Supporting Information

Co-doped $Zn_{1-x}Cd_xS$ nanocrystals from Metal–Organic Framework precursors: porous microstructure and efficient photocatalytic hydrogen evolution

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1. Experimental Section:

1.1 Chemicals: $Cd(NO_3)_2·4H_2O$, $Zn(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, thiourea and 1,2-Dimethylimidazole (MIM) (Shanghai Macklin Biochemical Technology Co., Ltd) are analytical grade and used as received without further purification.

1.2 Sample preparation.

1.2.1 Synthesis of ZIF-8 and ZnCo-ZIF precursors: In a typical synthesis, methanol solution (25 ml) of $Zn(NO_3)_2•6H_2O$ (2 mmol) was slowly added into a methanol solution (25 ml) of MIM (16 mmol) with stirring for 24 h. After stirring for 24 h, the milky dispersion was centrifuged at 11000 rpm for 10 min, and the precipitate was washed three times with methanol and then dried at 60 °C overnight in the vacuum oven to evaporate the solvent ethanol.

In typical fabrication procedure of ZnCo-ZIF nano particle with different content of Co^{2+}, methanol solution (25 mL) of $Zn(NO_3)_2•6H_2O$ and $Co(NO_3)_2•6H_2O$ mixture solution (with nominal Co/Zn molar ratios of 0.5, 1, 5 at%) was slowly added into a methanol solution (25 ml) of MIM (16 mmol) with stirring for 24 h. Afterwards, the purple dispersion was centrifuged at 11000 rpm for 10 min, and the precipitate was washed three times with methanol and then dried at 60 °C overnight in the vacuum oven to evaporate the solvent ethanol.

1.2.2 Synthesis of the $Zn_{1-x}Cd_xS$ solid solutions derived from ZIF-8: For the synthesis of a series of samples with nominal Cd/(Zn+Cd) molar ratio x are labeled as ZCx (x = 0, 10, 30, 50, 70 at%), deionized water (12 mL) of ZIF-8, $Cd(NO_3)_2·4H_2O$ (the total amount of ZIF-8 and $Cd(NO_3)_2·4H_2O$ equaling to 2 mmol) and 4 mmol thiourea mixture solution (with nominal Cd/(Zn+Cd) molar ratios of 10, 30, 50, and 70 at%) under ultrasound for a few minutes till ZIF-8 and $Cd(NO_3)_2•4H_2O$ was well-dispersed. After several minutes, the obtained solution was transferred into 15 mL autoclave and maintained 220 ^oC for 18 h. The final products with different concentrations of Cd^{2+} were respectively rinsed with distilled deionized water and ethanol for three times, and dried at 60 ^oC overnight in the vacuum oven to evaporate the solvent ethanol.

1.2.2 Synthesis of the $Zn_{0.5}Cd_{0.5}S$ (HZC50) solid solutions through hydrothermal method: Suitable contents of $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol) and 4 mmol thiourea was dissolved in 12 mL deionized water under ultrasound for a few minutes. Afterwards, the obtained solution was transferred into 15 mL autoclave and maintained at 220 ^oC for 18 h. The final products were rinsed with distilled deionized water and ethanol for three times, respectively, and dried at 60 ^oC overnight in the vacuum oven to evaporate the solvent ethanol.

1.2.3 Synthesis of $Zn_{0.5}Cd_{0.5}Co_yS$ derived from ZnCo-ZIF crystals with different Co content: The $Zn_{0.5}Cd_{0.5}Co_yS$ (denoted as CoZCy) were prepared according to the same reaction conditions with the optimized amount of the Cd/(Zn+Cd) (50 at%) using ZnCo-ZIF with different Co content as precursor (the $Zn_{0.5}Cd_{0.5}Co_yS$ samples were denoted as CoZCy with the Co content of 0, 0.5, 1, 5 at%, respectively).

2. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54060$ Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. The atomic structure of the CdS phase junction was characterized using an ARM-200CF (JEOL, Tokyo, Japan) transmission electron microscope operated at 200 kV and equipped with double spherical aberration (Cs) correctors. Element content analysis was tested on an inductively coupled plasma (ICP) spectroscope (Prodigy, Leeman, America). The UV−Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with BaSO4 as a reflectance standard. The transient photocurrent responses experiments were carried out at room temperature using a conventional three-electrode system with a glassy carbon electrode (3mm in diameter), (sheet resistance 20−25 Ω/square) with a geometrical area of 1.0 ± 0.1 cm^2 as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. All the samples were dispersed in deionized water with a concentration of 1.5 mg/mL and deposited on the glassy carbon electrode and dried infrared light irradiation. Na_2S (0.1 M) and Na_2SO_3 (0.02 M) mixture solution was used as the supporting electrolyte. The transient photocurrent responses measurements were performed with a CHI 660E electrochemical station (Shanghai Chenhua Co. Ltd, China) under 365 nm of irradiation in 0.1 M Na_2S + 0.02 M Na_2SO_3 mixed solutions. Moreover, Mott-Schottky (M-S) plots under dark conditions were also investigated to compare the charge carrier density of differentfilm electrodes using a CHI 660E electrochemical station in 0.1 M Na_2S + 0.02 M Na_2SO_3 mixed solutions under 1000 Hz. The Brunauer−Emmett−Teller (BET) specific surface area (S_{BET}) of the heterojunction samples analyzed by nitrogen adsorption and water vapor adsorption is investigated by an Autosorb-iQ adsorption apparatus (Quantachrome instruments, USA). All of the prepared samples were degassed at 90 °C for 3 hours prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using adsorption data in the relative pressure (P/P0) range of 0.05 − 0.3. A desorption isotherm was used to determine the pore size distribution via the Barret−Joyner−Halender (BJH) method, assuming a cylindrical pore model. The nitrogen adsorption volume at a relative pressure (P/P0) of 0.972 was used to determine the pore volume and average pore size. Electrochemical impedance spectra (EIS) measurements were carried out in three-electrode system and recorded over a frequency range of 0.05-10^5 Hz with ac amplitude of 10 mV at 0.5 V in dark using EC-lab (SP-150, VMP3-based instruments, France) under a surface power density of about 0.1 mW/cm^2. Na_2S (0.1 M) and Na_2SO_3 (0.02 M) mixture solution was used as the supporting electrolyte.

3. Photocatalytic Hydrogen Production.

The photocatalytic H_2 production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 420−800 nm, which was positioned 13 cm away from the reaction solution, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was about 200 mW·cm^{-2}, which was measured by a FZ-A visible-light radiometer (CEAULight, China). In a typical photocatalytic H_2-production experiment, 5 mg of the prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing Na_2S (0.35 M) and Na_2SO_3 (0.25 M). Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments. H_2 content was analyzed by gas chromatography (GC-7900, CEAULight, China). All glassware was carefully rinsed with deionized water prior to use. The quantum efficiency (QE) of 5 mg CoZC0.5 catalyts for H_2 evolution was measured using a 420 ± 8 nm band-pass filter. The average intensity of irradiation is determined to be 10.13 mW·cm^{-2} by an FZ-A visible-light radiometer. The number of incident photon is 7.84×10^{20}, and the QE for H_2 evolution is calculated as 39.2 % according to the following equation:

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

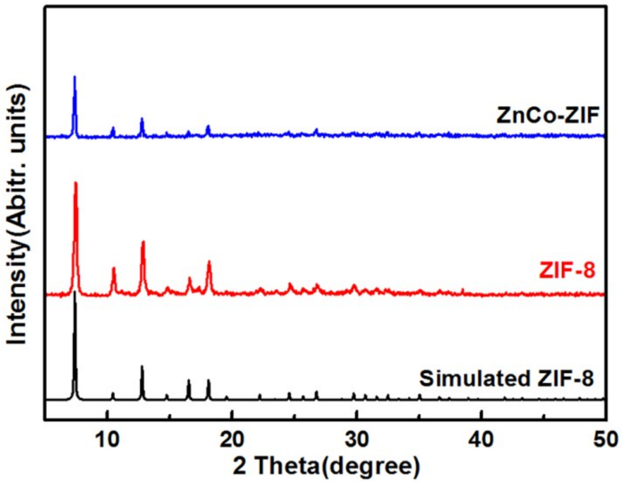

Fig. S1. The X-ray diffraction patterns of the ZIF-8 and ZnCo-ZIF with Co content of 0.5 at%.

