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Local hydrophobic environment in metal–organic framework for boosting photocatalytic CO_2 reduction in the presence of water

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Supplementary Index

Experimental section

Materials and Methods. All reagents were commercially available and used without further purification. 1,4,7,10-tetrazazcyclododecane-*N*,*N*',*N*'',*N*'''-tetra-*p*-methylbenzoic acid (H_4tactmb) was synthesized according to literature method.[*CrystEngComm*, 2012, **14**, 6115.] X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Scientific ESCALAB 250 instrument. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8-Advance diffractometer with Cu Kα radiation and a LynxEye detector. Thermogravimetry (TG) analyses were performed on a TA Q50 thermogravimetric analyzer under nitrogen gas at a heating rate of 10 °C/min. Scanning electron microscope (SEM) images were obtained from an Ultra-high Resolution electron microscope (FE-SEM, SU8010). Inductively coupled plasma-atomic emission spectrometry (ICPAES) was performed on an IRIS(HR) spectrometer (TJA, USA). Gas sorption isotherms were measured on a Micromeritics ASAP 2020M instrument. Before the sorption experiments, the as-synthesized samples were first solvent exchanged by MeOH, and then activated for 12 h under vacuum. CO_2 (99.999%) was used for all measurements. The temperature was controlled by an acetone-dry ice bath (195 K).

Synthesis of $[Zr_6(OH)_4O_4(tactmb)_3]$ (denoted as MCF-55). A mixture of $ZrCl_4$ (23.3 mg, 0.1 mmol), H_4tactmb (35.4 mg, 0.05 mmol), benzoic acid (BA, 1.2 g) and *N*,*N*-Dimethylformamide (DMF, 4.0 mL) were ultrasonically dissolved in a Pyrex vial, heated in an oven at 100 °C for 72 h, and then cooled to room temperature at a rate of 10 °C h^{-1}, giving small colorless block-shape crystals. The resultant product were washed with MeOH for three times and collected by filtration (yield 70%).

Synthesis of $[Zr_6(OH)_4O_4(tactmb\text{-}Co)_3(Cl)_6]$ (denoted as MCF-55-Co). $CoCl_2{\cdot}6H_2O$ (60 mg) and MCF-55 (50 mg) was added to a 10 mL DMF solution, the solution was heated at 100 °C for 48 hours. The microcrystalline powder was collected by filtration and washed with DMF for three times. The DMF within the pores of the samples was then exchanged with methanol (5 × 30 mL) over a five-day period. Finally, the methanol was removed by evacuation for 24 hours.

Synthesis of $[Zr_6(OH)_4O_4(tactmb\text{-}Ni)_3(Cl)_6]$ (denoted as MCF-55-Ni). The synthesis process of MCF-55-Ni is much similar to that of MCF-55-Co, except that $NiCl_2{\cdot}6H_2O$ (60 mg) was used to replace the $CoCl_2{\cdot}6H_2O$ (60 mg).

Photocatalytic Measurements. Microcrystals of the MOF catalysts (5 mg) were dispersed in water (5 mL) with ultrasonication for 30 min, and the amount of catalyst was determined by the volume of the suspension. The photocatalytic CO_2 reduction was conducted under 1 atm of a certain atmosphere (pure CO_2 or CO_2/Ar mixed gas, *v*/*v* = 10:90) at 25 °C in a 16-mL reactor containing catalyst (n(Co^{2+}) = 30 nmol), $[Ru(phen)_3]Cl_2 \cdot 6H_2O$ (2 μmol), TEOA (0.3 M), and CH_3CN/H_2O (*v*/*v* = 4:1, 5 mL). The reaction mixture was continuously stirred with a magnetic bar and irradiated under a LED light (λ = 450 nm). The generated gas samples were analyzed by an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) and a TDX-01 packed column. The oven temperature was held constant at 60 °C, and the inlet and detector temperature were set at 80 °C and 200 °C, respectively. The products in the liquid phase of the photocatalytic CO_2 reaction were analyzed by a Thermo Scientific Dionex ion chromatography (IC) system 5000 with an AS11HC column. Each photocatalytic reaction was repeated at least three times to confirm the reliability of the data.

