

**Supporting information:**

**In Situ Fabrication of TiO<sub>2</sub> Nanoparticles/2D Porphyrin Metal-Organic Frameworks for Enhancing the Photoreduction of CO<sub>2</sub> to CO**

Xiaoqian Xu,<sup>a</sup> Abdelkader. Labidi,<sup>a</sup> Tian Luo,<sup>a</sup> Ting Gao,<sup>a</sup> Nurxat Nuraje,<sup>b,c</sup> Chuanyi Wang<sup>a</sup> \*

<sup>a</sup> School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, P. R. China

<sup>b</sup> Department of Chemical & Materials Engineering, School of Engineering & Digital Science, Nazarbayev University, Astana, Kazakhstan;

<sup>c</sup> Renewable Energy Laboratory, National Laboratory Astana, Nazarbayev University, Astana, Kazakhstan;

\*Authors for Correspondence: Prof. Chuanyi Wang

E-mail: wangchuanyi@sust.edu.cn (C. Wang)

## **Experimental Section**

### **Materials**

Copper (II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), 4,4'-Dipyridyl (BPY), 5, 10, 15, 20-tetrakis (4-carboxyl-phenyl)-porphyrin (TCPP), Polyvinylpyrrolidone (PVP), tetrabutyl titanate, were purchased from Alfa Aesar. N, N-dimethylformamide (DMF), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) triethanolamine (TEOA), trifluoroacetic acid were obtained from Sigma-Aldrich. All the chemicals are analytical grade and used without further purification. Deionized water was prepared with a Milli-Q purification system and used throughout all the experiments.

### **Synthesis**

#### **Synthesis of titanium dioxide nanoparticles ( $\text{TiO}_2$ )**

According to the method reported in the literature <sup>[1]</sup>,  $\text{TiO}_2$  nanoparticles were synthesized by a similar method. A mixing of 2 ml deionized water, 10 ml ethanol, 1 ml glacial oleic acid, 10 ml tertbutyl titanate and 0.5 g sodium hydroxide were stirred at room temperature for 0.5 h, then the mixed solution was transferred to a 50 ml polytetrafluoroethylene reactor for reaction at  $180^\circ\text{C}$  for 24 h. After the reaction cooled to room temperature, and the bottom product was separated and dispersed in cyclohexane solution by centrifugal tube. The product was then precipitated with ethanol to separate the product then dried at  $60^\circ\text{C}$  in oven for 8 h. After that, the dry material is ground into powder and calcined at  $450^\circ\text{C}$  for 4 hours to obtain titanium dioxide nanoparticles.

#### **Synthesis of 2D Porphyrin Metal-Organic Frameworks (Al-MOF)**

$\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (3.6 mg, 0.015 mmol), BPY (3.0 mg, 0.02mmol), trifluoroacetic acid ( $1.0\text{ M} \times 10\ \mu\text{L}$ ), PVP (10.0 mg) and TCPP (3.5 mg, 0.0045 mmol) were dissolved in a mixture solution of 6 mL N, N-dimethylformamide (DMF), 3 ml Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and 1ml  $\text{H}_2\text{O}$  forming a homogeneous solution. After that, transfer the mixture to a glass bottle with lid then heated at  $120^\circ\text{C}$  for 12 h in oven. After cooling down to room temperature, the product was centrifuged at 8000 r.p.m. for 10 min and washed three times with ethanol and water, respectively.

#### **Synthesis of Al-MOF@ $\text{TiO}_2$**

The synthesis of Al-MOF@TiO<sub>2</sub> was using in-situ synthesis method by add 30 mg of TiO<sub>2</sub> to the materials for MOF synthesis.

### **Synthesis of Al-MOF/TiO<sub>2</sub>**

1 g Al-MOF and 30 mg of TiO<sub>2</sub> ethanol solution dispersed in 30 ml ethanol solution and refluxing at 12 °C for 12 hours. After cooling down to room temperature, filter and wash by water then dry at 80 °C for 6 h.

