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Supporting Information

Metal-organic Framework-derived $Zn_{1-x}Cd_xS$/CdS Heterojunction for Efficient Visible Light-driven Photocatalytic Hydrogen Production

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Experimental section

Chemicals and materials. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, AR, Aladdin), cadmium chloride ($CdCl_2$, AR, Aladdin), 2-methylimidazole (MeIM, AR, Aladdin), thioacetamide (TAA, AR, TCI), and methanol (AR, 99.7%, Tianjin Concord)

All chemicals were used directly after purchased from commercial corporations without any further purifications.

Synthesis of nanosized ZIF-8. According to the reported method, the nanosized ZIF-8 was synthesized with some modifications as follows: typically, $Zn(NO_3)_2 \cdot 6H_2O$ (2.9740 g) and 2-methylimidazole (MeIM, 2.4630 g) were dissolved in 200 mL of methanol to form a clear solution, respectively. Then, the former was added into the latter rapidly under magnetic stirring, and the mixture solution was sustained stirred for 15 min at room temperature until turned into white suspensions. Subsequently, the white suspensions were centrifuged at 8500 rpm. The precipitate obtained was washed with methanol for three times and dried under 40 °C in vacuum.

Synthesis of ZnS QDs. Take 650.0 mg obtained nanosized ZIF-8 was dispersed into the mixture of 30 mL deionized water and 30 mL methanol with sonication, and then thioacetamide (TAA, 1.5030 g) was added under magnetic stirring. The mixture was stirred at 45 °C for 8 h. The white suspensions turned into turbid, and were separated by centrifugation at 9500 rpm. The precipitate obtained was washed with deionized water for three times and dried under 40 °C in vacuum.

Synthesis of $Zn_{1-X}Cd_XS$ QDs. Firstly, 50.0 mg ZnS QDs was dispersed in 40 mL of deionized water, and then appropriate amount of $CdCl_2$ (953.3 mg, 317.8 mg, 190.7 mg, 136.2 mg, 105.9 mg) was added, which make the ratio of Zn:Cd is 0.1, 0.3, 0.5, 0.7, and 0.9. After ultrasonically dispersing the mixture evenly, heat it to 65 °C for 10 hours with magnetic stirring. Then, the yellow turbid mixture was centrifuged at 8000 rpm and the solid product was washed with deionized water for three times. Finally, the yellow precipitate was dried at 40 °C in vacuum.

Synthesis of $Zn_{1-X}Cd_XS$/CdS QDs. Take 100.0 mg $Zn_{0.7}Cd_{0.3}S$, (16.5 mg, 33.0 mg, 49.5 mg, 66.0 mg or 82.5 mg) $CdCl_2$ and 135.2 mg TAA to dispersed in 40 mL of deionized water evenly, heated to 70 °C and maintained for 7h with magnetic stirring, then the yellow turbid mixture was centrifuged at 8000 rpm. The obtained product was washed with deionized water for three times. Finally, the yellow precipitate was dried at 40 °C in vacuum.

Physical Characterization. The powder X-ray diffraction (PXRD) patterns were collected by a Rigaku MiniFlex600 diffraction meter over a 2θ range of 3-80 ° at a scanning speed of 8 ° min^{-1}. An X-ray diffractometer was used with a Cu Kα radiation (λ ¼ 1.5406 Å) at 40 kV and 15 mA. Transmission electron microscopy (TEM) (JEOL, JEM-2800) with energy dispersive X-ray spectrum (EDS) elemental mapping. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, SPECTRO-BLUE IL) were used to characterize the components of the samples obtained. The PL spectrum was performed on a Hitachi F7000 fluorescence spectrophotometer. The room temperature PL spectra were recorded with an excitation wavelength of 400 nm. The time-resolved PL spectrum were performed on the Edinburgh FLS980. The XPS analysis of the samples was carried out on an Axis Ultra DLD system with an Al Kα X-ray source (E = 1486.7 eV). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. The specific surface areas were calculated from the N_2 isotherms at 77 K using the BET method. The pore distribution was calculated using the DFT method. The optical absorbance measurement of all samples was performed using a Shimadzu UV-2550 spectrophotometer. On the basis of the Kubelka-Munk (KM) method and the UV-visible diffuse absorption spectra by the following equation: $\alpha h\nu = A(h\nu\text{-Eg})^{0.5}$, the Eg of all samples can be calculated experimentally, where α, A, h, and $h\nu$ are the absorption coefficient, constant, and Planck's constant, and photon energy, respectively.[1]

