

Supporting Information

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Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, AR), cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, AR) and sodium hydroxide (NaOH) were supplied by Shanghai Aladdin Biochemical Technology Co. Ltd. Thioacetamide (TAA), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, AR) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. TEOA was purchased from Tianjin Best Chemical Co. Ltd. All reagents were used as received without additional purification. Throughout the entire preparation process, deionized water (18.25 M) was used.

Physic characterization

The structural and morphological characteristics of the prepared samples were determined by X-ray diffraction pattern (Rigaku, XRD), scanning electron microscopy (JEOLJSM-6390 system) and transmission electron microscopy (TecnaiG2F20S-TWIN). X-ray photoelectron spectroscopy (XPS) was performed by Kratos (AXIS NOVA) to elucidate the chemical state and elemental composition of the catalyst. The light absorption properties of the samples were measured using a UV-Vis spectrophotometer (Shimadzu UV-3600) using BaSO_4 as a reference. The photoluminescence spectra were obtained using an F-7000 Fluorescence Spectrophotometer with a wavelength of 325 nm. Brunner-Emmet-Teller (BET Quantachrome NOVA 2000e, N_2 adsorption and desorption isotherms) was used to measure the specific surface area of the samples. Electron paramagnetic resonance (EPR) spectra were obtained on an ELEXSYS-II E500 electron paramagnetic resonance spectrometer.

Photocatalytic H₂ evolution test

The photocatalytic water splitting experiments for hydrogen production were carried out by an online detection system (Lab Solar III-AG, Beijing Perfect Light Technology Co., Ltd., China) and gas chromatography (TechcoMp, GC7900). Under constant stirring, 10 mg of the catalyst was dispersed into 100 mL of an aqueous solution containing 20 vol% TEOA in a 250 mL heat-resistant flask reactor. Using circulating water to maintain a constant temperature of 30 °C. A 300 W Xe lamp was used as the light source, 15 cm from the liquid level. The system was vacuumed before irradiation. The amount of H₂ was tested by GC7900 gas chromatography using N₂ as the carrier gas.

Test of Photoelectrochemical Performance

3.0 mg of catalyst was dispersed in a centrifuge tube containing 9 mL of deionized water and then sonicated for 30 min to form a homogeneous suspension. 1mL solution was moved to the FTO glass, then naturally dried to obtain the FTO working electrode.

The photoelectrochemical (PEC) performance of the samples was measured by an electrochemical workstation (Shanghai Chenhua) with a bias potential of 0.5 V, and all measurements were performed in a neutral electrolyte solution (0.5 M Na₂SO₄, pH = 7.0). The Hg/HgCl₂ electrode was used as the reference electrode, the Pt wire was used as the counter electrode, and the sample was the working electrode. Transient photocurrent density plots (i-t), linear sweep voltammetry plots (LSV), electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) plots were obtained.^{1,2}

The reversible hydrogen electrode (RHE) potential is calculated according to the Nernst equation:³

$$E_{\text{RHE}} = E_{\text{Hg/HgCl}_2} + 0.059 \times \text{pH} + E^{\circ}_{\text{Hg/HgCl}_2}$$

Where E_{RHE} was the calculated potential vs. RHE, $E_{\text{Hg/HgCl}_2}$ was the applied electrode potential against the Hg/HgCl₂, $E^{\circ}_{\text{Hg/HgCl}_2}$ referred to the standard potential

of Hg/HgCl₂ (the value was 0.24 V), and the pH of 0.5 M Na₂SO₄ solution was 7.0.

