Supporting Information

NiS nanoparticles decorated MoS_2 nanosheets as efficient promoter for Enhanced Solar H_2 Evolution over $Zn_xCd_{1-x}S$ Nanorods

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1. Experimental Section

All the chemical reagents were of analytical grade and were purchased from Sinopharm chemical reagent company.

Synthesis of $Zn_xCd_{1-x}S/MoS_2$(y%) hybrid. Briefly, x mmol of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 1-x mmol of cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) were dissolved in 10 mL of ethylenediamine (EN) and 5 mL of water to form a homogeneous solution. Then 5 mL of aqueous solution containing 4 mmol of thiourea and a certain amount of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was added under magnetic stirring. The nominal atomic ratios of Mo to (Zn+Cd) were 0, 10, 15, 20%, respectively. After stirring for 1 h, the mixture was transferred to a 30 mL Teflon-lined autoclave and heated at 200 ^oC for 24 h. The obtained precipitates were collected by centrifugation, washed with deionized water 3 times and dried at 60 ^oC overnight. The as-prepared sample was labelled as $Zn_xCd_{1-x}S/MoS_2$(y%).

Synthesis of $Zn_xCd_{1-x}S/MoS_2/NiS$(z%) hybrid. After the aforementioned mixture was cooled to room temperature, a cetain amount of $Ni(NO_3)_2 \cdot 6H_2O$ was added into the autoclave. Then the suspension is mixed and the autoclave was sealed and maintained at 200 ^oC for additional 12 h. The nominal atomic ratios of Ni to (Zn+Cd) were 1%, 2%, 3%, 6%, 9%, 12%, 15%, 18%, respectively. The following treatments were the same as above mentioned procedure. The obtained samples were assigned as $Zn_xCd_{1-x}S/MoS_2/NiS$(z%). For comparison, The $Zn_{0.2}Cd_{0.8}S/NiS$(z%) were prepared by the same method except for the addition of the $Na_2MoO_4 \cdot 2H_2O$.

2. **Characterization.**

The XRD patterns of the as-prepared samples were recorded on a Philips X'Pert diffractometer with Cu $K\alpha$ radiation (λ = 0.15418 nm). The TEM and HRTEM analyses were conducted on a JEM-2100UHR transmission microscope (TEM, JEOL, Japan) at 200 kV. The UV-*vis* diffuse reflectance spectra were investigated with a Shimadzu UV-2600 spectrophotometer with $BaSO_4$ as a reflectance sample. Photoluminescence (PL) spectra were measured at room temperature using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). The excitation wavelength was 380 nm, the scanning speed was 1200 $nm \cdot min^{-1}$, and the PMT voltage was 700 V. The width of excitation slit and emission slit were about 10.0 nm. X-ray photoelectronic spectroscopy (XPS) was performed using the ThermoFisher Scientific ESCALAB 250 X-ray photoelectron spectrometer. The Brunauer-Emmett-Teller (BET) specific surface area and porous structure of the samples were analyzed by using a Micromeritics Tristar 3000 apparatus.

3. **Photocatalytic H_2 production evaluation.**

Photocatalytic assays were carried out in a gas-closed circulation system (LabSolar-III AG reaction cell, Beijing Perfect Light Company) with optical flat quartz glass of ca. 40.7 cm^2. In a typical experiment, 20 mg of sampling photocatalyst was dispersed in 60 mL aqueous solution containing Na_2S (0.25 M) and Na_2SO_3 (0.35 M), which act as the sacrificial agents. Prior to irradiation, the system was sonicated for 3 min to obtain a uniform suspension. The suspension was then thoroughly degassed and then irradiated by a Xe lamp (300 W). The amount of H_2 produced was determined by using online gas chromatography (Tianmei, GC7900).

Ultrafast transient absorption spectroscopy measurement. The femtosecond transient absorption setup used for this study is based on a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ/pulse, and 1 kHz repetition rate), nonlinear frequency mixing techniques and the Helios spectrometer (Ultrafast Systems LLC). Briefly, the 800 nm output pulse from the regenerative amplifier was split into two parts with a 50% beam splitter. The transmitted part was used to pump a TOPAS Optical Parametric Amplifier (OPA), which generates a wavelength-tunable laser pulse from 250 nm to 2.5 μm. Here a 380 nm laser with 2 nJ/pulse was used as pump beam. The reflected 800 nm beam was split again into two parts. One part with less than 10% was attenuated with a neutral density filter and focused into a 2 mm-thick CaF_2 window to generate a white light continuum (WLC) from 350 nm to 760 nm used for probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. Behind the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 1 KHz. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). All experiments were performed at room temperature. During data collection, the samples were kept in a 2 mm-thick cuvette and constantly stirred by a magnetic stirrer.

