Cu-Fe bimetallic MOF enhanced selectivity of photocatalytic CO_2 reduction for product CO

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Supplementary Figures

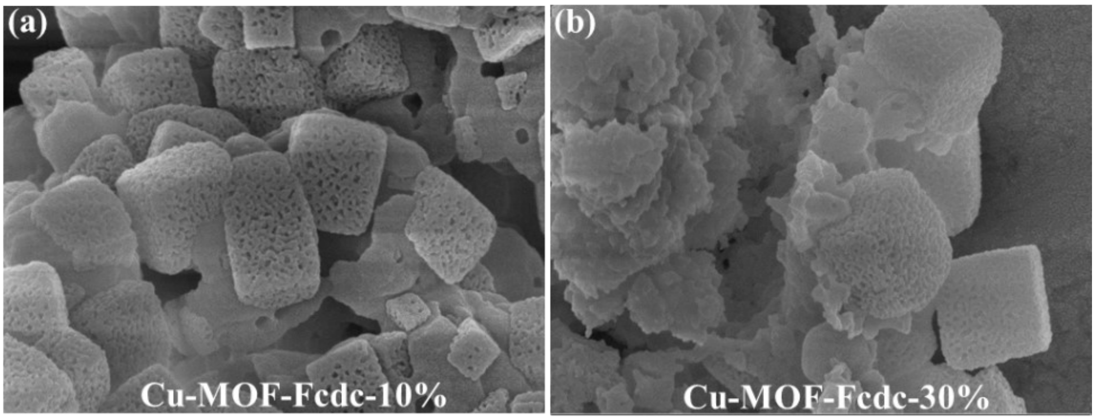

Fig. S1 SEM images of Cu-MOF-10% (a) and Cu-MOF-Fcdc-30% (b).

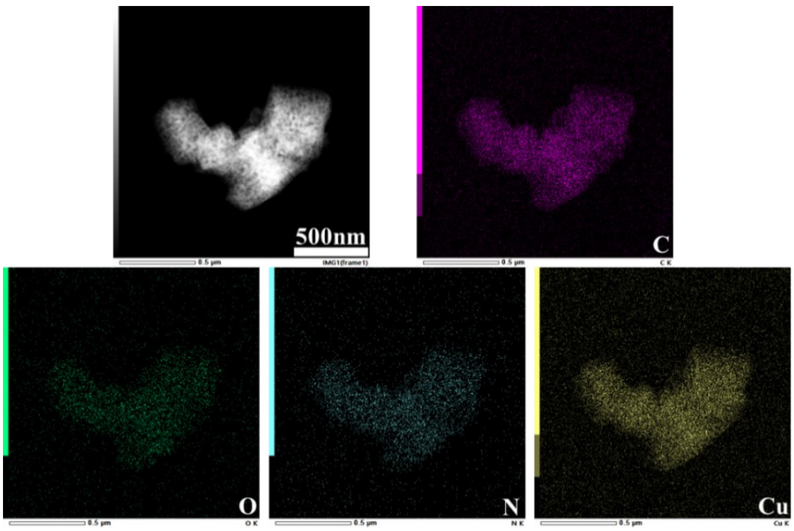

Fig. S2 TEM elemental mappings of Cu-MOF.