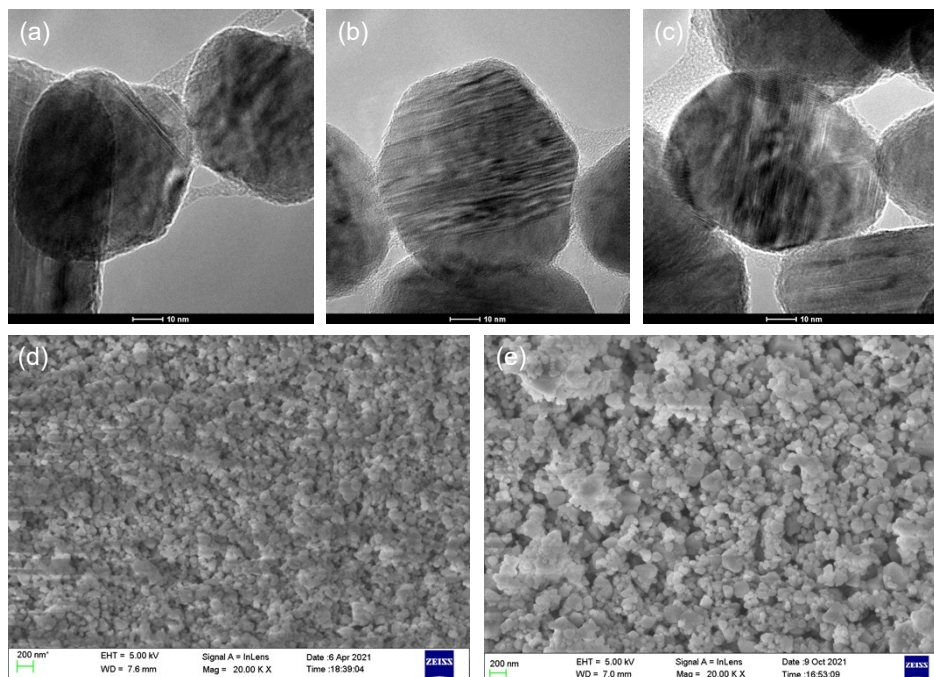


Fig. S1 (a-c) TEM images of T-CZS, SEM images of (d) T-CZS, (e) CoS_x.

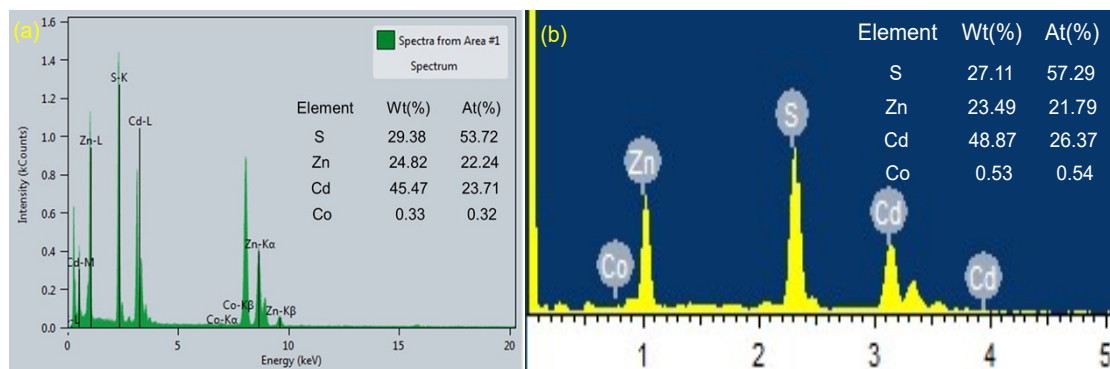


Fig. S2 (a) EDX and (b) EDS spectrum of 4 wt% CoS_x/T-CZS.

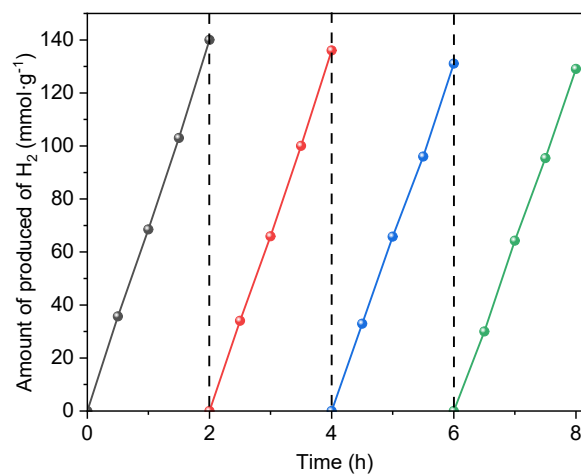


Fig. S3 Cycling measure of 4 wt% CoS_x/T-CZS.

