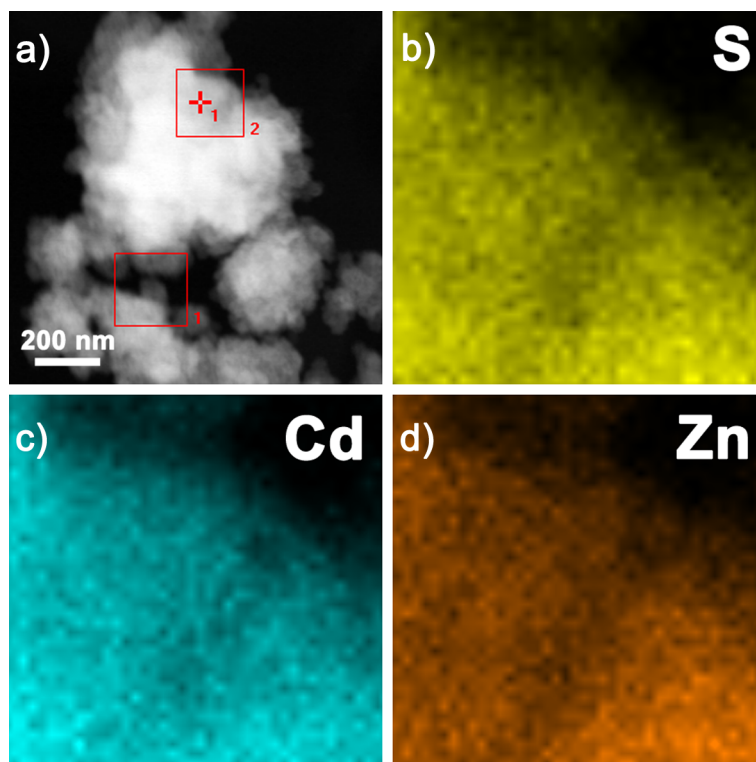


Fig. S4 The XEDS analysis results of Cd<sub>0.6</sub>Zn<sub>0.4</sub>S-0.6 photocatalyst: a) HAADF image and XEDS energy mapping of b) S (yellow), c) Cd (cyan) and d) Zn (orange). The XEDS spectra were acquired at a probe dwell time of 2 s and step size of 5 nm to distinguish spatial uniformity of the elemental distribution.

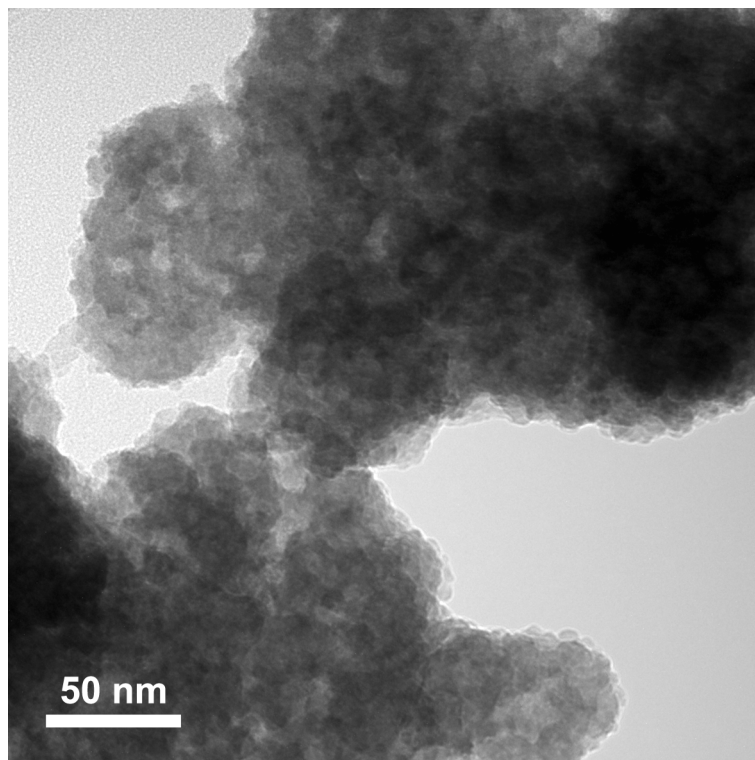


Fig. S5 TEM image of porous structure in  $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}-0.6$  photocatalyst. Wormhole-like mesopores can be found in the self-assembled structures with the diameter between 3 and 10 nm.

