

Supporting Information

A novel bicomponent Co₃S₄/Co cocatalyst on CdS accelerating charge separation for highly efficient photocatalytic hydrogen evolution

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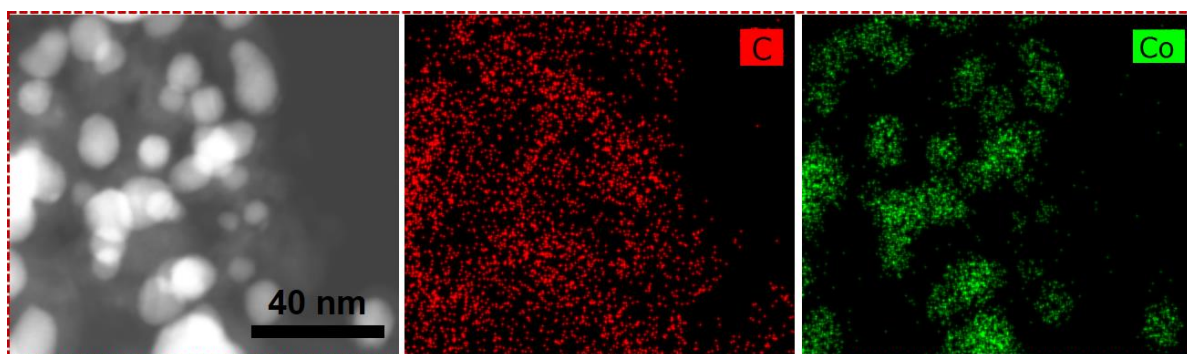


Fig. S1 HAADF-STEM images and the corresponding elemental mapping images of Co@C.

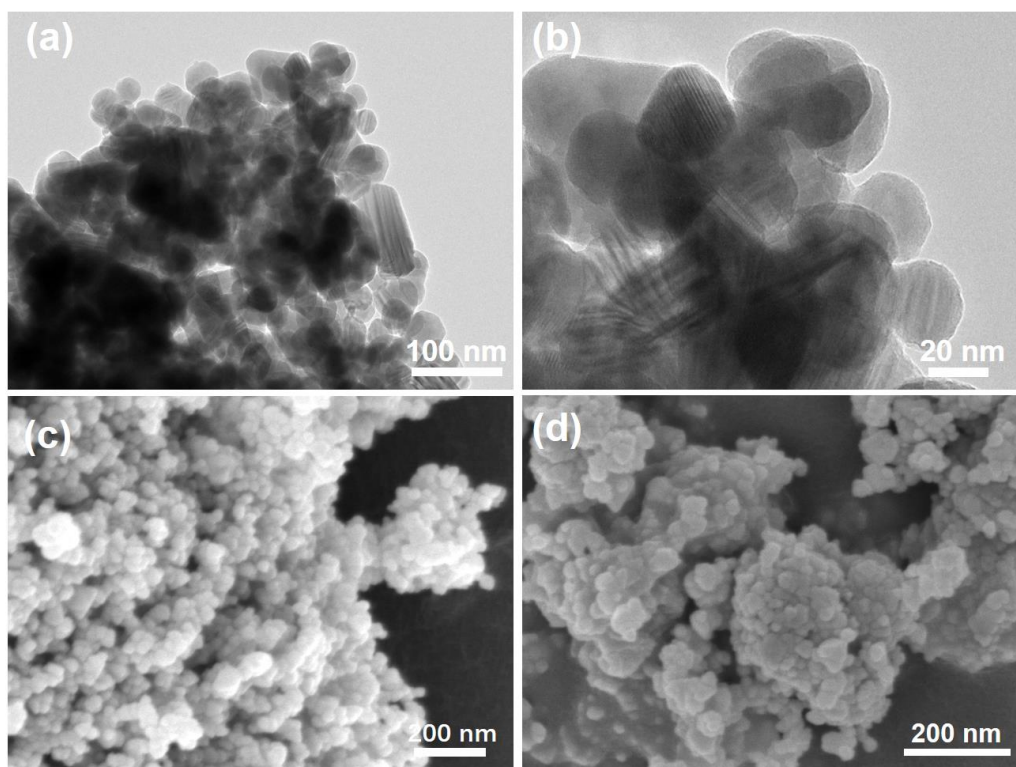


Fig. S2 (a, b) TEM images of CdS. SEM images of (c) CdS and (d) SCS-5.