The concentration of Ni in the filtrate was detected by the inductively coupled plasma–mass spectrometry. After photocatalytic CO_2 reduction (10 nmol catalysts in 5 mL solution), 3 mL of the filtrate was digested and diluted to 10 mL for tests. The concentration of Ni in the concentrated filtrate was detected as 1.07 ng/mL. Therefore, the dissolved Ni ions of the MOF was (1.07 ng mL^{-1} × 10 mL)/(6 nmol × 3 × 59 g mol^{-1}) = 1.01%.

Computational Methods. All simulations/calculations were performed by the Materials Studio 5.0 package. All energies were calculated by the periodic density functional theory (PDFT) method by the Dmol3 module. Full geometry optimizations with fixed cell parameters were performed to the systems. The widely used generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and the double numerical plus d-functions (DNP) basis set, TS for DFT-D correction as well as the Effective Core Potentials (ECP) were used. The energy, force and displacement convergence criterions were set as 1×10^{-5} Ha, 2×10^{-3} Ha and 5×10^{-3} Å, respectively.

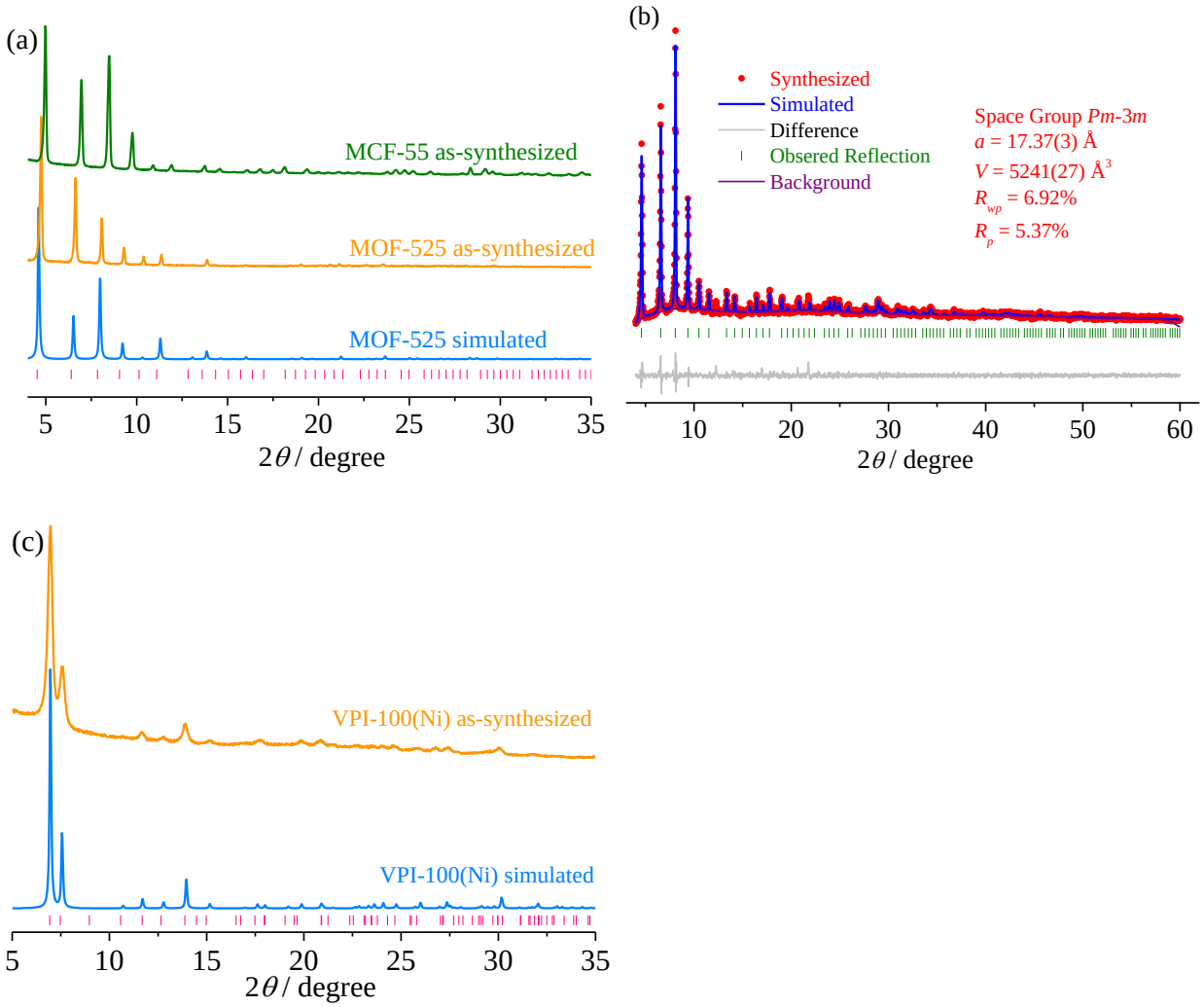

Figure S1. (a) PXRD patterns of MOF-525 and MCF-55. (b) Rietveld refinement results of MCF-55. (c) PXRD patterns of VPI-100(Ni).

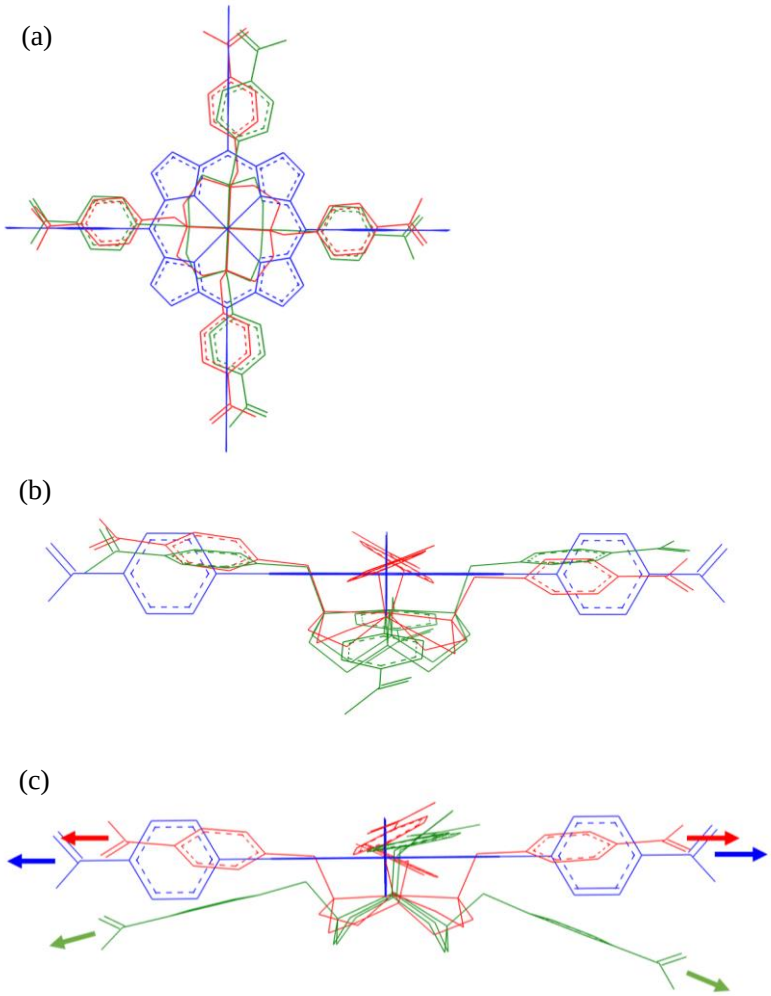

Figure S2. (a) Top and (b-c) side views of the optimized structures of *cis*-H_4tactmb (green), *trans*-H_4tactmb (red) and H_4TCPP-H_2 (blue). H atoms are omitted for clarity.

