

Supporting Information

Design of Well-defined Shell-Core Covalent Organic Frameworks/Metal Sulfide as an Efficient Z-Scheme Heterojunction for Photocatalytic Water Splitting

Yan Wang,^a Zhao Hu,^c Wei Wang,^a Haichuan He,^a Liu Deng,^{*ab} Yi Zhang,^a Jianhan Huang,^a Ning Zhao,^b Guipeng Yu,^{*a} and You-Nian Liu^{*ab}

^a Hunan Provincial Key Laboratory of Micro & Nano Materials Interface Science, College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, P R China

E-mail: dengliu@csu.edu.cn; gilbertyu@csu.edu.cn; liuyounian@csu.edu.cn

^b State Key Laboratory of Coal conversion, Institute of Coal Chemistry, CAS, Taiyuan, Shanxi 030001, P R China

^c State Key Laboratory of Breeding Base of Green Pesticide & Agricultural Bioengineering, Key Laboratory of Green Pesticide & Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for R&D of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, P R China.

1. Experimental Section

Materials

Polyvinyl pyrrolidone, thiourea and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were brought from Sigma Aldrich (Missouri, USA), 2,4,6-tris(4-aminophenyl)-1,3,5-triazine and 1,3,5-benzenetricarboxaldehyde were purchased from Yanshen Technology (Jilin, Changchun, China). All other solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise.

Synthesis of CdS: CdS was prepared by solvothermal method. A mixture of thiourea (0.53 g, 7.0 mmol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.16 g, 7.0 mmol), polyvinyl pyrrolidone (0.78 g, 7.0 mmol) were dissolved into 70.0 mL of polyethylene glycol and heated at 120 °C for 12 h. After the reaction was cooled to room temperature, the mixture was filtered and washed with methanol for several times, and then dried in a vacuum oven at 60 °C for 10 h. The final product CdS was obtained as a saffron yellow powder.

Synthesis of T-COF: 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (0.04 mmol 14.2 mg), 1,3,5-benzenetricarboxaldehyde (0.04 mmol, 6.5 mg) and acetonitrile (5 mL) were added in a glass vial. After 30 min of ultrasonication, 12 M CH_3COOH_3 (0.4 mL) was added to the reaction system, then the glass vial was sealed and kept at room temperature for 96 h without stirring. The product was separated, washed with *N,N*-dimethylformamide and then dried in a vacuum oven at 70 °C for 12 h to obtain yellow solid in a yield of 97%.

Synthesis of T-COF@CdS-X: 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (0.04 mmol, 14.2 mg), acetonitrile (3 mL) and a certain amount of CdS were added in a glass vial. After 60 min of ultrasonication, the mixture of 1,3,5-benzenetricarboxaldehyde (0.04 mmol, 6.5 mg) and acetonitrile (2 mL) were added to the reaction system. Then sonicating for another 30 min, 12 M CH_3COOH_3 (0.4 mL) was added to the solution, then the glass vial was sealed and kept at room temperature for 96 h without stirring. The obtain yellow solid was filtrated, washed with *N,N*-dimethylformamide, then dried in a vacuum oven at 70 °C for 12 h. By varying the amount

of CdS, the different weight ratios of T-COF@CdS-X hybrid materials were obtained. (T-COF@CdS-1 (T-COF:CdS = 5:1), T-COF@CdS-2 (5:2), T-COF@CdS-3 (5:3) T-COF@CdS-4 (5:4)).

Synthesis of T-COF/CdS-3: For comparison, T-COF/CdS-3 (5:3) was prepared by physical mixing of T-COF and CdS.

Photocatalytic water splitting: The photocatalytic water splitting was carried out in a gas-closed system Labsolar 6A (PerfectLight, Beijing, China) equipped with a gas-circulated pump. Typically, 10 mg of photocatalysts, 30 mL ascorbic acid aqueous solution (0.1 M) and 1 mL $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution (1 mg mL^{-1}) were dispersed in a Quartz and Pyrex glass hybrid reaction cell. The airtight system was completely evacuated by using a vacuum pump. Then the photoreactor was irradiated with a 300 W Xe lamp (PLS-SXE300, PerfectLight, Beijing, China), and the reaction system was kept at 5 °C as controlled by cooling water. The product H_2 was analyzed by gas chromatography (7890B, Agilent, CA, USA).

2. Method section

Characterization

The morphologies and microstructures were probed utilizing scanning electron microscope (SEM, JSM-7610F JEOL, Japan) and transmission electron microscop (Tecnai G2 F20 S-Twin, FEI, USA). Powder X-Ray Diffraction data were collected over the 2θ range 2–60 ° on a Bruker Advance D8 (Bruker, Germany) at room temperature with a scan speed of 5° min^{-1} . The Zeta potential of CdS and T-COF was obtained on a Zeta Nano-ZS instrument (ZEN3600, Malvern Instruments, UK). N_2 ad/desorption isotherms were performed at 77 K over an Autosorb-iQ2-MP gas sorption analyzer (Quantachrome, USA). The surfaces areas were calculated using the Brunauer-Emmett-Teller (BET) model of N_2 adsorption isotherms. The pore size distribution curves were derived from the N_2 adsorption isotherms using nonlocalized density function theory (NLDFT). The UV-vis diffuse reflectance spectroscopy (DRS) was obtained on a U-4100 spectrometer. Photoluminescence (PL) spectra was obtained on an FLS-1000 fluorescence

