

Supporting Information

Solvent-Free Photoreduction of CO₂ to CO Catalyzed by Fe-MOFs with Superior Selectivity

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EXPERIMENTAL SECTION

Chemicals. 2-Aminoterephthalic acid (NH₂-BDC) was purchased from Tokyo Chemical Industry Co., Ltd, iron chloride hexahydrate (FeCl₃·6H₂O) and triethanolamine (TEOA) were purchased from Aladdin Industrial Corporation and solvents such as *N, N*-dimethylformamide (DMF) and methanol are of reagent grade obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water with a resistivity of above 18.2 MΩ·cm was obtained using a JL-RO100 Millipore-Q Plus water purifier and used throughout the experiments. All chemicals are of analytical grade and used directly without further purification during the experiments.

Characterization. The phase and crystalline structure of the obtained samples was characterized by powder X-ray diffraction (PXRD) (Bruker D8 Advance X-ray diffractometer) with Cu Kα radiation (1.5478 Å). The morphology and microstructural observations were carried out on field emission scanning electron microscope (SEM) (Hitachi S-4800) at an acceleration voltage of 5 kV and the compositions of resulting products were examined by

energy-dispersive X-ray spectroscopy (EDX) attached to SEM. Fourier transform Infrared (FT-IR) spectra were recorded using KBr discs in the range of 400-4000 cm^{-1} on a Bruker Vector 22 FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was measured on UIVAC-PHI 5000 VersaProbe using monochromatized Al K α X-ray source, in which all of the binding energies were calibrated with reference to the C 1s peak (284.8 eV). UV-Vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-3600 spectrophotometer in the wavelength range of 200-800 nm (BaSO_4 was used as reference). BaSO_4 for UV-Vis diffuse reflectance spectra was purchased from Sigma-Aldrich. The photoelectrochemical measurements were carried out on an electrochemical workstation (CHI730E, Shanghai Chenhua Limited, China) and the electrochemical impedance spectroscopy was achieved on Zahner electrochemical workstation (IM6ex, Zahner Scientific Instruments, German). All the gas adsorption isotherms were measured on a Belsorp-max volumetric gas sorption analyzer by employing a standard volumetric technique up to saturated pressure. Prior to sorption measurements, all samples were degassed at 120 $^{\circ}\text{C}$ for 6h. Photoluminescence spectra were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as light source. ^1H -NMR spectra were measured on Bruker-DRX 500 MHz instruments at room temperature.

Photocatalytic Reduction of CO_2 Experiments. The photocatalytic performances were carried out in a batch-type reaction system (CEL-SPH2N-D9, CeAulight, China) equipped with a homemade photoreactor together with a homemade condensate circulating water filter to shield photothermal effect. Firstly, 2 mg of as-synthesized photocatalyst was scattered in 1 mL acetone and ultra-sonicated to form suspension, then the suspension was uniformly dispersed onto a glass fiber film ($\Phi 25$ mm, 0.22 μm micro-pore diameter). The film was activated in vacuum at 120 $^{\circ}\text{C}$ for 12 h. Then the film was fixed in the reaction cell by a static bed, 2 mL of TEOA was added into the reactor, and the reactor was held at 50 $^{\circ}\text{C}$ using oil bath. After the

complete evacuation of the reaction system (no O₂ or N₂ could be detected), pure CO₂ gas (80 kPa, 99.999%, Shangyuan Gas) was injected into the closed system. A 300 W xenon arc lamp (Sirius-300P, Zolix Instruments Co., Ltd., China) with a 400-780 nm filter (CeAulight, China) was used as the light source. The optical power density was set at 400 mW cm⁻² measured by optical power meter (CEL-NP2000-2, CeAulight, China). The gas products were monitored by using gas chromatography (GC-9860, Luchuang Instrument, China), equipped with a TCD detector and a FID detector. The gas was separated by a 1 m TDX-01 column with N₂ (99.999%) as carrier gas, the temperatures for TCD and FID are 100 and 150 °C, respectively. The retention time of CO, CH₄ and H₂ are 1.290, 2.540 and 0.578 min, respectively. Calibration curves for gases were established separately.