Photoelectrochemical Measurements. All the PEC tests were conducted in a standard three-electrode quartz cell with an electrochemical station (CHI 660E, Chenhua Ltd., Shanghai, China). The reference electrode and counter electrode were Ag-AgCl and Pt foil respectively, the photoanodes as the working electrode, and the 20 mL Na_2SO_4 aqueous solution (0.1 M, pH 6.8) as the electrolyte. To prepare the working electrode, the as-synthesized samples (2 mg) were added into 10 μL Nafion and 1 mL ethanol mixed solution, and the mixture was ultrasonicated for 30 min to dispersed completely. Finally, took 200 μL of suspension and dropped evenly onto the surface of a prepared FTO substrate. All the working electrodes were dried at room temperature for 6 h. For the transient photocurrent response test and the electrochemical impedance spectroscopy (EIS) measurements, the 350 W Xe lamp with a 420 nm cut-off filter was acted as light source. In the photocurrent response test, a bias voltage of 0.62 V (1.23 V *vs.* RHE) was applied and the illuminated area of the working electrode was about 1 cm^2. The electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 100 to 10^4 Hz with a bias potential of 1.0 V. The instruments used for the steady-state surface photovoltage test are built by the test platform. The light source adopts CHF-XM500 Xe lamp (Beijing), the monochromator adopts SBP300 three-grating monochromator (Beijing), the chopper model is SR540 (Stanford Company), and the lock-in amplifier model is SR830 (Stanford Company). During the test, the sample is placed between the ITO conductive glass to form a "sandwich" structure of electrodes. The atmosphere control test system consists of the vacuum system, the carrier gas system (N_2 as the carrier gas) and a special sealable sample cell.

Photocatalytic Hydrogen Production. The photocatalytic hydrogen evolution experiments were performed using Perfectlight Labsolar 6A system with a 100 mL quartz reactor at 5 °C. In the typical procedure, before the photocatalytic reaction, the reaction vessel was evacuated for 30 min to remove the dissolved gas and ensure the vacuum conditions. 10 mg of the as-obtained powder photocatalyst and sacrificial agents (1.2000 g Na_2S and 0.6300 g Na_2SO_3) were dispersed uniformly in 100 mL of aqueous solution by sonication. In the process of photocatalytic hydrogen evolution, a 350 W xenon lamp with the cut-off filter ($\geqslant$ 420 nm), was applied to trigger the photocatalytic reaction，which was placed 10 cm away from the reactor, and the irradiation intensity on the reactor was ~100 $mW\cdot cm^{-2}$, which was tested by the FZ-A visible-light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China). To maintain the photocatalyst suspended in the mixture，constantly magnetic stirring was used at the bottom of the reactor. The amount of hydrogen produced was analyzed through a thermal conductivity detector（TCD）of an online gas chromatograph (Fuli GC9790) instrument with the high-purity Ar as the carrier-gas (99.999%). The apparent quantum efficiency (AQE) of 5 mg of catalyst for H_2 evolution is measured using the CHROMATOGRAPH and 300W xenon lamp with 400 nm band-pass filter. The number of incident photon is 4.99 × 1020, and the AQE for H_2 evolution is calculated as 3.84% according to the following equation:

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

Calculation method. The present first principle DFT calculations are performed by Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method.[2, 3] The exchange-functional is treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional.[4] The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.03 eV/Å was set for convergence criterion of geometry relaxation. The Brillouin zone integration is performed using 5×5×1 k-point sampling. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. The DFT-D3 method was employed to consider the van der Waals interaction.[5]

Table S1 The Zn/Cd ratio results of $Zn_{1-x}Cd_xS$ samples.

Samples	**Theoretical Zn/Cd ratio**	**Zn/Cd ratio (ICP-AES)**	**H_2 production rate (mmol g^{-1} h^{-1})**
$Zn_{0.1}Cd_{0.9}S$	0.10	0.11	0.031
$Zn_{0.3}Cd_{0.7}S$	0.30	0.35	0.043
$Zn_{0.5}Cd_{0.5}S$	0.50	0.52	0.073
$Zn_{0.7}Cd_{0.3}S$	0.70	0.76	0.110
$Zn_{0.9}Cd_{0.1}S$	0.90	0.93	0.067

Table S2 Summary of some reported ZnCdS-based photocatalysts.