spectrophotometer (Edinburgh, UK). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IS50 FT-IR spectrometer (Thermo Fisher Scientific, USA) in the region of 500–4000 cm^{-1} . *In-situ* and *ex-situ* X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) with Al K α excitation source. *In-situ* XPS measurement of samples were performed under dark conditions and light irradiation (300 W Xe lamp was used as simulated solar source), respectively. XPS valence band spectra and ultraviolet photoelectron spectroscopy (UPS) were recorded on ESCALAB 250Xi spectrometer with helium discharge excitation source. Photocurrent and electrochemical impedance (EIS) were measured in a three-electrode cell. 5 mg of catalyst were dispersed in the mixed solution of Nafion (10 μL), ethanol (792 μL) and distilled water (198 μL). After sonicating for 30 min, 20 μL the catalyst ink was deposited on conductive glass of 1 cm $\times$ 0.5 cm as working electrode, and Na₂SO₄ solution (0.4 M) was used as electrolyte. Then transient photocurrent responses was recorded at Xe lamp source irradiation. EIS was carried out at under open circuit potential. All spin-polarized DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP code 5.4.1). The generalized gradient approximation was used as the exchange-correlation functional. The Gaussian trailing width and cut-off energy were set to 0.2 and 400 eV, respectively, while the K-points were 3 $\times$ 3 $\times$ 1. All geometries and energies were converged to below 0.01 eV.

AQY calculation

The apparent quantum yield (AQY) for photocatalytic H₂ evolution of T-COF@CdS-3 was measured under the same photocatalytic reaction conditions but with different monochromatic light. The photocatalytic process of Z-scheme systems is regarded as two-step excitation process and the calculation process is as follows.^{1, 2}

$$\text{AQY (\%)} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

$$= \frac{\text{number of evolved } H_2 \text{ molecules} \times 4}{\text{number of incident photons}} \times 100\%$$

Take AQY (365 nm) of T-COF@CdS-3(10 mg) as example:

$$N = \frac{P \times \lambda \times t}{h \times c} = \frac{27.62 \times 10^{-3} \times 365 \times 10^{-9} \times 3600}{6.626 \times 10^{-34} \times 3 \times 10^8} = 1.825 \times 10^{20}$$

$$\text{AQY}(365) = \frac{\text{number of evolved } H_2 \text{ molecules} \times 4}{N} \times 100\%$$

$$= \frac{N_A \times n \times 4}{N} \times 100\%$$

$$= \frac{6.02 \times 10^{23} \times 17.41 \times 10^{-6} \times 4}{1.825 \times 10^{20}} \times 100\%$$

$$= 22.97\%$$

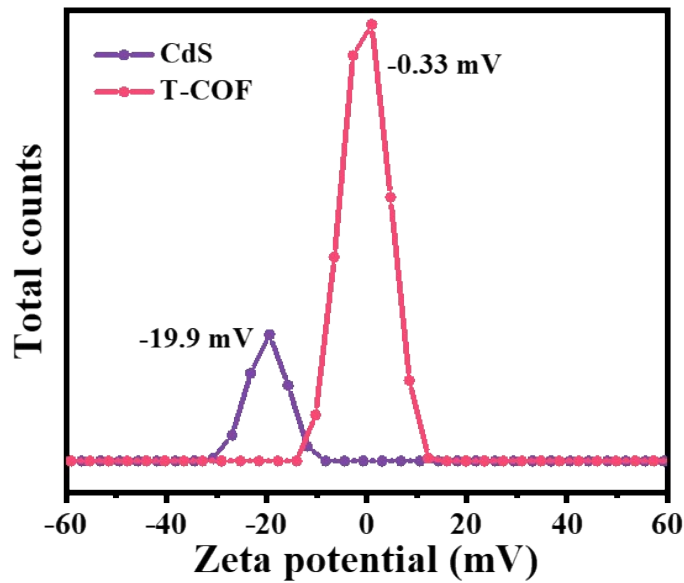


Fig. S1 Zeta potential of CdS and T-COF dispersed in deionized water at pH 7.

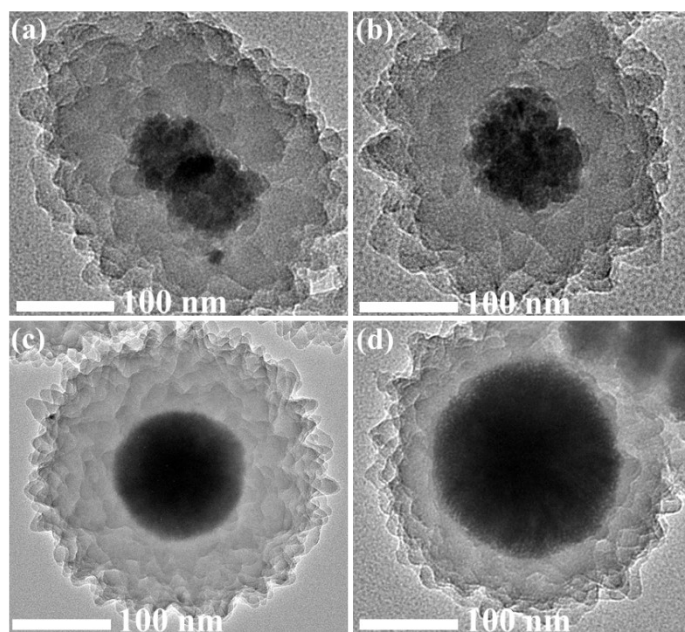


Fig. S2 TEM images of (a) T-COF@CdS-1, (b) T-COF@CdS-2, (c) T-COF@CdS-3 and (d) T-COF@CdS-4.