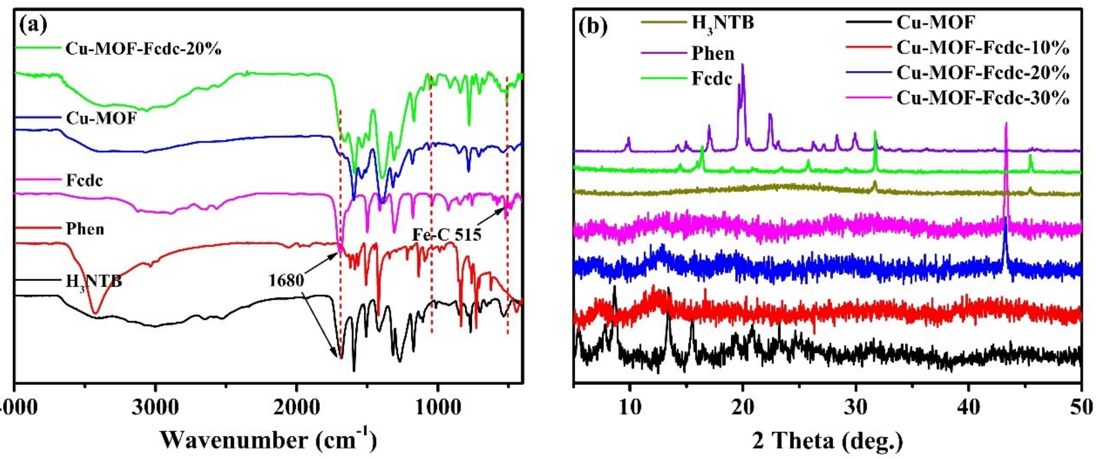

Fig. S3 The IR spectra (a) and XRD curves (b) of the series samples.

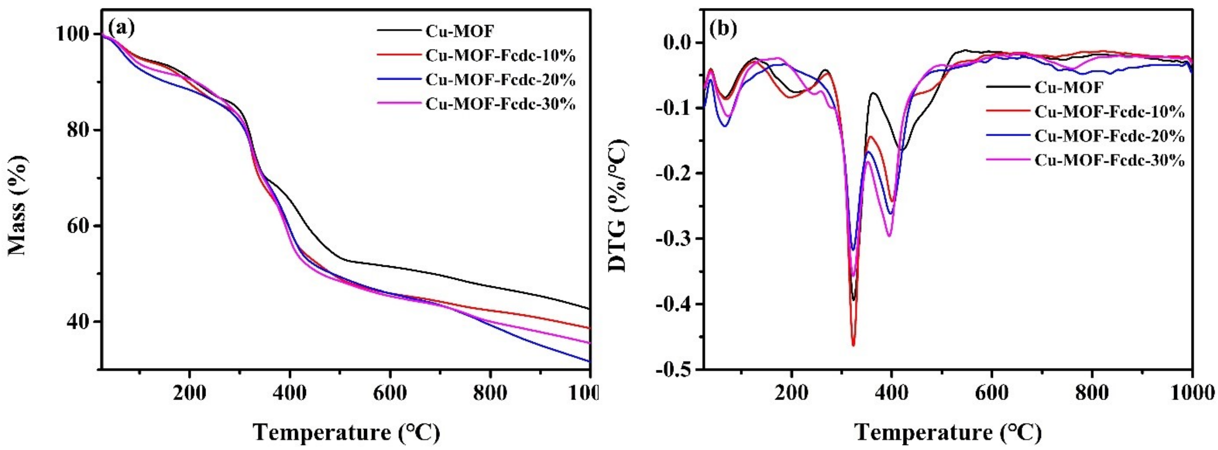

Fig. S4 The TG (a) and DTG (b) curves of Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%).

