Supporting Information

MOF@MOF-derived hierarchical MIL-125(Ti)@TiO_2\Co_3S_4 hollow nanodiscs for remarkable photocatalytic CO_2 reduction

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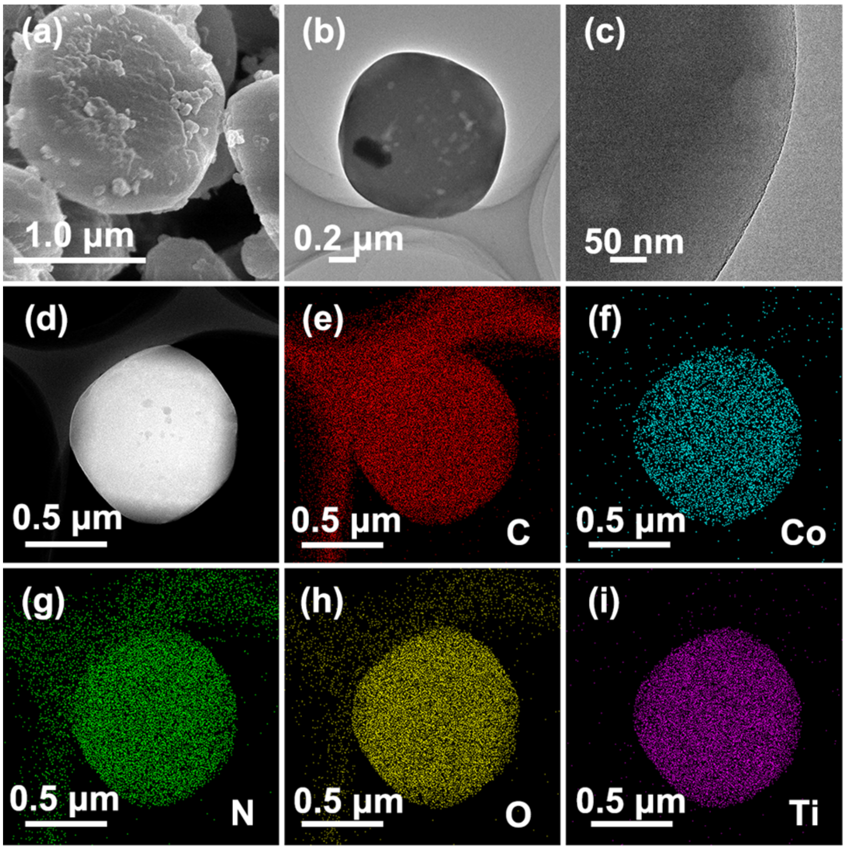

Fig. S1. (a) SEM, and (b, c) TEM images of MIL-125(Ti)@ZIF-67. (d) STEM image and corresponding elemental mappings for (e) C, (f) Co, (g) N, (h) O, and (i) Ti elements of MIL-125(Ti)@ZIF-67.

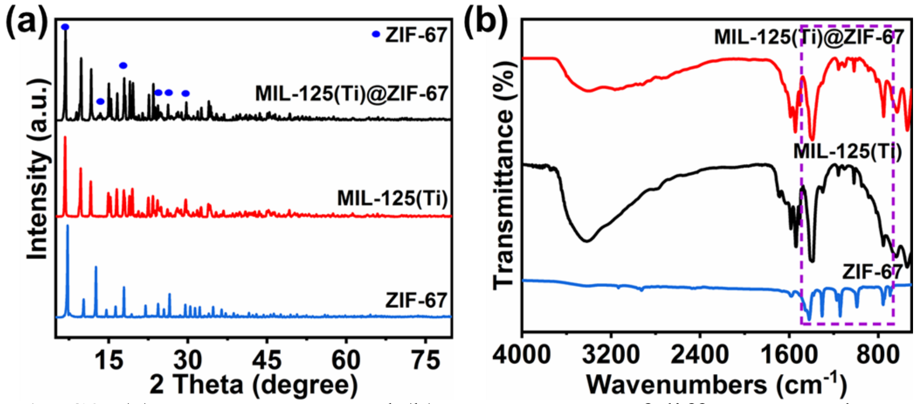

Fig. S2. (a) XRD patterns and (b) FTIR spectra of different samples.