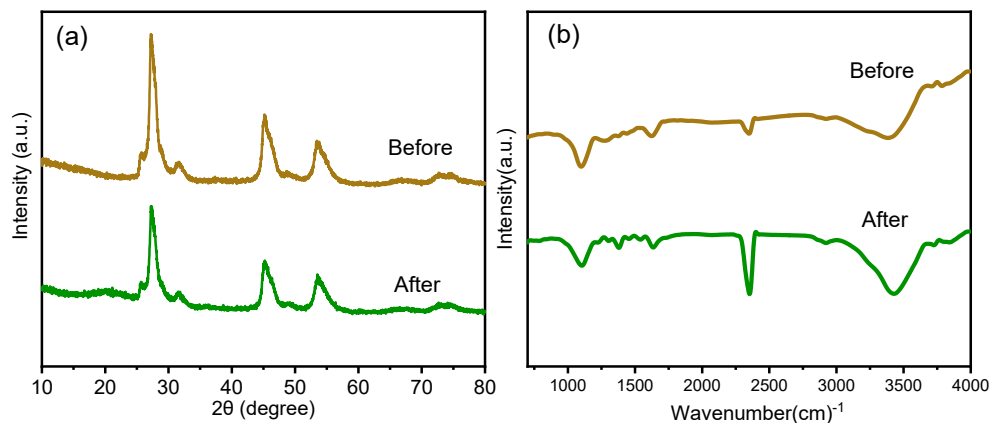


Fig. S4 (a) XRD, (b) FTIR of 4 wt% $\text{CoS}_x/\text{T-CZS}$ composite before and after use.