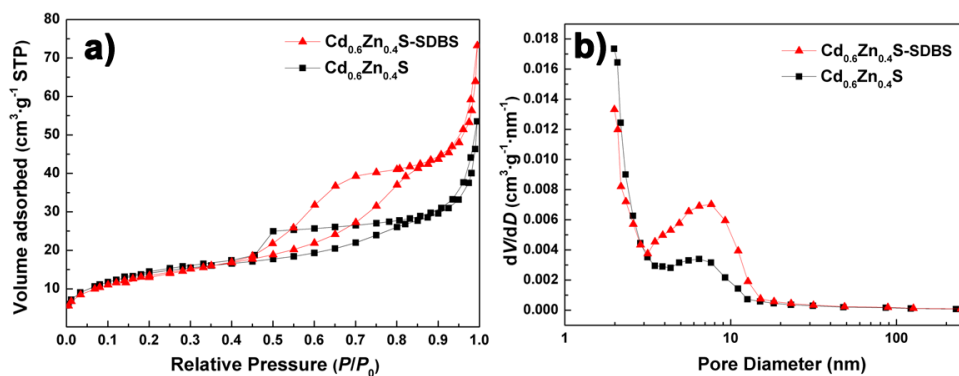


Fig. S6 Nitrogen adsorption/desorption isotherms and (b) pore size distribution curves of  $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$  solid solution synthesized in the absence of SDBS and in the presence of  $0.6 \text{ mmol}\cdot\text{L}^{-1}$  SDBS. The pore-size distribution curves show that the pore sizes of both  $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}$  solid solutions synthesized in the absence of SDBS and in the presence of  $0.6 \text{ mmol}\cdot\text{L}^{-1}$  SDBS are also concentrated between 3 and 10 nm.



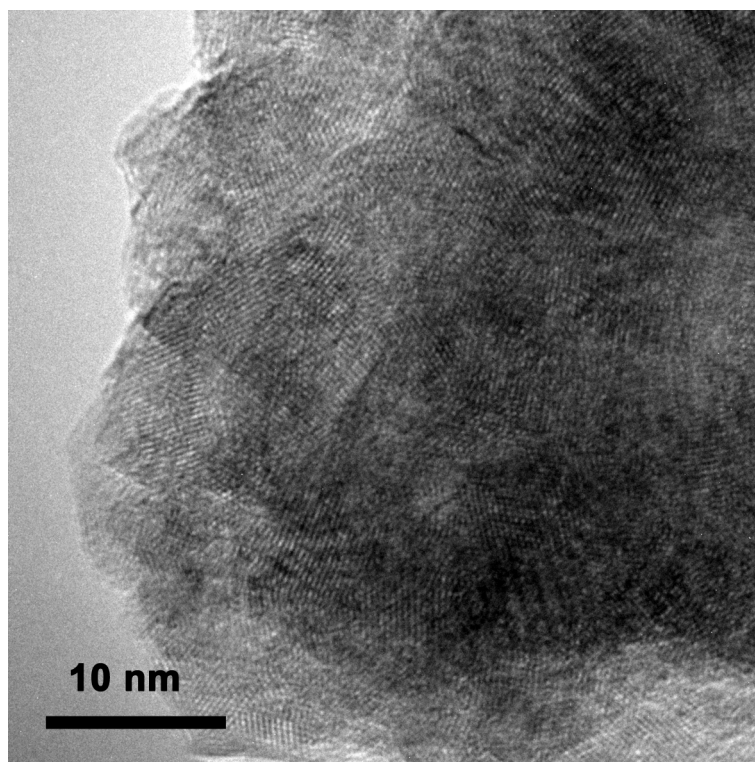


Fig. S7 HRTEM image of Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalyst prepared without SDBS.