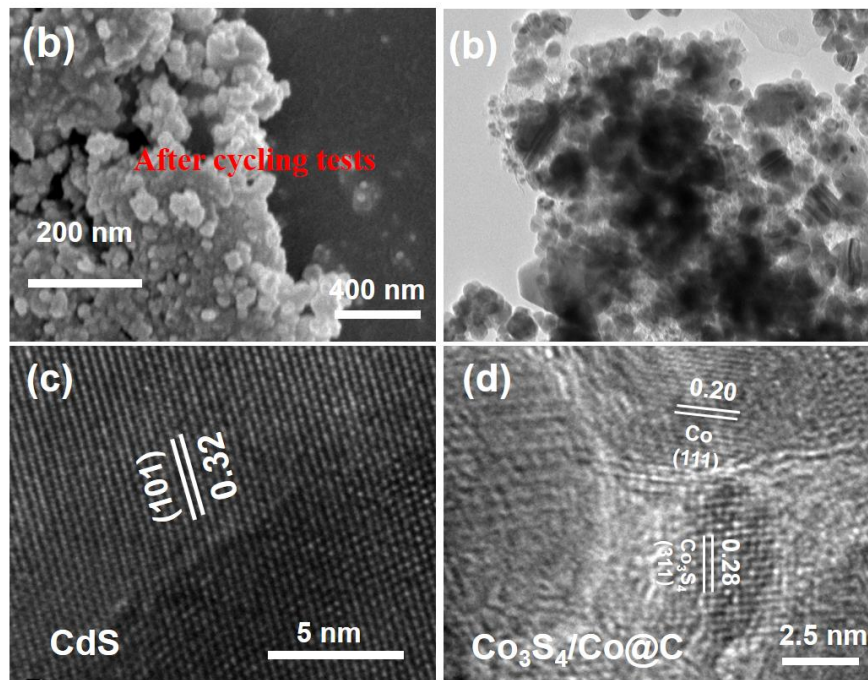


Fig. S3 (a) SEM, (b) TEM, and (c, d) HR-TEM images of SCS5 after cycling tests.

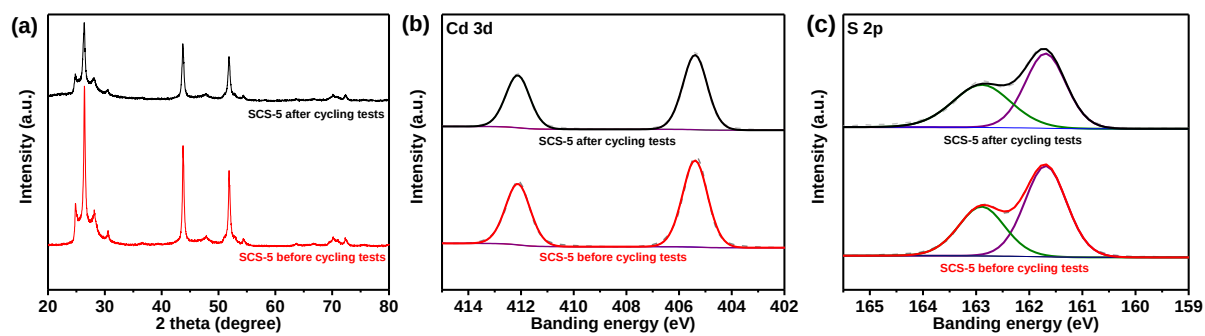


Fig. S4 (a) XRD patterns, (b) Cd 3d XPS spectra, and (c) S 2p XPS spectra of SCS5 sample

before and after cycling tests.