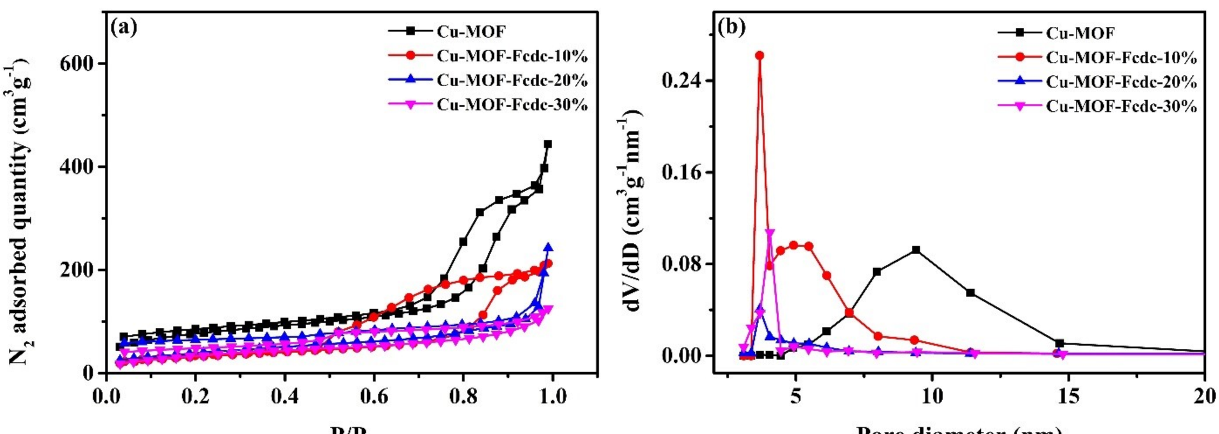

Fig. S5 The N_2 adsorption/desorption isotherms of Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%) (a), and the corresponding pore size distribution curves (b).

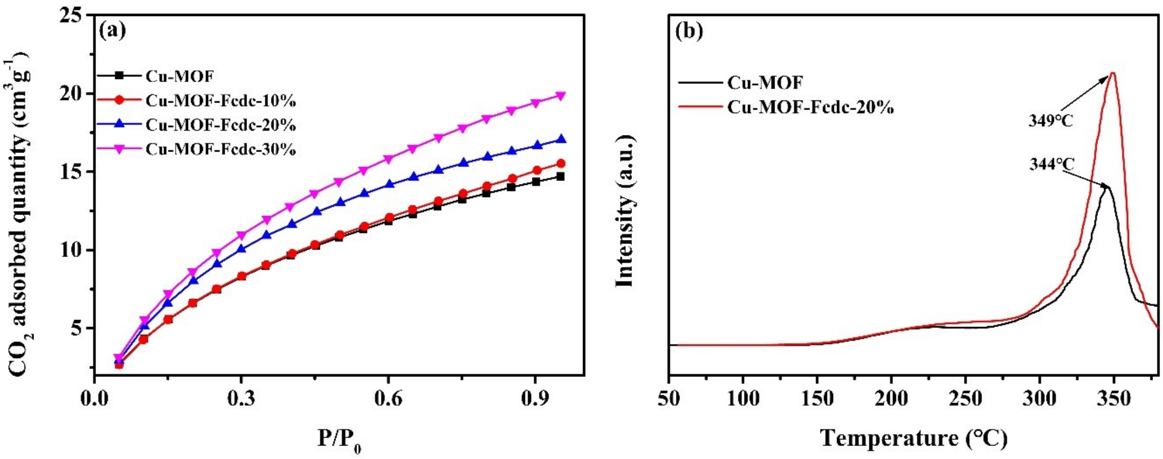

Fig. S6 The CO_2 adsorption isotherms of Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%) (a), and CO_2-TPD curves (b).