Electrochemical Measurements. Photocurrent measurements were performed on a CHI 730E electrochemical work station (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with the photocatalyst-coated ITO as working electrode, Pt plate as counter electrode and Ag/AgCl as reference electrode. A 0.1 M Na₂SO₄ solution was used as the electrolyte. The as-synthesized sample (3 mg) was added into 20 μL Nafion and 1.0 mL methanol mixed solution, and the working electrode was prepared by dropping the suspension (300 μL) onto the surface of an ITO plate. The working electrode was dried at room temperature, and the photo-responsive signals of the samples were measured under chopped light at 0.5 V.

The electrochemical impedance spectroscopy was performed on the Zahner electrochemical workstation in a standard three-electrode system with photocatalyst-coated glassy carbon ($\Phi = 3$ mm) as the working electrode, Pt plate as the counter electrode and Ag/AgCl as the reference electrode. A 0.1 M Na₂SO₄ solution was used as the electrolyte. The as-synthesized samples (3 mg) were added into 20 μL Nafion and 1.0 mL methanol mixed solution, and the working electrode was prepared by dropping the suspension (10 μL) onto the

surface of the glassy carbon electrode. The working electrode was dried at room temperature, and then EIS measurement was performed with a bias potential of -0.3 V in the dark with a frequency range from 10^{-2} to 10^5 Hz in nitrogen atmosphere.

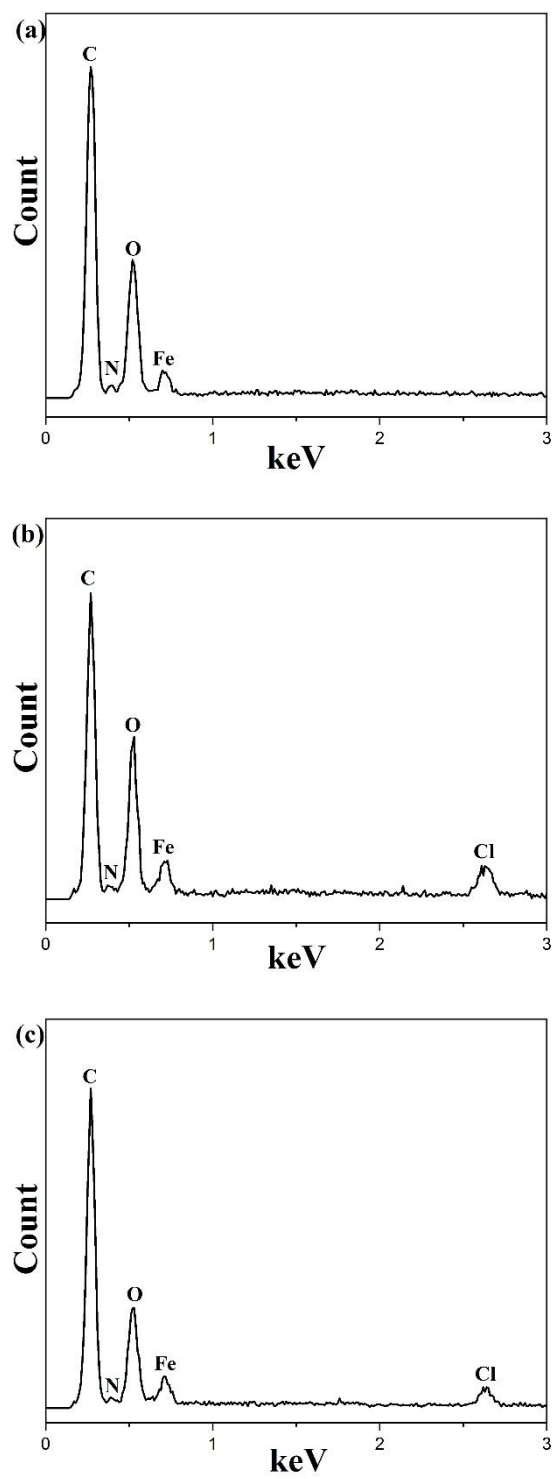


Figure S1. EDX spectra of NH₂-MIL-53(Fe) (a), NH₂-MIL-88B(Fe) (b) and NH₂-MIL-101(Fe) (c).

