Electronic Supplementary Information for:

Green synthesis of 3D core-shell SnS_2/SnS-$Cd_{0.5}Zn_{0.5}S$ multi-heterojunction for efficient photocatalytic H_2 evolution

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1. Preparation of SnS

1 mmol of $SnCl_2 \cdot H_2O$ and 4 mmol of thiourea were dissolved in 20 mL deionized water, and were ultrasonically stirred for 1 h. Then, the solution was transferred to a 50 mL Teflon liner, and heated at 190°C for 12 h. After the autoclave was allowed to cool to room temperature, the final product was centrifuged and washed with deionized water and ethanol several times, and dried in an oven at 70°C. The final product was labelled as SnS.

2. Characterization

The phase composition of the as-prepared materials was analyzed by X-ray diffractometer (XRD, SmartLab-9kW, Cu Kα radiation, 45 keV, 200 mA). The morphologies of samples were investigated by field-emission scanning electron microscope (SEM, FIB Helios G4) and transmission electron microscope (TEM, Talos F200X G2). X-ray photoelectron spectroscope (XPS) measurements were measured on a Thermo Escalab 250 Xi with Mg Kα as the excitation source. The UV-Vis diffuse reflection spectra (DRS) were obtained on a Shimadzu UV-3600 spectrophotometer with an integrated sphere attachment and $BaSO_4$ used as the reference. Steady-state fluorescence spectra, time resolved fluorescence spectra, and fluorescence quantum yields were measured with FLS1000 (Edinburgh instrument Ltd, England). The absolute fluorescence quantum yields of all samples were obtained by using an integrating sphere and photoluminescence decay curves were measured on the single photon counting (TCSPC) mode. N_2 adsorption-desorption isotherms were measured at 77 K after heating the samples at 120℃ for 6 h to remove any moisture and solvent molecules in the pore with a Beckman Coulter SA3100 analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate specific surface areas (S_{BET}). By using the Barrett-Joyner-Halenda model, the pore size and volume distributions were derived from the adsorption branches of isotherms.

3. Calculation of AQY

The apparent quantum yields (AQY) were tested by adding different bandpass filters and calculated using equation (S1):

$$\mathrm{AQY}=\frac{2\times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}}\times 100\%$$

$$=\frac{2\times n\times N_A}{\frac{S\times P\times t}{h\nu}}\times 100\% \quad =\frac{2\times n\times N_A\times h\times c}{S\times P\times t\times \lambda}\times 100\% \qquad (S1)$$

Where n is the yield of the H_2 evolution (mmol), N_A is 6.022×10^{23} /mol, h is 6.626×10^{-34} J·S, S is effective lighting area (cm^2), P is the light intensity (mW/cm^2), t is reaction time (s), λ is corresponding monochromatic wavelength (nm), respectively.

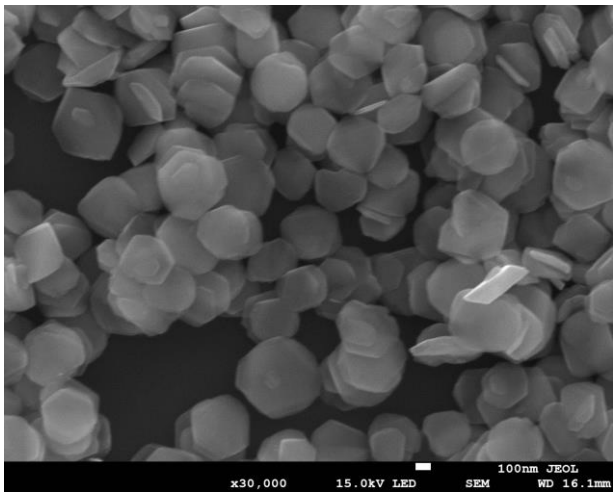

Fig. S1 SEM image of SnS_2 nanosheets.

