Supporting Information for

Steering Electron Flow by Constructing Integrated Structure in Metal-Organic Frameworks (MOFs) via Iminopyridine Units for Efficient CO_2 Photoreduction to C_2H_4 and C_2H_6

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Experimental Section

Materials 2-Aminoterephthalate (H_2ATA) were purchased from Alfa Aesar Co. $Ti(OC_3H_6CH_3)_4$ were purchased from Shanghai Chemical Reagent Co. Anhydrous N,N-dimethylformamide (DMF) was purchased from Sigma-Aldrich Co. 2-Pyridinecarboxaldehyde and methanol (CH_3OH) were purchased from Aladdin. $C_{20}H_{16}Cl_2N_4Ru\cdot 2H_2O$ was purchased from Shanghai Maclin Biochemical Technology Co. All the reagents were analytical grade and used without further purification.

Synthesis of Ti-MOF Ti-MOF was prepared following a previous reported procedure with a slight modification[31]. Typically, 2-aminoterephthalic acid (H_2ATA) (0.5 g, 3 mmol) and tetra-n-butyl titanate Ti (OC_4H_9)$_4$ (0.26 ml, 0.75 mmol) were added into a solution containing dimethylformamide (DMF) (9 ml) and dry MeOH (1 ml). The above mixture was stirred at room temperature for 30 min and was transferred to a 50 ml Teflon liner and heated at 150°C for 72 hours. After hydrothermal treatment, the resultant suspension was filtered, washed with DMF and methanol, respectively, and vacuum-dried to obtain the product.

Synthesis of Ti-MOF-Py The 2-pyridinecarboxaldehyde functionalized Ti-MOF is denoted as Ti-MOF-Py, which was prepared by following the previous report. Typically, 165.37 mg of Ti-MOF (0.1 mmol) was dispersed in toluene (10 mL) containing 58.2 μL of 2-pyridinecarboxaldehyde. This mixture was stirred at room temperature for 2 days and then stand unperturbed for another 1 day. Subsequently, the resultant yellow powder was washed with 3×10 mL of CH_2Cl_2 and dried at 60 °C under vacuum.

Synthesis of CuCo/Ti-MOF-Py 82.7mg of the obtained Ti-MOF-Py was dispersed in 5 mL isopropyl alcohol containing 13.3mg of $CuCl_2\cdot 2H_2O$ in a 10 mL round-bottom flask. The suspension was then refluxed for 5 h under continuously stirring. The resultant was washed many large amounts of ethanol to ensure the removal of unreacted reactants and dried at 60 ℃. Subsequently, 50 mg of the obtained product was dispersed in 50 mL of ethanol/H_2O (v:v=1:4) and photoreduced for 1 h. The suspension was separated by centrifugation and the solid product was washed with methanol several times and dried at 60 ℃ to obtain the final product.

Synthesis of CuCo/Ti-MOF-Py-Ru 50 mg CuCo/Ti-MOF-Py and 3 mg cis-bis (2,2' -dipyridyl) ruthenium (II) dichloride dihydrate were dissolved in 6 mL methanol and ultrasonic for

5 min, stirring at room temperature for 24 h. The resulting product is washed many times with large amounts of methanol. Then dry at 60 °C.

Characterizations XRD patterns were collected on a D8 Advance X-ray diffractometer (DX2700, China) with Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scanning rate of 2^{o}/min in the 2θ range of $5–50^{o}$. FT-IR spectra of powder samples were recorded on a Nicolet iS50 FTIR spectrometer (ThermoFisher, USA). The XPS was carried out on ThermoFischer, ESCALAB Xi+ apparatus. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was performed on Optima 8000 (PerkinElmer). Before ICP-OES experiment, the solid sample was digested in mixture of HNO_3 and milli-Q water. The TEM and energy dispersive X-ray spectroscopy (EDS) mapping images were acquired by high-resolution transmission electron microscopy (Talos F200S G2 instrument). UV–visible diffuse reflectance spectra (UV-DRS) was obtained for the dry-pressed disk samples using a Shimadzu UV-2600 (Japan) with $BaSO_4$ as a reflectance standard. Photoluminescence (PL) emission spectroscopy were performed with (Hitachi F-7100; Japan) at room temperature.

Photocatalytic CO_2 reduction The photocatalytic CO_2 reduction was performed by using a 300 W Xe lamp with a cut-off filter of 400 nm as a visible light source. In a typical experimental process, 20 mg of the photocatalysts was added to the reaction vessel, the system was bubbled with high-purity CO_2 (99.999 %) for 30 min to remove the dissolved oxygen. A pre-prepared mixture of 50ml water, acetonitrile and triethanolamine (v:v:v=1:3:1) is then injected into the reaction vessel. Xenon lamps were then used to illuminate the reaction system for six hours. The gas and liquid products were detected by gas GC and ^{1}H NMR.

Photoelectrochemical characterization The photoelectrochemical tests were performed in a 0.5 M Na_2SO_4 electrolyte solution using a three-electrode system. The as-obtained films, Ag/AgCl (saturated KCl), and platinum foil (1×1 cm^{2}) were used as the working electrode, reference electrode, and counter electrode, respectively, and collected on an electrochemical station (CHI760E, Shanghai Chenhua). Five milligrams of the as-prepared photocatalysts is dispersed in 400 μL of ethanol and 600 μL of water, and then sonicated for 5 min. Then 30 μL of the catalyst ink was spread on the Fluorine-doped tin oxide (FTO) (1.0×1.0 cm^{-2}) and dried at room temperature to form working electrode.

