Electronic Supplementray Information (ESI)

Twisted Graphene-Like MOFs for Efficient CO_2 Photoreduction

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1. Experimental section

1.1 Materials

Hexahydrated nickel(II) nitrate ($Ni(NO_3)_2·6H_2O$, >98%), 1,3,5-benzenetriacetic acid (H_3BTC, >98%) were all purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).N,N-dimethylformamide (C_3H_7NO, >99.5%), N-methylformamide (C_2H_5NO, >99%), dichloromethane (CH_2Cl_2, >99.5%), acetonitrile (CH_3CN, >99.8%), pyrazine ($C_4H_4N_2$, >98%), pyridine (C_5H_5N, >98%), triethanol ($C_6H_{15}NO_3$, >99%) were all purchased from Sinopharm Group Chemical Reagents Co., Ltd. (Shanghai, China).

1.2 Synthesis

Synthesis of Ni-BTC-pyz-0°: Dissolve the mixture of $Ni(NO_3)_2·6H_2O$ (38 mg), H_3BTC (24 mg) , and pyrazine (26 mg) in a 20 mL glass bottle containing 4 mL NMF. Perform ultrasonic treatment for 30 minutes, then heat the mixed solution to 70°C and let it react for 48 hours. After washing the product with fresh DMF, obtain green column-shaped crystals.[1]

Synthesis of Ni-BTC-pyz-30°: Dissolve the mixture of $Ni(NO_3)_2·6H_2O$ (145 mg), H_3BTC (105 mg), and pyrazine (40 mg) in a 20 mL glass bottle containing 10 mL DMF. Perform ultrasonic treatment for 30 minutes, then heat the mixed solution to 130°C and let it react for 72 hours. After washing the product with fresh DMF, obtain light green column-shaped crystals.[2]

Synthesis of Ni-BTC-pyz-60°: Dissolve the mixture of $Ni(NO_3)_2·6H_2O$ (95 mg), H_3BTC (58 mg), and pyrazine (66 mg) in a 20 mL glass bottle containing 10 mL DMF. Perform ultrasonic treatment for 30 minutes, then heat the mixed solution to 70°C and let it react for 48 hours. After washing the product with fresh DMF, obtain dark green column-shaped crystals.[3]

Synthesis of Ni-BTC-py-60°: Dissolve the mixture of $Ni(NO_3)_2·6H_2O$ (29 mg), H_3BTC (21 mg), and pyridine (81 μL) in a 20 mL glass bottle containing 10 mL DMF. Perform ultrasonic treatment for 30 minutes, then heat the mixed solution to 100°C and let it

react for 48 hours. After washing the product with fresh DMF, obtain green column-shaped crystals.[4]

Synthesis of Ni-BTC-dmf-60°: Dissolve the mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (145 mg) and H_3BTC (105 mg) in a 20 mL glass bottle containing 10 mL DMF. Perform ultrasonic treatment for 30 minutes, then heat the mixed solution to 130°C and let it react for 72 hours. After washing the product with fresh DMF, obtain yellowish green column-shaped crystals.[4]

Sample activation: Soak the synthesized samples in dichloromethane for 3 days. Perform solvent replacement twice a day during this period. Then, vacuum dry at 80°C for 12 hours.

2. Photocatalytic CO_2 reduction performance measurements

Before the photocatalytic reaction, all samples were activated to retain the original pore structure and avoid the side effect of small solvent molecules on the results. The CO_2 photoreduction properties were evaluated using a quartz photocatalytic reaction system. Add 5 mg of the activated sample, $[Ru(bpy)_3]Cl_2 \bullet 6H_2O$ (5 mg), CH3CN (8 mL), TEOA (2 mL), and H_2O (2 mL) to a 180 mL quartz photochemical reactor. The reactor was vacuumed for 1 min aer sealing, and then CO_2 gas was passed through the reactor for 15 min until the mixture was CO_2 saturated. A 300 W xenon lamp with $\lambda > 400$ nm filter was used as the irradiation light source. The gas products were analysed by gas chromatography (GC), and the liquid products were analysed by ^1H nuclear magnetic resonance (^1H-NMR) spectroscopy. The incident light intensity was determined using a PL-MW2000 optical power meter.

3. Photoelectrochemical measurements

Photoelectrochemical experiments were performed in a threeelectrode system with 0.2 M Na_2SO_4 as the electrolyte. For the preparation of the working electrode, 20 mg as-synthesized photocatalyst was dissolved in 10 µL Nafion solution and 1 mL methanol. Then, 200 µL of the aforementioned suspension was deposited on the FTO

and dried at room temperature. An Ag/AgCl electrode and a platinum electrode were used as the reference electrode and the counter electrode, respectively. All electrochemical characterization tests were performed on a CHI 760E electrochemical workstation.