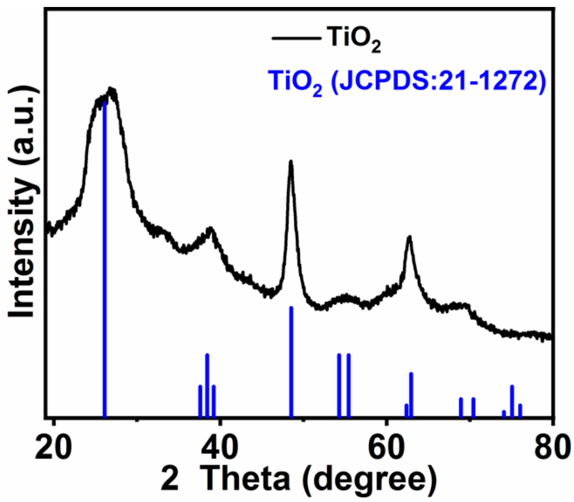

Fig. S3. XRD pattern of TiO_2.

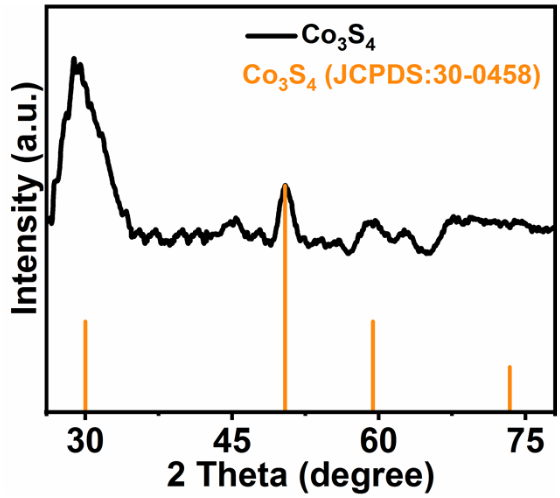

Fig. S4. XRD pattern of Co_3S_4.

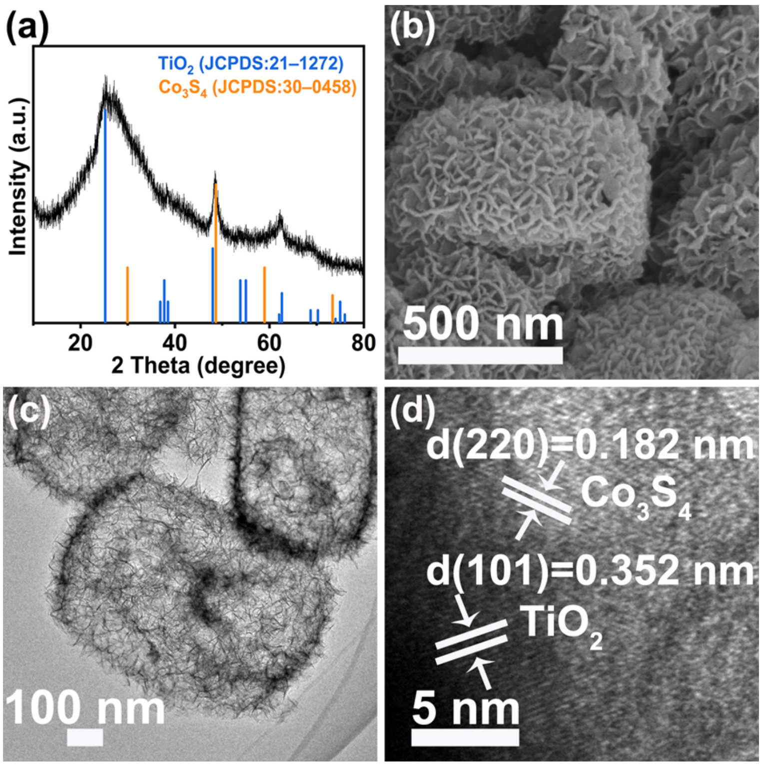

Fig. S5. (a) XRD pattern, (b) SEM, (c) TEM, and (d) HRTEM images of TiO_2\Co_3S_4.