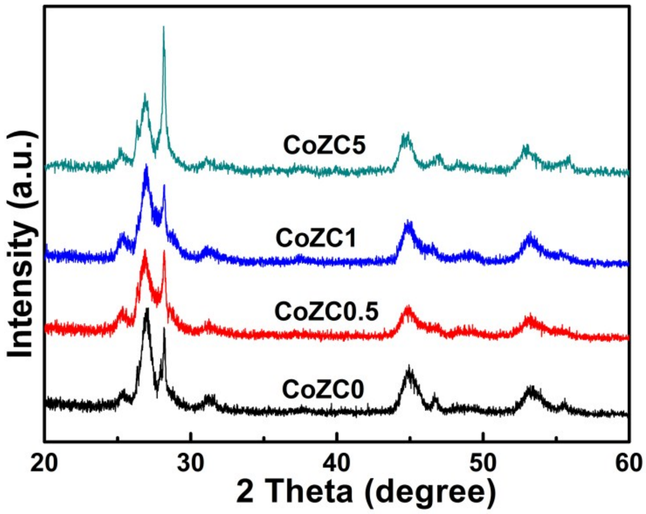

Fig. S2. Effect of the Co doping on the X-ray diffraction patterns of the $Zn_{0.5}Cd_{0.5}Co_yS$ samples. Due to the tiny content of Co, there was no dramatically differences in the XRD patterns of the as-prepared samples.

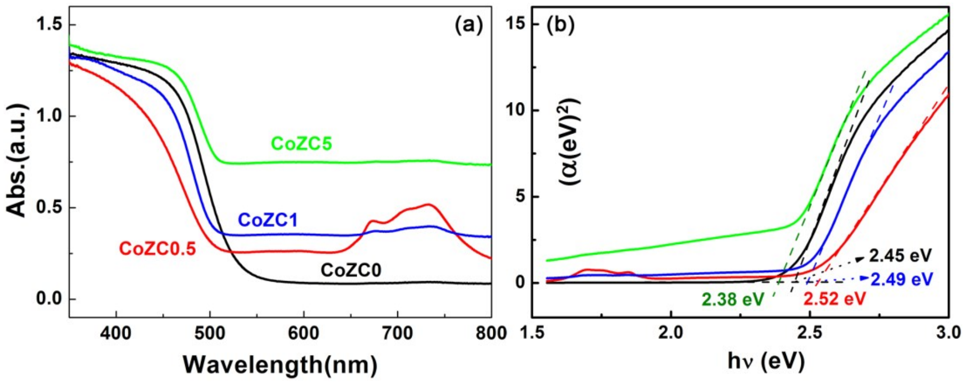

Fig. S3. The (a) UV−visible diffuse reflection spectra and (b) the band gaps of the $Zn_{1-x}Cd_xS$ solid solutions with different Co concentration.

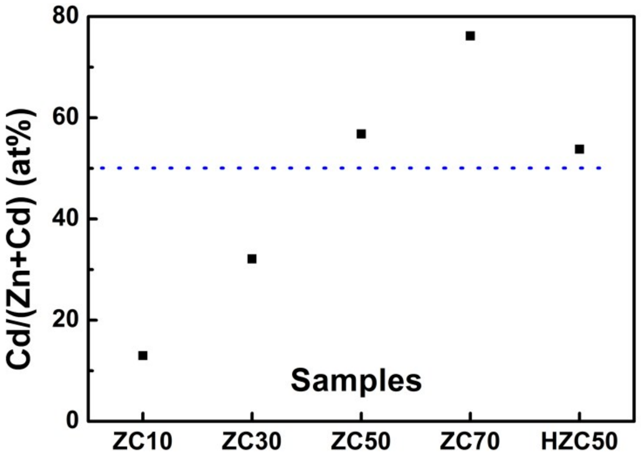

Fig. S4. Inductively coupled plasma (ICP) results for the samples prepared with different Cd content. There was no dramatically variation between the setting and tested Cd and Co concentration.

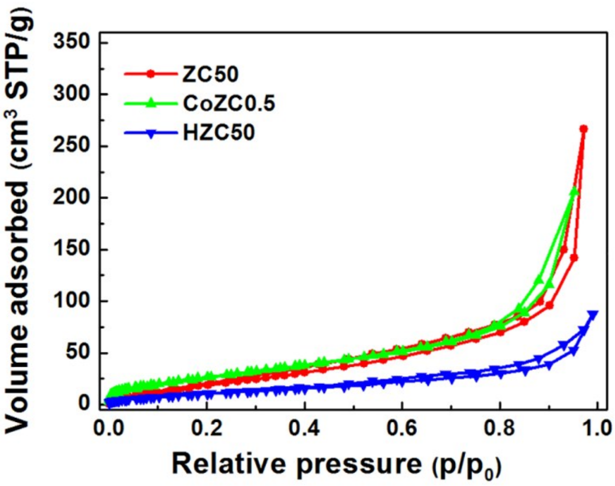

Fig. S5. Nitrogen adsorption/desorption isotherms of the $Zn_{0.5}Cd_{0.5}S$ samples (HZC50: prepared with hydrothermal; ZC50 and CoZC50 represent the sample derived from ZIF-8 and CoZn-ZIF (Co=0.5 at%), respectively). Thanks to the highly porous precursors, ZC50 and CoZC-0.5 exhibits much larger N_2 adsorption volume and S_{BET} (87.4 and 68.9 m^2/g respectively) than that of HZC50 (17.3 m^2/g).