4. In situ FT-IR spectroscopy

At room temperature, in-situ diffuse reflectance infrared tests were conducted using an infrared spectrometer (Bruker INVENIO S). The sample powder was added to the high-temperature diffuse reflection reaction chamber, with KBr used as the background. Then, under the irradiation of a deuterium lamp, carbon dioxide gas was introduced into the distilled water through bubbling, and data were collected at different time points.

5. Supplementary Figures and Tables

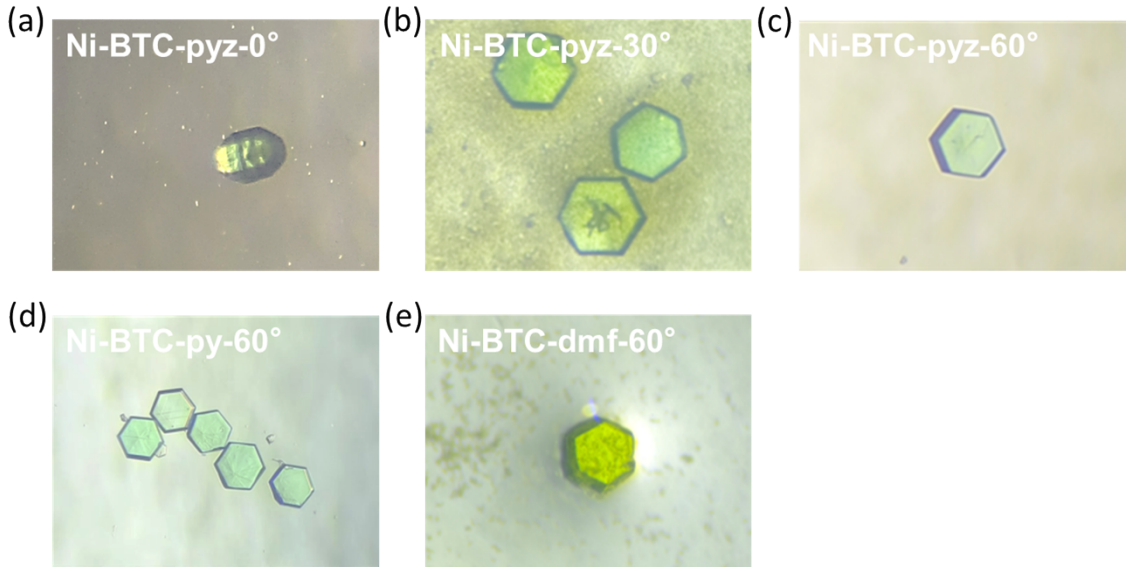

Fig. S1 Optical photos of the Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60° single crystals.

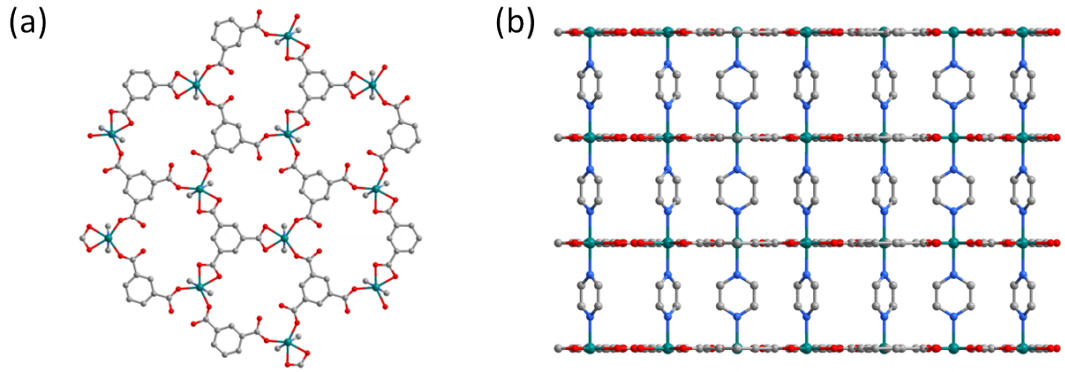

Fig. S2 (a) The three-dimensional structure of Ni-BTC-pyz-0° along the c-axis direction, and (b) the three-dimensional structure of Ni-BTC-pyz-0° along the b-axis direction.