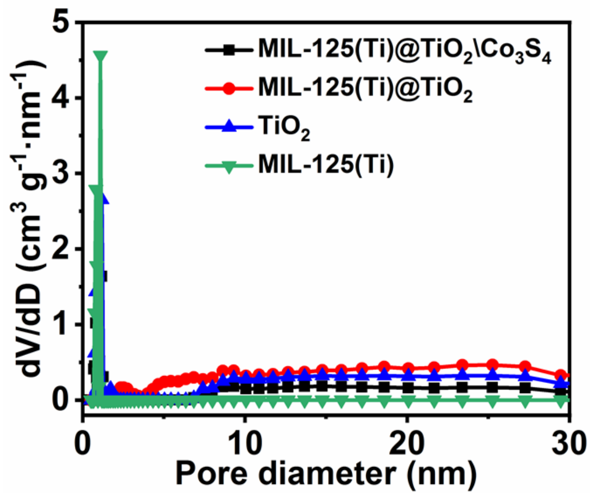

Fig. S6. Pore size distribution of different samples.

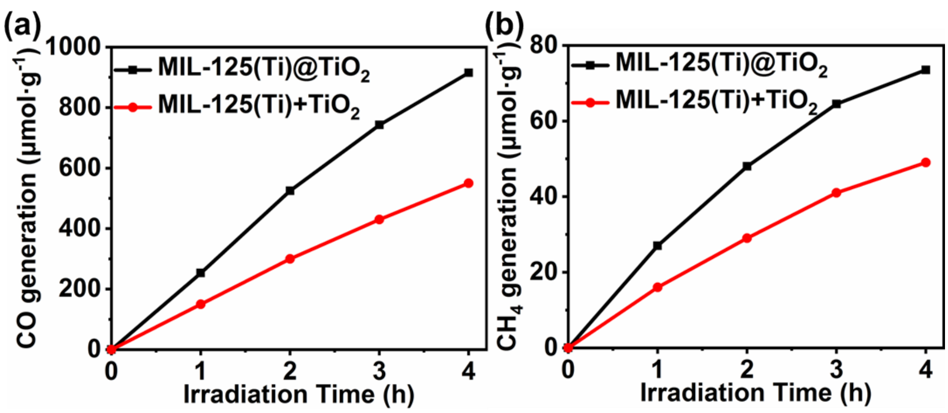

Fig. S7. Time courses of (a) CO and (b) CH_4 production from the single-component catalysts (MIL-125(Ti) and TiO_2) and physical mixture of MIL-125(Ti) and TiO_2.

Table S1. Summary of the surface area (S_{BET}), pore volume and average pore size of the different samples.

Samples	S_{BET} (m^2 g^{-1})	pore volume (cm^3 g^{-1})	pore size distribution (nm)
MIL-125(Ti)@TiO_2\Co_3S_4	306.2	0.854	0.80, 1.20, 5-30
MIL-125(Ti)@TiO_2	371.8	0.244	0.80, 1.18, 5-30
TiO_2	214.2	0.060	0.80, 1.16, 5-30
MIL-125(Ti)	872.5	0.056	0.80, 1.08

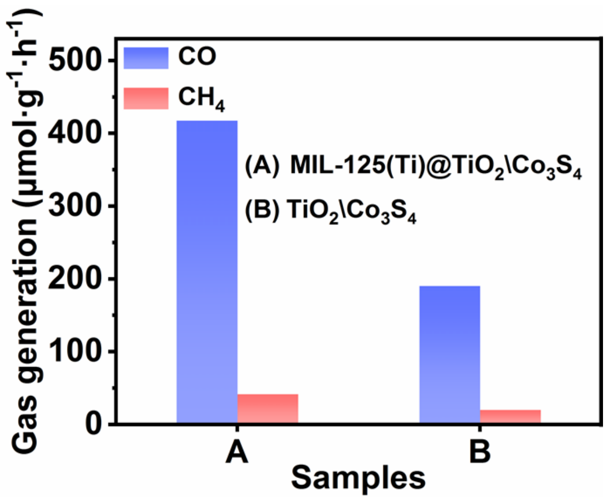

Fig. S8. Average CO and CH_4 generation rates over different catalysts, over MIL-125(Ti)@TiO_2\$Co_3S_4$ and TiO_2\$Co_3S_4$.