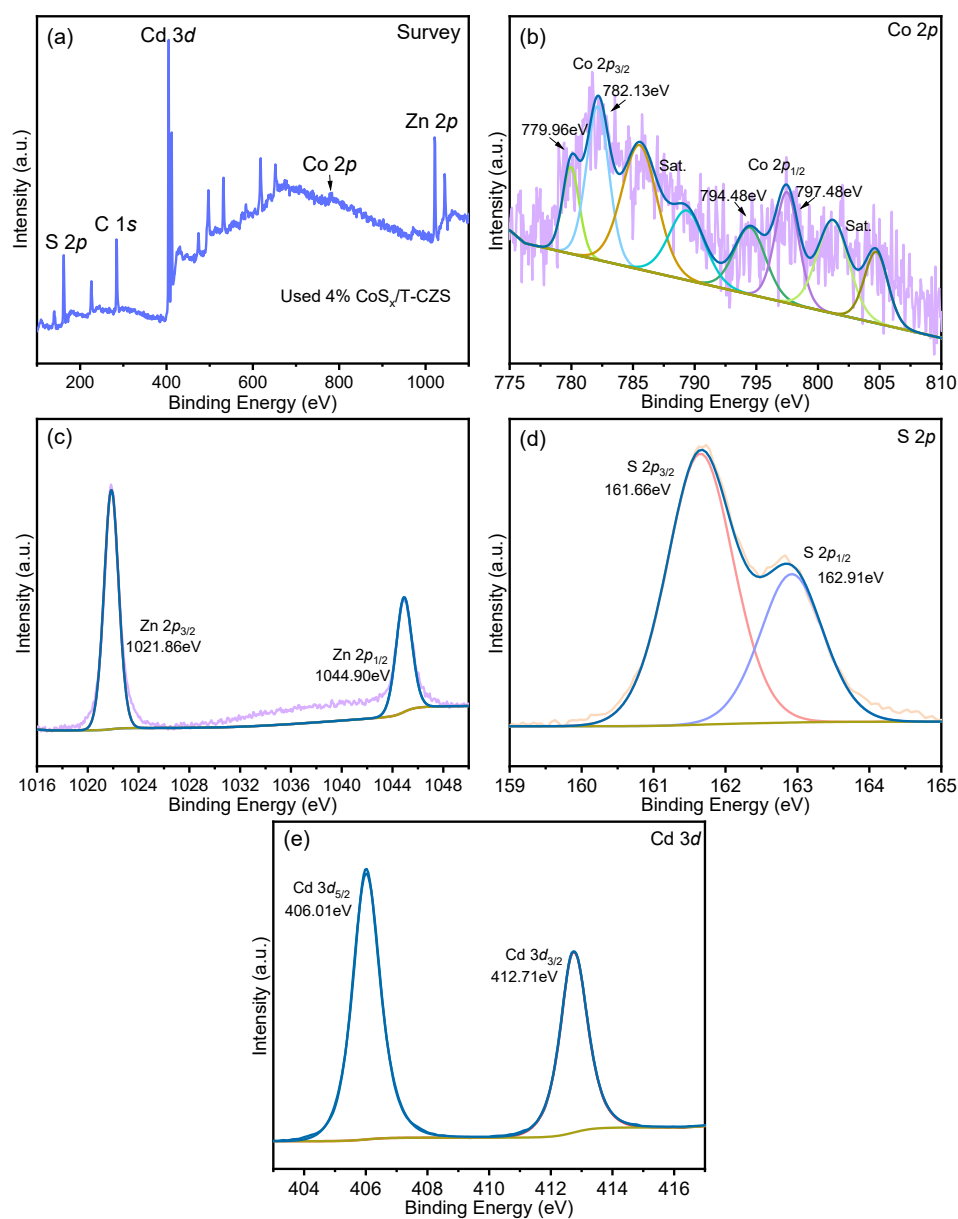


Fig. S5 The XPS survey spectra of (a) survey spectra, (b) Co 2p, (c) Zn 2p, (d) S 2p, (e) Cd 3d for used

4 wt% CoS_x/T-CZS composite.

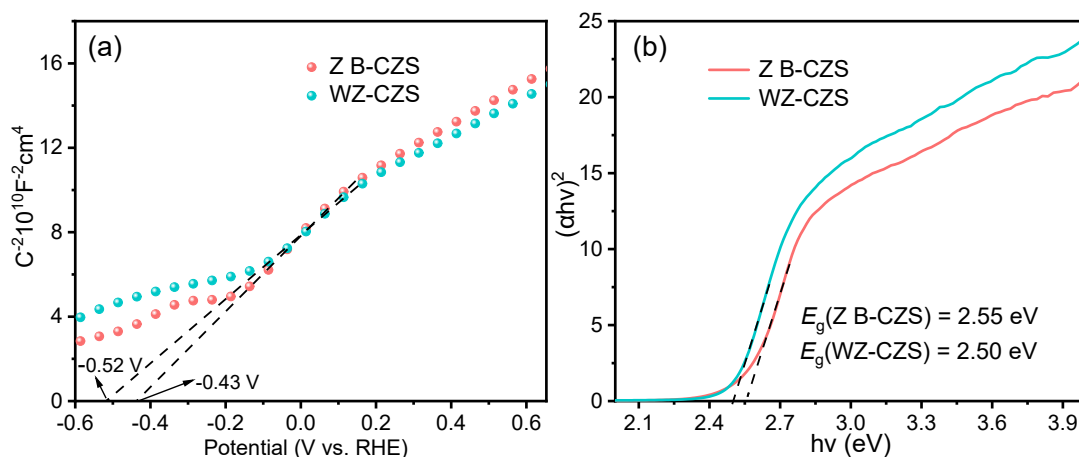


Fig. S6 (a) Mott-Schottky curve and (b) Kubelka-Munk plots of ZB-CZS and WZ-CZS.