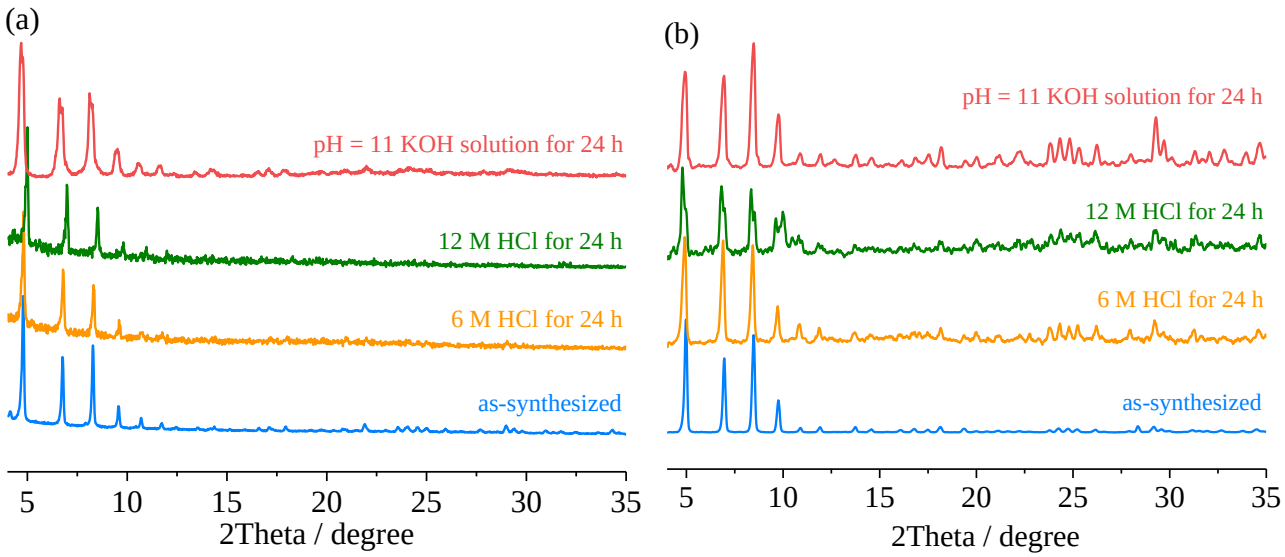

Figure S3. PXRD patterns of (a) MCF-55-Ni and (b) MCF-55-Co after immersed in different solutions.

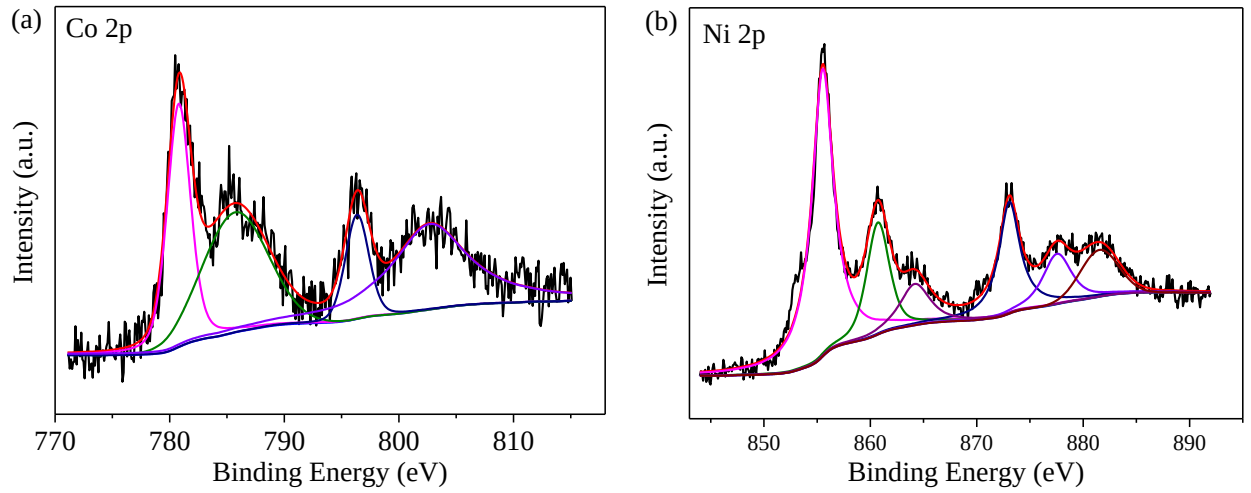

Figure S4. XPS Co2p spectrum of MCF-55-Co and Ni2p spectrum of MCF-55-Ni.