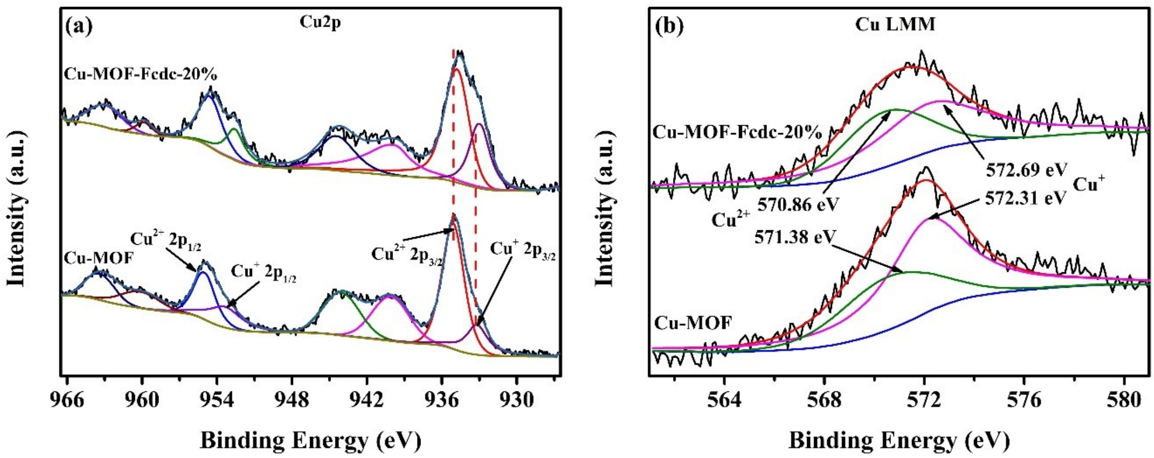

Fig. S7 (a) The Cu2p XPS spectra of Cu-MOF and Cu-MOF-Fcdc-20%; (b) The Cu LMM Auger spectra.

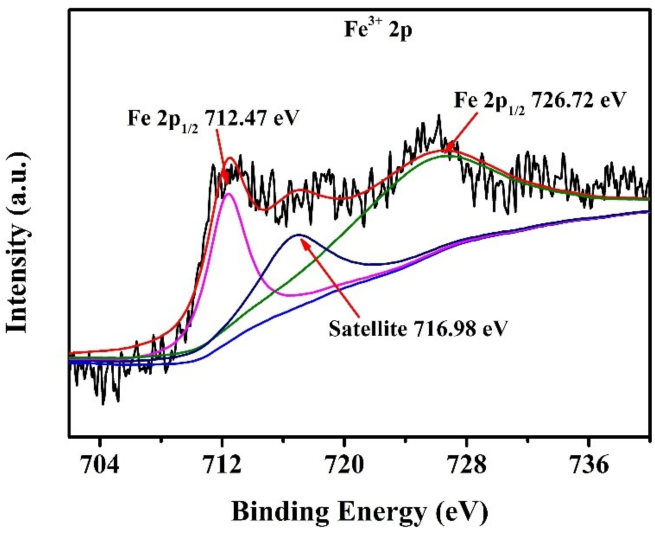

Fig. S8 The Fe2p (Fe^{3+}) XPS spectra of Cu-MOF-Fcdc-20%.

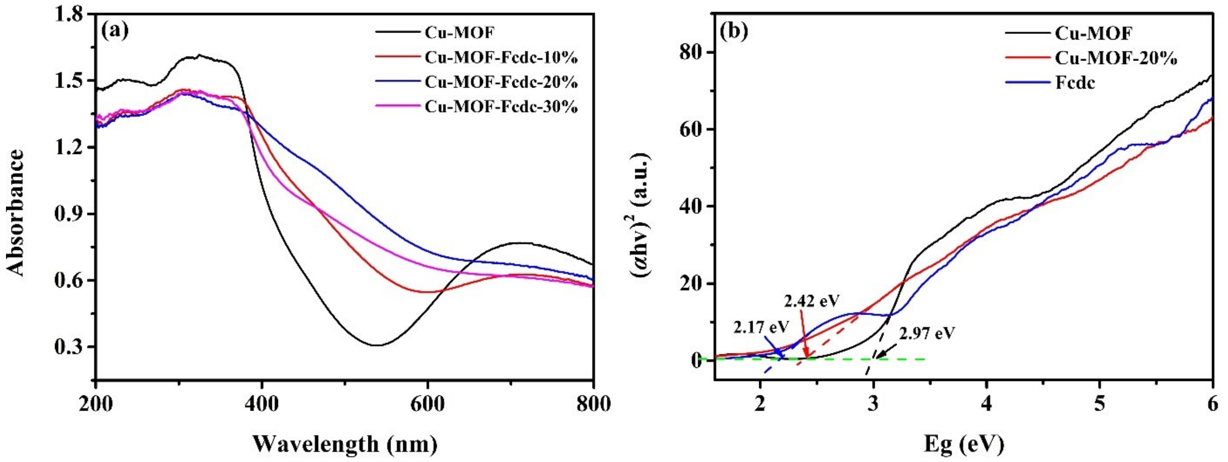

Fig. S9 (a) The UV-vis DRS spectra of Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%), and (b)The Tauc curves of Cu-MOF, Cu-MOF-Fcdc-20% and Fcdc ligand.