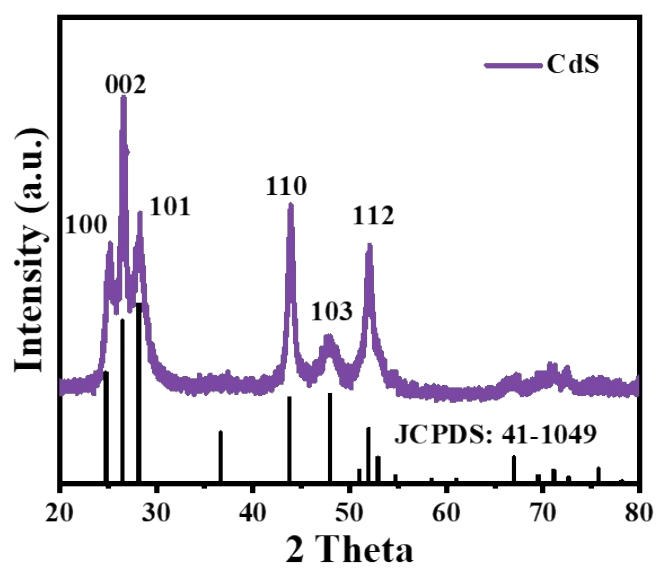


Fig. S3 PXRD pattern of CdS.

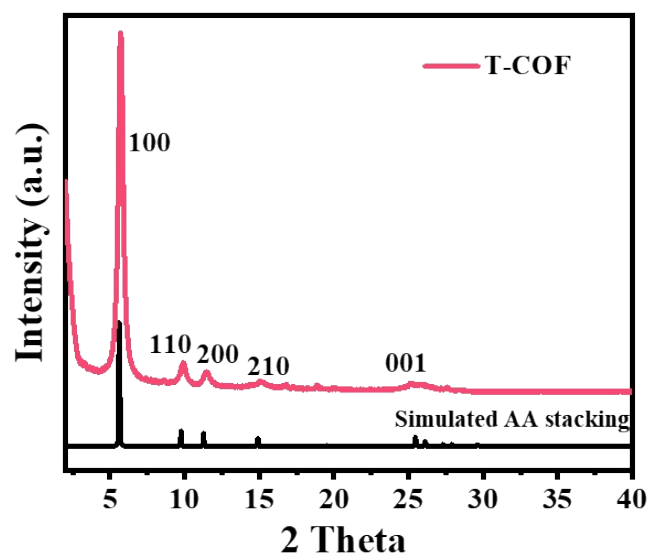


Fig. S4 PXRD pattern of T-COF.

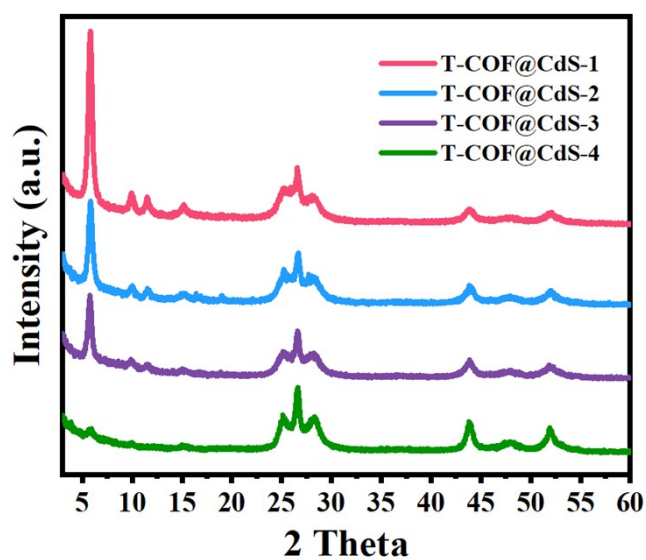


Fig. S5 PXRD pattern of T-COF@CdS.

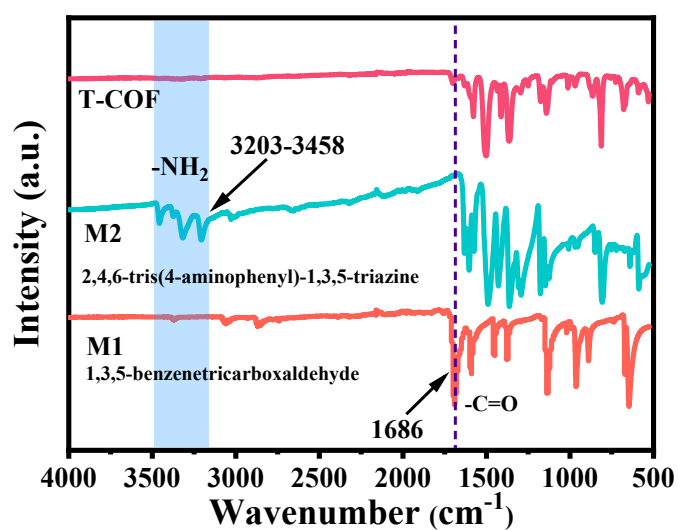


Fig. S6 FT-IR spectra of monomers and T-COF.

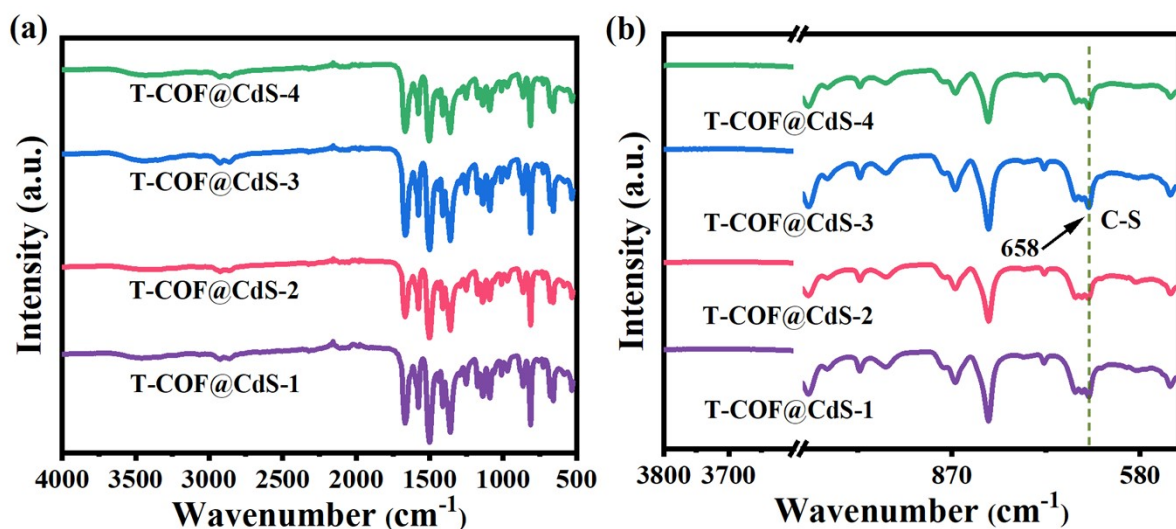


Fig. S7 FT-IR spectra of T-COF@CdS-X.