Ref.	**Sample**	**Test conditions**	**Light Source**	**H_2 production rate**
This Work	ZCS-C-3	$H_2O/Na_2S/Na_2SO_3$	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	2.7 mmol g^{-1} h^{-1}
[1][6]	α-Fe_2O_3 / $Zn_{0.4}Cd_{0.6}S$	$H_2O/Na_2S/Na_2SO_3$	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	536.8 μmol h^{-1}
[2][7]	$Zn_{1-x}Cd_xS$ / CdS	$H_2O/Na_2S/Na_2SO_3$	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	667.5 μmol h^{-1} (per 5 mg)
[3][8]	(RGO)-$Zn_xCd_{1-x}S$	$H_2O/Na_2S/Na_2SO_3$	AM 1.5G	1824 μmol g^{-1} h^{-1}
[4][9]	$Zn_xCd_{1-x}In_2S_4$ / g-C_3N_4	H_2O/TEOA	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	170.3 μmol h^{-1}
[5][10]	$Cd_{0.2}Zn_{0.8}S$@UiO-66-NH_2	$H_2O/Na_2S/Na_2SO_3$	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	5846.5 μmol g^{-1} h^{-1}
[6][11]	VS_2-ZnCdS / CdS-P	$H_2O/Na_2S/Na_2SO_3$	Visible light ($\lambda \geq 420$ nm, 300W Xe lamp)	192.3 μmol h^{-1}

Table S3 Parameters of equivalent circuit for the impedance data of ZnS, ZnCdS, CdS, and ZCS-C-X samples.

Samples	**R_s (Ω)**	**R_{ct} (Ω)**
ZnS	50.62	4826
$Zn_{0.7}Cd_{0.3}S$	50.06	4368
ZCS-C-1	51.87	4224
ZCS-C-2	43.68	3539
ZCS-C-3	51.63	2462
ZCS-C-4	50.07	3111
ZCS-C-5	52.23	3711
CdS	48.62	4621

Table S4 Third-order fitting results of the time-resolved PL spectra of the ZCS-C-X samples.

Samples	**τ_1 (ns)**	**A_1 (%)**	**τ_2 (ns)**	**A_2 (%)**	**τ_3 (ns)**	**A_3 (%)**	**τ_{AVE} (ns)**	χ^2
ZCS-C-1	1.3254	39.85	5.2678	43.41	27.2062	16.74	7.37	1.114
ZCS-C-2	1.4102	42.58	5.8441	41.55	39.3263	15.87	9.27	1.079
ZCS-C-3	0.9819	26.52	4.6505	34.83	46.7513	38.65	19.95	1.144
ZCS-C-4	1.2698	33.89	5.2584	39.92	36.2258	26.19	12.02	1.173
ZCS-C-5	1.2691	34.24	4.4222	40.76	26.1928	25.00	8.79	1.149

Table S5 The bandgap energy (Eg), H_2 production rate results, and Quantum Yield (QY) of ZCS-C-X samples.

Samples	**Eg (eV)**	**H_2 production rate (mmol g^{-1} h^{-1})**	**Quantum Yield (%)**
ZCS-C-1	2.42	0.32	3.32
ZCS-C-2	2.37	0.96	0.86
ZCS-C-3	2.30	2.70	0.56
ZCS-C-4	2.25	1.10	0.69
ZCS-C-5	2.16	0.55	2.06
$Zn_{0.7}Cd_{0.3}S$	2.82	0.11	3.58
CdS	2.13	0.062	/