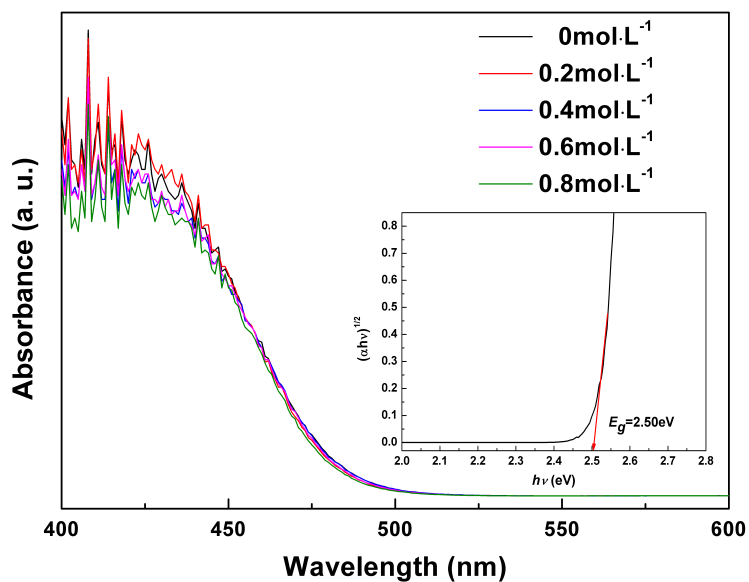


Fig. S8 UV-vis absorption spectra for Cd<sub>0.6</sub>Zn<sub>0.4</sub>S solid solution synthesized with variable amount of SDBS. The inset is the representative tauc plot of Cd<sub>0.6</sub>Zn<sub>0.4</sub>S-0.6 photocatalyst.

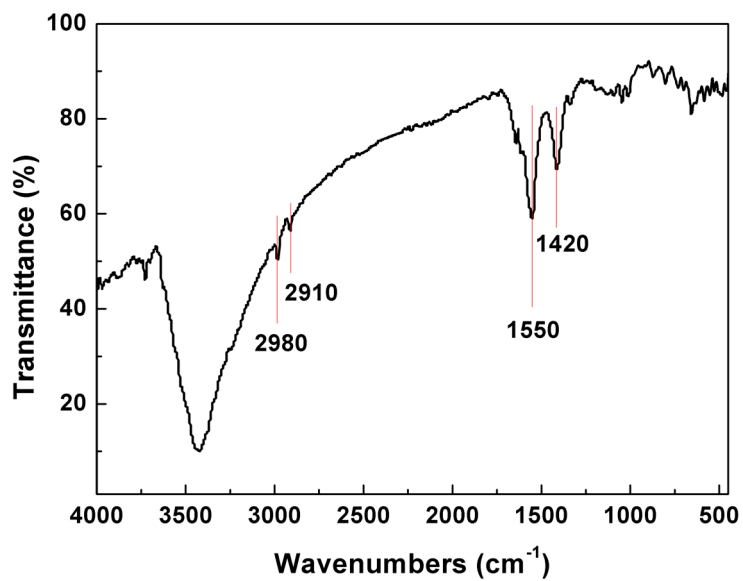


Fig. S9 FT-IR spectra of Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalyst synthesized with 0.8 mmol·L<sup>-1</sup> SDBS.

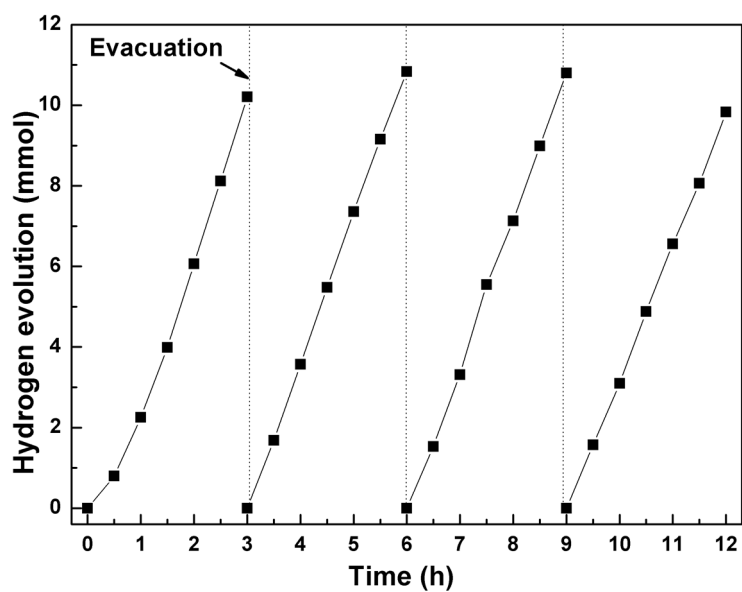


Fig. S10 Amount of H<sub>2</sub> evolution according to reaction time for Cd<sub>0.6</sub>Zn<sub>0.4</sub>S photocatalyst.