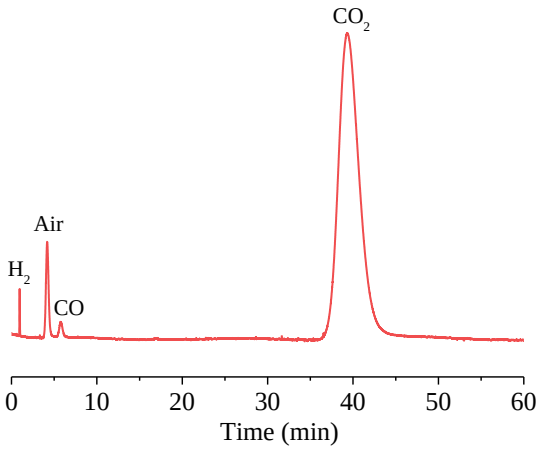

Figure S5. The GC profiles for the gaseous products from the photocatalytic CO_2 reduction by using MCF-55-Ni as catalysts.

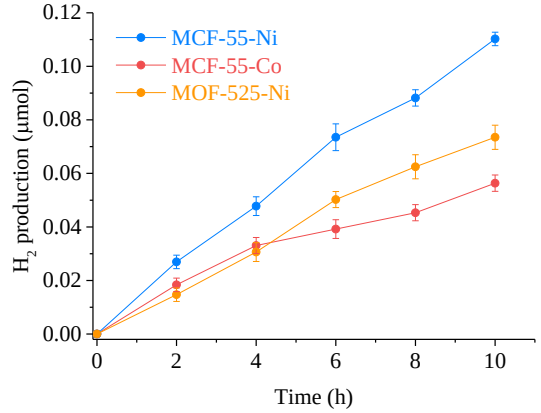

Figure S6. H_2 production rates of photocatalytic CO_2 reduction by using catalysts MCF-55-Ni, MCF-55-Co and MOF-525-Ni.

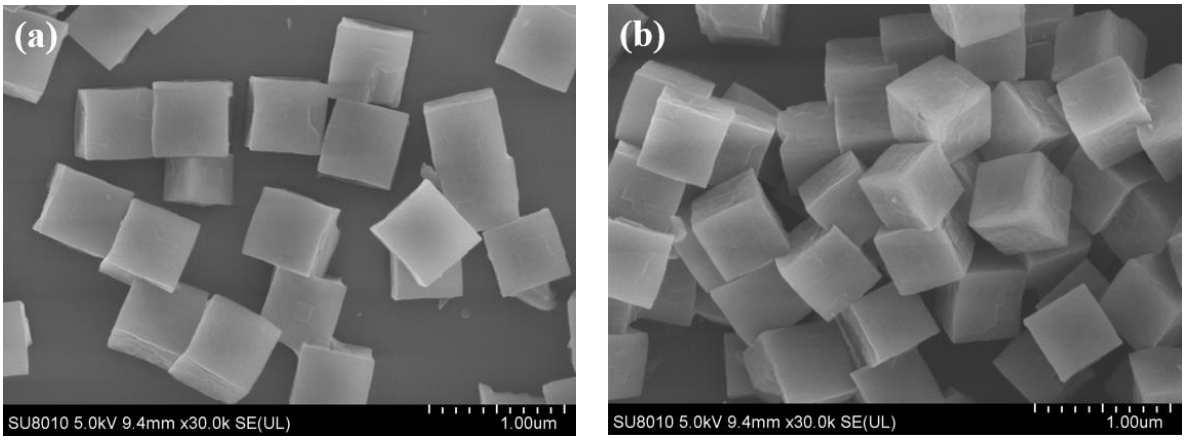

Figure S7. SEM images of the (a) MCF-55-Co and (b) MCF-55-Ni. According to the SEM images, the particle sizes of MCF-55-Co and MCF-55-Ni are similar, meaning that the different photocatalytic activities are not because of the particle sizes.