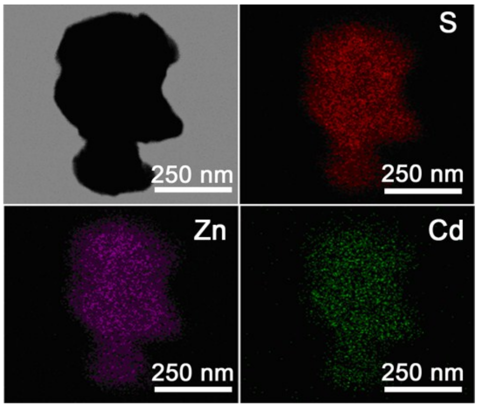

Fig. S6. The element mapping images of the $Zn_{0.5}Cd_{0.5}S$ with Co content of 0.5 at% derived from ZnCo-ZIF.

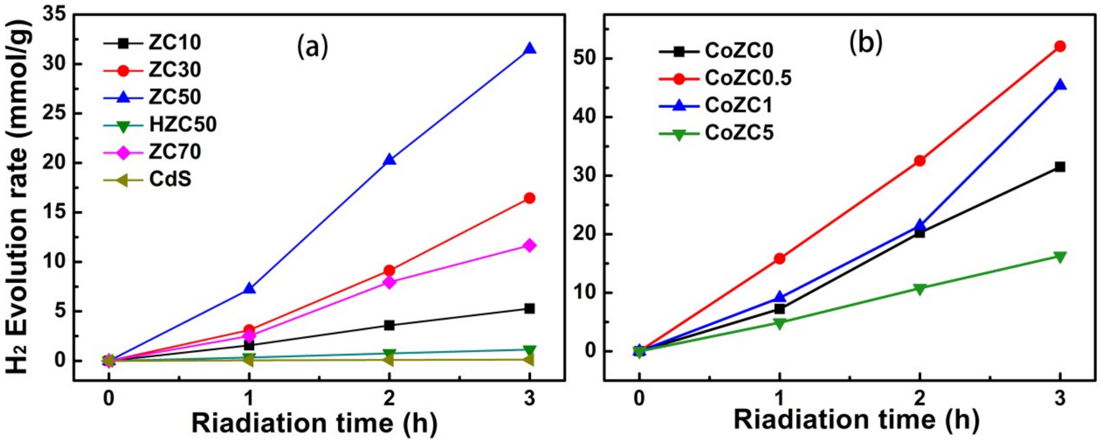

Fig. S7. Comparison of the action spectra of H_2-evolution for the samples with the (a) different Cd content derived from ZIF-8 and (b) different Co doping derived from ZnCo-ZIF.

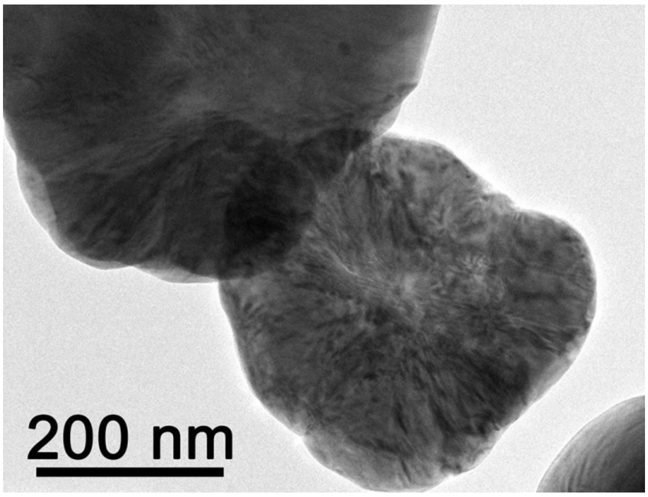

Fig. S8. Transmission electron microscope image of CoZC0.5 after the photocatalytic reaction over 30 h.