4. Supporting Figures

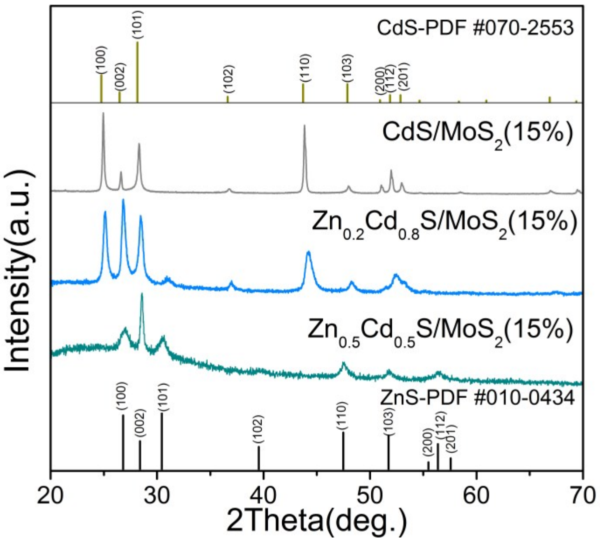

Fig. S1. XRD patterns of the $Zn_xCd_{1-x}S/MoS_2$(15%) nanocomposites.

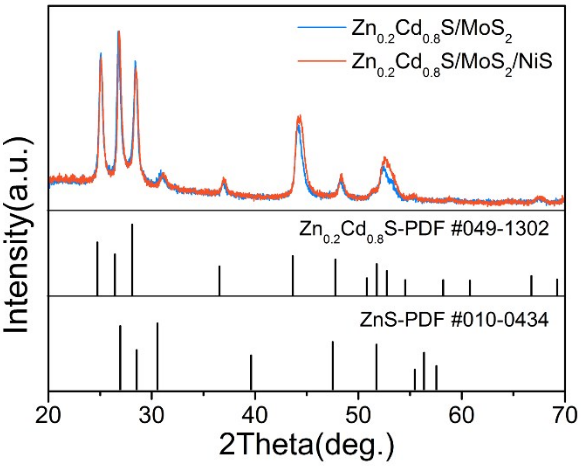

Fig. S2. XRD patterns of the as-prepared $Zn_{0.2}Cd_{0.8}S/MoS_2$ and $Zn_{0.2}Cd_{0.8}S/MoS_2/NiS$.

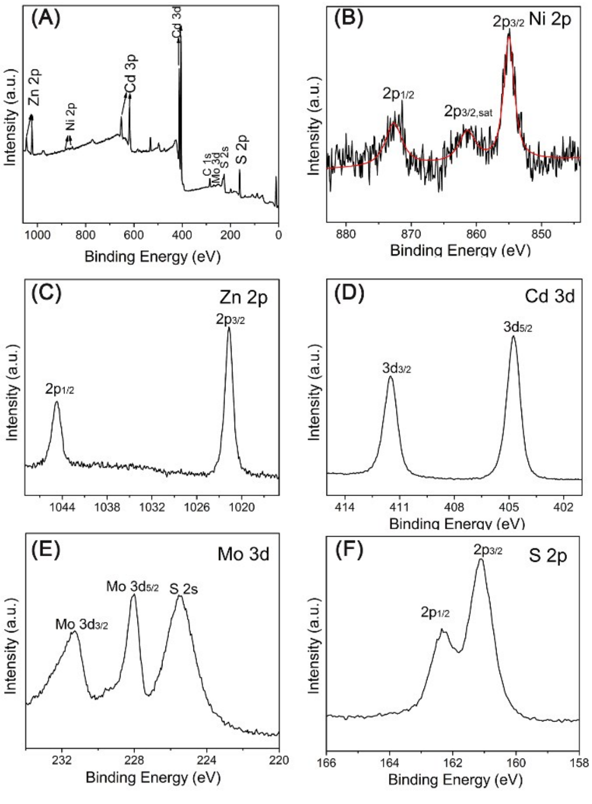

Fig. S3. XPS of the typical $Zn_{0.2}Cd_{0.8}S/MoS_2/NiS$: (A) survey spectrum, (B) high resolution Ni2p spectrum, (C) Zn2p spectrum, (D) Cd3d spectrum, (E) Mo3d spectrum and (F) S2p spectrum.