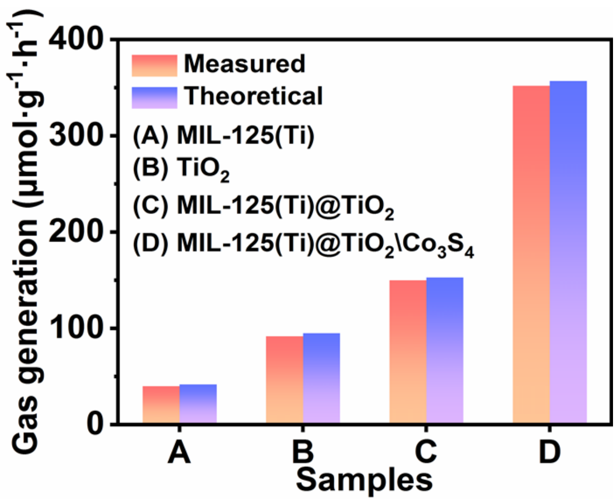

Fig. S9. The O_2 evolution rate over different photocatalysts.

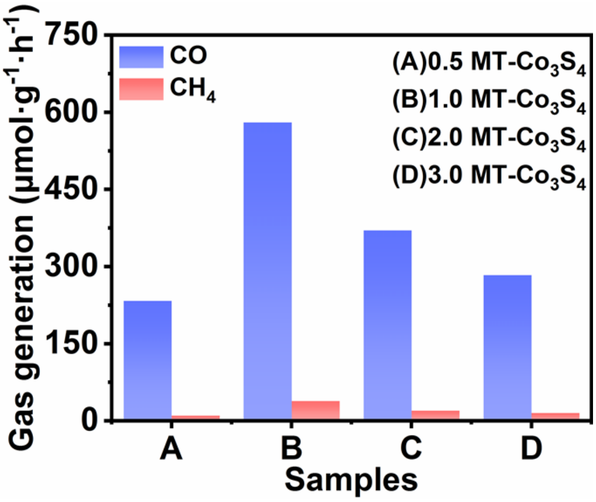

Fig. S10. Yields of different products with different contents of Co_3S_4.