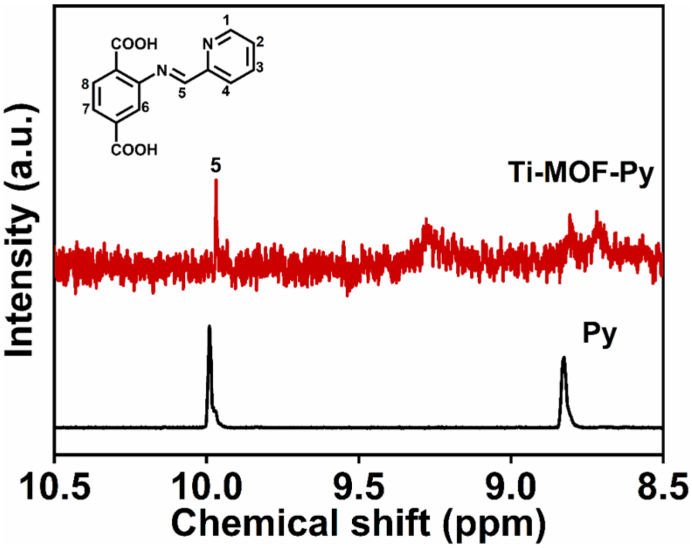

Fig. S1 ^{1}H NMR spectra of Ti-MOF-Py and Py.

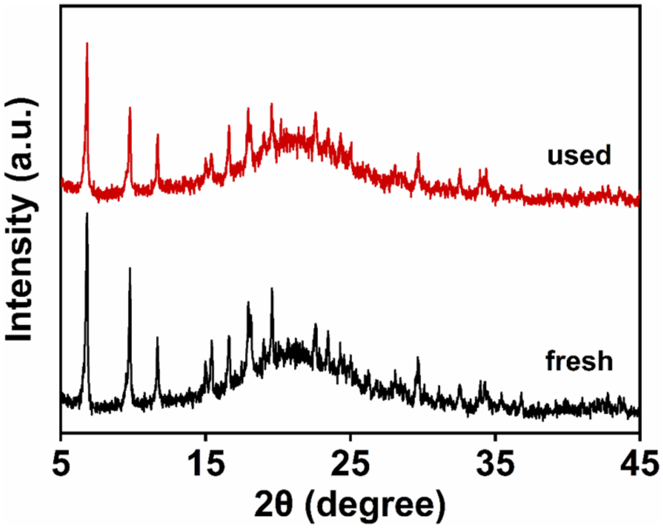

Fig. S2 XRD patterns of CuCo-Ti-MOF-Py-Ru before and after reaction.

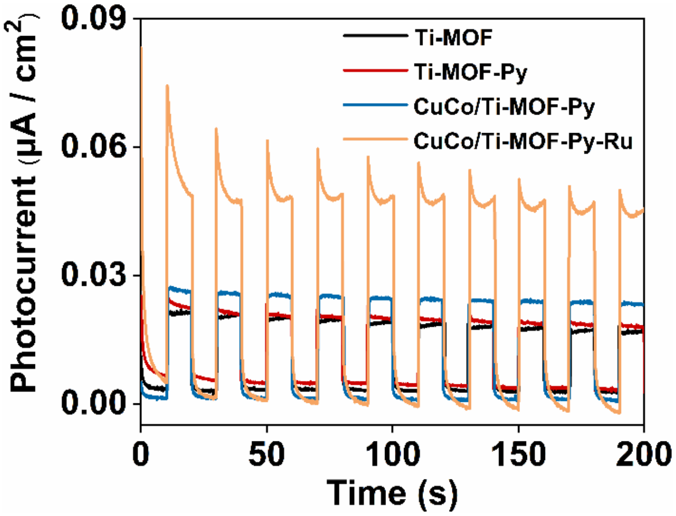

Fig. S3 Transient photocurrent response of different samples.

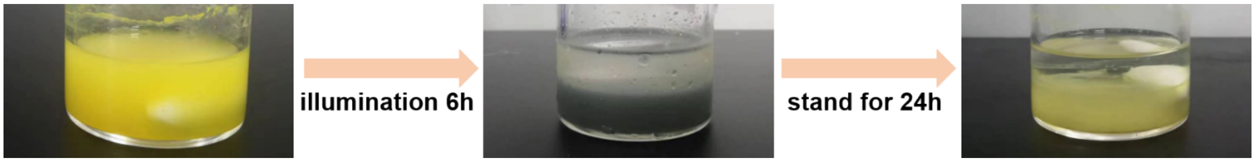

Fig. S4 The color change of the photocatalyst during the reaction.

Samples	Contents of Cu (wt%)	Contents of Co (wt%)
Cu/Ti-MOF-Py	1.03 wt%	-
CuCo/Ti-MOF-Py	0.52 wt%	0.91 wt%

Table S1 The contents of Cu and Co in the samples according to ICP-OES.