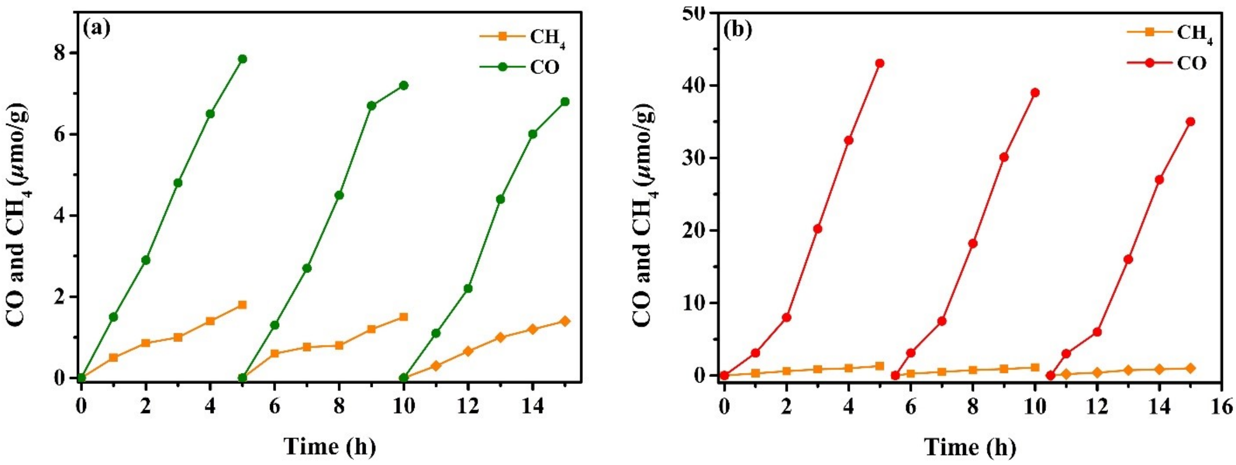

Fig. S10 The yields of CH_4 and CO for Cu-MOF (a) and Cu-MOF-Fcdc-20% (b) as composite photocatalysts in the CO_2 reduction process.

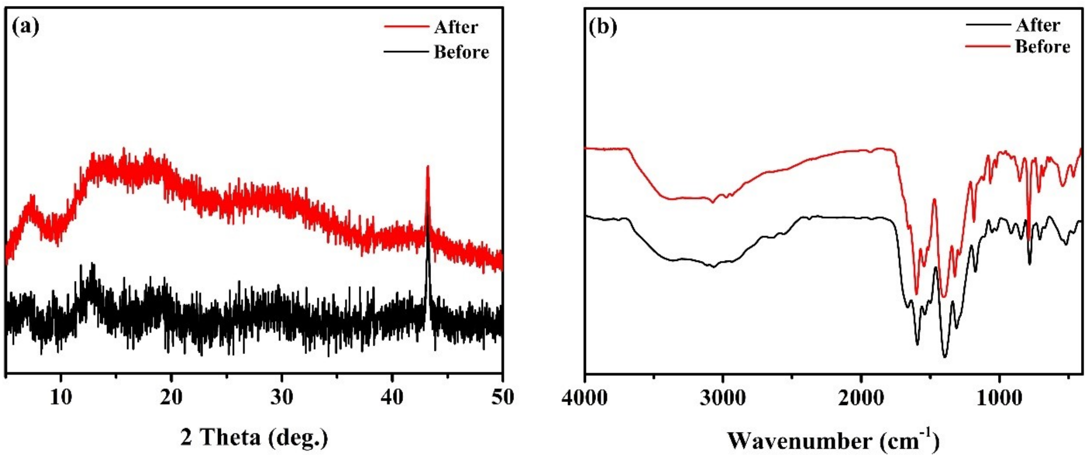

Fig. S11 XRD curves (a) and FTIR spectra (b) of Cu-MOF-Fcdc-20% before and after photocatalytic CO_2 reduction.