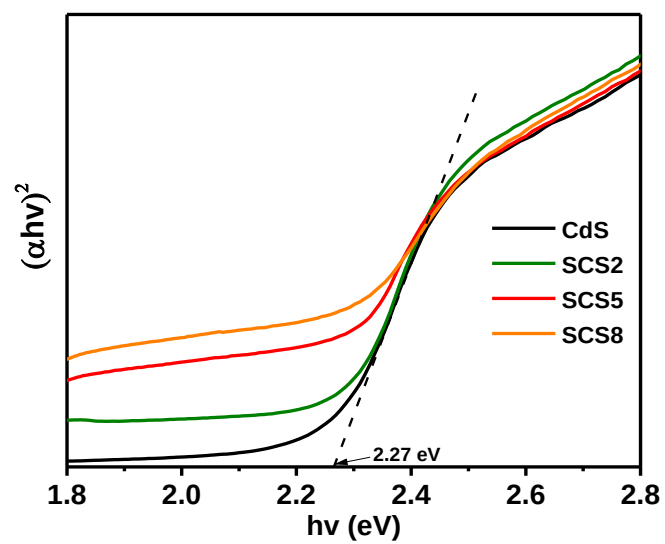


Fig. S5 Tauc plots of the samples.

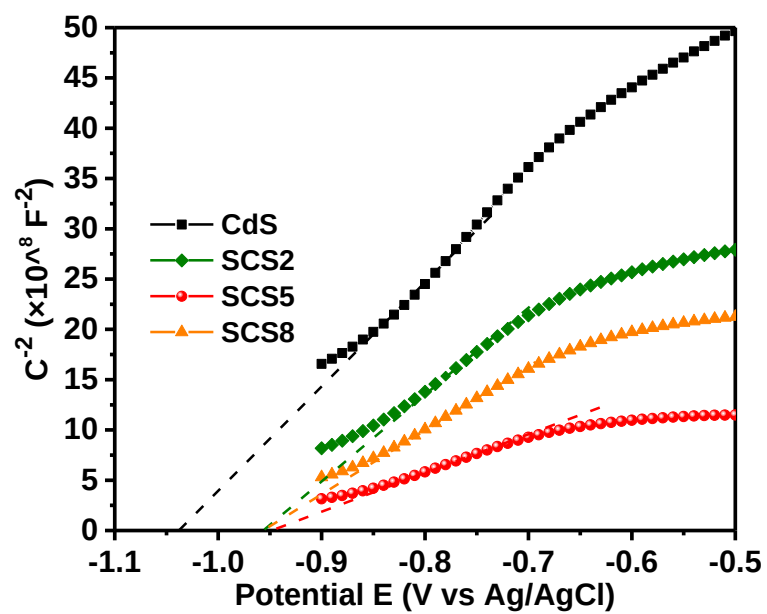


Fig. S6 Mott–Schottky plots of CdS, SCS2, SCS5 and SCS8.

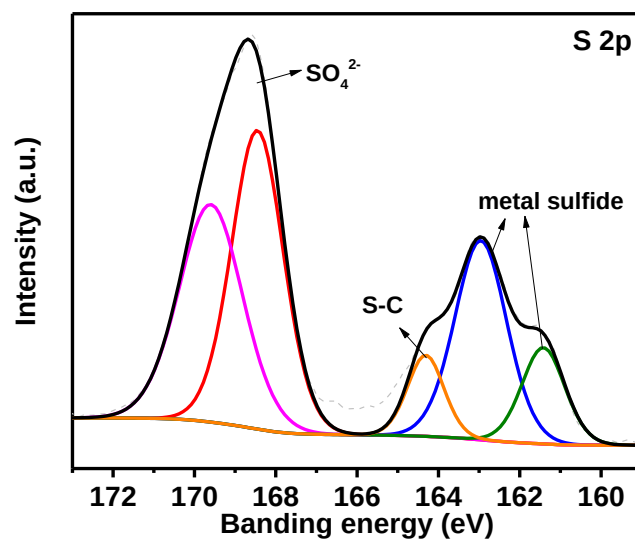


Fig. S7 S 2p XPS spectrum of $\text{Co}_3\text{S}_4/\text{Co}@C$.