Table. S1 Related reports of Cd_xZn_{1-x}S Schottky junction photocatalysts in the literature

Photocatalyst	Sacrificial reagents	Light source	HER μmol·g ⁻¹ ·h ⁻¹	Reference
NiS/Cd _{0.4} Zn _{0.6} S	Na ₂ S (0.1 M) + Na ₂ SO ₃ (0.1 M)	300 W Xe lamp λ > 400 nm	1200 μmol·g ⁻¹ ·h ⁻¹	1
Ni ₁₂ P ₅ /Cd _{0.5} Zn _{0.5} S	TEOA	300 W Xe lamp λ > 400 nm	46820 μmol·g ⁻¹ ·h ⁻¹	2
NiCo ₂ S ₄ /Cd _{0.5} Zn _{0.5} S	water	300 W Xe lamp	2436 μmol·g ⁻¹ ·h ⁻¹	3
Ni ₂ P/T-Cd _{0.9} Zn _{0.1} S	Na ₂ S + Na ₂ SO ₃	300 W Xe lamp	1800 μmol·g ⁻¹ ·h ⁻¹	4
Ni(OH) ₂ /T-Zn _{0.5} Cd _{0.5} S	TEOA	300 W Xe lamp λ > 400 nm	14000 μmol·g ⁻¹ ·h ⁻¹	5
Ni ₂ P/Cd _{0.5} Zn _{0.5} S	Na ₂ S + Na ₂ SO ₃	300 W Xe lamp λ > 400 nm	65.6 μmol·h ⁻¹	6
Co ₂ P/Cd _{0.5} Zn _{0.5} S	lactic acid	300 W Xe lamp λ > 400 nm	68020 μmol·h ⁻¹	7
Ni ₂ S/Cd _{0.5} Zn _{0.5} S	Na ₂ S (0.35 M) + Na ₂ SO ₃ (0.25 M)	300 W Xe lamp λ > 400 nm	1400 μmol·h ⁻¹	8
Cu/Ni/Cd _{0.5} Zn _{0.5} S	Na ₂ S (0.3 M) + Na ₂ SO ₃ (0.3 M)	300 W Xe lamp λ > 400 nm	58330 μmol·h ⁻¹	9
CoS _x /T-Cd _{0.5} Zn _{0.5} S	TEOA	300 W Xe lamp	76200 μmol·h ⁻¹	This work

Reference

- 1 X.-L. Yin, L.-L. Li, J.-H. Jiang, X.-X. Du, D.-H. Pang, J. Yang, Z.-J. Li, Y.-X. Wang, X.-Y. Li, D.-C. Li and J.-M. Dou, *Chem. Eng. J.*, 2019, **375**, 121970.
- 2 W. Xue, W. Chang, X. Hu, J. Fan and E. Liu, *Chin. J. Catal.*, 2021, **42**, 152-163.
- 3 J. Zhao, Y. Cheng, Y. Chen, W. Zhang, E. Liu, J. Fan, H. Miao and X. Hu, *Appl. Surf. Sci.*, 2021, **568**, 150917.

- 4 J. Wang, B. Li, J. Chen, N. Li, J. Zheng, J. Zhao and Z. Zhu, *Appl. Surf. Sci.*, 2012, **259**, 118-123.
- 5 H. Sun, W. Xue, J. Fan, E. Liu and Q. Yu, *J. Alloys Compd.*, 2021, **854**, 156951.
- 6 Z. Shao, X. Meng, H. Lai, D. Zhang, X. Pu, C. Su, H. li, X. Ren and Y. Geng, *Chin. J. Catal.*, 2021, **42**, 439-449.
- 7 B. Debnath, S. Dhingra, V. Sharma, V. Krishnan and C. Nagaraja, *Appl. Surf. Sci.*, 2021, **550**, 149367.
- 8 S. Peng, Y. Yang, J. Tan, C. Gan and Y. Li, *Appl. Surf. Sci.*, 2018, **447**, 822-828.
- 9 Z. Liang and X. Dong, *J. Photochem. Photobiol., A*, 2021, **427**, 113081.
- 10 N. Li, B. Zhou, P. Guo, J. Zhou and D. Jing, *Int. J. Hydrogen Energy.*, 2013, **38**, 11268-11277.
- 11 Ya. Hao, S.-Z. Kang, X. Liu, X. Li, L. Qin and J. Mu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 1165-1172.
- 12 C. Wang, X. Ma, Z. Fu, X. Hu, J. Fan and E. Liu, *J. Colloid Interface Sci.*, 2021, **592**, 66-76.