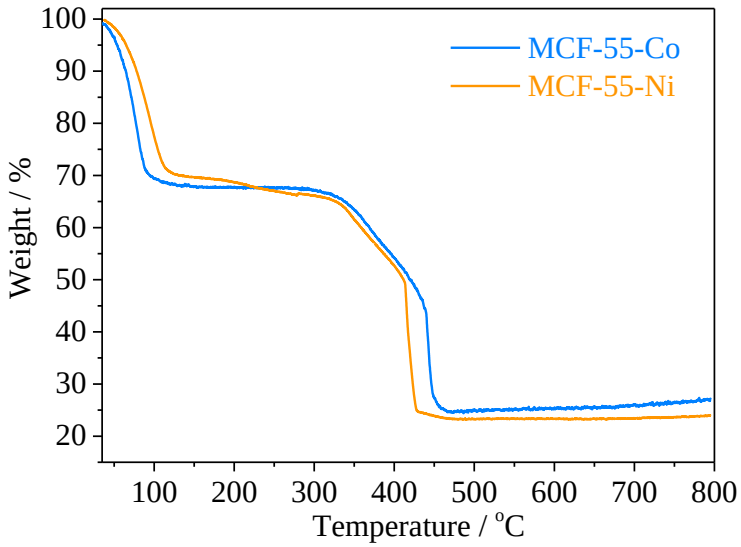

Figure S8. TG curves of MCF-55-Co and MCF-55-Ni.

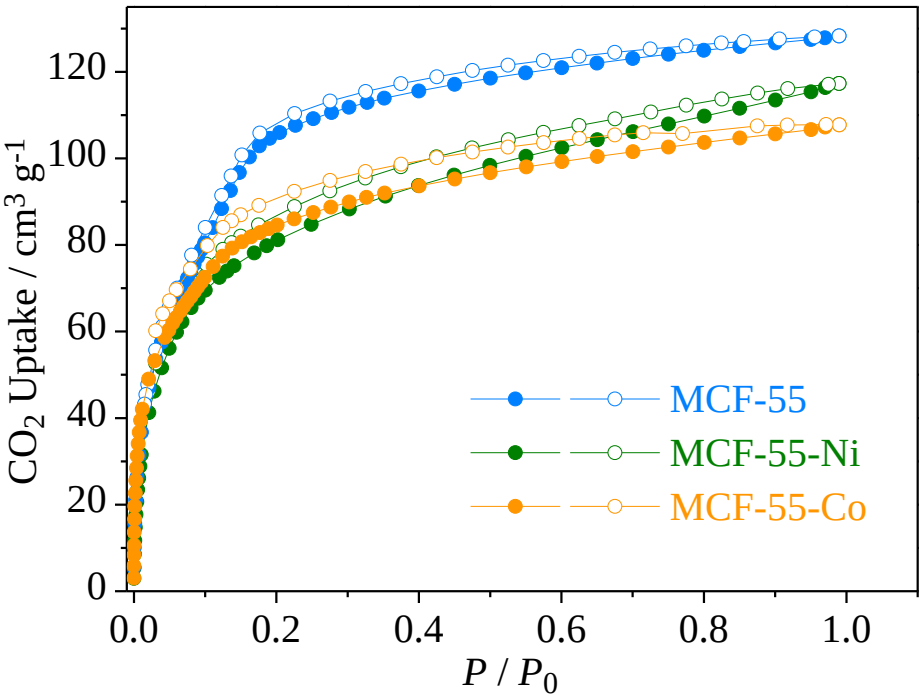

Figure S9. CO_2 adsorption (solid symbols) and desorption (open symbols) isotherms of MCF-55, MCF-55-Ni and MCF-55-Co at 195 K.

