Electronic supplementary information (ESI)

Huaizhi Yang, [a] Yuqi Wan, [a] Qingrong Cheng, *[a], Hong Zhou, [a] Zhiquan Pan, [a] Yan Liu. [b]

[a] School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan, 430205, PR China.

[b] Shenzhen Puhua System Technology Co., Ltd， Shenzhen, 518129, PR China.

Corresponding authors:

*(Q.C.) E-mail: chengqr383121@sina.com

Total number of pages: 9

Total number of Tables: 2

Total number of Figures: 6

The characterization methods and evaluation of photocatalytic performance

Transmission electron microscopy (TEM, FEI TALOS F200) was used to characterize the internal and microstructural information of the samples (HRTEM measures the lattice information of substances), and the basic element composition distribution (EDX) was obtained by equipped with an energy dispersive X-ray spectrometer. Ultraviolet-Visible (UV-Vis) diffuse reflectance spectroscopy (DRS) was measured using a West Wisteria UV-2600 spectrometer with barium sulfate as a reference. X-ray photoelectron spectroscopy (XPS) was performed using the 250Xi-XPS photoelectron spectrometer of the thermal calibration laboratory and aluminum Kα ray resources. The change in binding energy was taken as the internal standard at the C1s level at 284.8 eV. The patterns collected on a BrukerD8 advanced X-ray diffractometer (XRD) were used to analyze the surface phase composition of the materials, scans over a test angle range of 5° to 90° at a rate of 5° min^{-1}. ESR measured by German Bruker (A300), it is used to detect the content of active species in the process of photoreaction.

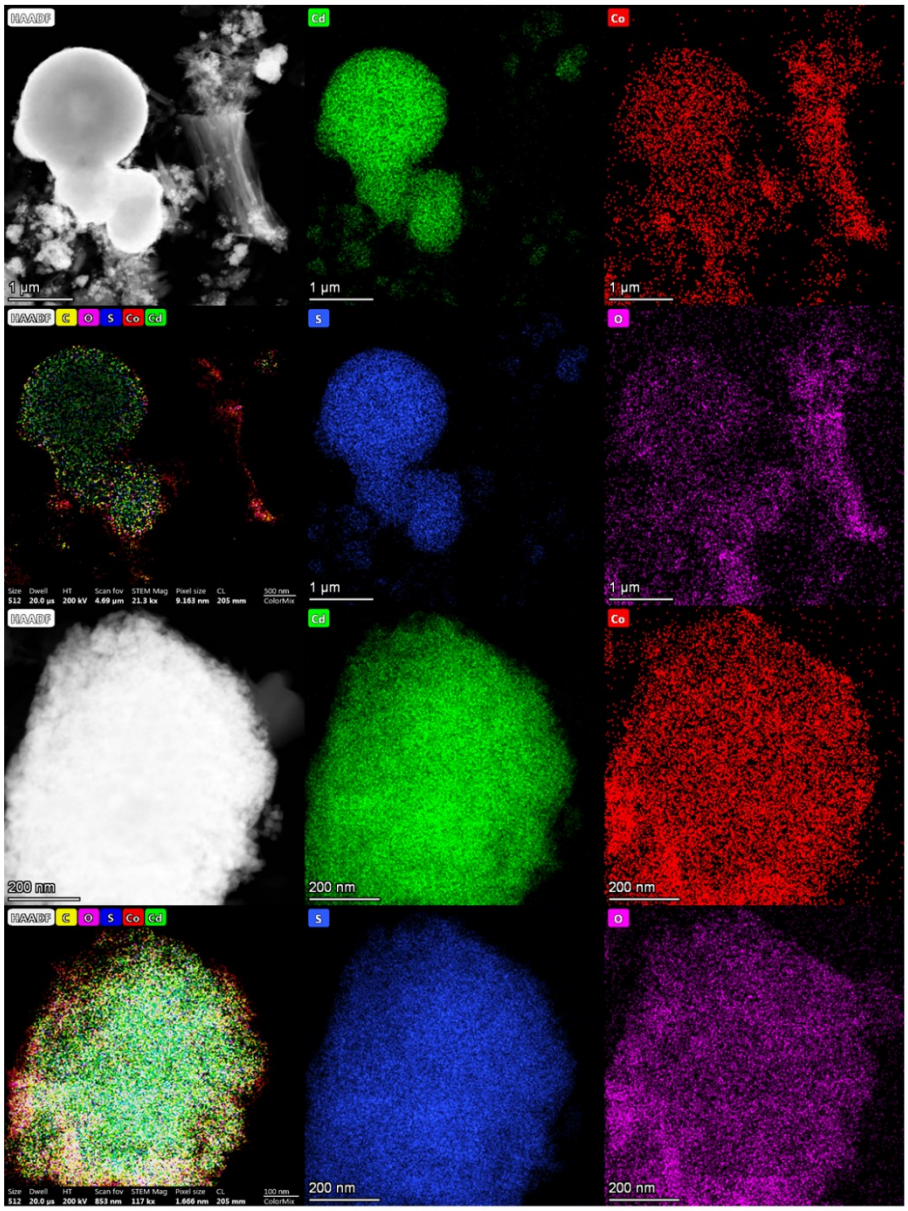
Electrochemical measurements were carried out on an electrochemical workstation (CHI760E instruments) connected to a standard three-electrode system, namely the working electrode prepared from the test sample, a platinum plate as the counter electrode, and a saturated Ag/AgCl as the reference electrode. The working electrode was prepared as follows: Weigh 10mg of the sample and pour it into a 5 mL EP tube, added 2 mL Nafion injection solution (Nafion: isopropanol = 1:25), and sonicated for 15 min. Each time, 10 microliters were dropped onto the conductive glass surface with a micro-injector, dispersed evenly, dried under a sun lamp, and the operation was repeated 3 times. The test solution was 0.5 M sodium sulfate aqueous solution. Electrochemical impedance spectroscopy (EIS) data were measured directly at the electrochemical workstation, the frequency range of the circuit potential was 1 Hz to 100 kHz, and the test voltage was 1.5 eV. The EIS was fitted by ZView2 software. Transient Photocurrent Response (PC) of the sample was carried out under sun light conditions (300 W xenon lamp), with the light on for 30 s and the light off for 30 s as a cycle, for 6 consecutive cycles. Mott-Schottky's measurement experiments were performed at frequencies at 500 Hz and 1000 Hz, and the potential changed