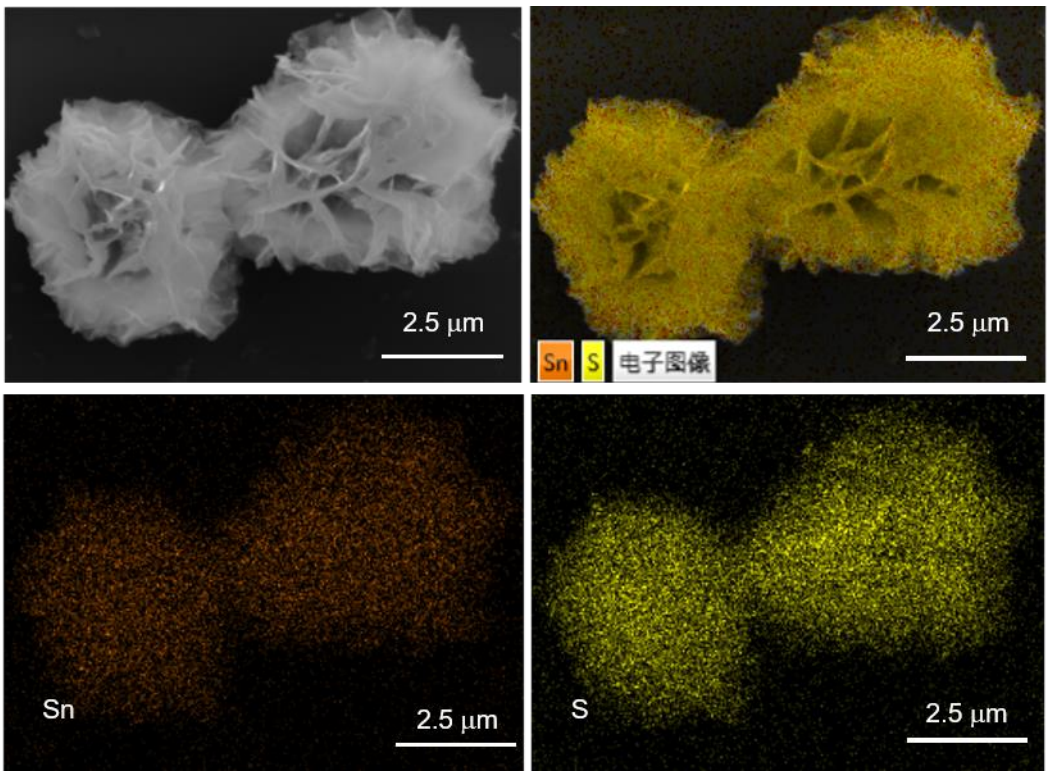

Fig. S2 EDS mapping images of SS nanoflowers.

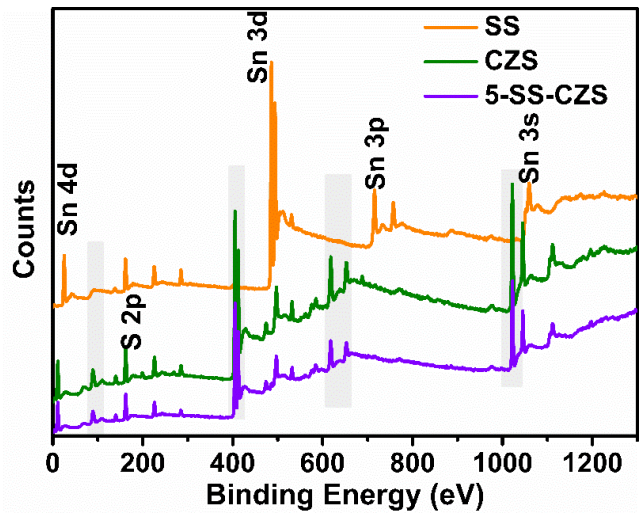

Fig. S3 The survey XPS spectra of samples.