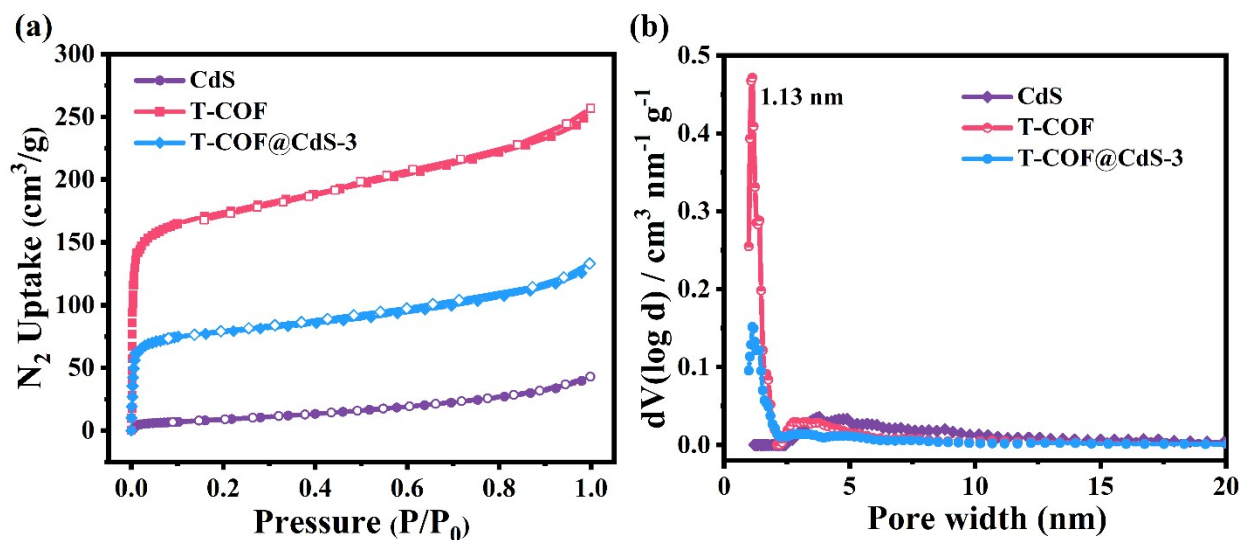


Fig. S8 (a) N_2 adsorption (solid symbols) and desorption (open symbols) isotherms of CdS, T-COF and T-COF@CdS-3 at 77 K. (b) Pore size distribution profiles of CdS, T-COF and T-COF@CdS-3.

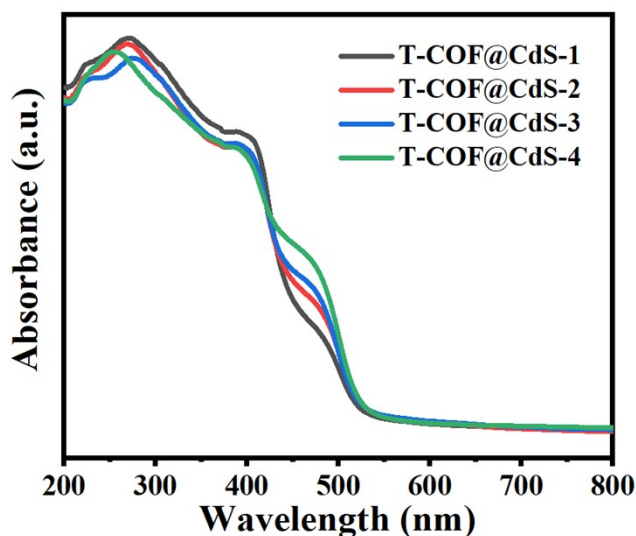


Fig. S9 UV-visible DRS of T-COF@CdS.

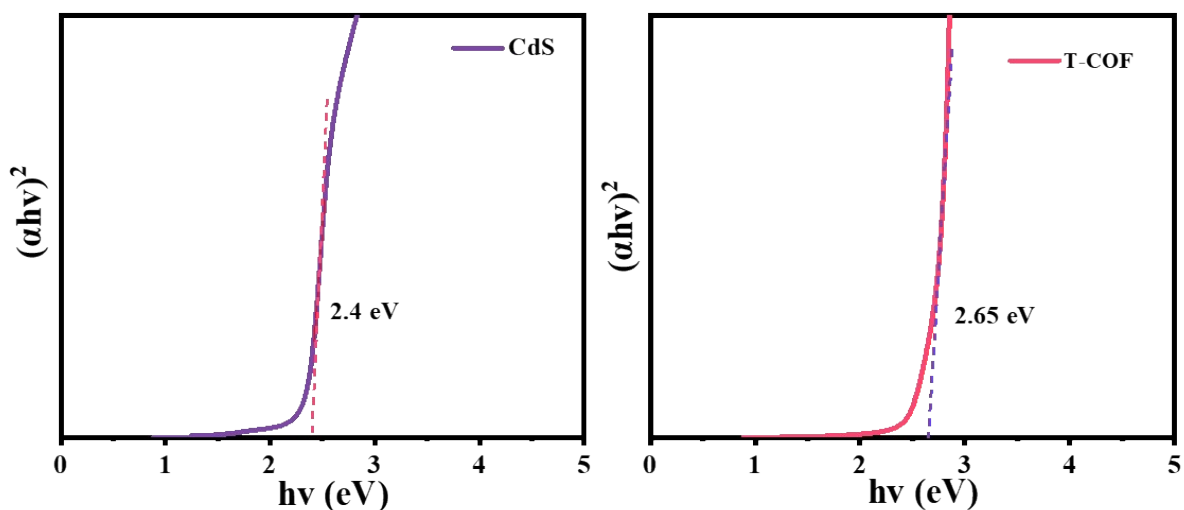


Fig. S10 Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of CdS and T-COF.