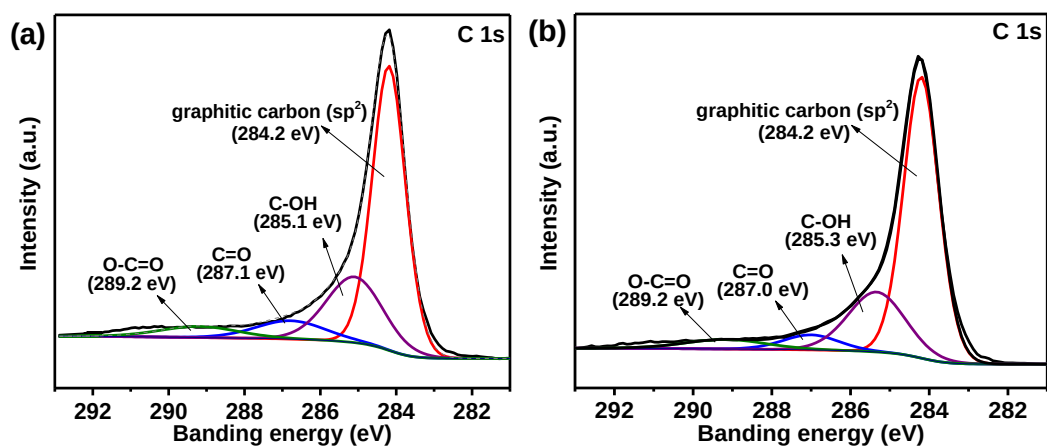


Fig. S8 C 1s XPS spectra of (a) Co@C and (b) Co₃S₄/Co@C.

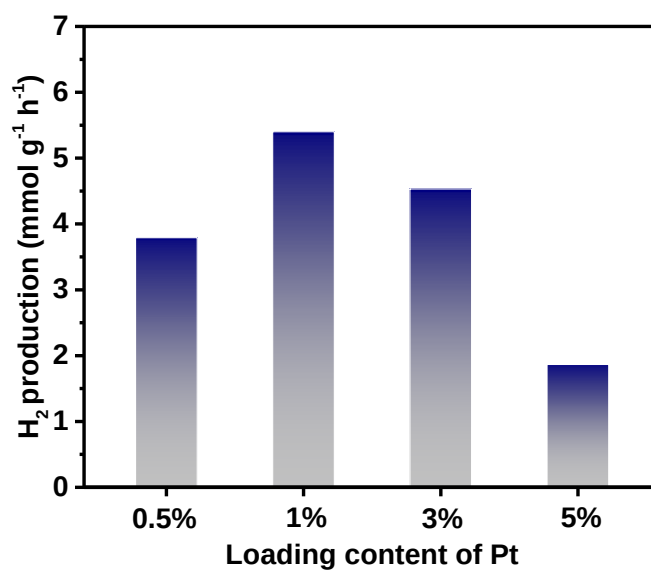


Fig. S9 Photocatalytic H₂ evolution of Pt-CdS with different Pt loadings.

Different amounts of H₂PtCl₆ aqueous solution were used to prepare the Pt-CdS with different loading content of Pt. The result shows that the most optimum loading content of Pt is 1%. The optimal sample Pt-CdS is used to compare with SCS5 for photocatalytic H₂ evolution.

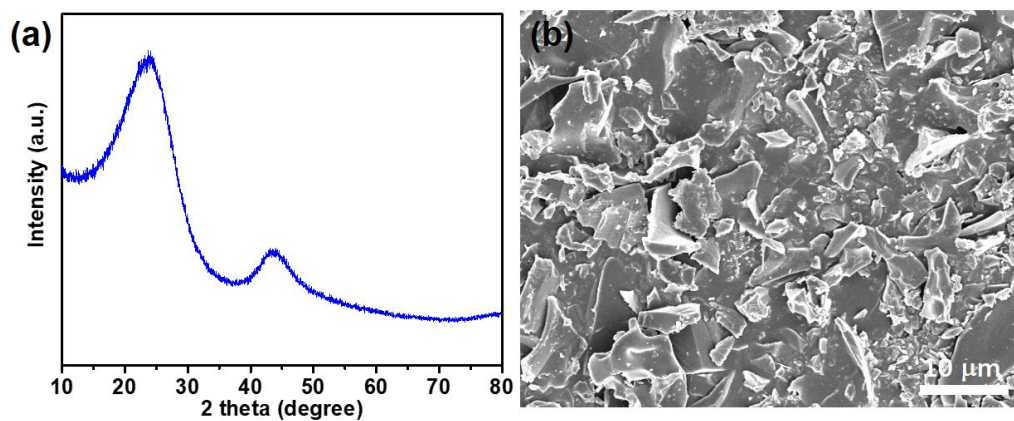


Fig. S10 (a) XRD pattern and (b) SEM image of C.