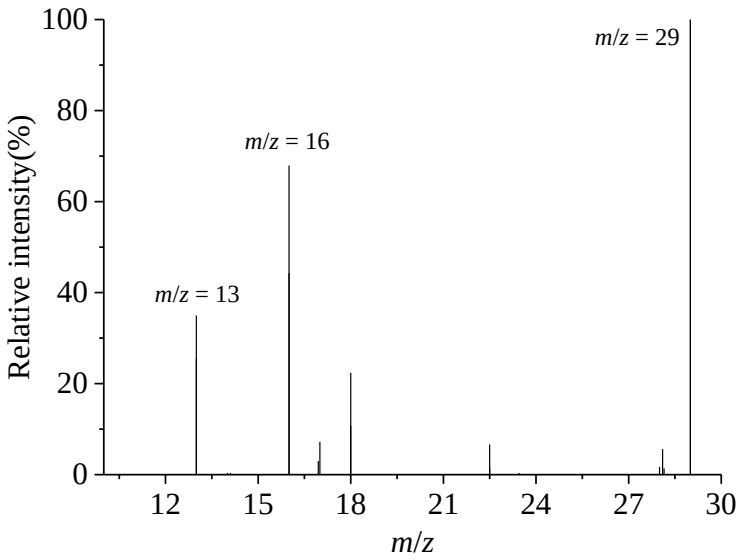

Figure S10. Mass spectra of reaction products of photocatalytic CO_2 reduction using MCF-55-Ni as the catalyst by using $^{13}CO_2$ as the gas environment. The peak at m/z = 29.1 can be assigned to and ^{13}CO.

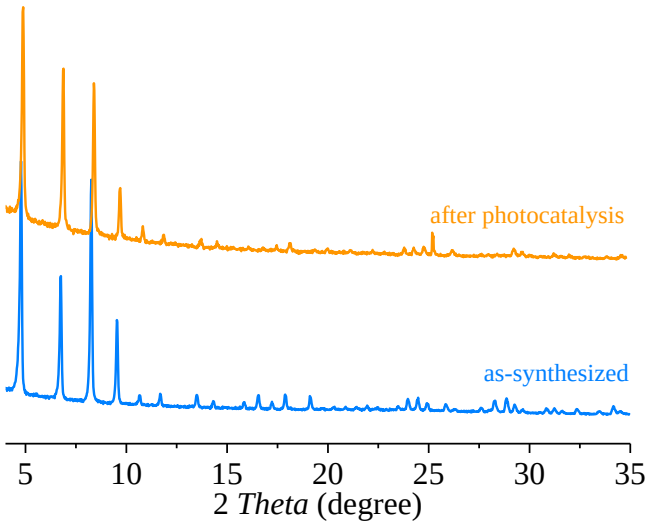

Figure S11. PXRD patterns of MCF-55-Ni before and after photocatalytic reaction.

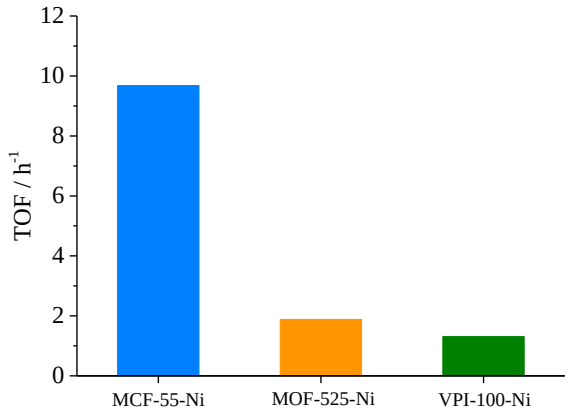

Figure S12. CO production TOFs of MCF-55-Ni, MOF-525-Ni and VPI-100-Ni.

Table S1. ICP-AES results of MCF-55-M (M = Ni, Co).

Materials	n/mmol·L^{-1}		Zr:M		Ratio
	Zr	M	Theoretical	Experimental	
MCF-55-Ni	0.0438	0.0215	2:1	2.04:1	98.7%
MCF-55-Ni21%	0.0603	0.0064	2:1	9.42:1	21.2%
MCF-55-Ni1.7%	0.0690	0.00059	2:1	116.9:1	1.7%
MCF-55-Co	0.0709	0.0320	2:1	2.22:1	90.1%

Table S2. Comparison of the photocatalytic activities of **MCF-55-M** and MOF catalysts.