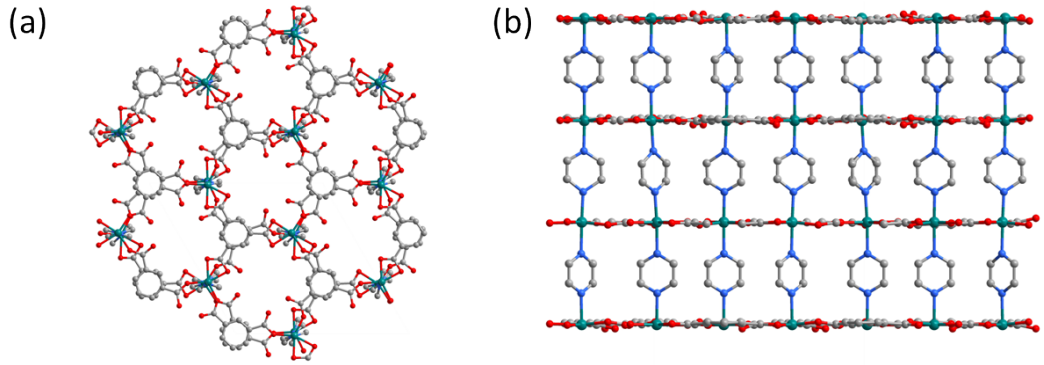

Fig. S3 (a) The three-dimensional structure of Ni-BTC-pyz-30° along the c-axis direction, and (b) the three-dimensional structure of Ni-BTC-pyz-30° along the b-axis direction.

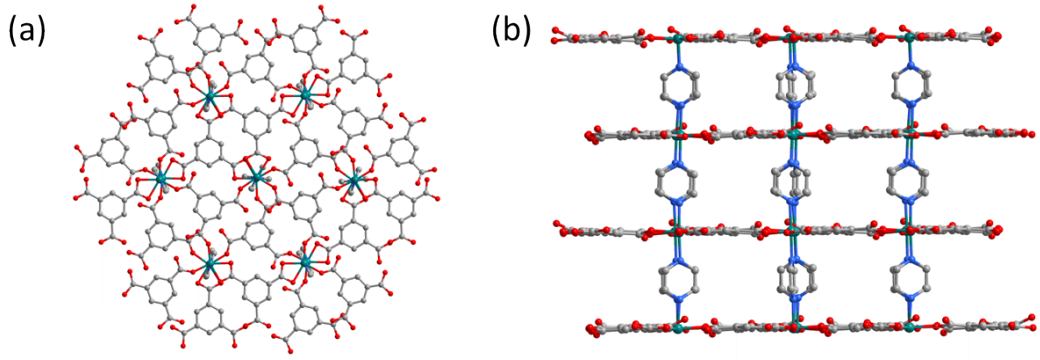

Fig. S4 (a) The three-dimensional structure of Ni-BTC-pyz-60° along the c-axis direction, and (b) the three-dimensional structure of Ni-BTC-pyz-60° along the b-axis direction.

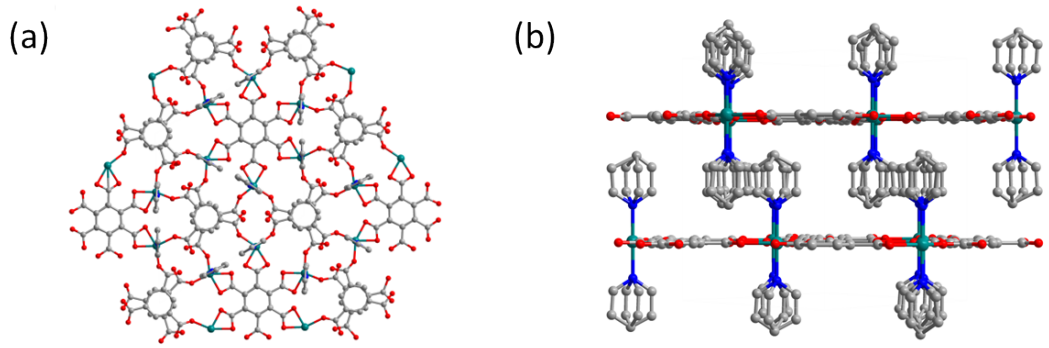

Fig. S5 (a) The three-dimensional structure of Ni-BTC-py-60° along the c-axis direction, and (b) the three-dimensional structure of Ni-BTC-py-60° along the b-axis direction.