Fig. S10a is the XRD pattern of C cocatalyst without metallic Co. Compared with those of Co@C and Co₃S₄/Co cocatalysts, the SEM image in Fig. S10b shows the different structural morphology of C cocatalyst. The C-CdS photocatalyst was prepared using this C cocatalyst as precursor.

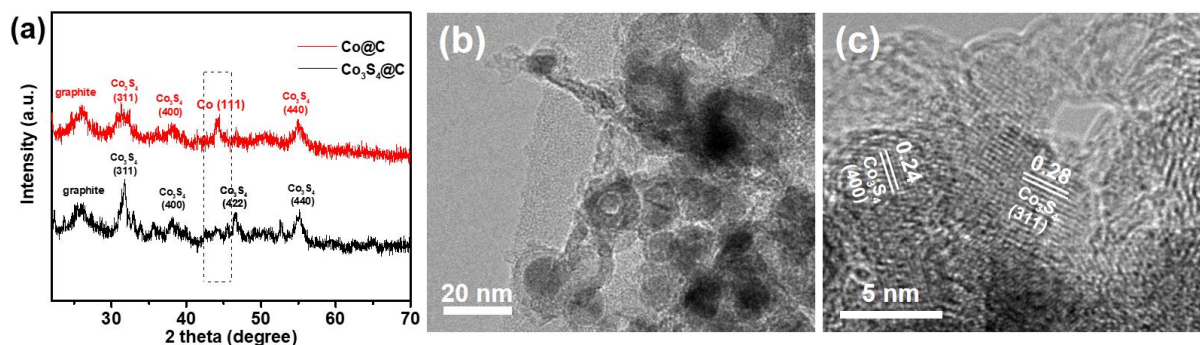


Fig. S11 (a) XRD pattern of $\text{Co}_3\text{S}_4@\text{C}$ and $\text{Co}@\text{C}$, (b) TEM and HR-TEM of $\text{Co}_3\text{S}_4@\text{C}$.

$\text{Co}_3\text{S}_4@\text{C}$ was also prepared by a method similar to $\text{Co}@\text{C}$, but the hydrothermal time was extended to 48 h when the metal Co was almost vulcanized into Co_3S_4 . Fig. S11a is the XRD pattern of $\text{Co}_3\text{S}_4@\text{C}$ and $\text{Co}@\text{C}$. Compared with the XRD pattern $\text{Co}@\text{C}$, the $\text{Co}_3\text{S}_4@\text{C}$ shows no XRD peak of Co (111), which indicates that the metal Co is was almost vulcanized into Co_3S_4 . Furthermore, the TEM images in Fig. S11b shows that the lattice spacing values of 0.24 and 0.28 nm are corresponded to (400) facet and (311) facet of Co_3S_4 , further confirming that the existence of Co_3S_4 in $\text{Co}_3\text{S}_4@\text{C}$. The $\text{Co}_3\text{S}_4\text{-CdS}$ photocatalyst was prepared using this $\text{Co}_3\text{S}_4@\text{C}$ cocatalyst as precursor.

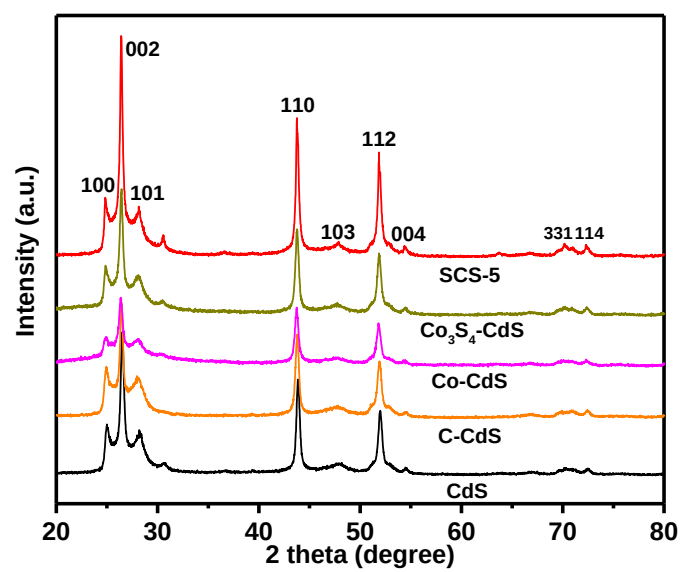


Fig. S12 XRD patterns of different samples.