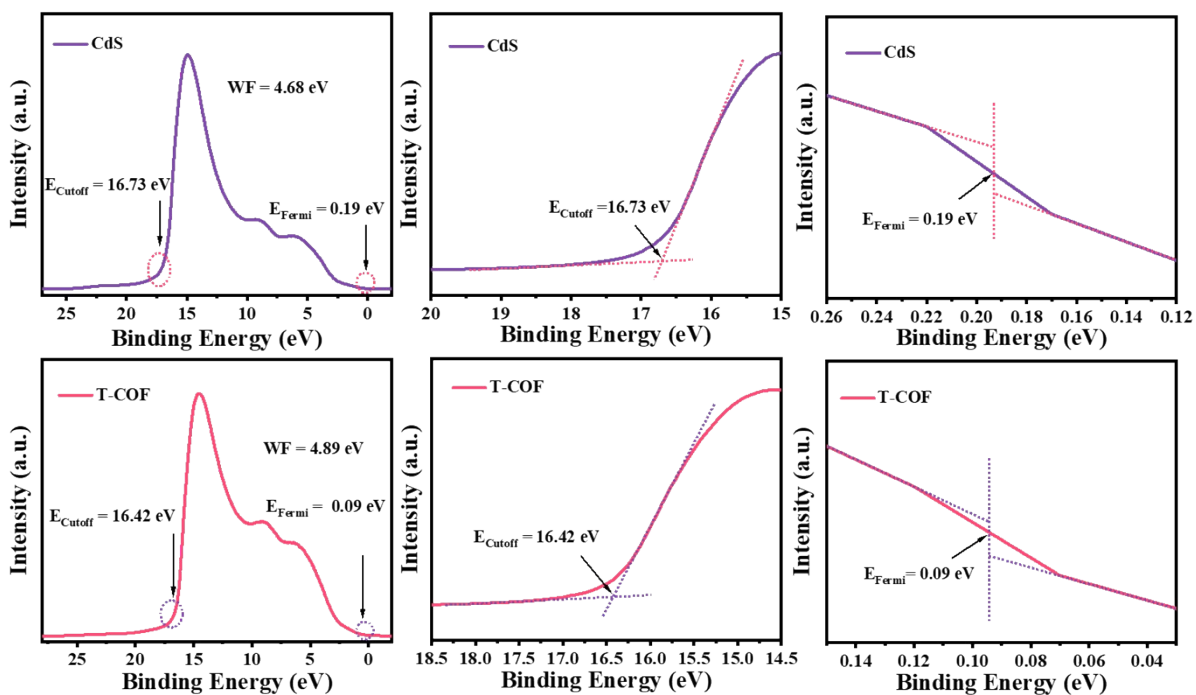


Fig. S11 UPS spectra of CdS and T-COF. UPS was used to determine the work function (WF). According to the linear intersection method, WF of CdS and T-COF were calculated to be 4.68 and 4.89 eV from the equation $WF = h\nu - (E_{\text{Cutoff}} - E_{\text{Fermi}})$ ($h\nu$ of 21.22 eV: the excitation energy of the He I Source). Then VB potential measured via the XPS valence band (VB) spectra can be calibrated by work function and vacuum level (4.44 eV). The VB position vs RHE, RHE of CdS and T-COF are calculated to be 1.66 and 2.04 eV (vs RHE) by the equation $VB \text{ (vs NHE)} = WF + VB_{\text{XPS}} - 4.44$.³

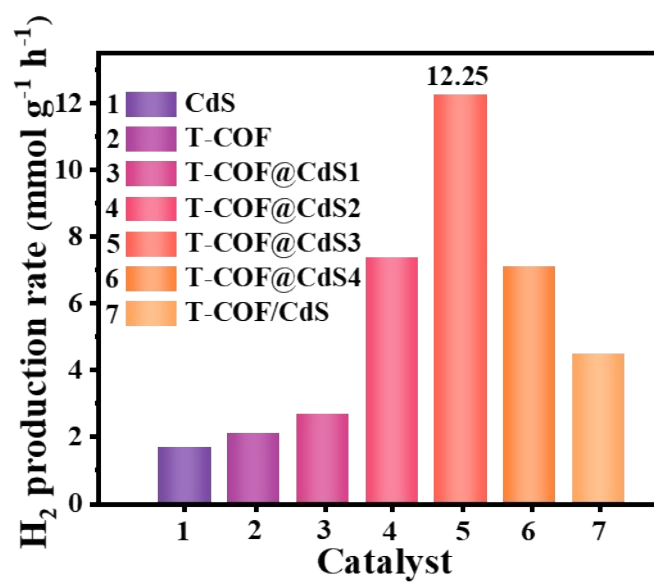


Fig. S12 H₂ evolution rates per gram of various catalysts.