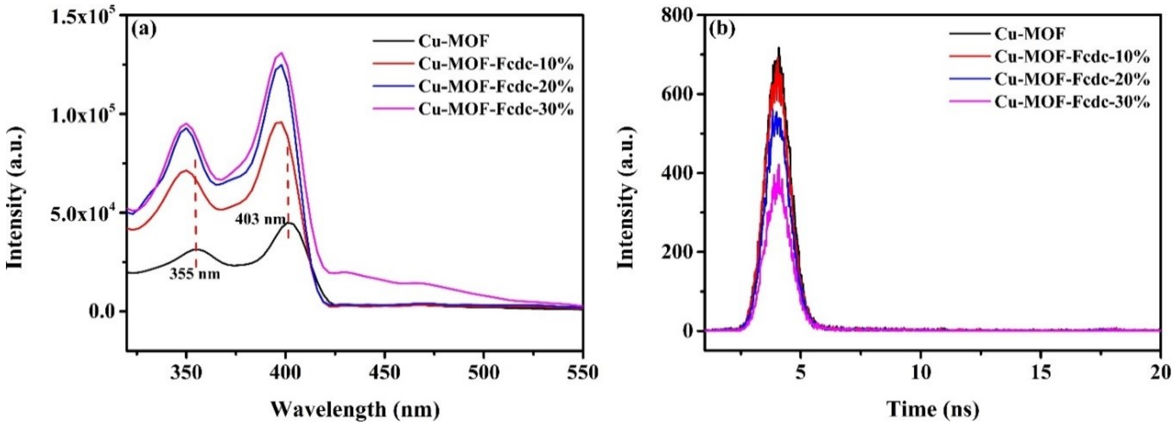

Fig. S12 PL emission spectra (a) and lifetime decay curves (b) for Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%).

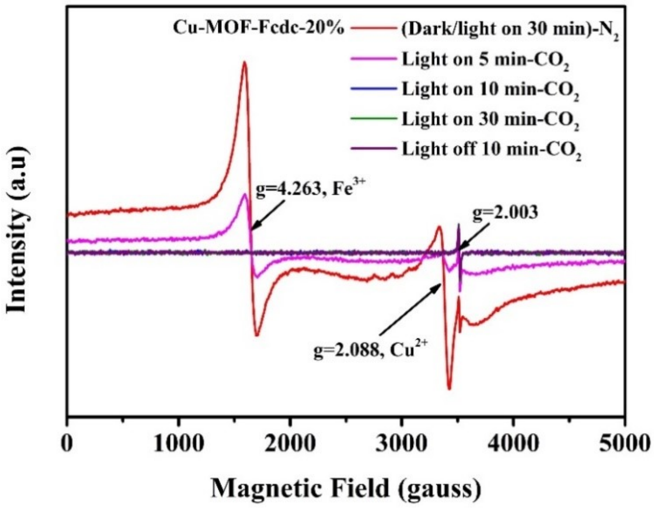

Fig. S13 The EPR spectra of Cu-MOF-Fcdc-20% illuminated in CO_2 atmosphere.

Tables

Table S1. The contents of Cu and Fe elements in different Cu-MOF-Fcdc(10%, 20%, and 30%) by SEM.

Samples	Cu、Fe (mmol)	Wt%	At%
Cu-MOF-Fcdc-10%/SEM			
Cu	0.1	9.59	2.22
Fe	0.01	0.99	0.26
Cu-MOF-Fcdc-20% /SEM			
Cu	0.1	15.45	3.75
Fe	0.02	3.20	0.88
Cu-MOF-Fcdc-30%/SEM			
Cu	0.1	8.44	1.95
Fe	0.03	3.09	0.81

Table S2. The Cu and Fe element contents of Cu-MOF and Cu-MOF-Fcdc (-10%, 20%, and 30%) by ICP-OES.