from -2.0 to 1.5 eV.

Photocatalysis experiments included organic pollutant degradation experiments and hydrogen production experiments. The ability of photocatalysts to degrade organic pollutants can be judged by measuring the changes in the absorbance (positions of characteristic peaks) of organics under visible light irradiation. The light source was visible light (with a 420 nm filter). First, 50 mL of 30 mg/L TC solution was poured, 3 mL of the solution was taken out, and the measured absorbance was recorded as the initial absorbance (C_{-30}). Then, 10 mg of the photocatalyst was added, and the catalyst was magnetically stirred for 30 min in the dark to reach the adsorption-desorption equilibrium. After the light-proof treatment, 3 ml of the solution was taken out, and the measured absorbance was recorded as the absorbance at 0 min of illumination (C_0). During the photoreaction, 3 mL samples were withdrawn from the reactor every 10 min (It is represented by C_t, and it is denoted as C_{10} and C_{20} in turn.). All samples were filtered photocatalysts using organic filters (0.22 μm. organic). The absorption intensity at the maximum wavelength of 357 nm was measured with a UV-Vis spectrophotometer, and the concentration change was reflected by the change of absorbance to evaluate the degradation efficiency. In the photocatalytic degradation cycle experiments, the products were collected by a common centrifugation method. Considering the mass loss, the amount of catalyst added was changed to 20 mg. In each cycle, we only collected samples before dark (C_{-30}), after dark (C_0), and after 60 min of light (C_{60}). At the end of a cycle, the catalyst in the remaining liquid was collected by centrifugation and washed with methanol and after vacuum drying, and then enter a new round of photocatalytic degradation test with a new tetracycline solution. A total of four cycles were carried out to test the stability of the prepared composite photocatalyst. The photocatalytic hydrogen production experiments were carried out in a 150 mL cylindrical quartz reactor with an irradiation area of 28.12 cm^2 and a 300 W xenon lamp as the light source (PerfectLight, Labsolar-IIIAG Photocatalytic system). Mixed 30 mg of photocatalyst, 80 mL of distilled water, and the prepared sacrificial agent (10 mL of 0.35 M sodium sulfite solution, 10 mL of 0.25 M sodium sulfide solution) evenly, and replaced the air in the container with nitrogen before the reaction, turned on stirring and kept the catalyst suspend in the reaction system, used a syringe needle draws 300 μL of gas per hour from the reactor, and the H_2 generation rate was calculated by gas chromatography (Timei GC7900, TCD, N_2 as carrier). The operation of the photocatalyst cycle test was as follows: after the first hydrogen production

experiment, the photocatalyst was collected by centrifugation, washed three times with ethanol, the obtained solid was dried, and transferred to a new solution system, filled with nitrogen again, and carried out for the next hydrogen production experiment, the entire process was repeated four times.