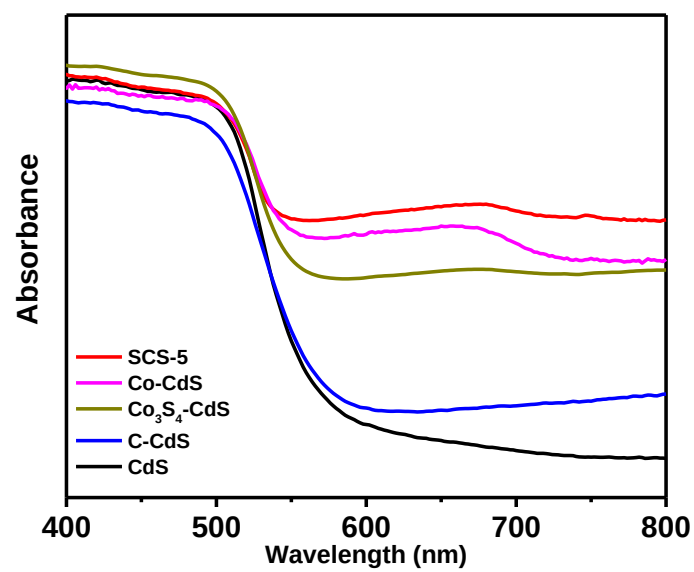


Fig. S13 UV-vis diffuse reflectance spectra of different samples.