Material	**Solvent**	**λ**	**Major Products**	**Generation Rate / μmol g^{-1} h^{-1}**	**TOF/ h^{-1}**	**TON**	**CO Selectivity**	**Ref.**
MCF-55-Ni	MeCN-H_2O (4:1 *v*/*v*)	> 450 nm	CO、H_2	CO 9377	CO 9.69	CO >448	96.1%	**This work**
MCF-55-21%Ni	MeCN-H_2O (4:1 *v*/*v*)	> 450 nm	CO、H_2	CO 4551	CO 22.2	CO >88.8	97.1%	
MCF-55-1.7%Ni	MeCN-H_2O (4:1 *v*/*v*)	> 450 nm	CO、H_2	CO 1214	CO 73.8	CO >295	95.9%	
MCF-55-Co	MeCN-H_2O (4:1 *v*/*v*)	> 450 nm	CO、H_2	CO 7097	CO 7.41	CO >37.1	96.5%	
MOF-525-Ni	MeCN-H_2O (4:1 *v*/*v*)	> 450 nm	CO、H_2	CO 1674	CO 1.76	CO >17.3	86.9%	
MOF-525-Co	MeCN	> 400 nm	CO、CH_4	CO 200.6	CO 0.216	/	84.6%	*Angew. Chem. Int. Ed*. **2016**, *55*, 14310
ZrPP-1-Co	MeCN	> 420 nm	CO、CH_4	CO 14	/	/	**96.4%**	*Adv. Mater*. **2018**, *30*, 1704388.
PCN-222	MeCN	> 420 nm	$HCOO^-$	/	0.0717	/	/	*J. Am. Chem. Soc.*, **2015**, *137*, 13440
Co-ZIF-9	MeCN-H_2O (4:1 *v*/*v*)	> 420 nm	CO、H_2	/	CO 104.5	CO 89.6	58.3%	*Angew. Chem. Int. Ed*. **2014**, *53*, 1034
Co-MOF-74	MeCN-H_2O (4:1 *v*/*v*)	> 420 nm	CO、H_2	/	/	CO 23.8	61.6%	
MAF-X27*l*-OH	MeCN-H_2O (4:1 *v*/*v*)	> 420 nm	CO、H_2	/	CO 212.4	/	**98.2%**	*J. Am. Chem. Soc.*, **2018**, *140*, 38
Hf_{12}-Ru-Re	MeCN	> 400 nm	CO、HCOOH	/	/	CO 8613	**98%**	*J. Am. Chem. Soc.*, **2018**, *140*, 12369
Ni MOLs	MeCN-H_2O (3:2 *v*/*v*)	> 400 nm	CO、H_2	CO 12500	/	/	**97.8%**	*Angew. Chem. Int. Ed*. **2018**, *57*, 1

Table S3. Summary of photocatalytic CO_2 reduction experiments.

	H_2 / μmol	**TOF / h^{-1}**	**CO / μmol**	**TOF / h^{-1}**	**CO selectivity**
MCF-55-Ni	0.15	0.63	2.71	12.96	95.41%
Without catalyst	0.01	0.04	0.33	1.10	96.39%
Without photosensitizer	0.01	0.02	0	0	0
Without sacrificial agent	0.04	0.12	0	0	0
Without light	0.01	0.02	0	0	0
Using dry CH_3CN to replace CH_3CN/H_2O mixture	0.02	0.07	0	0	0
Using H_2O to replace CH_3CN/H_2O mixture	0.01	0	0	0	0
Using filtrate to replace catalyst	0.01	0	0	0	0

*Basic reaction condition: $[Ru(phen)_3]Cl_2 \cdot 6H_2O$ (2 μmol), catalysts (30 nmol on the basis of Ni), solvent (5 mL, CH_3CN/H_2O = 4:1), triethanolamine (TEOA, 1.5 mmol), LED light (λ = 450 nm), 25 °C, 1.0 atm.