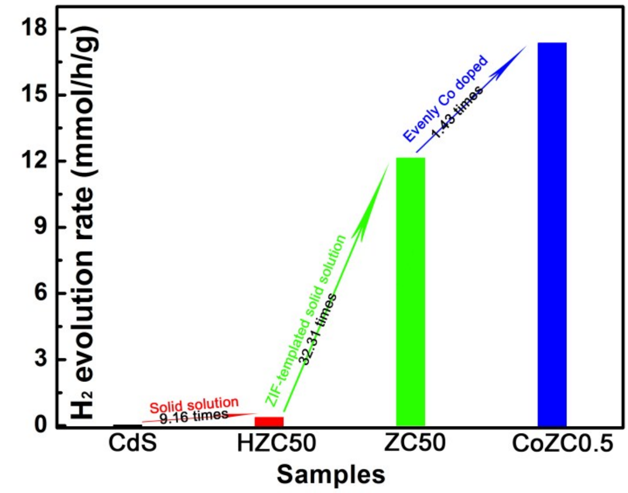

Figure S9. The comparison results of the photocatalytic hydrogen production rate of CdS, $Zn_{0.5}Cd_{0.5}S$ derived from hydrothermal method (HZC50), ZIF-8 (ZC50) and ZnCo-ZIF (CoZC0.5).

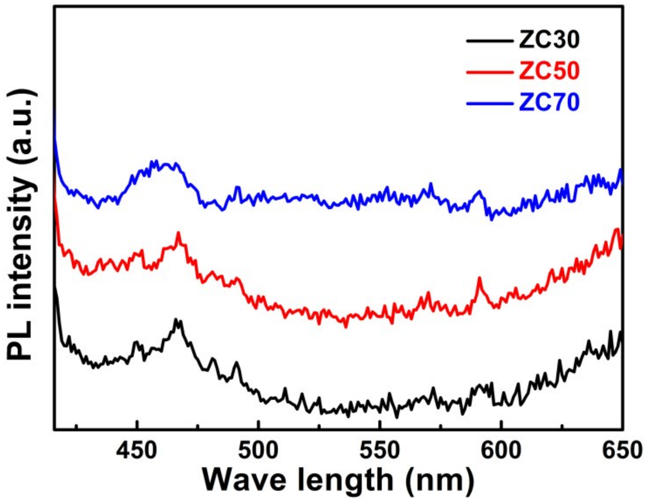

Fig. S10. Room temperature photoluminescence (PL) excitation spectra of the solid solutions with different Cd content derived from ZIF-8.

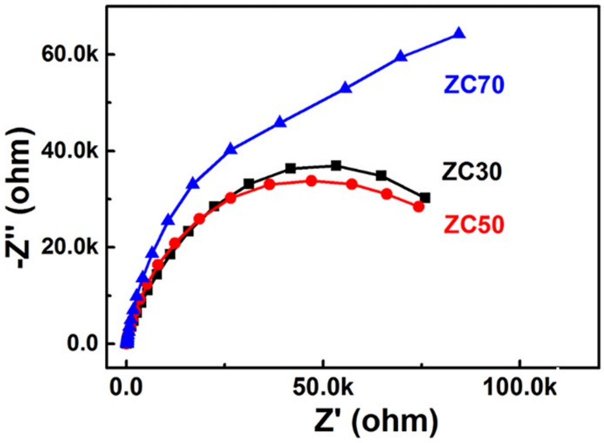

Fig. S11. Effect of the Cd content and on the Nyquist plots of the solid solution samples in 0.1 M Na_2S + 0.02 M Na_2SO_3 aqueous solution under a surface power density of about 10 mW/cm^2. Electrochemical impedance spectra (EIS) analysis is a powerful method to investigate charge transfer process occurring in the three-electrode system and the EIS. The intermediate-frequency response is associated with the electron transport and transfer at the semiconductor sample/electrode interface. The optimal solid solution (ZC50) shows the smallest semicircle in the middle-frequency region, indicating its faster interfacial electron transfer, indicating the significantly enhance the photocatalytic H_2-production activity through using ZIFs as template.

Table S1. Comparison results of H_2-production rate in the CdS based photocatalysts via water splitting.

Photocatalyst	S_{BET} (m^2/g)	Eg (eV)	Activity (mmol/h/g)
ZC30	——	2.60	5.48
ZC50	87.4	2.45	12.13
ZC70	——	2.38	3.89
CoZC0.5	68.9	2.52	17.36
HZC50	17.3	2.41	0.37