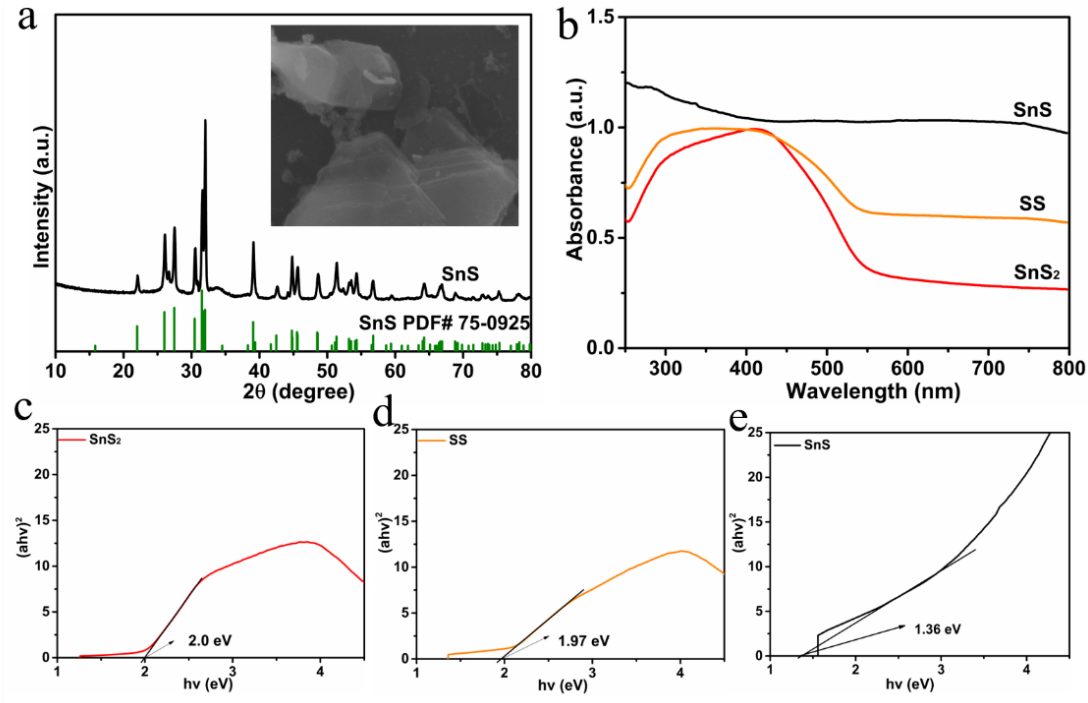

Fig. S4 (a) XRD pattern of SnS (inset of SEM), (b) UV-Vis diffuse reflectance spectroscopy and (c-e) energy bandgap Tauc plots of SnS_2, SS, and SnS.

Notes: As-prepared SnS sample is investigated by XRD, SEM, UV-Vis DRS spectra. To demonstrate the electron transfer pathway between SnS and SnS_2 in SS, E_{CB} and E_{VB} of SnS_2 and SnS are obtained by combing the UV-Vis DRS spectra and the following equation S2.

$$E_{CB}=\chi-E_e-0.5E_g \qquad E_{VB}=E_g-E_{CB} \qquad (S2)$$

Where χ represents the absolute electronegativity of the semiconductor, E_e is the energy of the free electrons on the hydrogen scale (4.5 eV), and E_g is the bandgap. The bandgaps of SnS, SnS_2, and SS are 1.36, 2.0, and 1.97 eV, respectively. The absolute electronegativity of the semiconductors (χ) is 4.34 eV and 4.66 eV for SnS and SnS_2.[9] Based the above results, the calculated E_{CB} and E_{VB} are determined to be -0.87 eV and 0.55 eV for SnS, -0.84 eV and 1.16 eV for SnS_2.