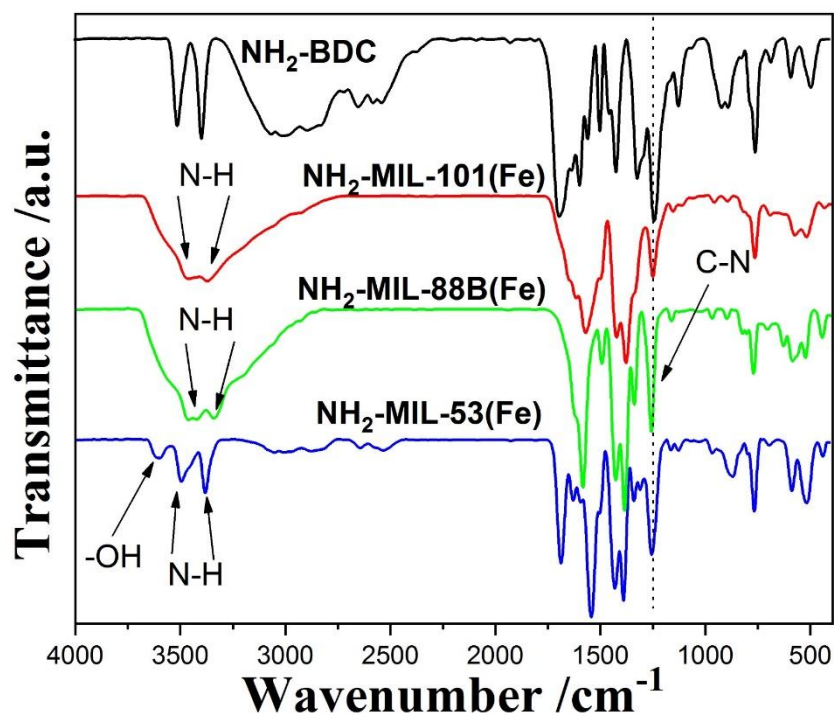


Figure S2. FTIR spectra of NH₂-BDC, NH₂-MIL-53(Fe), NH₂-MIL-88B(Fe) and NH₂-MIL-101(Fe).