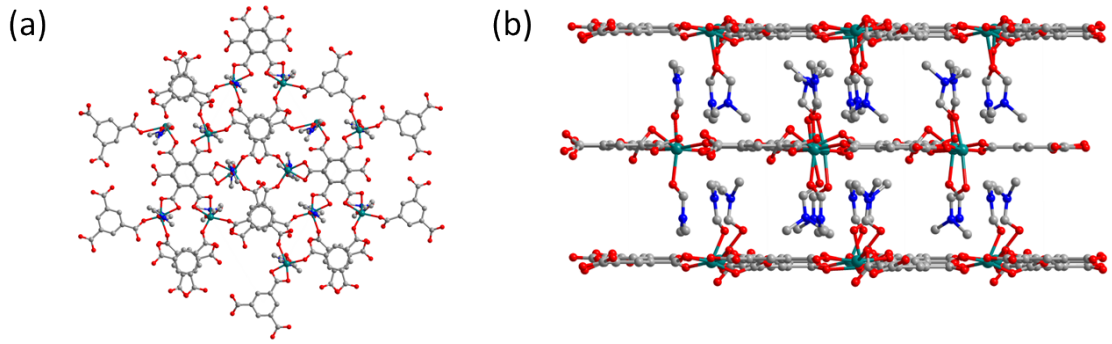

Fig. S6 (a) The three-dimensional structure of Ni-BTC-dmf-60° along the c-axis direction, and (b) the three-dimensional structure of Ni-BTC-dmf-60° along the b-axis direction.

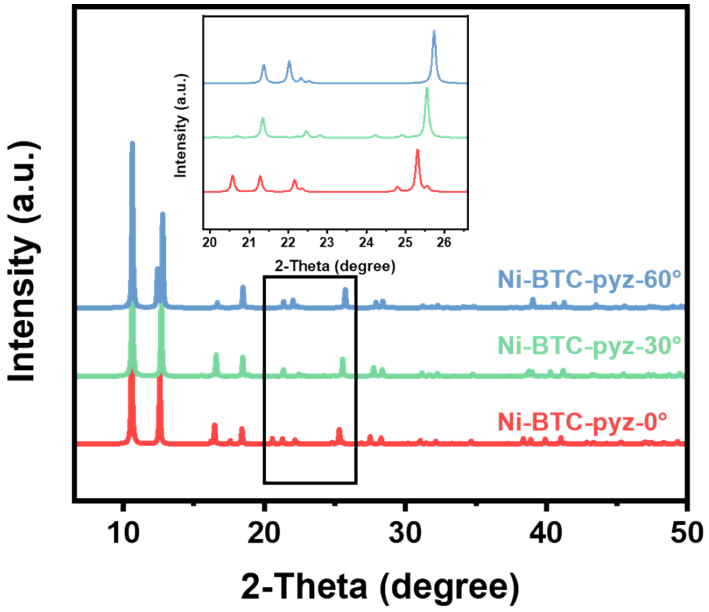

Fig. S7 A comparison of PXRD patterns for Ni-BTC-pyz-0°, Ni-BTC-pyz-30° and Ni-BTC-pyz-60°.

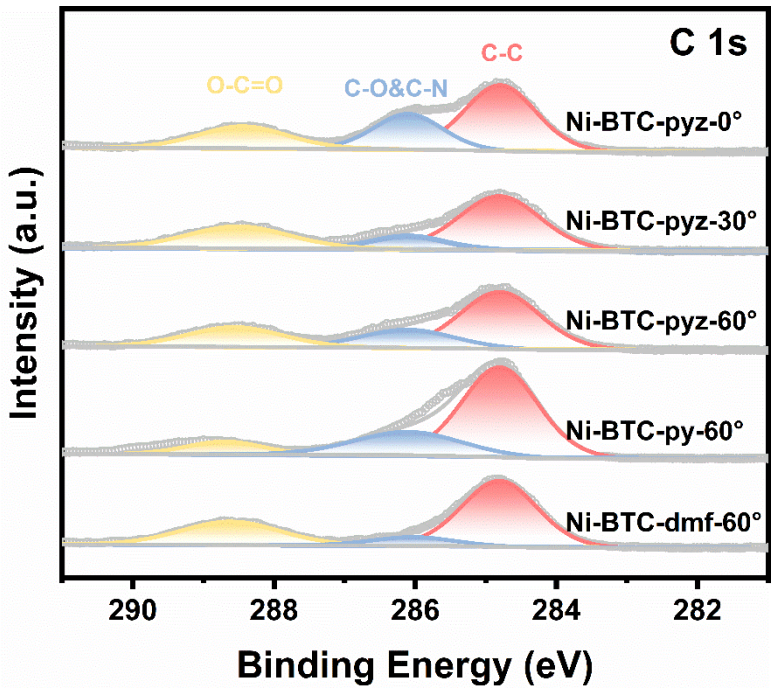

Fig. S8 XPS spectra of C 1s in Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60.