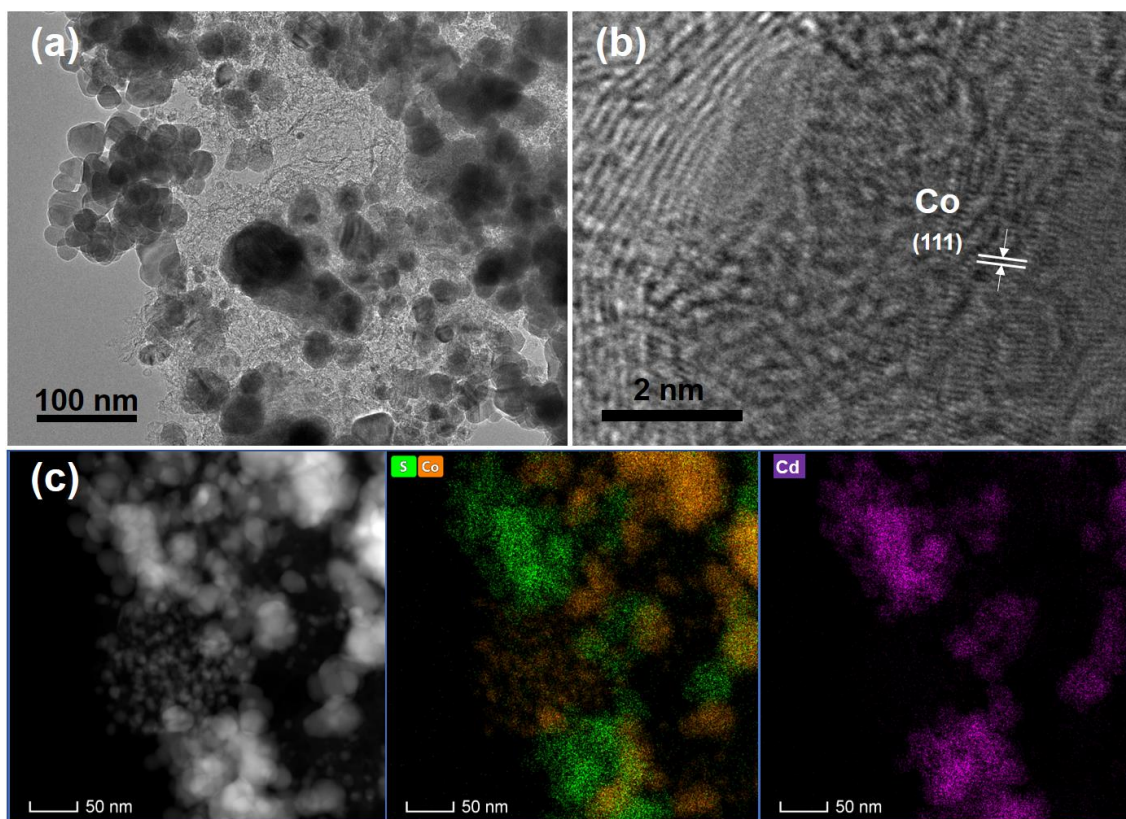


Fig. S14 (a) TEM, (b) HR-TEM, (c) HAADF-STEM images and EDX element mapping of mechanically mixed $(\text{Co}_3\text{S}_4/\text{Co})\text{-CdS}$.

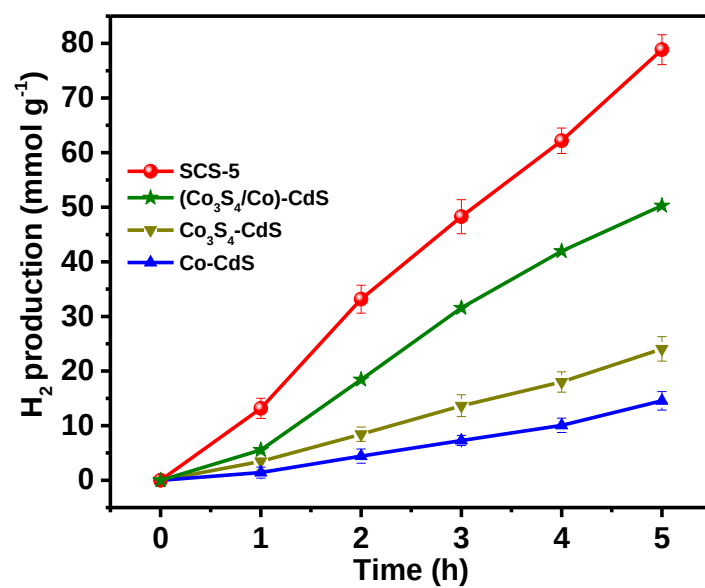


Fig. S15 Comparison of photocatalytic H₂ evolution of Co-CdS, Co₃S₄-CdS, SCS5 and the mechanically mixed (Co₃S₄/Co)-CdS.

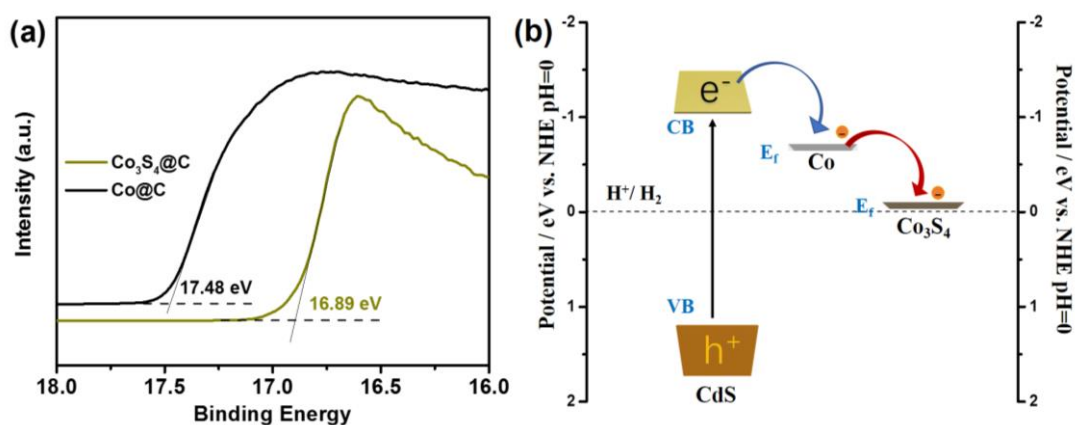


Fig. S16 (a) UPS spectra of Co@C and Co₃S₄@C. (b) Band gap structures of CdS, Co and Co₃S₄.