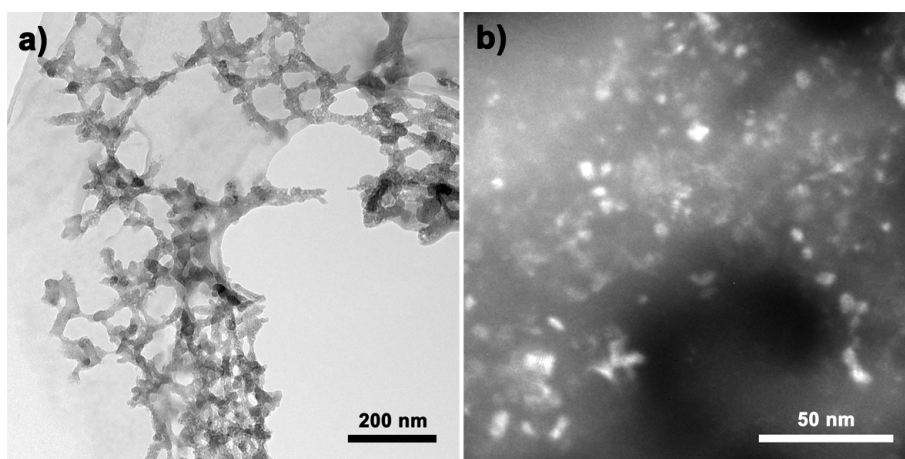


Fig. S11 a) TEM image and b) dark field image of  $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}-0.6$  sample after photocatalytic reaction for 2h.

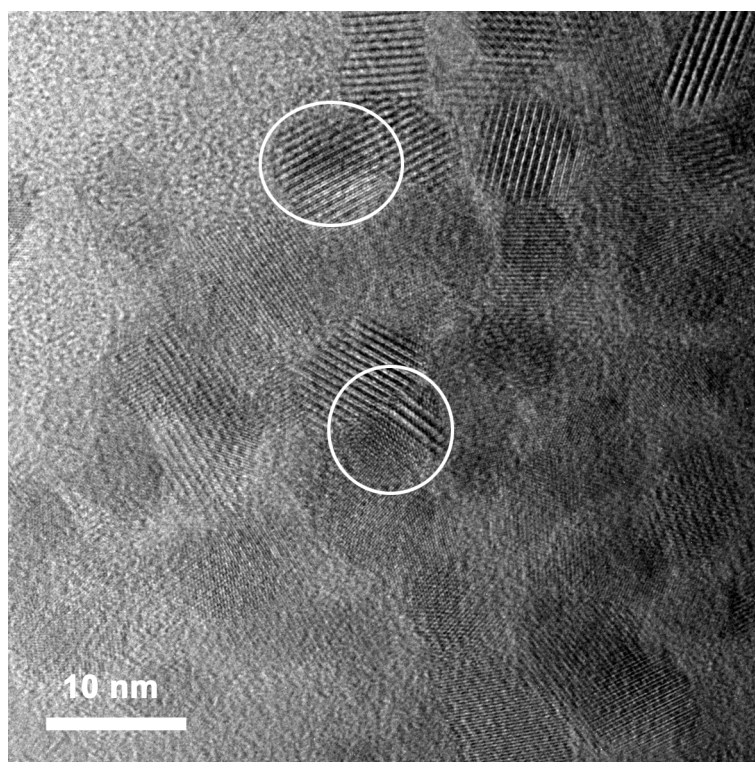


Fig. S12 HRTEM image of  $\text{Cd}_{0.6}\text{Zn}_{0.4}\text{S}-0.6$  sample after photocatalytic reaction for 2h. Nanocrystals with twin structure were marked with white circles.