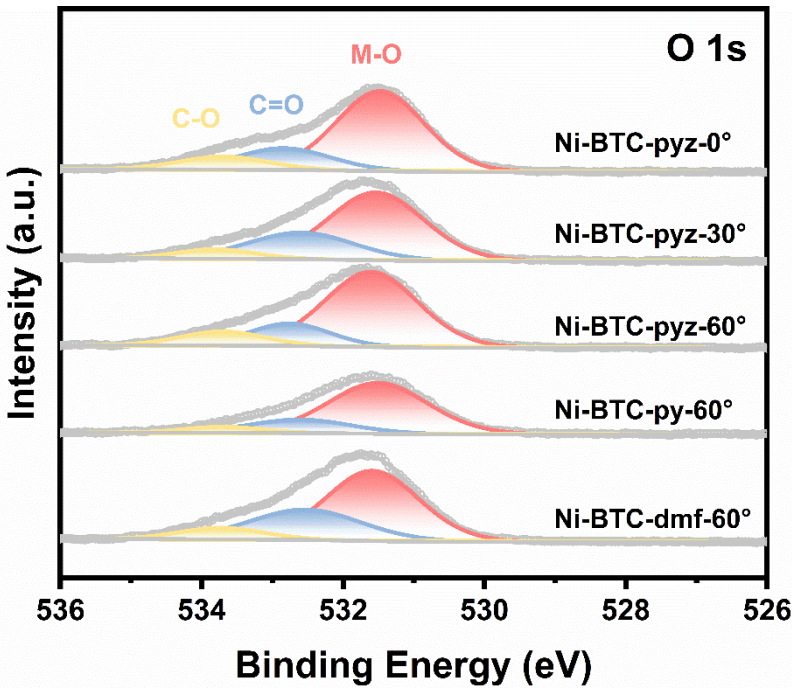

Fig. S9 XPS spectra of O 1s in Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60.

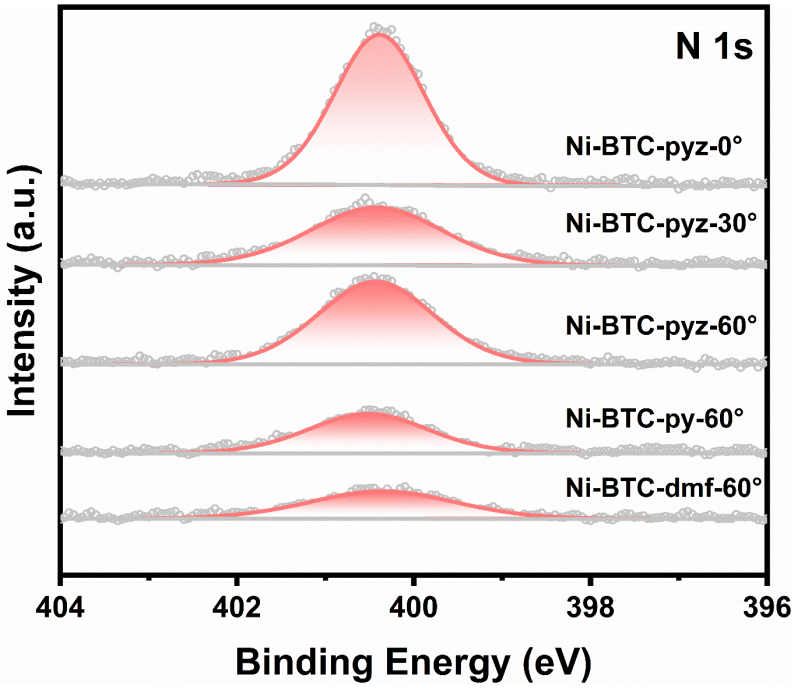

Fig. S10 XPS spectra of N 1s in Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60.

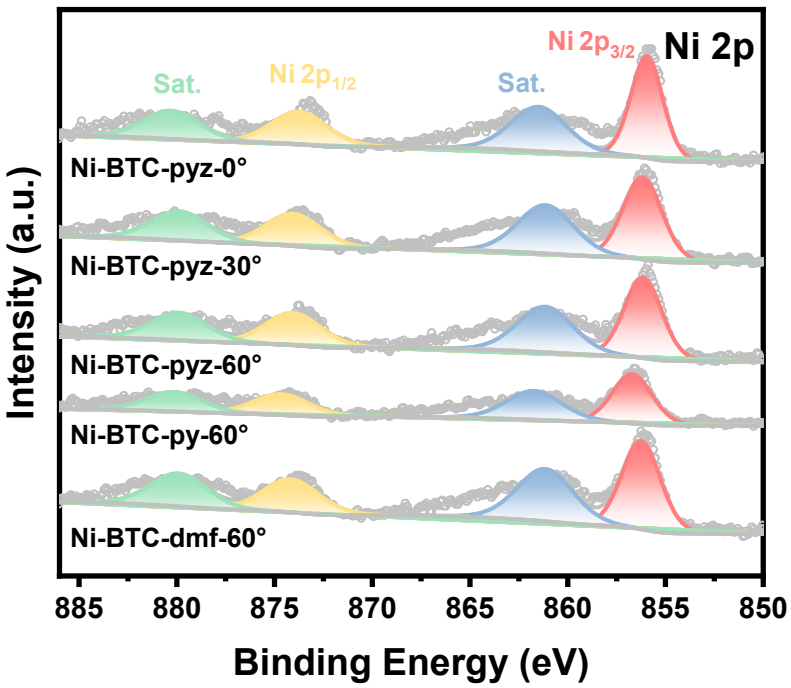

Fig. S11 XPS spectra of Ni 2p in Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60