Samples	Cu content (mg/L)	Fe content (mg/L)	wt% (Fe)
Cu-MOF	85.00	0.00	0.00
Cu-MOF-Fcdc-10%	83.10	2.80	2.80%
Cu-MOF-Fcdc-20%	78.60	3.70	3.70%
Cu-MOF-Fcdc-30%	66.40	4.90	4.90%

1.00 mg Cu-MOF sample was dissolved in 500.00 μL HNO_3 and filled with water to 10.00 mL. Then, take 1.00 mL clear liquid and dilute it again to 10.00 mL for ICP-OES test. Perform the same operation as above for other samples.

Table S3. Summary of specific surface area, pore size and pore volume data of each sample

Samples	Surface Area m^2/g	Pore Diameter/nm	Total pore volume cc/g
Cu-MOF	267.997	9.411	0.6866
Cu-MOF-Fcdc-10%	215.606	3.671	0.5616
Cu-MOF-Fcdc-20%	144.557	3.677	0.375
Cu-MOF-Fcdc-30%	131.249	4.046	0.1936

Table S4. Activity data of photocatalytic CO_2RR in controlled experiments

Samples	CH_4 (μmol/g/h)	CO (μmol/g/h)	Selectivity
Cu-MOF	0.36	1.57	81.35%
Cu-MOF-Fcdc-10%	0.14	2.04	93.58%
Cu-MOF-Fcdc-20%	0.26	8.61	97.07%
Cu-MOF-Fcdc-30%	0.31	6.42	95.39%
Cu-Fcdc	0.17	5.81	98.81%
Mixed Cu-MOF and Cu-Fcdc (m, 4:1= Cu:Fcdc)	1.26	0.76	37.62%
Cu-NTB-Fcdc-20%	0.75	2.79	78.81%
Cu-phen-Fcdc-20%	0.52	2.12	80.30%
Cu-MOF-Fca-20%	0.96	4.21	81.43%
Cu-MOF-Fc-20%	0.6	2.22	78.72%
Cu-MOF-Fcdc-20%-N_2	0	0	

Table S5. Performance comparison of recently reported MOF- based photocatalysts applied in the literature for CO_2 reduction to CO

Catalyst	Reaction medium	Light range	Products	Yield (μmol/g/h), Selectivity	Reference
Cu-MOF-Fcdc-20%	Gas–Solid, H_2O	> 360 nm, 210mW/cm^2	CO CH_4	8.61, 97.07% 0.26	This work
Co-MOF/Cu_2O	Gas–Solid, H_2O	> 420 nm,	CO	3.83, 100%	1

		480mW/cm^2			
COF@Ti–MOF	Gas–Solid, H_2O	> 360 nm,	CO CH_4	78.7, 100%	2
Mn-MOF	Gas–Solid, H_2O	> 360 nm, 100mW/cm^2	CO CH_4	50, 70.4% 21	3
Co-MOF/GR	Gas-Solid, H_2O	> 420 nm, 300mW/cm^2	CO CH_4	20.25, 92.63% 1.61	4
CdS/Ni-MOF	Gas–Solid, H_2O	> 360 nm, 300mW/cm^2	CO CH_4	1.75, 93.1% 0.13	5
$Co_{0.1}Ni_{0.9}$-MOF	Gas–Solid, H_2O	> 360 nm	CO	38.74 ,100%	6
Zn-MOF/BiV_4	Gas–Solid, H_2O	> 420 nm	CO CH_4	4.30, 87.40% 0.62	7
PCN-250-Fe_3	Gas–Solid, H_2O	> 420 nm, 480mW/cm^2	CO CH_4	1.01, 19.84% 4.08	8

Table S6. PL lifetime of different samples

Samples	Cu-MOF	Cu-MOF-Fcdc-10%	Cu-MOF-Fcdc-20%	Cu-MOF-Fcdc-30%
A_1	761.54	713.54	436.84	594.95
τ_1/ns	0.57	0.61	0.74	0.60
R^2	0.99	1.04	1.02	1.03

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