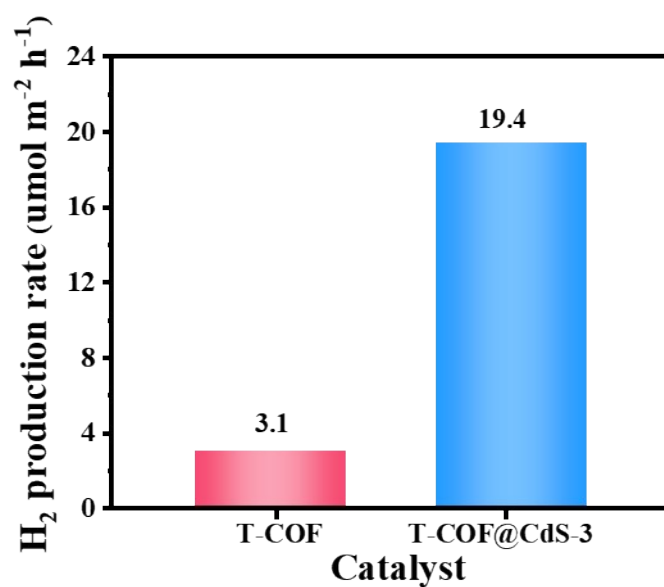


Fig. S13 H₂ evolution rates per surface area of various catalysts.

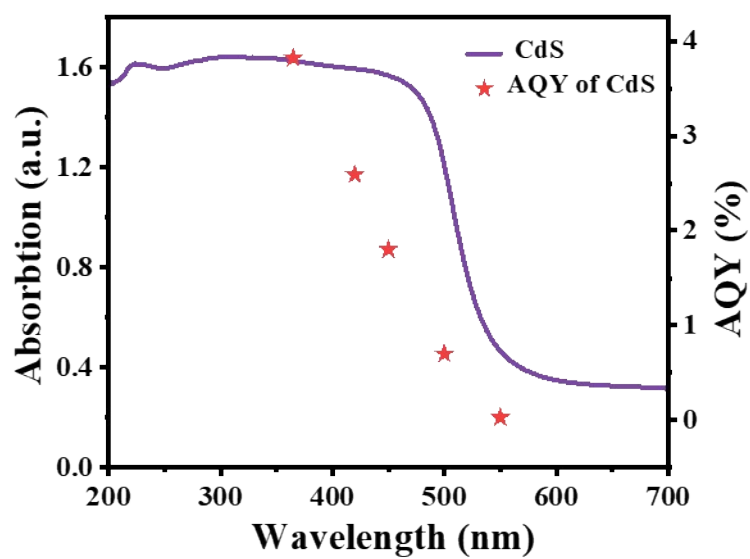


Fig. S14 AQY values of CdS (10 mg) at different monochromatic light irradiation and UV-visible DRS spectra.

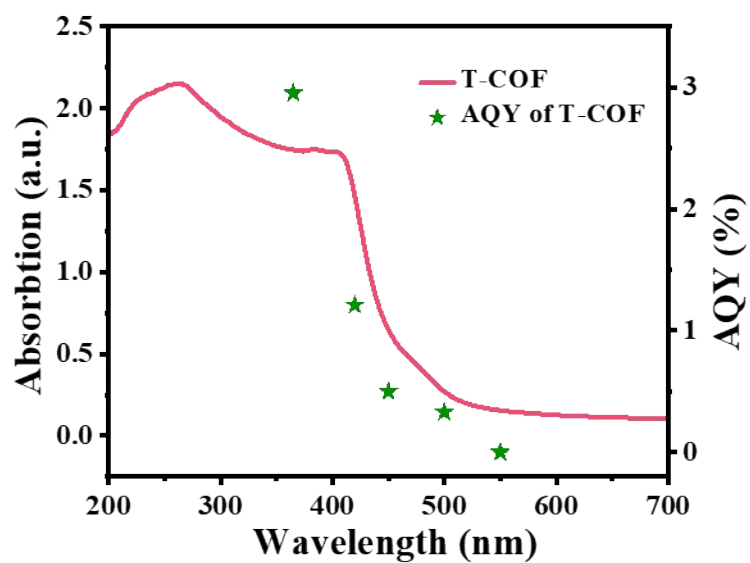


Fig. S15 AQY values of T-COF (10 mg) at different monochromatic light irradiation and UV-visible DRS spectra.

Table S1. Summary of detailed performance of photocatalytic hydrogen production for CdS-based hybrid photocatalysts.

Material	Sacrificial reagent	AQY(%)	Light	Ref.
CdS@NC(B)	Na ₂ S, Na ₂ SO ₃	9.12 (30 mg)	300 W Xe lamp	4
PVDF-HFP/CNT/CdS-Pt	triethanolamine	16.9 (300 mg)	300 W Xe lamp	5
CdS/TiO ₂ Nanofibers	methanol	10.14	350 W Xe lamp	6
H-CdS@C ₃ N ₄ -5	Na ₂ S, Na ₂ SO ₃	10.97	300 W Xe lamp	7
CdS/PT	Lactic acid	24.3 (10 mg)	350 W Xe lamp	8
CdS/NiCo-LDH	Lactic acid	14	300 W Xe lamp	9
CdS/MoS ₂	Lactic acid	3.66	300 W Xe lamp	10
CdS/graphene QDs	Lactic acid	4.2 (40 mg)	300 W Xe lamp	11
COF@CdS-3	ascorbic acid	37.8 (30 mg)	300 W Xe lamp	This work

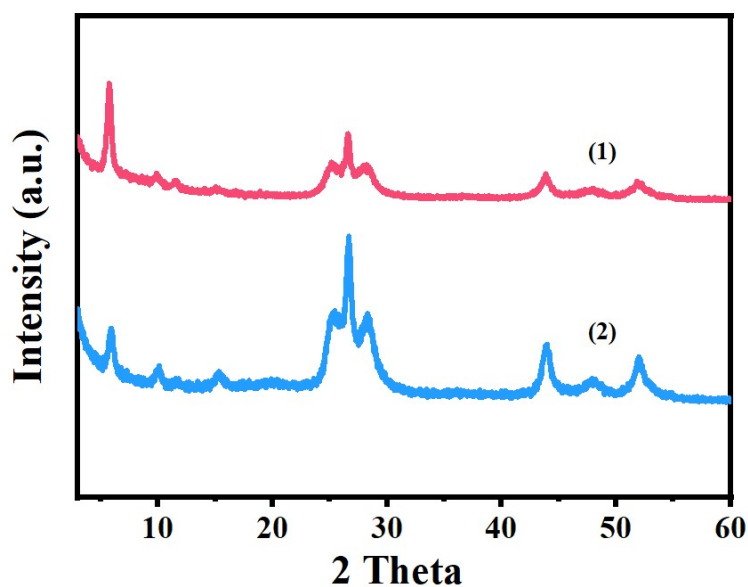


Fig. S16 XRD of T-COF@CdS-3 before (1) and after (2) photocatalytic water splitting reaction.