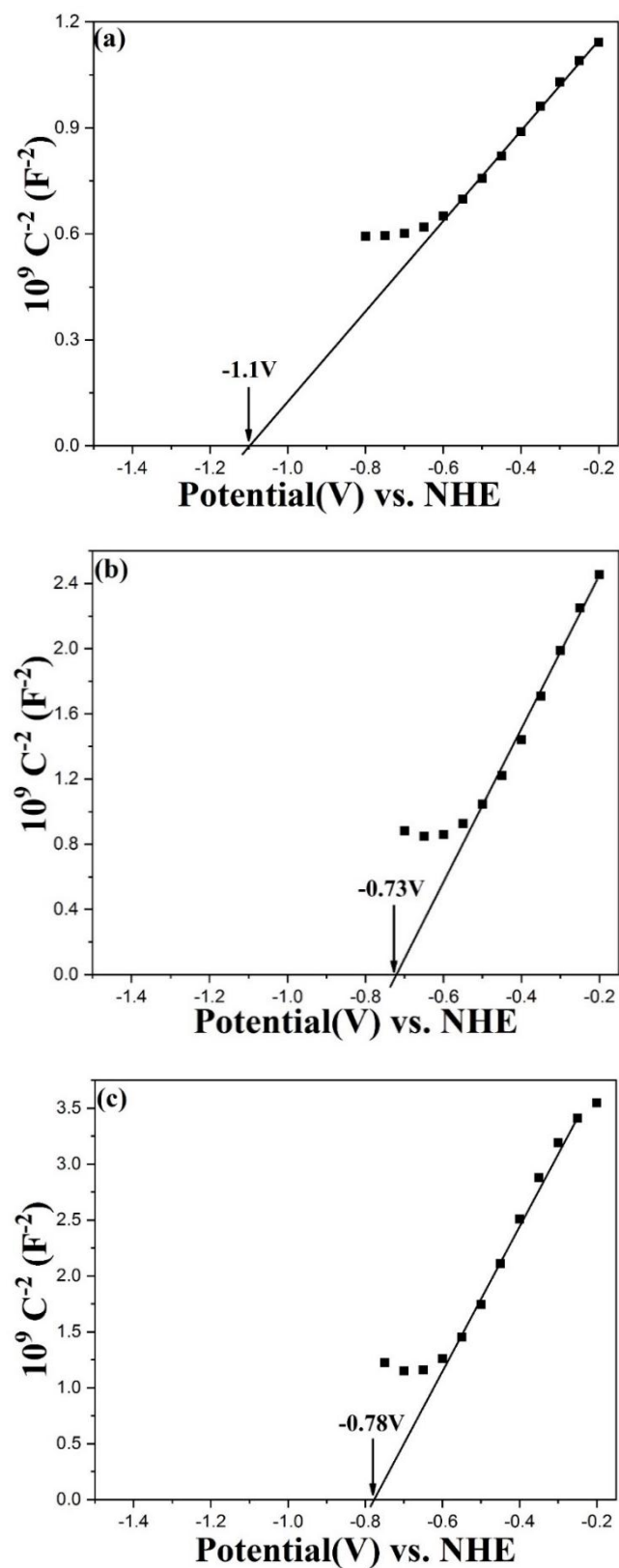


Figure S3. Mott-Schottky plots of $\text{NH}_2\text{-MIL-53(Fe)}$ (a), $\text{NH}_2\text{-MIL-88B(Fe)}$ (b) and $\text{NH}_2\text{-MIL-101(Fe)}$ (c).

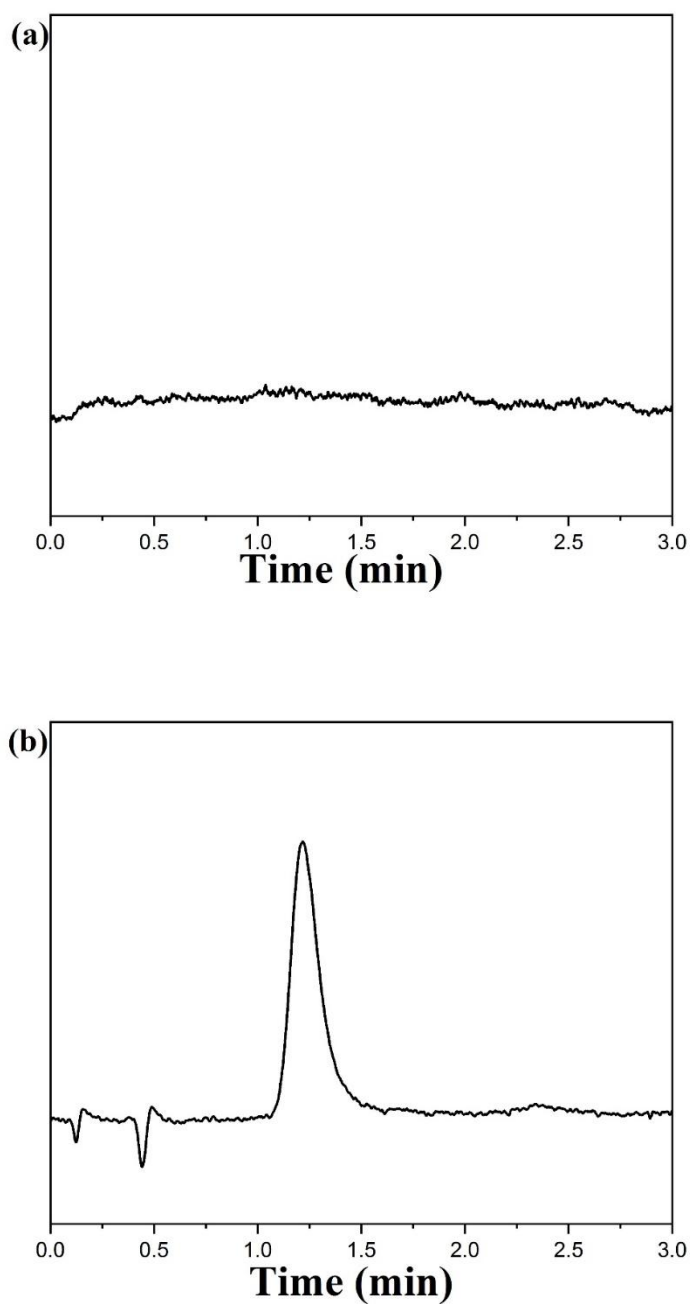


Figure S4. The gas products from irradiation analyzed by gas chromatograms: (a) TCD detector for H_2 detecting, which no H_2 (retention time: 0.578 min) detected; (b) FID detector for CO and CH_4 monitoring, CO was detected with retention time of about 1.290 min, and no CH_4 (retention time: 2.540 min) was detected.