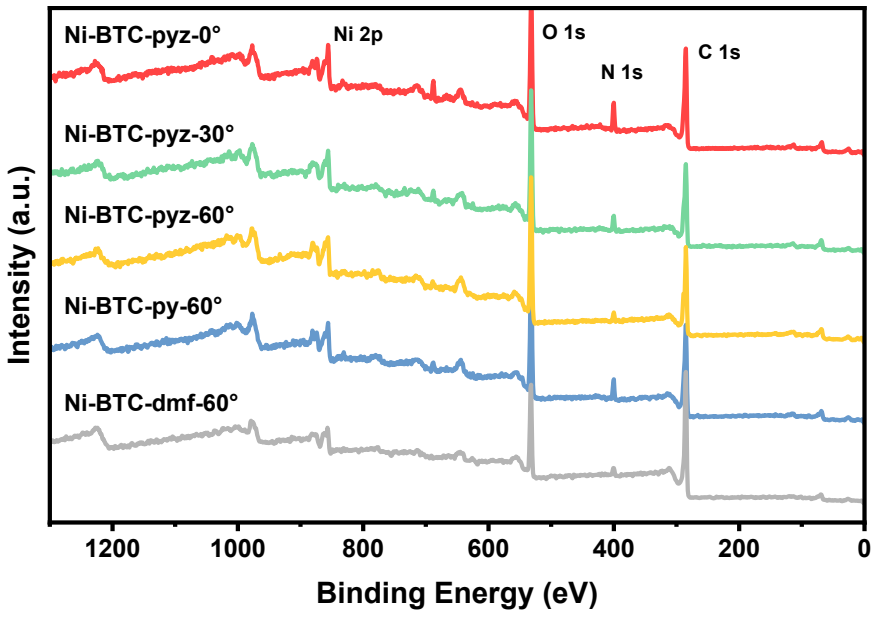

Fig. S12 The full XPS spectra of Ni-BTC-pyz-0°, Ni-BTC-pyz-30°, Ni-BTC-pyz-60°, Ni-BTC-py-60° and Ni-BTC-dmf-60.

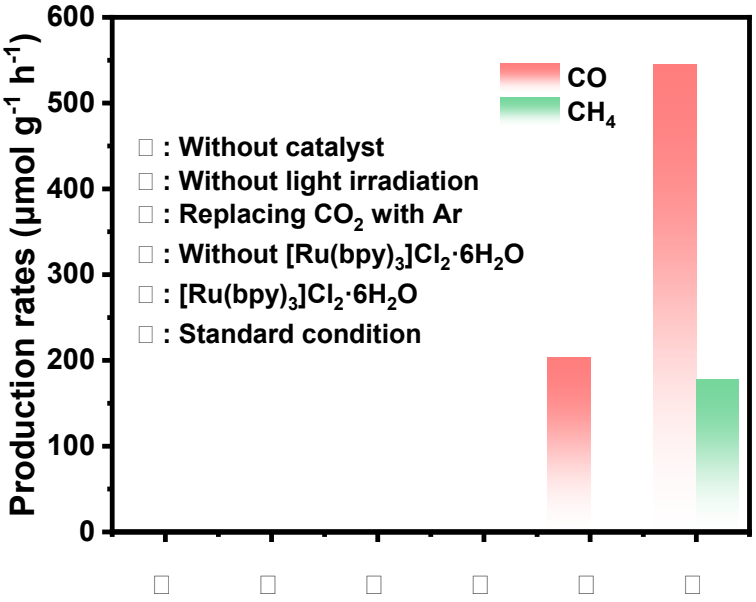

Fig. S13 Control experiments in various conditions over Ni-BTC-pyz-60°.