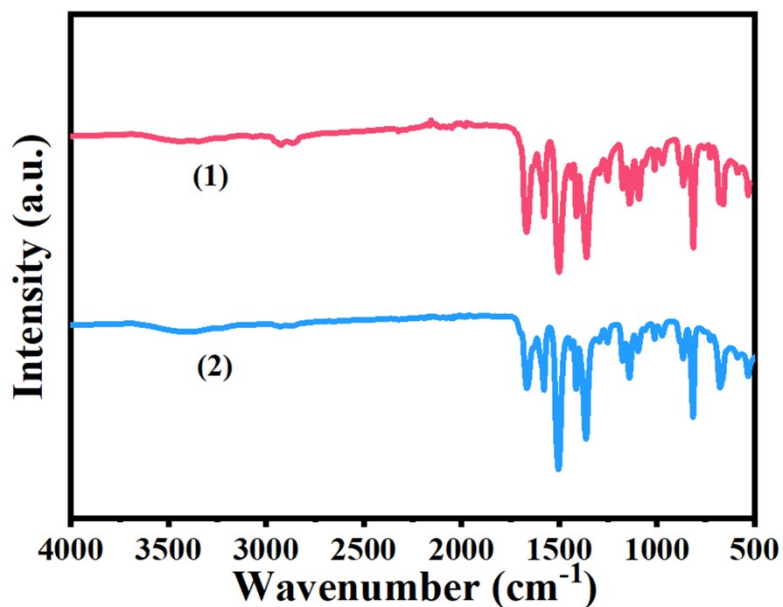


Fig. S17 FT-IR of T-COF@CdS-3 before (1) and after (2) photocatalytic water splitting reaction.

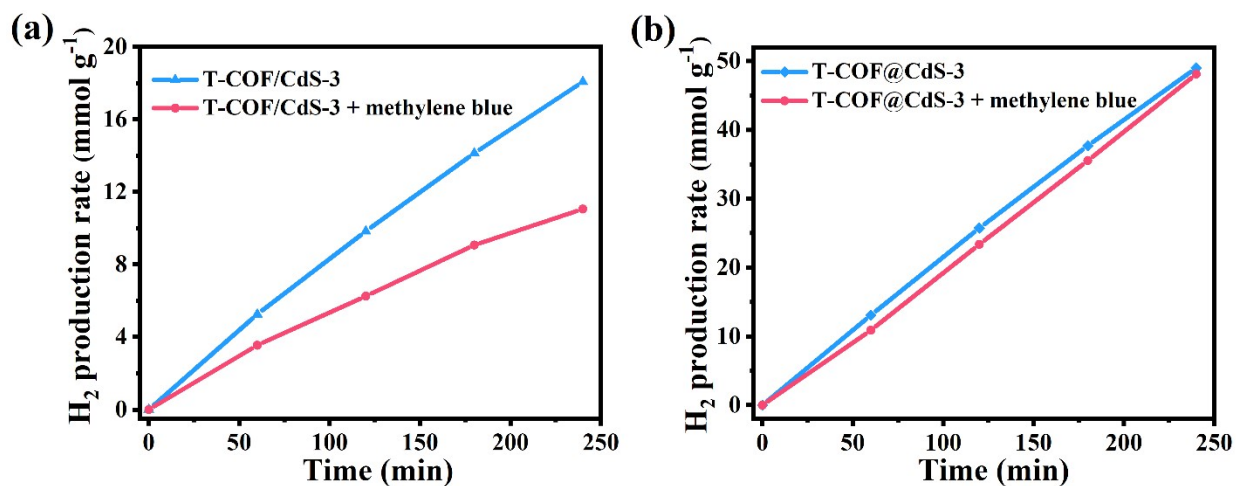


Fig. S18 photocatalytic H_2 evolution amount of (a) T-COF/CdS-3 and (b) T-COF@CdS-3 before and after adding methylene blue ($2 \text{ mL } 100 \text{ mg L}^{-1}$) in the reaction solution.

