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

Haitao Zhao $^a$,*, Baohua Zhao $^b$, Heyuan Liu $^c$, Xiyou Li $^c$,*

$^a$ Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, P. R. China

$^b$ College of Science, China University of Petroleum (East China), Qingdao, P. R. China

$^c$ School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, P. R. China

* Corresponding authors

E-mail: xiyouli@upc.edu.cn, zhaohaitao_2014@163.com,
1. **Preparation of SnS**

1 mmol of SnCl$_2$·H$_2$O 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 spectrooscope (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°C 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 ($S_{\text{BET}}$). 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):

$$\text{AQY} = \frac{2 \times \text{Number of evolved H}_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{2 \times n \times N_A}{S \times P \times t \times h \nu} \times 100\% = \frac{2 \times n \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$  \hspace{1cm} (S1)

Where \( n \) is the yield of the \( \text{H}_2 \) evolution (mmol), \( N_A \) is \( 6.022 \times 10^{23} \) /mol, \( h \) is \( 6.626 \times 10^{-34} \) J·S, \( S \) is effective lighting area (cm\(^2\)), \( P \) is the light intensity (mW/cm\(^2\)), \( t \) is reaction time (s), \( \lambda \) is corresponding monochromatic wavelength (nm), respectively.

![Fig. S1 SEM image of SnS\(_2\) nanosheets.](image)
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.

\[
E_{CB} = \chi - E_e - 0.5E_g \quad E_{VB} = E_g - E_{CB}
\]  

Where $\chi$ 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 (\(\chi\)) 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 ($\lambda \geq 420$ nm).

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

Fig. S7 Transient photocurrent and Nyquist impedance plots of x-SS-CZS photocatalysts.
### Table S1 Comparisons of H₂ evolution rate of Cd₅Zn₁₋₅S-based photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Catalyst mass (mg)</th>
<th>Light source</th>
<th>Sacrificial agent</th>
<th>PHE rates (mmol·g⁻¹·h⁻¹)</th>
<th>H₂ rate (mmol·h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-CZS</td>
<td>10</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>100 mL of H₂O containing</td>
<td>168.85</td>
<td>1.688</td>
<td>Recent work</td>
</tr>
<tr>
<td>1%-Ni:Cu/T-Zn₅Cd₅S</td>
<td>50</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>0.25 M Na₂S/0.35 M Na₂SO₃</td>
<td>15.66</td>
<td>0.783</td>
<td>[1]</td>
</tr>
<tr>
<td>Zn₅Cd₅S/PdP-0.33S-1.67</td>
<td>1</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>0.25 M Na₂S/0.25 M Na₂SO₃</td>
<td>246.04</td>
<td>0.246</td>
<td>[2]</td>
</tr>
<tr>
<td>Zn₅Cd₅S/TiC/TiO₂-2%</td>
<td>10</td>
<td>300 W Xe lamp (λ &gt; 400 nm)</td>
<td>0.75 M ascorbic acid</td>
<td>372.12</td>
<td>0.372</td>
<td>[3]</td>
</tr>
<tr>
<td>NiCo₂O₄/Zn₅Cd₅S</td>
<td>50</td>
<td>300 W Xe lamp (λ &gt; 400 nm)</td>
<td>0.3 M Na₂S/0.3 M Na₂SO₃</td>
<td>34.4</td>
<td>1.720</td>
<td>[4]</td>
</tr>
<tr>
<td>20%-W₁O₅Os/Cd₅SZn₅S</td>
<td>20</td>
<td>300 W Xe lamp (λ &gt; 200 nm)</td>
<td>0.35 M Na₂S/0.25 M Na₂SO₃</td>
<td>147.7</td>
<td>2.954</td>
<td>[5]</td>
</tr>
<tr>
<td>15%NMPP₂/Zn₅Cd₅S</td>
<td>30</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>0.35 M Na₂S/0.25 M Na₂SO₃</td>
<td>83.54</td>
<td>2.506</td>
<td>[6]</td>
</tr>
<tr>
<td>MoS₂/Zn₅Cd₅S/ZnS</td>
<td>50</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>50 mL of 20 vol% lactic acid</td>
<td>79.3</td>
<td>3.965</td>
<td>[7]</td>
</tr>
<tr>
<td>Ni-MOFs/Cu-Zn₅Cd₅S/Pt-3%</td>
<td>50</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>100 mL of 20 vol% TEOA aqueous solution</td>
<td>5.7712</td>
<td>0.289</td>
<td>[8]</td>
</tr>
</tbody>
</table>

### 4. The Calculation of average fluorescence lifetime:

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

\[
\tau_{ave} = \frac{\sum_{i=1}^{3} B_i \tau_i^2}{\sum_{i=1}^{3} B_i \tau_i}
\]  

(S3)

Where \(\tau_{ave}\) is the average lifetime; \(\tau_i\) are the respective decay times; \(B_i\) are the corresponding weight factors.

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\tau_1) (ns)</th>
<th>(\tau_2) (ns)</th>
<th>(\tau_3) (ns)</th>
<th>(\tau_{ave}) (ns)</th>
<th>(\Phi_{PL}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZS</td>
<td>0.3174(16.58%)</td>
<td>2.4667(34.70%)</td>
<td>10.5786(48.72%)</td>
<td>9.34</td>
<td>4.97%</td>
</tr>
<tr>
<td>5-SS-CZS</td>
<td>0.9846(25.31%)</td>
<td>4.0089(33.54%)</td>
<td>22.6753(41.15%)</td>
<td>19.88</td>
<td>0.24%</td>
</tr>
</tbody>
</table>
References