The survey spectrum in Fig. S3A indicates the presence of Ni, Zn, Cd, Mo and S elements. The high-resolution XPS spectrum of Ni2p (Fig. S3B) shows the binding energy at 855.0 eV corresponds to Ni^{2+} in NiS, which has a strong interaction with MoS_2.[1,2] The peaks at 861.4 eV and 872.34 eV are assigned to the satellites of $Ni2p_{3/2}$ and Ni $2p_{1/2}$ in NiO, respectively, showing that a trace of NiO was formed.[3,4] For Zn2p and Cd3d (Fig. S3C and Fig. S3D), the peaks centred at 1021.7 eV and 1047.1 eV are attributed to Zn^{2+} and the peaks at 411.5 eV and 404.7 eV are attributed to Cd^{2+}.[5] Moreover, XPS analysis shows the Zn:Cd molar ratio was 1:4.14 in a wide scan XPS spectrum, which is consistent with the composition of $Zn_{0.2}Cd_{0.8}S$. In addition, XPS signals of doublet Mo3d in Fig. S3E are observed at binding energies of 228.0 ($Mo3d_{5/2}$) and 231.35 eV ($Mo3d_{3/2}$) along with a S2s peak at 225.46 eV, which are consistent with the reported values.[6]

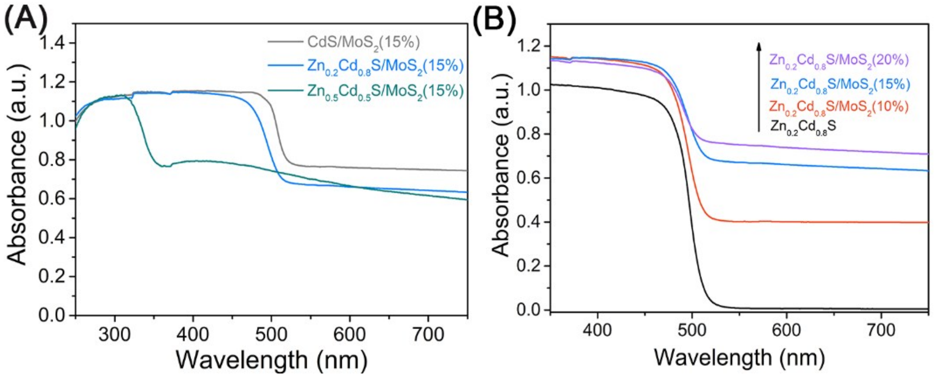

Fig. S4. UV−visible diffuse reflection spectra of (a) Zn$_x$Cd$_{1-x}$S/MoS$_2$(15%) samples and (b) Zn$_{0.2}$Cd$_{0.8}$S/MoS$_2$(y%, y=0, 10, 15, 20) samples.

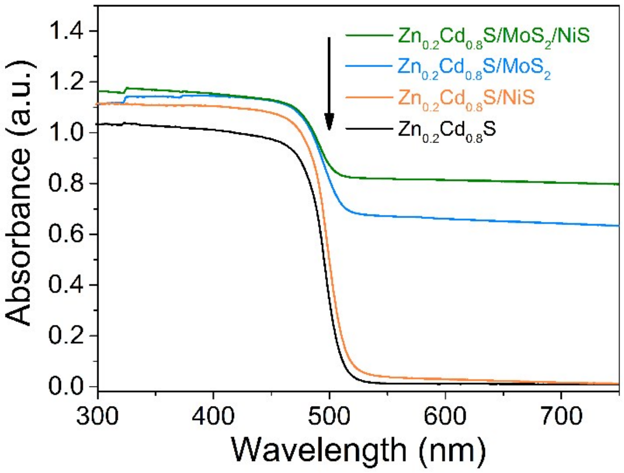

Fig. S5. UV-vis diffused reflectance spectra of the typical Zn$_{0.2}$Cd$_{0.8}$S-based samples.

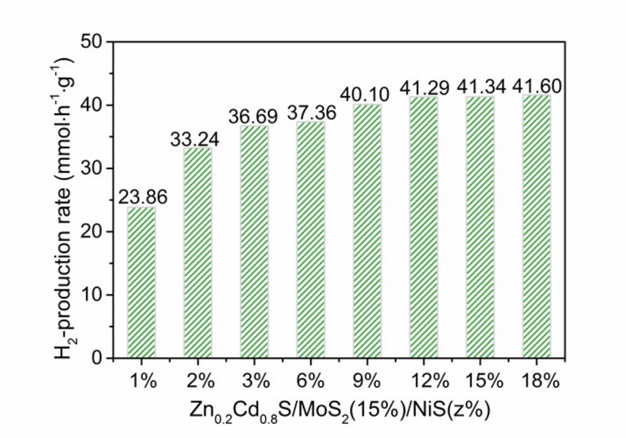

Fig. S6. Photocatalytic H_2-production rate comparison of different $Zn_{0.2}Cd_{0.8}S/MoS_2(15\%)/NiS(z\%)$ composites.