The Cambridge Series Total Energy Package (CASTEP) module of Materials Studio program was used to all the DFT calculations. It was calculated using the function GGA-PBE(general gradient approximation- Perdew-Burke-Ernzerhof) and the hybrid functional HSE06 (Heyd-Scuseria-Ernzerhof). Herein, the geometry optimization conditions for CdS and CoO were as follows, the cutoff energies were set to 500 eV and 750 eV, respectively, and the k-points were set to 8×8×5 and 9×9×9, respectively. The convergence tolerance parameter for the max step size was 0.001 Å, the maximum force was 0.01 eV/Å, the energy change was 1.0×10^{-6} eV/atom, and the maximum stress was 0.02 GPa. For surface structure calculations and heterogeneous junction structure calculations, the interface between CdS and CoO by taking the supercell of 3×3 CdS (12.60Å×12.60Å) and 4×4 CoO (12.69Å×12.69Å), k-points were taken as 2×2×1, a vacuum layer of 15 Å was constructed to eliminate interactions between periodic structures of surface models, and all the above calculations had been tested for convergence.



105

106 Figure S1. EDX mapping of the composite photocatalyst.

107

108

109

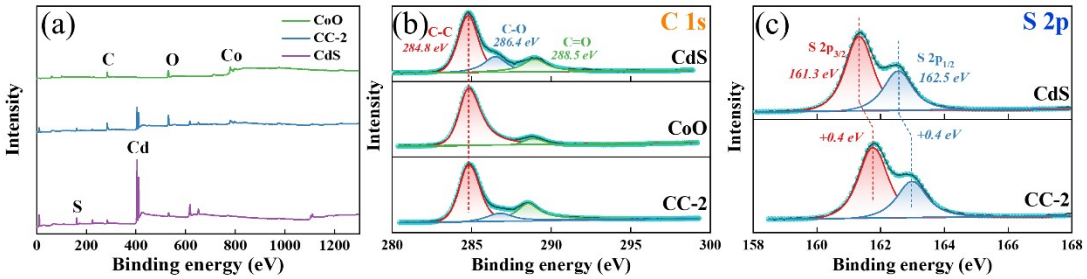


Figure S2. (a) XPS survey spectra of CdS, CoO and CC-2, (b) C 1s fine spectra of CdS, CoO and CC-2, (c) S 2p fine spectra of CdS, and CC-2.

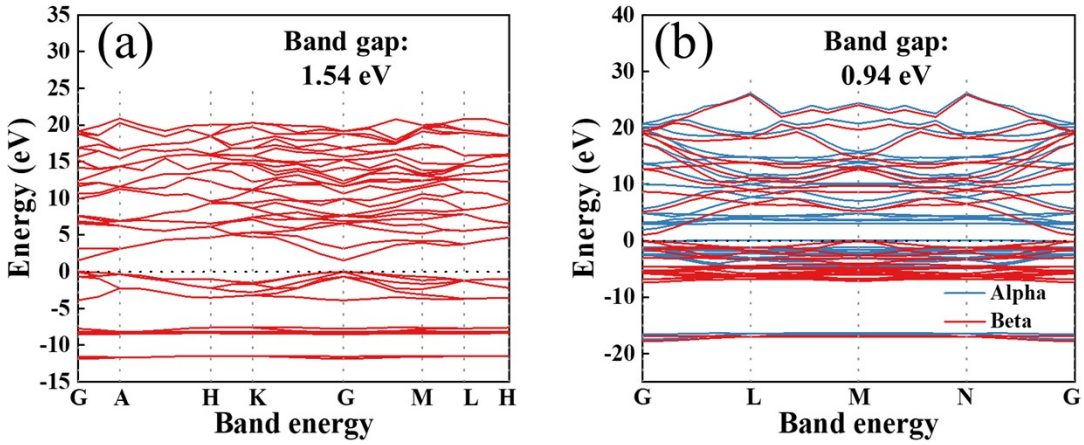


Figure S3. The band energy a of the (a) CdS and (b) CoO, calculated with GGA-PBE.