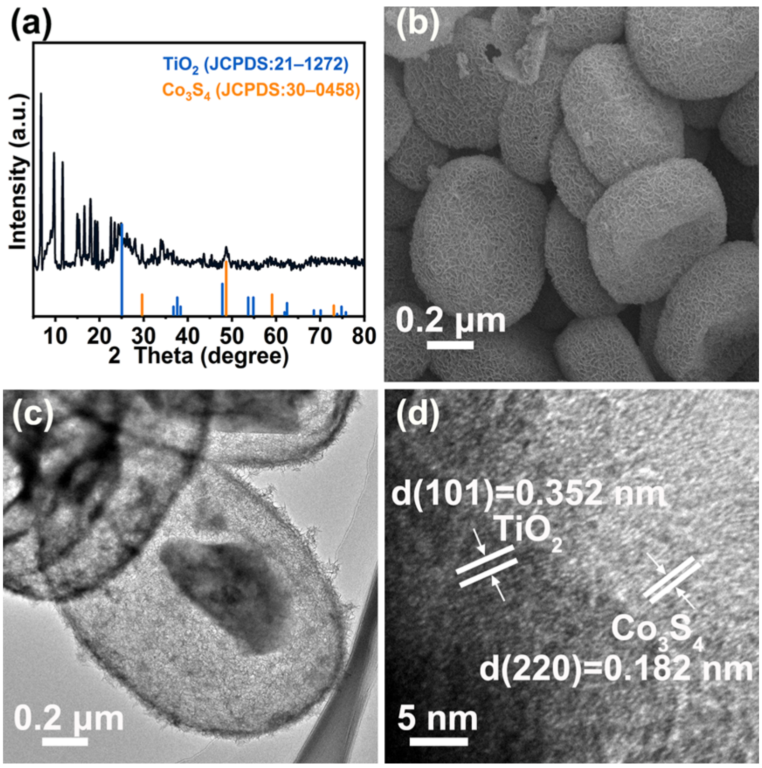

Fig. S11. (a) XRD pattern, (b) SEM, (c) TEM, and (d) HRTEM images of MIL-125(Ti)@TiO_2\Co_3S_4 after cycle tests.

Table S2. Comparative photocatalytic performance of different photocatalysts.

Photocatalytic	Yield Rate of CO (μmol·g^{-1}·h^{-1})	Yield Rate of CH_4 (μmol·g^{-1}·h^{-1})	Selectivity for CO (%)	Apparent Quantum Efficiency (%)
MIL-125(Ti)	83.49	9.12	69.59	2.81
TiO_2	159.01	16.60	70.54	5.28
MIL-125(Ti)@TiO_2	213.53	20.30	72.44	6.90
MIL-125(Ti)@TiO_2\Co_3S_4	587.50	38.43	79.26	17.36

The equation for CO (%) selectivity was calculated as shown below:

Selectivity for CO (%) = [2n (CO)]/ [2n (CO) + 8n (CH_4)]

Calculation of Apparent Quantum Yield (QE %):

The apparent quantum yield (QE) is defined as the ratio of the number of reaction electrons to the number of incident photons. In principle, it takes two electrons to produce a CO molecule and eight electrons to produce a CH_4 molecule. The apparent quantum yield (QE) is measured using the following equation:

$$QE\ (\%) = \frac{2 \times Na \times N_{(CO)} + 8 \times Na \times N_{(CH_4)}}{I \times A \times \frac{\lambda}{hc} \times t} \times 100\%$$

where Na is Avogadro's number (N = 6.022 × 10^{23} mol^{-1}), N(CO) and N(CH_4) are the number of CO (mole) and CH_4 (mole) evolved at time "t" (1 h), respectively, I is the incident solar irradiance (I = 1.5 mW cm^{-2}), the 400 nm LED (5 W, Beijing Putian Light Technology Co. Ltd., China) is located 3.5 cm above the reactor, and the focusing area of the LED in the reactor is 6.25 cm^2. λ is the wavelength of this study (420 nm), h is Planck's constant (6.626 × 10^{-34} J·s), and c is the speed of light (3.0 × 108 m s^{-1}).

Table S3. The catalytic activity reported in the literature for the production of CO by photocatalysis.

Catalysts	**Light source and intensity (mW/cm^2)**	**CO production ($\mu mol\cdot g^{-1}\cdot h^{-1}$)**	**Ref**
0D/2D Au/TiO_2	300W Xe lamp; 100	19.75	[S1]
NH_2-MIL-125	300W Xe lamp; not provided	8.25	[S2]
TiO_2@CTF-Py/$CoCl_2$	300W Xe lamp; not provided	43.34	[S3]
Co-ZIF-67@a-TiO_2	300W Xe lamp; not provided	43.8	[S4]
TiO_2@NH_2-MIL-125	300W Xe lamp; 203	106.16	[S5]
Co_3O_4/TiO_2	300W Xe lamp; not provided	1256	[S6]
MIL-125(Ti)@TiO_2\Co_3S_4	300W Xe lamp; 100	587.5	This work

Table S4. The determined energy band parameters of the samples

Sample	E_g (eV)	E_f (V)	XPS VB (eV)	E_{VB} (V)	E_{CB} (V)
MIL-125(Ti)	3.62	-0.70	3.61	2.91	-0.71
TiO_2	3.24	-0.40	2.98	2.58	-0.66
Co_3S_4	2.17	0.73	0.42	1.15	-1.02

References

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