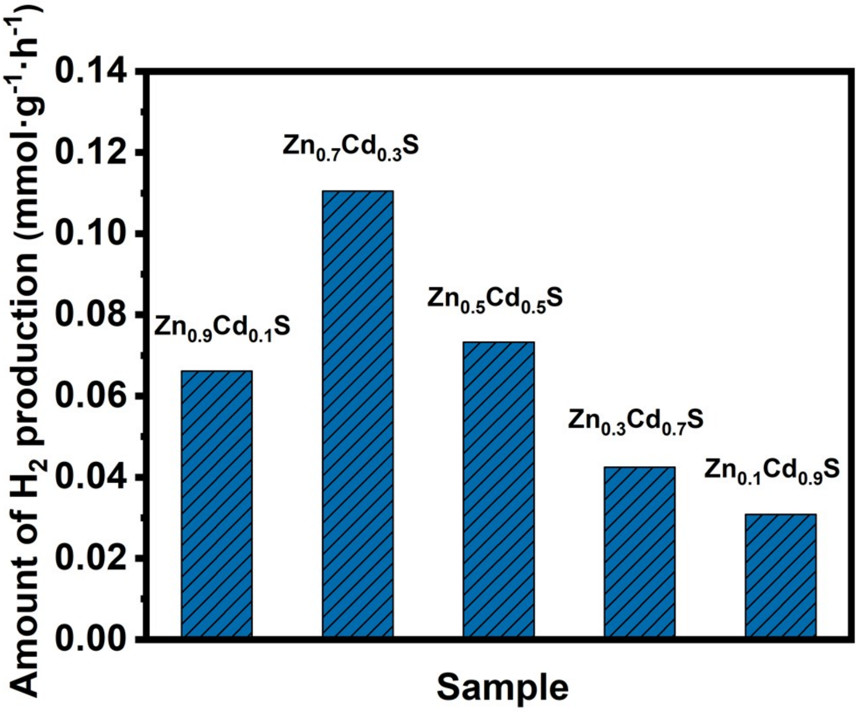

Fig. S1 Photocatalytic hydrogen production rates of $Zn_{1-x}Cd_xS$

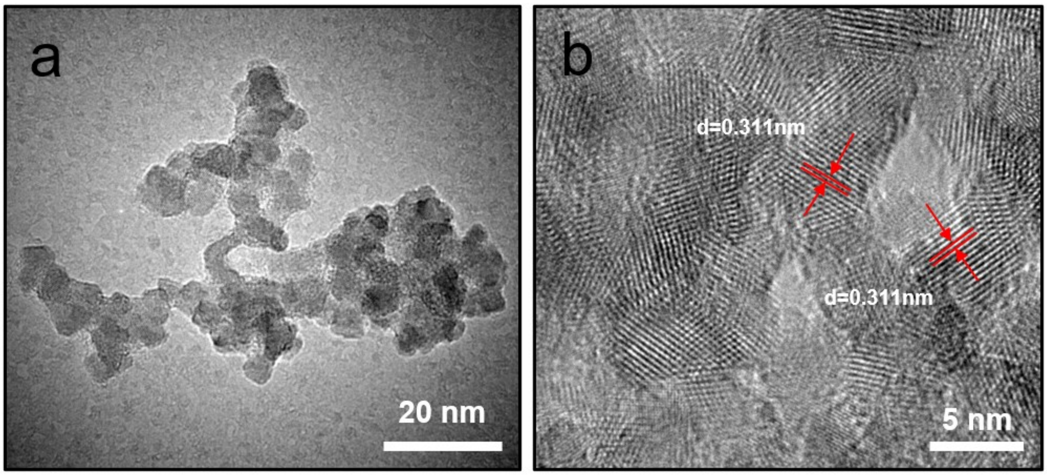

Fig. S2 (a) the TEM image of ZnS; (b) the HRTEM image of ZnS

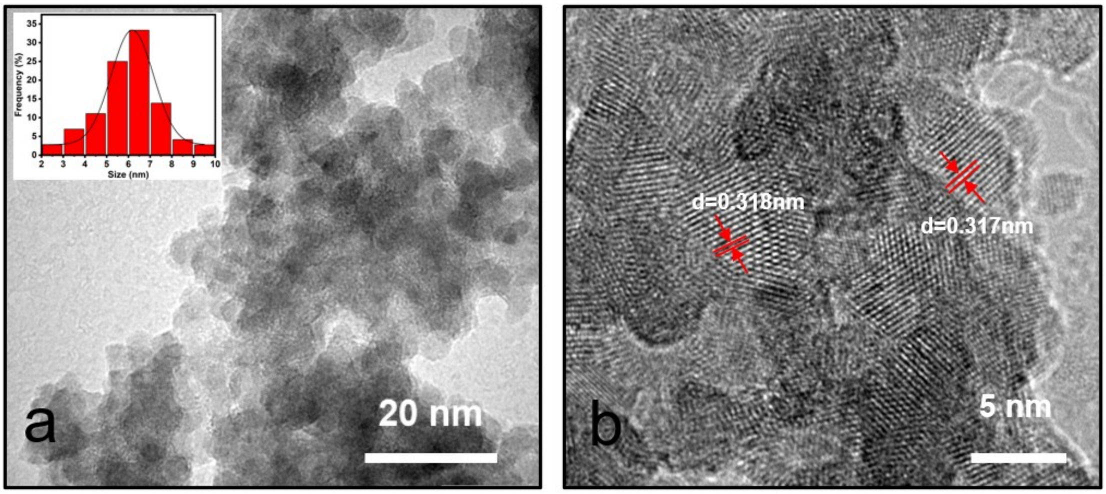

Fig. S3 (a) the TEM image of $Zn_{0.7}Cd_{0.3}S$; (b) the HRTEM image of $Zn_{0.7}Cd_{0.3}S$

