Electronic Supplementary Information

Experimental details

Characterizations: The crystal phases of the samples were analyzed by X-ray diffraction (XRD) on a Bruker D8 Advance instrument (Cu K α irradiation, $\lambda =$ 1.5406 Å). The morphology and structure of the samples were examined by field emission scanning electron microscope (SEM; JEOL-6700) and transmission electron microscope (TEM; JEOL, JEM-2010). The TEM instrument was employed to capture elemental mapping images. The compositions of the samples were determined by energy-dispersive X-ray spectroscopy (EDX) attached to a scanning electron microscope (SEM; Quanta250). N2 and CO2 adsorption isotherms were collected on an ASAP2020M apparatus. The samples were degassed in vacuum at 100 °C for 6 h, and then measured at -77 K and 0 °C to determine N₂ and CO₂ adsorption, respectively. UV-vis diffuse reflectance spectra (DRS) spectra were obtained on a Varian Cary 500 UV-Vis-NIR spectrophotometer with BaSO₄ as a reflectance standard. The X-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectra (UPS) were obtained using a PHI Quantum 2000 XPS system with C 1s binding energy (284.6 eV) as the reference and He I excitation (21.22 eV) as the monochromatic light source. Photoluminescence (PL) characterizations were carried out on a Hitachi-F-7000 spectrophotometer at room temperature. The fluorescence lifetime was determined by recording the time-resolved fluorescence emission spectra on a Deltapro Fluorescence Lifetime System. The electrochemical analysis carried out on CHI600E Electrochemical System, using a conventional three electrodes cell with Pt plate and Ag/AgCl electrode as the counter electrode and reference electrode, respectively. Typically, 5 mg of the sample was dispersed in 1 mL of N, N-dimethylformamide (DMF) by sonication to gain a slurry. Then, the resultant slurry was spread onto the FTO glass with an area of ca. 0.25 cm². The transient photocurrent response spectra were collected in Na₂SO₄ aqueous solution (0.2 M) with a 300 W xenon lamp ($\lambda \ge 420$ nm) as a light source. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the open circuit potential. An Agilent 7890B gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a packed column (TDX-01) was utilized to analyze and quantify the gases produced from the CO₂ photoreduction system with Ar as the carrier gas. An HP 5973 gas chromatography-mass spectrometer (GC-MS) was employed to analyze the gaseous products generated from the 13 CO₂ (97% enriched) isotopic experiment. The GC-MS split ratio in this experiment is 100: 1, the heating program is holding at 45 °C for 2.5 minutes, and then increased to 150 °C for 2 min at a rate of 15 °C min⁻¹ and further increased to 170 °C for 2 min at a rate of 20 °C min⁻¹.

*Photocatalytic CO*₂ *reduction:* In the typical photocatalytic CO₂ reduction reaction, 10 mg of photocatalyst, 400 μ mol of 2'2-bipyridine (bpy), 8 μ mol of CoCl₂, 4 mL of triethanolamine (TEOA), 4 mL of H₂O and 16 mL of acetonitrile were added into a gas-closed Schlenk flask reactor (80 mL in capacity). Then, high purity CO₂ was introduced into the reactor with a partial pressure of 1 atm. A 300W Xe lamp with a 400 nm cutoff filter was used as the light source. The temperature of the reaction system was kept at 30 °C by a circulating water. During the photocatalytic process, the reaction system was vigorously stirred with a magnetic stirrer. After the reaction, the generated products were analyzed and quantified by an Agilent 7890B GC.



Fig. S1 EDX of Co₃O_{4@}CdIn₂S₄.



Fig. S2 XPS survey spectrum of $Co_3O_4@CdIn_2S_4$.



Fig. S3 The pore-size distribution curves of (a) CdIn₂S₄ and (b) Co₃O₄@CdIn₂S₄.



Fig. S4 UV-vis absorption spectra of the photocatalytic CO_2 reduction systems before and after visible light irradiation.

Sample	Decay lifetime	Related intensity	
	$\tau_1 = 1.21 \text{ ns}$	a ₁ =17.41 %	
$CdIn_2S_4$	$\tau_2 = 68.83 \text{ ns}$ $\tau_3 = 0.43 \text{ ns}$	a ₂ =35.09 % a ₃ =47.5 %	
	$\tau_1 = 1.01 \text{ ns}$	a ₁ =30.7 %	
Co ₃ O ₄ @CdIn ₂ S ₄	$\tau_2 = 30.04 \text{ ns}$ $\tau_3 = 0.42 \text{ ns}$	a ₂ =3.93 % a ₃ =65.37 %	

Table S1. The decay lifetime and related intensity of time-resolved transient PL spectra in Fig. 5b.

catalyst (used amount)	cocatalyst	sacrificial agent	CO evolution rate (µmol h ⁻¹)	Refs.
Co ₃ O ₄ @CdIn ₂ S ₄ (10 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 53	This work
HR-CN (30 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 9.9	1
CdS/BCN (50 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 12.5	2
ZnS-DETA/CdS (4 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 33.3	3
Au(25)@CdS (4 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 15	4
$ZnIn_2S_4$ - In_2O_3 (4 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 12.3	5
PCN/ ZnIn ₂ S ₄ (50 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 44.6	6
CNU-BA0.03 (30 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 26.2	7
$In_2S_3 - CdIn_2S_4$ (4 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 3.3	8
$TiO_2/g-C_3N_4$ (5 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 1.2	9
Co ₄ @g-C ₃ N ₄ (50 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 5.4	10
DA-CTF (30 mg)	Co(bpy) ₃ ²⁺	TEOA	CO: 4.0	11

Table S2. Comparison of CO₂ photoreduction performance of Co₃O₄@CdIn₂S₄ with that of other catalysts in similar reaction systems under visible light irradiation ($\lambda \ge 400$ nm).

Supplementary References

- Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, Angew. Chem. Int. Ed., 2014, 53, 11926-11930.
- 2. M. Zhou, S. Wang, P. Yang, C. Huang and X. Wang, ACS Catal., 2018, 8, 4928-4936.
- B. Su, L. Huang, Z. Xiong, Y. Yang, Y. Hou, Z. Ding and S. Wang, *J. Mater. Chem. A*, 2019, 7, 26877-26883.
- 4. P. Zhang, S. Wang, B. Y. Guan and X. W. Lou, Energy Environ. Sci., 2019, 12, 164-168.
- 5. S. Wang, B. Y. Guan and X. W. Lou, J. Am. Chem. Soc., 2018, 140, 5037-5040.
- M. Zhou, S. Wang, P. Yang, Z. Luo, R. Yuan, A. M. Asiri, M. Wakeel and X. Wang, *Chem. Eur. J.*, 2018, 24, 18529-18534.
- 7. J. Qin, S. Wang, H. Ren, Y. Hou and X. Wang, Appl. Catal. B Environ., 2015, 179, 1-8.
- 8. S. Wang, B. Y. Guan, Y. Lu and X. W. Lou, J. Am. Chem. Soc., 2017, 139, 17305-17308.
- H. Shi, J. Du, J. Hou, W. Ni, C. Song, K. Li, G. G. Gurzadyan and X. Guo, J. CO2. Util., 2020, 38, 16-23.
- J. Zhou, W. Chen, C. Sun, L. Han, C. Qin, M. Chen, X. Wang, E. Wang and Z. Su, *ACS Appl. Mater. Interfaces*, 2017, 9, 11689-11695.
- H. Zhong, Z. Hong, C. Yang, L. Li, Y. Xu, X. Wang and R. Wang, *ChemSusChem*, 2019, **12**, 4493-4499.