### **Characterization**

The powder X-ray diffraction (PXRD) experiments were measured on a Bruker D8 Advance with Cu/K $\alpha$  radiation radiation ( $2\theta = 5\text{--}60^\circ$ ) at 20 kV and 20 mA. Fourier-transform infrared (FTIR) spectroscopy was conducted using a VECTOR-22 spectrometer in the range of 500-4000 cm<sup>-1</sup> with a KBr window. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was carried out using a PE Lambda 950 instrument. Photoluminescence (PL) spectral measurements and fluorescence lifetime measurements were measured on an XGT-7200V. The crystal structure of morphology was obtained on a scanning electron microscope (SEM, Hitachi S-4800). The transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were used on a FEI Tecnai G2 F20 S-TWIN high-resolution TEM. The XPS studies of the chemical valence state was evaluated on were performed on the AXIS SUPRA. Electron paramagnetic resonance (EPR) spectra were performed with a Bruker Elexsys E500-T equipment operating in the X-band at room temperature. EPR parameter settings are: microwave frequency, 9.79 GHz; power, 5.05 mW center field, 3500 G. Atomic force microscopy (AFM) observation was performed using Agilent 5100AFM. Raman spectra were obtained using a micro-Raman spectrometer (DXRxi) in a backscattering geometry with a 532 nm laser as an excitation source.

### **Photoelectrochemical tests**

The photoelectrochemical (PEC) measurements were recorded using a IGS1100 electrochemical workstation, which had a typical three-electrode system with a saturated Ag/AgCl electrode, prepare sample (sample-modified FTO) and a platinum foil as the reference electrode, working electrode, and counter electrode, 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte, respectively. The working electrode was prepared as

following: 10 mg samples was dispersed in ethanol to form a suspension, then dropped onto a 1×1cm FTO glass and the working electrode was obtained after air drying.

### **Activity tests of photocatalytic CO<sub>2</sub> reduction**

The activity test was carried out in a quartz glass photochemical reactor. The photocatalytic reduction of CO<sub>2</sub> was carried out with H<sub>2</sub>O and TEOA as a reductant in a glass reactor (volume: 100 mL) with a quartz window on the top. The photocatalytic reactions were processed by a 300 W Xe lamp (Beijing MC-PF300C) as light source. In a typical process, 20 mg photocatalysts were first dispersed on a flat quartz plate, while the 2 mL of deionized water was dropped to the reactor to engender water vapor to react with the photocatalyst during the photoreactions. During each run, the reactor was first passed into with Ar for at least 30 min to ensure the air were completely removed, after that inject pure CO<sub>2</sub> for 30 min to fill the reactor with CO<sub>2</sub> gas, then the reactor was sealed and the reaction temperature was kept at 25 °C with a circulating cold water bath system.

The photocatalytic reaction was performed for 1 h and the gas was collected with extraction syringes (1 mL) and measured by FULI GC-9790II gas chromatographic instrument. The amount of CO and CH<sub>4</sub> produced from CO<sub>2</sub> reduction was quantified by Flame ionization detector (FID) equipped with a 5 Å molecular column, CO was converted to CH<sub>4</sub> by reformer.

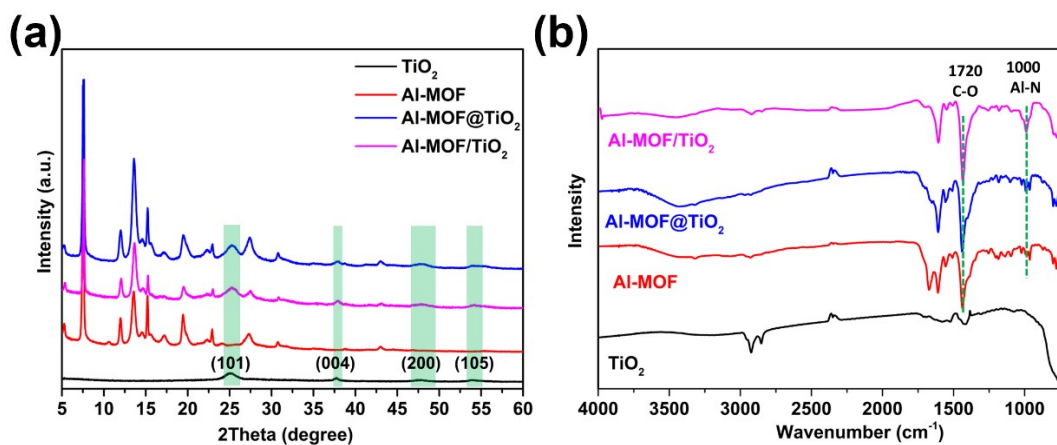


Figure S1. (a) PXRD and (b) FT-IR patterns of Al-MOF, Al-MOF@TiO<sub>2</sub> and Al-MOF/TiO<sub>2</sub>