ZCS-C-1	**ZCS-C-2**	**ZCS-C-3**	**ZCS-C-4**	**ZCS-C-5**
				

Fig. S4 Photographs of ZCS-C-X samples

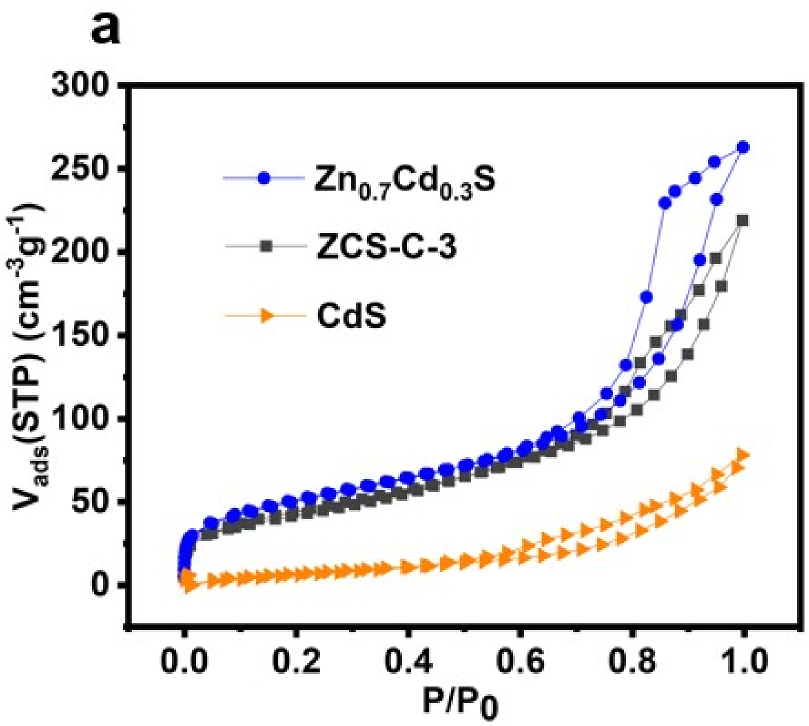

Fig. S5 N_2 isotherms and of $Zn_{0.7}Cd_{0.3}S$, ZCS-C-3, and CdS samples

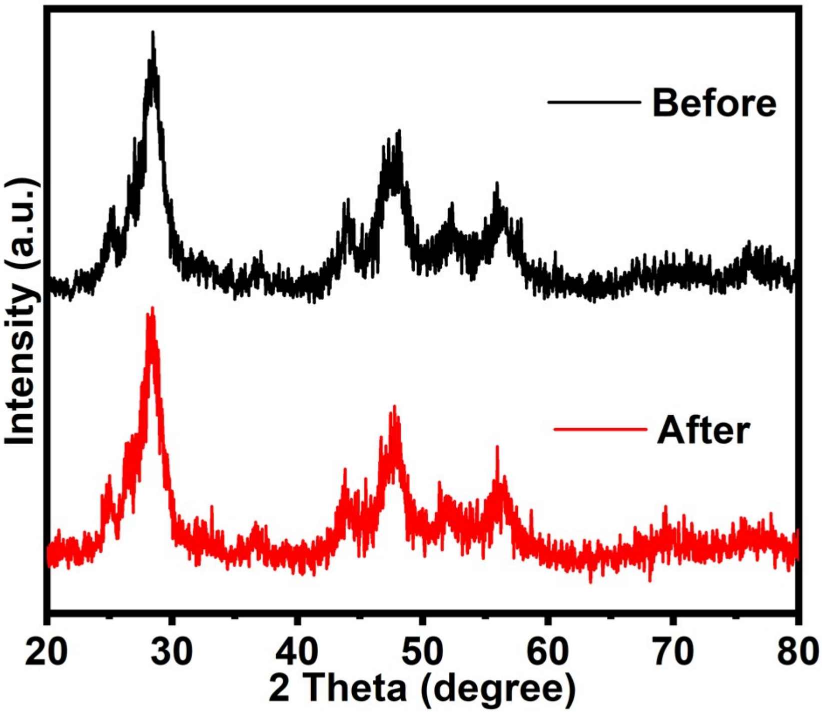

Fig. S6 XRD patterns for ZCS-C-3 sample before and after reaction