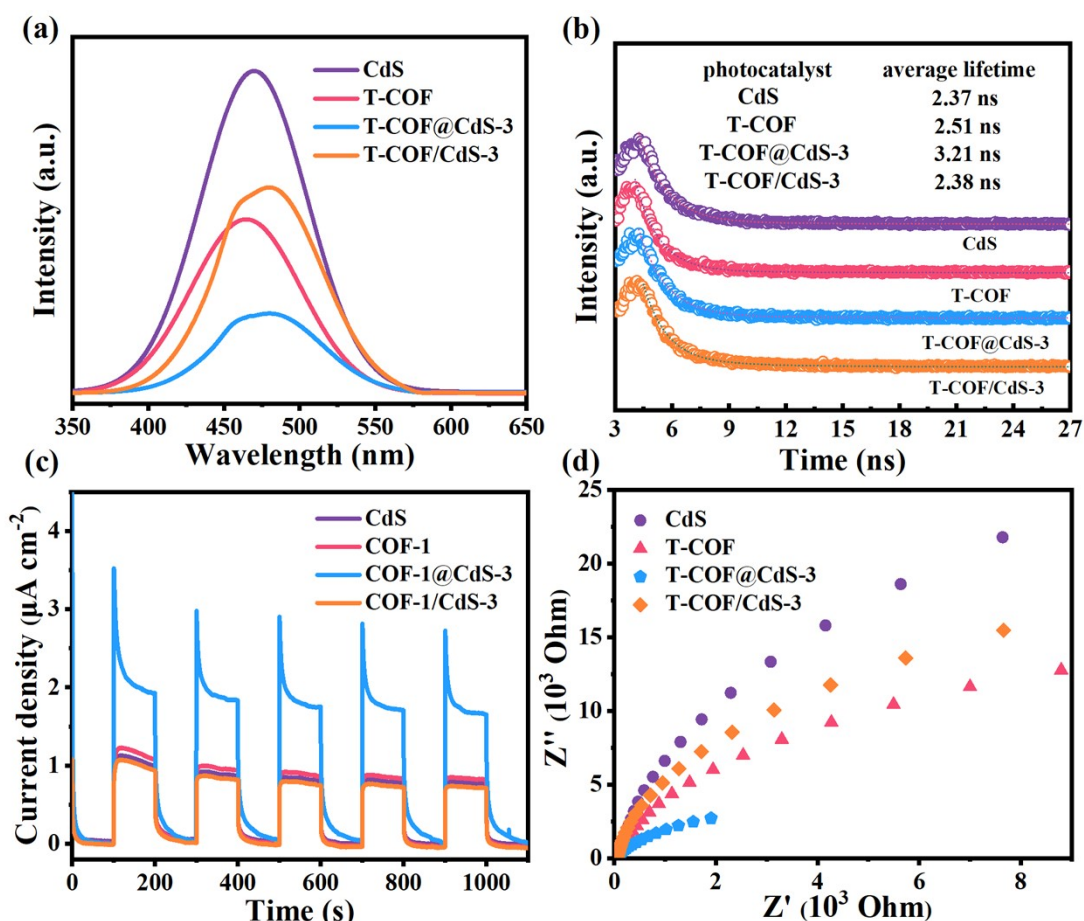


Fig. S19 (a) Photoluminescence spectra, (b) time-resolved photoluminescence spectra, (c) transient photocurrent responses and (d) electrochemical impedance spectroscopy of CdS, T-COF, T-COF@CdS-3 and T-COF/CdS-3.

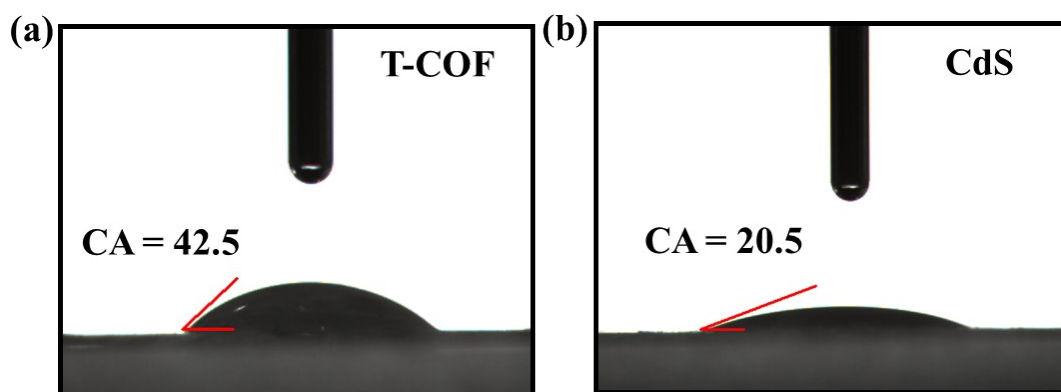


Fig. S20 The contact-angle of (a) T-COF and (b) CdS.

Reference

1. P. Zhou, J. Yu and M. Jaroniec, *Adv. Mater.*, 2014, **26**, 4920-4935.
2. D. Zhao, Y. Wang, C.-L. Dong, Y.-C. Huang, J. Chen, F. Xue, S. Shen and L. Guo, *Nat. Energy*, 2021, **6**, 388-397.

3. C. Feng, L. Tang, Y. Deng, J. Wang, J. Luo, Y. Liu, X. Ouyang, H. Yang, J. Yu and J. Wang, *Adv. Funct. Mater.*, 2020, **30**, 2001922.
4. C. Jiang, X. Xu, M. Mei and F.-n. Shi, *ACS Sustain. Chem. Eng.*, 2018, **6**, 854-861.
5. B. Dai, J. Fang, Y. Yu, M. Sun, H. Huang, C. Lu, J. Kou, Y. Zhao and Z. Xu, *Adv. Mater.*, 2020, **32**, 1906361.
6. H. Ge, F. Xu, B. Cheng, J. Yu and W. Ho, *ChemCatChem*, 2019, **11**, 6301-6309.
7. C. Yin, L. Cui, T. Pu, X. Fang, H. Shi, S. Kang and X. Zhang, *Appl. Surf. Sci.*, 2018, **456**, 464-472.
8. C. Cheng, B. He, J. Fan, B. Cheng, S. Cao and J. Yu, *Adv. Mater.*, 2021, **33**, 2100317.
9. S. Li, L. Wang, Y. Li, L. Zhang, A. Wang, N. Xiao, Y. Gao, N. Li, W. Song, L. Ge and J. Liu, *Appl. Catal. B*, 2019, **254**, 145-155.
10. Z.-W. Zhang, Q.-H. Li, X.-Q. Qiao, D. Hou and D.-S. Li, *Chinese J. Catal.*, 2019, **40**, 371-379.
11. Y. Lei, C. Yang, J. Hou, F. Wang, S. Min, X. Ma, Z. Jin, J. Xu, G. Lu and K.-W. Huang, *Appl. Catal. B*, 2017, **216**, 59-69.