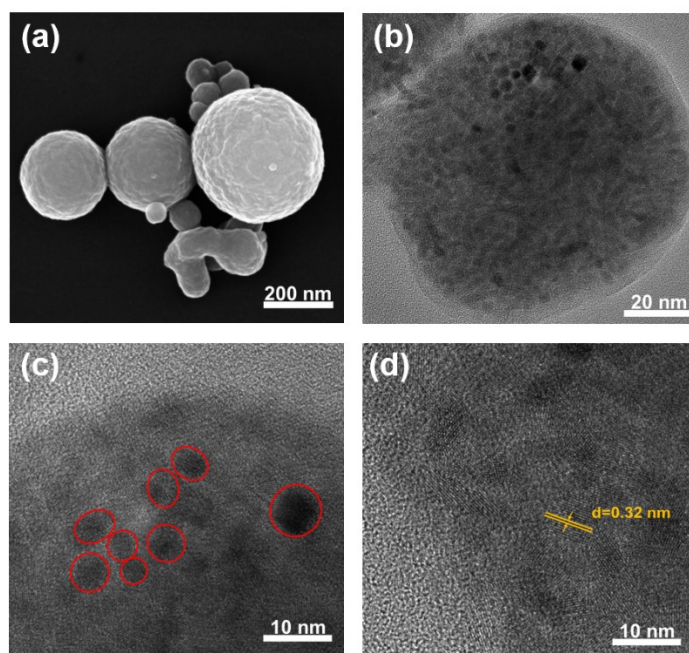


Figure S2. (a-b) SEM image of TiO<sub>2</sub>; (c-d) TEM image of TiO<sub>2</sub>.

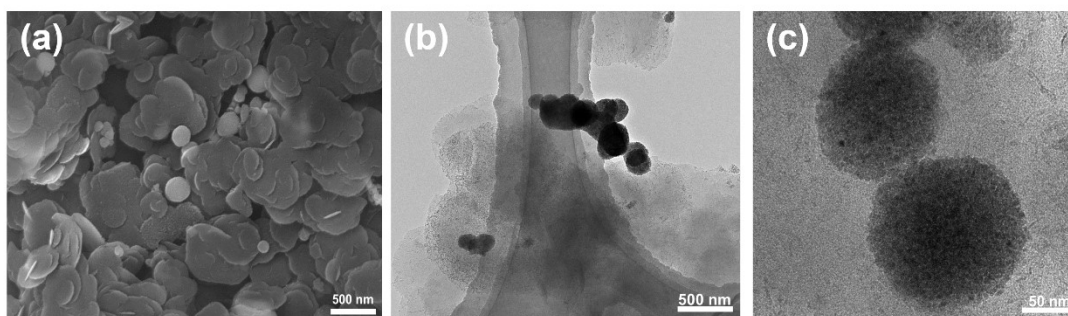


Figure S3. (a) SEM image of Al-MOF/TiO<sub>2</sub>, (b) TEM image of Al-MOF/TiO<sub>2</sub> and (c) HR-TEM image of Al-MOF/TiO<sub>2</sub>.

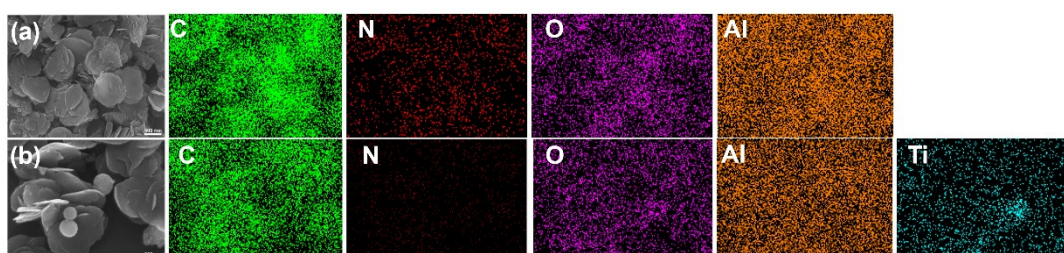


Figure S4. EDS of (a) Al-MOF and (b) Al-MOF/TiO<sub>2</sub>.