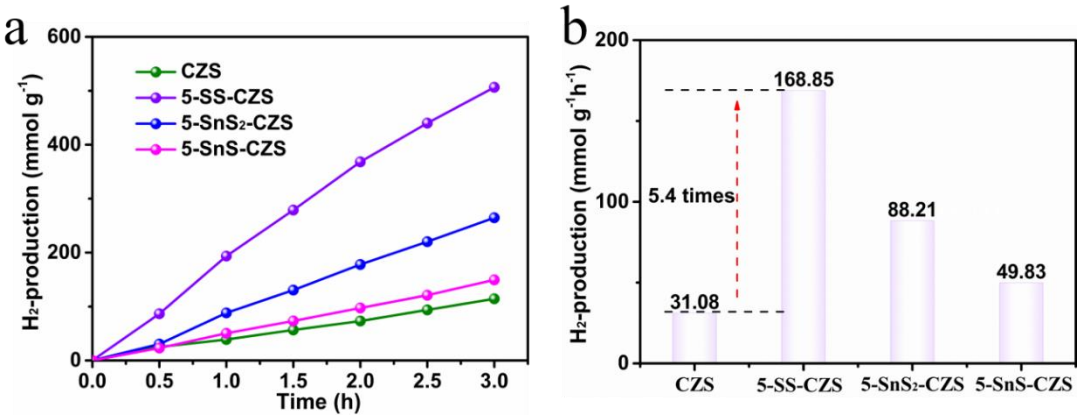

Fig. S5 The photocatalytic hydrogen evolution activity (a and b) of different samples under visible light irradiation (λ ⩾ 420 nm).

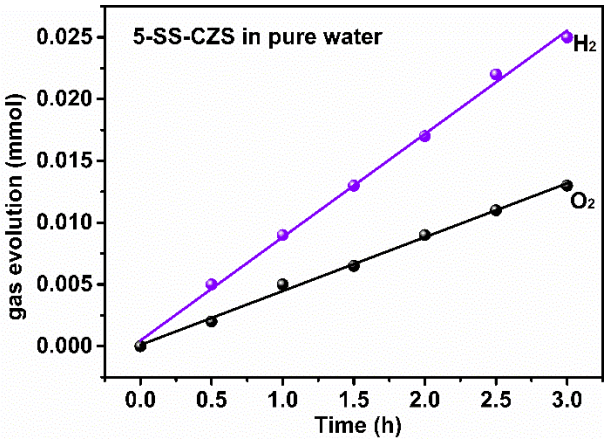

Fig. S6 Photocatalytic performance of 5-SS-CZS in pure water.

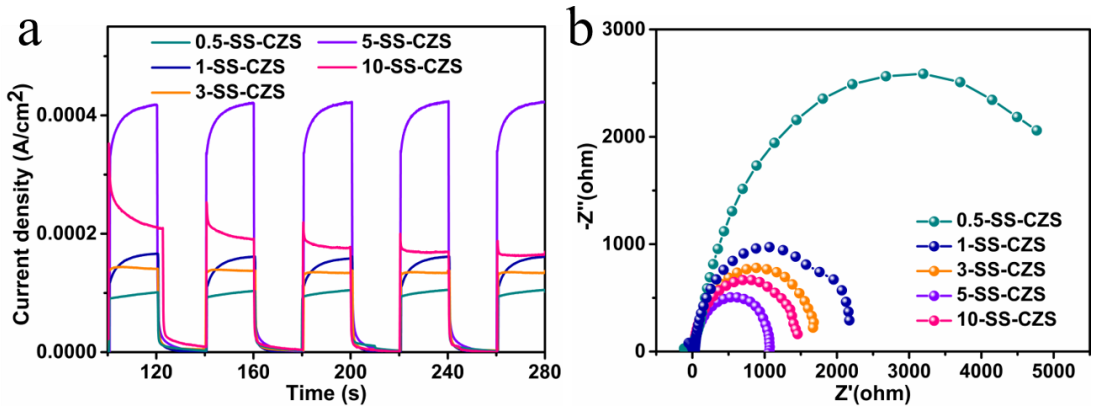

Fig. S7 Transient photocurrent and Nyquist impedence plots of x-SS-CZS photocatalysts.