The work function (ϕ) was determined by the difference between the photon energy of the Helium I light source at 21.2 eV and the binding energy of the secondary cutoff edge. Hence, the work function of Co@C and Co₃S₄@C are 3.72 and 4.31 eV, respectively.

Table S1 The performance comparison of this work with other similar composites

Photocatalyst	Light source	Reactant solution	Activity (mmol h ⁻¹ g ⁻¹)	Ref. (year)
Co ₃ S ₄ /Co-CdS	$\lambda > 420$ nm (300 W Xe)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	14.62	Our work
CdS-Co ₃ O ₄	$\lambda > 420$ nm (350 W Xe)	10 vol % of lactic acid	3.014	1 (2013)
Co-Pi-CdS	$\lambda > 420$ nm (300 W Xe)	10 vol % of lactic acid	13.3	2 (2016)
CdS/CoO _x	$\lambda > 420$ nm (350 W Xe)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	3.50	3 (2018)
CdS-Co ₉ S ₈	AM 1.5 (300 W Xe)	Na ₂ S and Na ₂ SO ₃	1.06	4 (2017)
a-CoMoS _x /CdS	$\lambda > 420$ nm (300 W Xe)	Lactic acid	3.57	5 (2018)
Co Single Atomic Cocatalysts-CdS	$\lambda > 420$ nm (300 W Xe)	1.0 M (NH ₄) ₂ SO ₃	7.27	6 (2017)
Co _x Mo _{1-x} S ₂ /CdS	$\lambda > 420$ nm (300 W Xe)	10 vol % of lactic acid	14.10	7 (2018)
MoS ₂ /G-CdS	$\lambda > 400$ nm (300 W Xe)	0.35 M Na ₂ S and Na ₂ SO ₃	6.00	8 (2014)
Co ₂ P-CdS	$\lambda > 400$ nm (300 W Xe)	10 vol % of lactic acid	6.06	9 (2018)
CdS/Co ₉ S ₈	$\lambda > 420$ nm (Xe)	0.35 M Na ₂ S and 0.25 M Na ₂ SO ₃	5.15	10 (2018)

References

- 1 D. Lang, F. Cheng and Q. Xiang, *Catal. Sci. Technol.*, 2016, **6**, 6207-6216.
- 2 T. Di, B. Zhu, J. Zhang, B. Cheng and J. Yu, *Appl. Surf. Sci.*, 2016, **389**, 775-782.
- 3 Y. Liu, S. Ding, Y. Shi, X. Liu, Z. Wu, Q. Jiang, T. Zhou, N. Liu and J. Hu, *Appl. Catal. B: Environ.*, 2018, **234**, 109-116.
- 4 B. Qiu, Q. Zhu, M. Du, L. Fan, M. Xing and J. Zhang, *Angew. Chem. Int. Edit.*, 2017, **56**, 2684-2688.
- 5 W. Liu, X. Wang, H. Yu and J. Yu, *ACS Sustain. Chem. Eng.*, 2018, **6**, 12436-12445.
- 6 Q. Zhao, W. Yao, C. Huang, Q. Wu and Q. Xu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 42734-42741.
- 7 J. Li, Y. Peng, X. Qian and J. Lin, *Appl. Surf. Sci.*, 2018, **452**, 437-442.
- 8 K. Chang, Z. Me, T. Wang, Q. Kang, S. Ouyang and J. Ye, *ACS Nano*, 2014, **8**, 7078-7087.
- 9 S. Li, L. Wang, S. Liu, B. Xu, N. Xiao, Y. Gao, W. Song, L. Ge and J. Liu, *ACS Sustain. Chem. Eng.* 2018, **6**, 9940-9950.
- 10 P. Tan, Y. Liu, A. Zhu, W. Zeng, H. Cui and J. Pan, *ACS Sustain. Chem. Eng.*, 2018, **6**, 10385-10394.