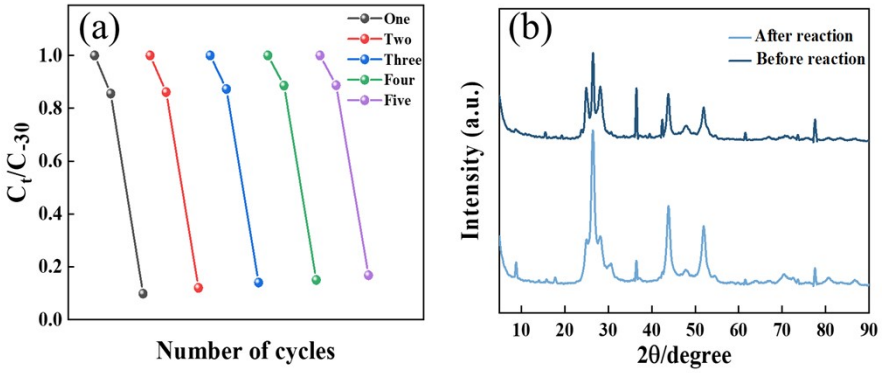


Figure S4 (a) Degradation efficiency of CC-2 in five cycles, (b) XRD patterns of CC-2 before and after cycling.

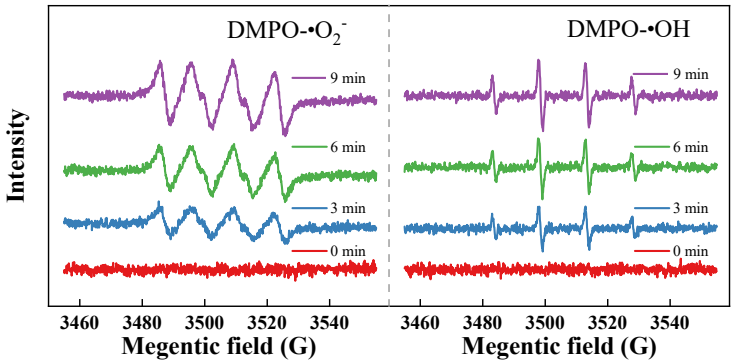


Fig.S5 The ESR spectrum of CC-2 for DMPO–•OH and DMPO–•O_2^-.

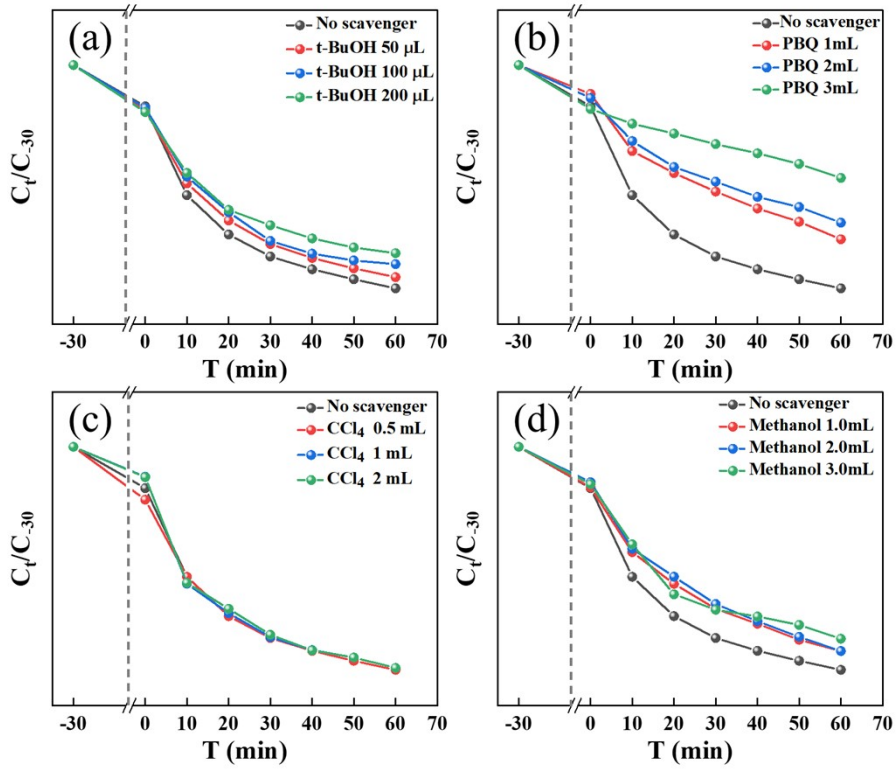


Fig.S6 (a-d) The radical trapping test for the CC-2.