Table S1 Comparisons of H_2 evolution rate of $Cd_xZn_{1-x}S$-based photocatalysts.

Photocatalyst	Catalyst mass (mg)	Light source	Sacrificial agent	PHE rates ($mmol \cdot g^{-1}h^{-1}$)	H_2 rate ($mmol\ h^{-1}$)	Ref
SS-CZS	10	300 W Xe lamp (λ > 420 nm)	100 mL of H_2O containing 0.25 M Na_2S/0.35 M Na_2SO_3	168.85	1.688	Recent work
1%-Ni_3C/T-$Zn_{0.5}Cd_{0.5}S$	50	300 W Xe lamp (λ > 420 nm)	80 mL of H_2O containing 0.25 M Na_2S/0.25 M Na_2SO_3	15.66	0.783	[1]
$Zn_{0.5}Cd_{0.5}S$/$PdP_{\sim0.33}S_{\sim1.67}$	1	300 W Xe lamp (λ > 420 nm)	100 mL of H_2O containing 0.7 M Na_2S/0.5 M Na_2SO_3	246.04	0.246	[2]
			0.75 M ascorbic acid	372.12	0.372	
$Zn_{0.5}Cd_{0.5}S$/Ti_2C/TiO_2-2%	10	300 W Xe lamp (λ > 400 nm)	100 mL of H_2O containing 0.3 M Na_2S/0.3 M Na_2SO_3	32.57	0.326	[3]
$NiCo_2O_4$/$Zn_{0.1}Cd_{0.9}S$	50	300 W Xe lamp (λ > 400 nm)	100 mL of H_2O containing 0.35 M Na_2S/0.25 M Na_2SO_3	34.4	1.720	[4]
20%-$W_{18}O_{49}$/$Cd_{0.5}Zn_{0.5}S$	20	300 W Xe lamp (λ> 200 nm)	100 mL of H_2O containing 0.35 M Na_2S/0.25 M Na_2SO_3	147.7	2.954	[5]
15%$NMPP_2$/$Zn_{0.5}Cd_{0.5}S$	30	300 W Xe lamp (λ > 420 nm)	100 mL of H_2O containing 0.35 M Na_2S/0.25 M Na_2SO_3	83.54	2.506	[6]
MoS_2/$Zn_{0.2}Cd_{0.8}S$/ZnS	50	300 W Xe lamp (λ > 420 nm)	50 mL of 20 vol% lactic acid	79.3	3.965	[7]
Ni-MOFs/Cu-$Zn_{0.5}Cd_{0.5}S$/Pt-3.0%	50	300 W Xe lamp (λ > 420 nm)	100 mL of 20 vol% TEOA aqueous solution	5.7712	0.289	[8]

4. The Calculation of average fluorescence lifetime:

Average lifetime (τ_{ave}) of samples was calculated by following equation:

$$\boldsymbol{\tau_{ave}} = \sum_{i=1,2,3} \boldsymbol{B_i\tau_i^2} \,/\, \sum_{i=1,2,3} \boldsymbol{B_i\tau_i} \qquad \text{(S3)}$$

Where τ_{ave} is the average lifetime; τ_i are the respective decay times; B_i are the corresponding weight factors.

Table S2 Decay parameters and PL quantum yield (Φ_{PL}) for CZS and 5-SS-CZS.

Samples	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_{ave} (ns)	Φ_{PL} (%)
CZS	0.3174(16.58%)	2.4667(34.70%)	10.5786(48.72%)	9.34	4.97%
5-SS-CZS	0. 9846(25.31%)	4.0089(33.54%)	22.6753(41.15%)	19.88	0.24%

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