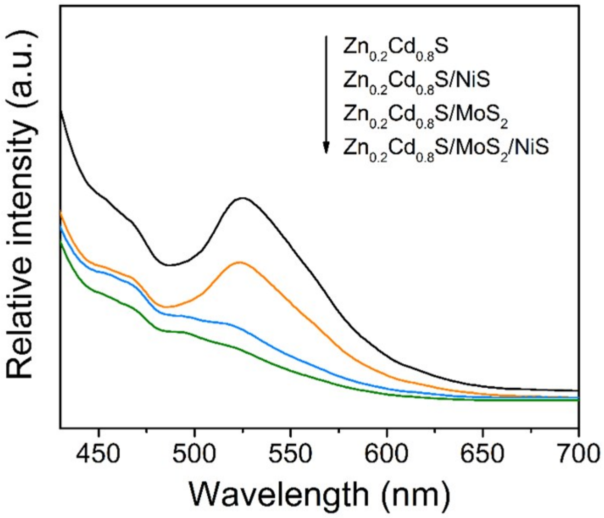

Fig. S7. Photoluminescent spectra of the prepared samples.

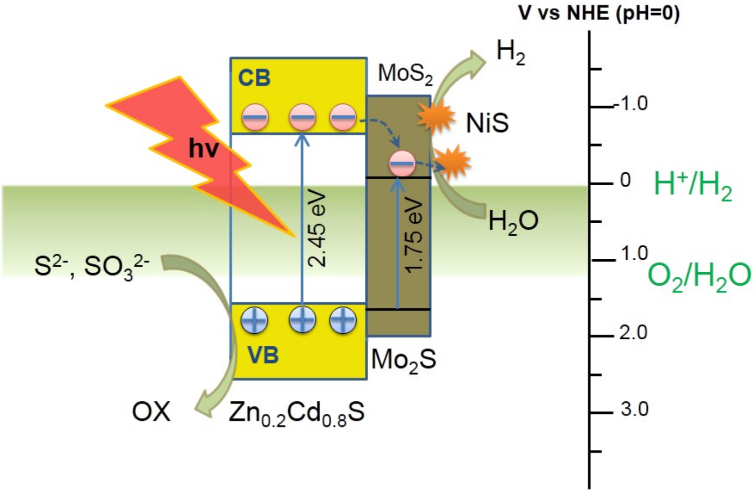

Fig. S8. Energy diagram of $Zn_{0.2}Cd_{0.8}S/MoS_2$(15%)/NiS(12%) photocatalysts under solar light irradiation.

Table S1 Comparisons of photocatalytic hydrogen evolution over reported ZnCdS based photocatalysts and the present samples.

Photocatalyst	**Light source**	**H_2 production rate (μmol/h)**	**Ref.**
$Zn_{0.5}Cd_{0.5}S$	300 W Xe lamp	770	[1]
$NiS/Zn_xCd_{1-x}S/RGO$	Newport 91160 100 mW cm^{-2}	375.7	[2]
$Zn_{1-x}Cd_xS/CdS$	300 W Xe lamp equipped with a cutoff filter (420 nm)	667.5	[3]

Ni(OH)$_2$-loaded Zn$_x$Cd$_{1-x}$S	300 W Xe lamp equipped with a UV cutoff filter	7160	[4]
Cu^{2+}- Zn$_x$Cd$_{1-x}$S	500 W Xe lamp equipped with a cutoff filter	4638.5	[5]
Zn$_x$Cd$_{1-x}$S/MoS$_2$	150 W Xe lamp equipped with a cut-off filter at 420 nm	7179.1	[6]
Zn$_{0.5}$Cd$_{0.5}$S@MoS$_2$/RGO	300 W Xe lamp	2310	[7]
RGO/ZnO@Zn$_x$Cd$_{1-x}$S	equipped with a cutoff filter (420 nm)	1865	[8]
Zn$_{0.2}$Cd$_{0.8}$S/MoS$_2$/NiS	300 W Xe lamp	41290	Present work

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