Table S1 Comparison of TC degradation over CC-2 and other photocatalysts.

Catalyst / mg	*V (mL) / C_{-30} ($mg \cdot L^{-1}$)*	*Light source*	*Time (min)*	*Result (%)*	*TOF*	*Ref*
CC-2(CdS/CoO)/10	50/30	Visible light	60	90%	2.25	This work

CDs-CoO/50	100/10	Visible light	60	87%	0.29	[1]
CdS/Ti_{32}-oxo-cluster composites /10	50/50	Visible light	60	96.3%	4.01	[2]
CdS/$Bi_4O_5Br_2$ /10	40/20	Visible light	60	85%	1.13	[3]
g-C_3N_4/CdS/25	50/50	simulated solar light	60	69.63%	1.16	[4]

TOF is calculated according to an equation:

$$TOF = \frac{C_{-30} \times V_{TC} \times \text{Degradation rate}}{m_{\text{catalyst}} \times t}$$

Table S2 Comparison of the photocatalytic H_2 evolution rates over CC-2 and other photocatalysts.

Photocatalysts	***Irrigation***	***Sacrificial agents***	***Activity μmol·g^{-1}h^{-1}***	***Ref***
CC-2(CdS/CoO)	Sun light	Na_2SO_3 and Na_2S	4463.5	This work
ZnS/CoO	Visible light	Na_2SO_3 and Na_2S	1763.17	[5]
CdS@Ti_3C_2@CoO	Visible light	nothing	134.46	[6]
CdS/MoS_2	Visible light		13129	[7]
CdS/Ni-MOF	Visible light	lactic acid	2508	[8]

References:

[1] W. Shi, F. Guo, H. Wang, M. Han, H. Li, S. Yuan, H. Huang, Y. Liu, Z. Kang, Carbon dots decorated the exposing high-reactive (111) facets CoO octahedrons with enhanced photocatalytic activity and stability for tetracycline degradation under visible light irradiation, Appl. Catal., B. 219 (2017) 36-44.

[2] Q. Zhu, Y. Sun, F. Na, J. Wei, S. Xu, Y. Li, F. Guo, Fabrication of CdS/titanium-oxo-cluster nanocomposites based on a Ti32 framework with enhanced photocatalytic activity for tetracycline hydrochloride degradation under visible light, Appl. Catal., B. 254 (2019) 541-550.

[3] W. Cao, C. Jiang, C. Chen, H. Zhou, Y. Wang, A novel Z-scheme CdS/Bi4O5Br2 heterostructure with mechanism analysis: Enhanced photocatalytic performance, J. Alloys Compd. 861 (2021) 158554.

[4] G. Li, B. Wang, J. Zhang, R. Wang, H. Liu, Rational construction of a direct Z-scheme g-C3N4/CdS photocatalyst with enhanced visible light photocatalytic activity and degradation of erythromycin and tetracycline, Appl. Surf. Sci. 478 (2019) 1056-1064.

[5] Q. Zhu, S. Xu, Y. Qin, J.C.-H. Lam, Y. Li, Multication and Structure Regulation: Utilizing X‐Doped (X = Co, Mn, Cu) ZnS/CoO Hollow Composites to Spatially Propel the Charge for Superior Solar Hydrogen Evolution, Solar RRL 7(2) (2022) 2200918.

[6] K.Z. Zizheng Ai, Bin Chang, Yongliang Shao, Lei Zhang, Yongzhong Wu, Xiaopeng Hao, Construction of CdS@Ti3C2@CoO hierarchical tandem p-n heterojunction for boosting photocatalytic hydrogen production in pure water, Chem. Eng. J. (2019) 123130.

[7] K. Zhuge, Z. Chen, Y. Yang, J. Wang, Y. Shi, Z. Li, In-suit photodeposition of MoS2 onto CdS quantum dots for efficient photocatalytic H2 evolution, Appl. Surf. Sci. 539 (2021) 148234.

[8] J. Guo, Y. Liang, L. Liu, J. Hu, H. Wang, W. An, W. Cui, Noble-metal-free CdS/Ni-MOF composites with highly efficient charge separation for photocatalytic H2 evolution, Appl. Surf. Sci. 522 (2020) 146356.