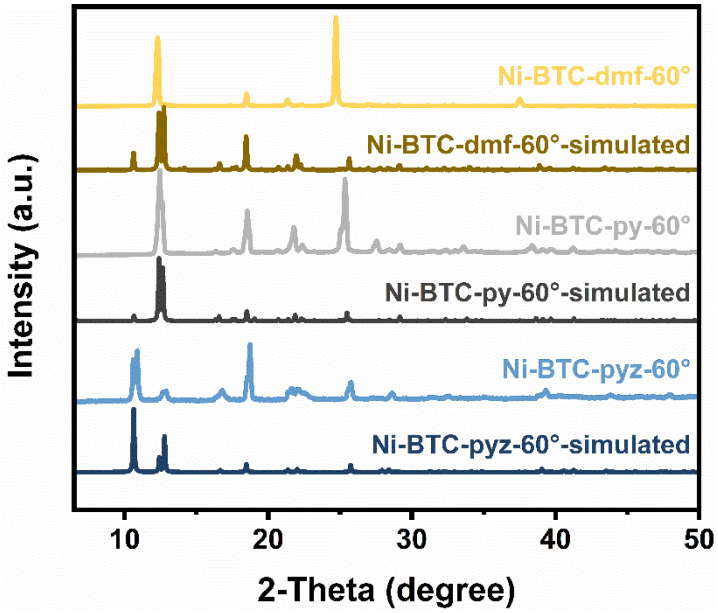

Fig. S14 PXRD of Ni-BTC-X-60° under different column ligands. Comparison of the photocatalytic.

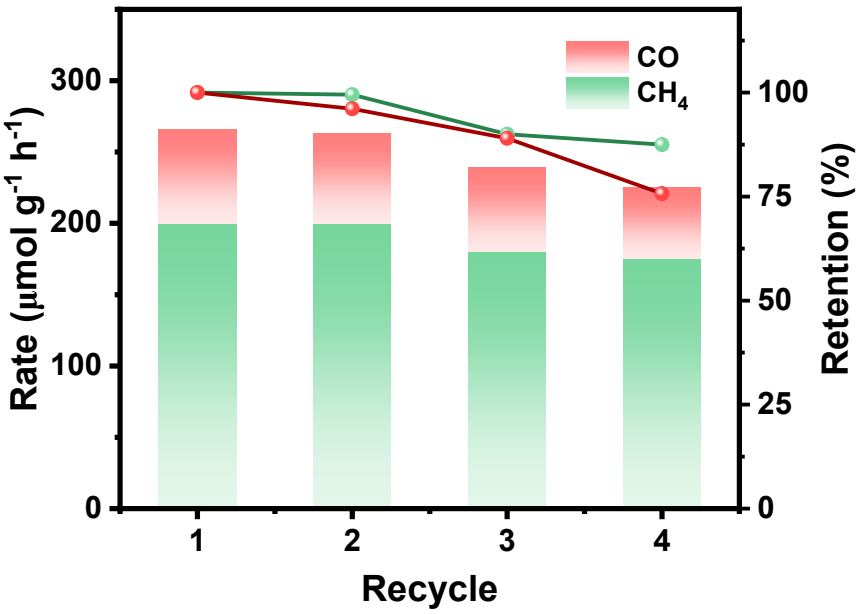

Fig. S15 Reusability of Ni-BTC-dmf-60° for four cycles.

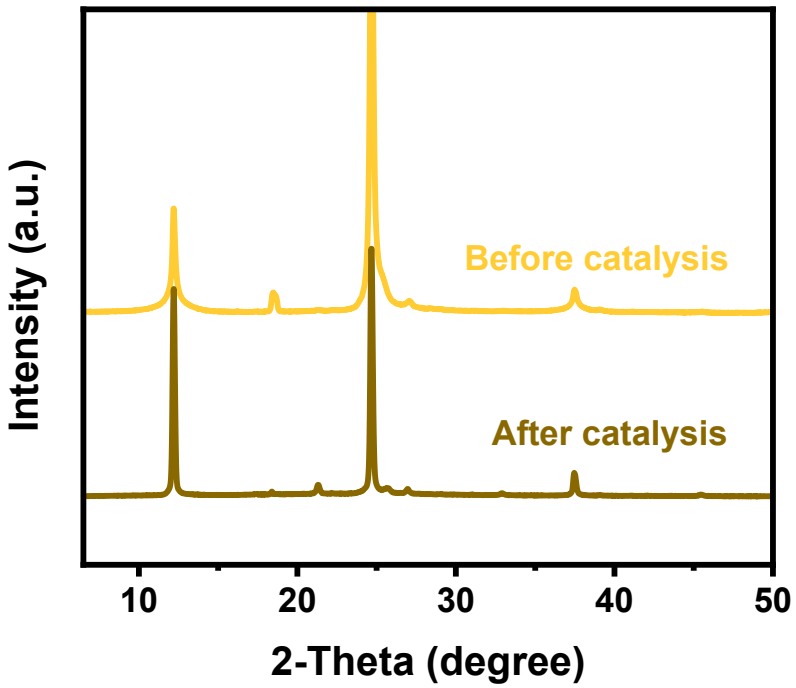

Fig. S16 PXRD patterns of Ni-BTC-dmf-60° before and after catalysis.