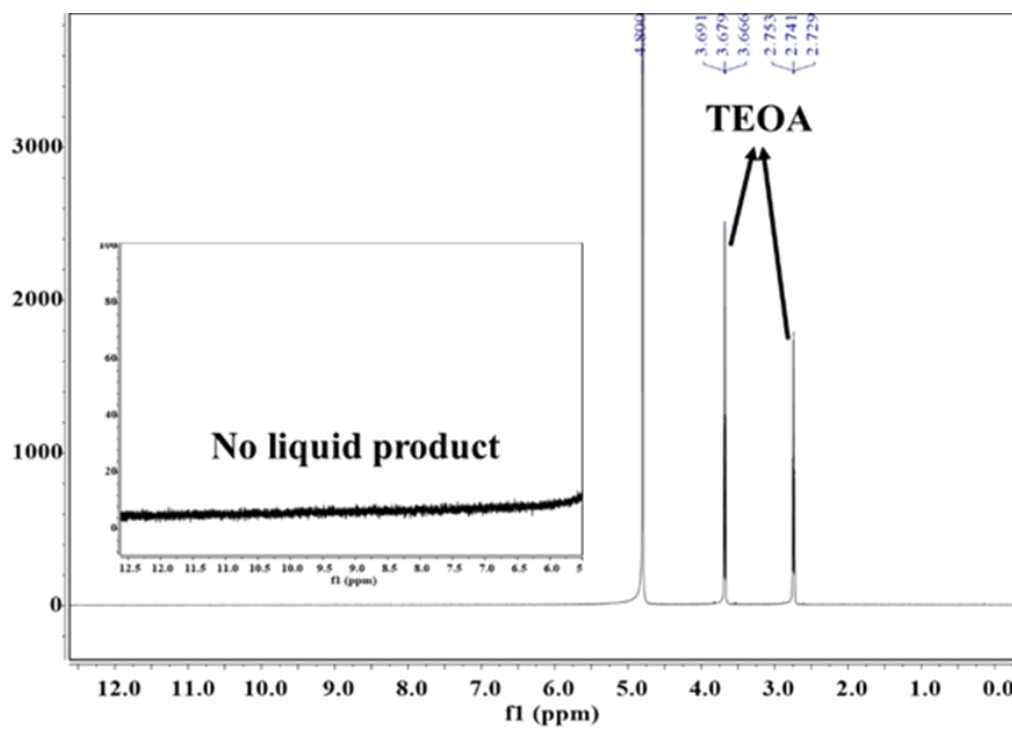


Figure S5. ^1H -NMR spectrum used to detect the liquid product from the photocatalytic reaction.