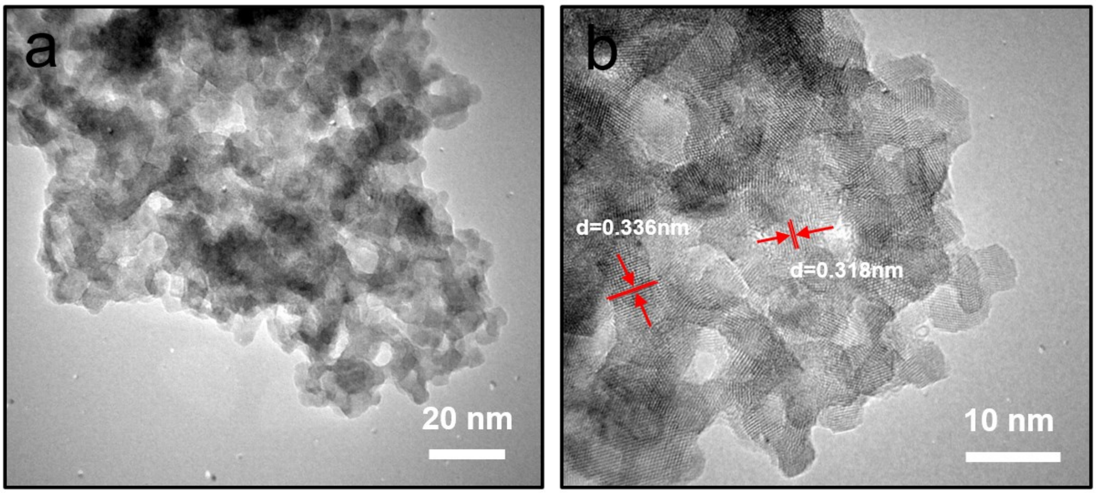

Fig. S7 TEM patterns for ZCS-C-3 sample after reaction

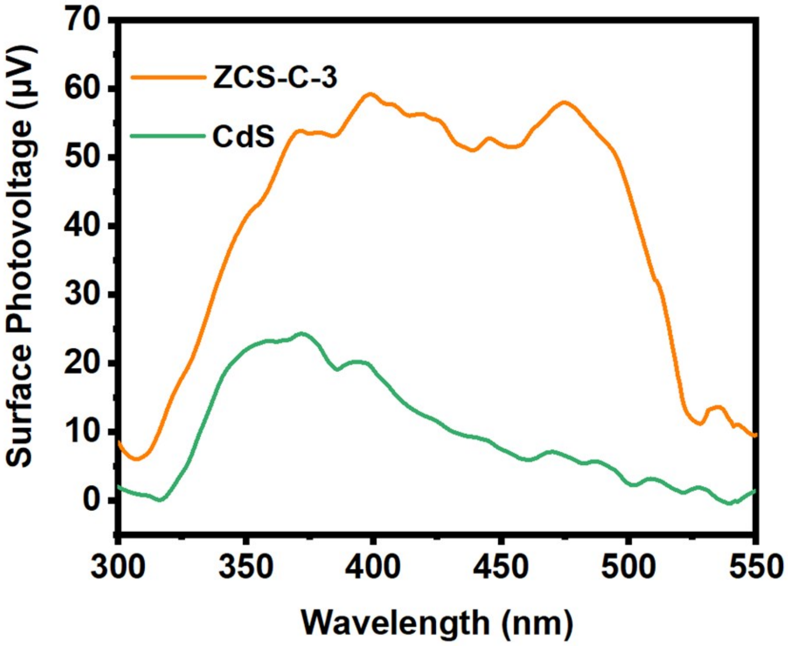

Fig. S8 Steady-state surface photovoltage (SPV) spectrum of ZCS-C-3 and CdS

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