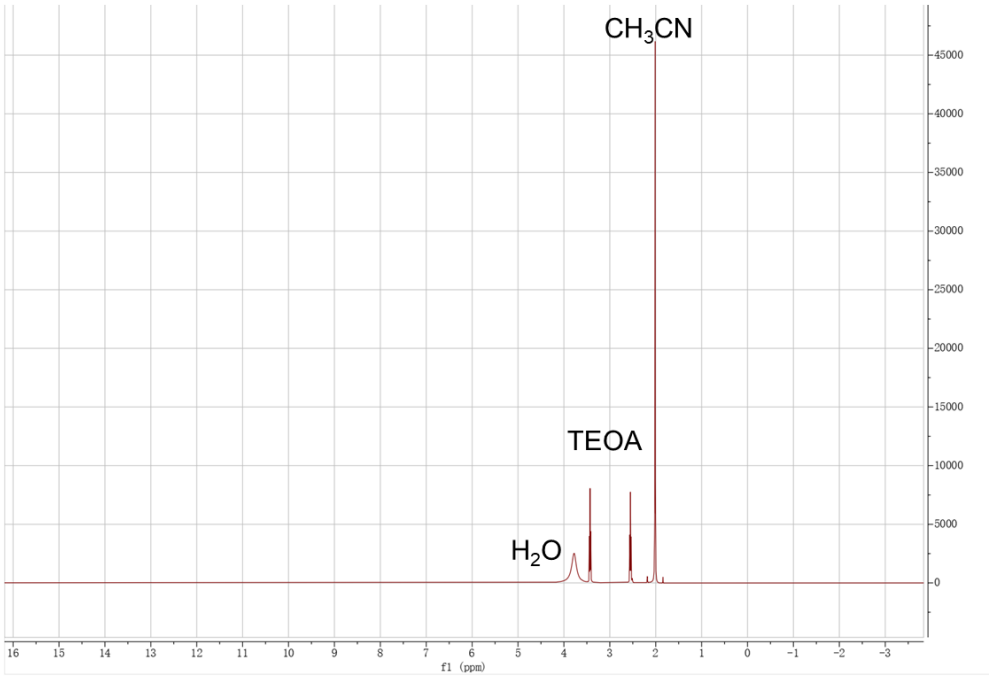

Fig. S17 The ^{1}H NMR spectra of the liquids after the photocatalytic experiments using Ni-BTC-dmf-60°.

Table S1. Summary of photocatalytic CO_2 to CO and CH_4 over MOF catalysts.

Photocatalysts	Conditions	Light intensity (W)	Yield of CO (μmol g^{-1} h^{-1})	Yield of CH_4 (μmol g^{-1} h^{-1})	Ref.
Ni-BTC-pyz-0°	CO_2, H_2O λ > 400 nm	300	548.2	3.9	This work
Ni-BTC-pyz-30°	CO_2, H_2O λ > 400 nm	300	108.5	1.4	This work
Ni-BTC-pyz-60°	CO_2, H_2O λ > 400 nm	300	544.7	177.8	This work
ZrPP-1-Co	CO_2, H_2O λ > 420 nm	300	14	0.5	5
MIL-100（Fe）	CO_2,TEOA 400-700nm	300	3.9	47.3	6
NH_2-MIL-125@Ni-BDC	CO_2, H_2O λ > 400 nm	300	41.38	5.91	7
MOF-525-Co	CO_2 MeCN/TEOA = 4:1 400-800nm	300	200.6	36.6	8
Monolayer MOF 1	CO_2 MeCN/H_2O/TEOA = 8:2:1 AM 1.5G filter	300	365.5	0	9
Bilayer MOF 2	CO_2 MeCN/H_2O/TEOA = 8:2:1 AM 1.5G filter	300	276.8	0	9
NH_2-UiO-66	CO_2, H_2O 420 - 800 nm	300	3.9	1.1	10
Zr-PS-FeTCPP	CO_2 ACE,TEA	500	247.8	36.6	11
NH_2-MIL-125(Ti)	CO_2, H_2O AM 1.5G filter	300	24.49	6.43	11

MOF-808	CO_2, H_2O 420 - 800 nm	300	0	102	12
pcn-222	CO_2, H_2O λ > 420 nm	300	6.8	0.2	13
Bi-PMOF-120-F	CO_2 MeCN,TEOA λ > 420 nm	300	28.61	8.81	14
MOF 1-OH	CO_2, H_2O 420 - 800 nm	300	33.9	23.6	15

6. Reference

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