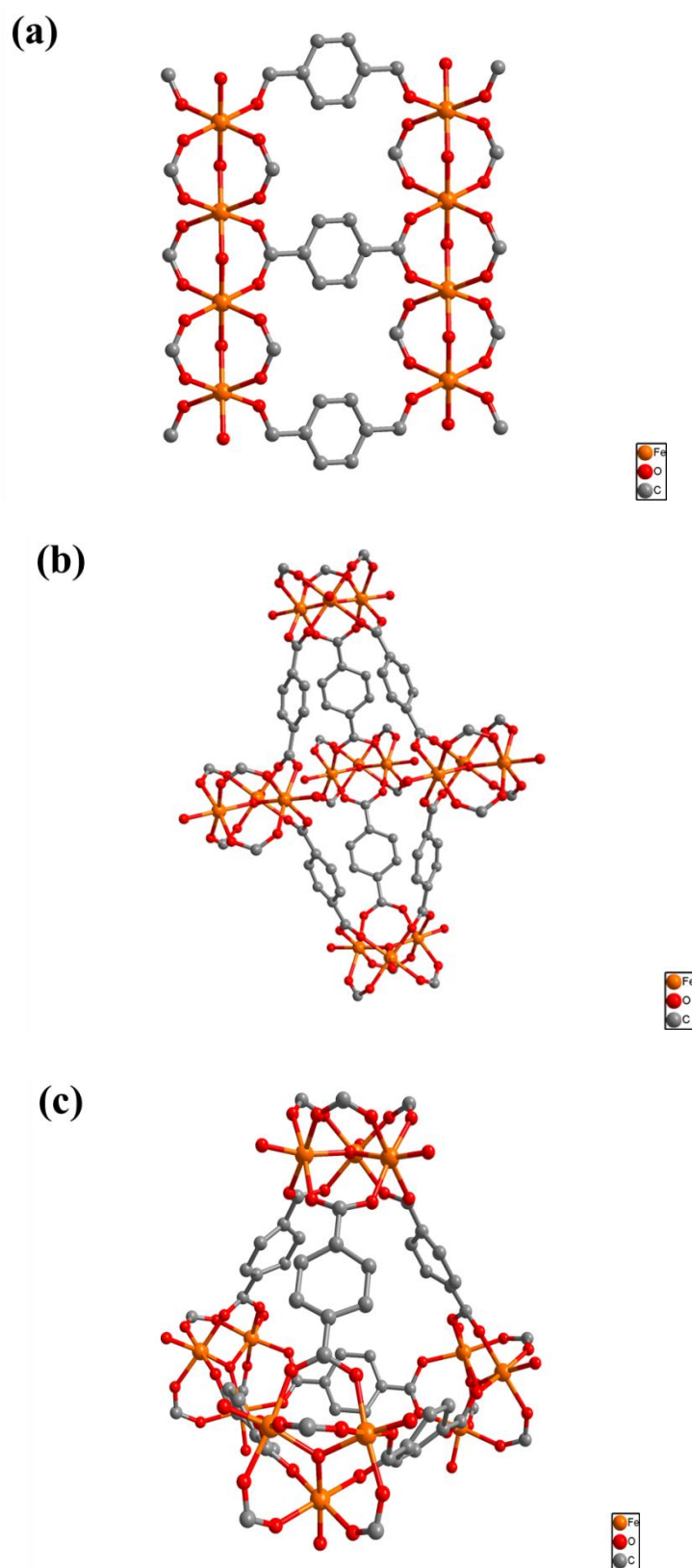


Figure S6. Structures of Fe-MOFs $\text{NH}_2\text{-MIL-53(Fe)}$ (a), $\text{NH}_2\text{-MIL-88B(Fe)}$ (b) and $\text{NH}_2\text{-MIL-101(Fe)}$ (c).

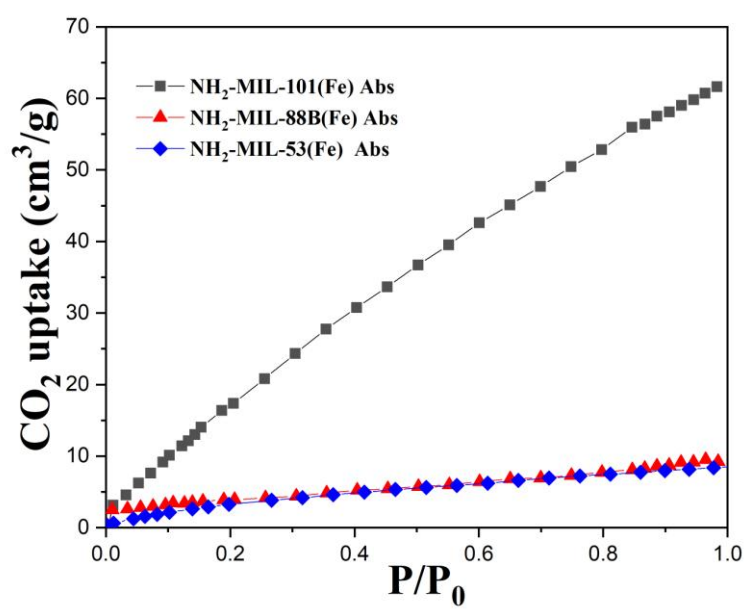


Figure S7. CO₂ sorption isotherms at 298 K.

Table S1. Photocatalytic reduction of CO₂ into CO under varied reaction conditions.

Entry	Catalyst	CO ₂	Light	TEOA	CO ($\mu\text{mol}\cdot\text{g}^{-1}$)
1	-	+	+	+	n.d.
2	+	-	+	+	n.d.
3	+	+	-	+	n.d.
4	+	+	+	-	n.d.

“+” stands for presence, “-” stands for inexistence, n.d. = not detectable.

Standard reaction conditions: catalyst (2 mg), CO₂ (80 kPa, 99.999%), TEOA (2 mL), visible light (300 W xenon arc lamp), reaction time is 5 h.