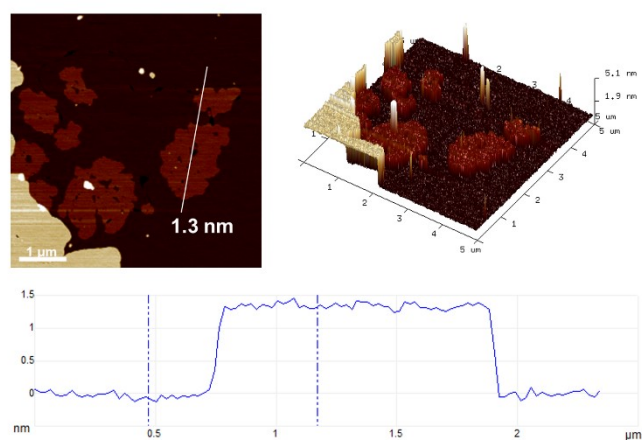


Figure S5. AFM images of Al-MOF/TiO<sub>2</sub>.

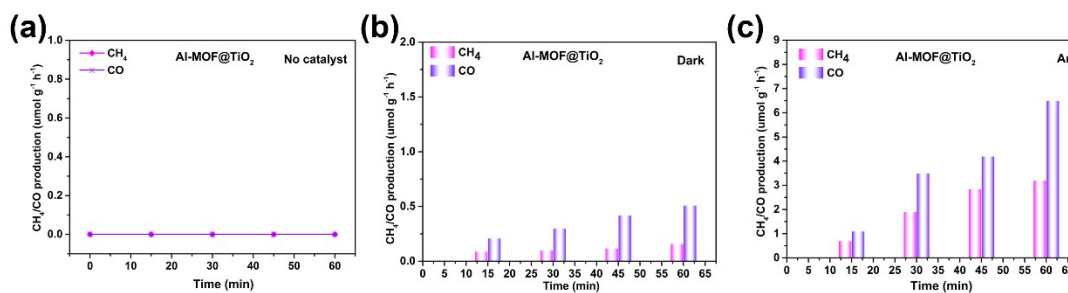


Figure S6. Comparative experiment of Al-MOF@TiO<sub>2</sub>. (a) photocatalytic activities for CO<sub>2</sub> conversion in no Al-MOF@TiO<sub>2</sub> catalysis condition; (b) photocatalytic activities for CO<sub>2</sub>

conversion of Al-MOF@TiO<sub>2</sub> in dark condition; (c) photocatalytic activities for CO<sub>2</sub> conversion of Al-MOF@TiO<sub>2</sub> in Ar condition.

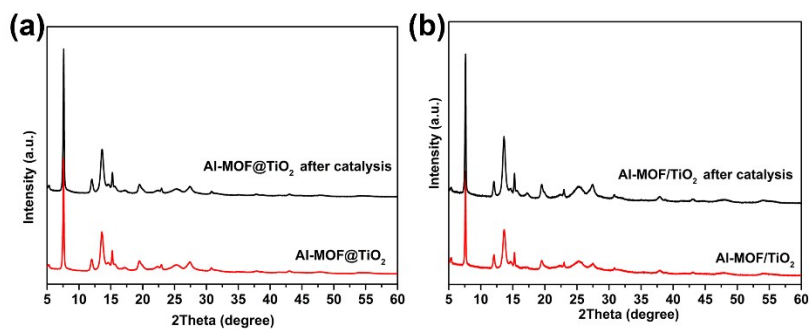


Figure S7. XRD patterns of Al-MOF@TiO<sub>2</sub> and Al-MOF/TiO<sub>2</sub> before and after the CO<sub>2</sub> photoreduction reaction.

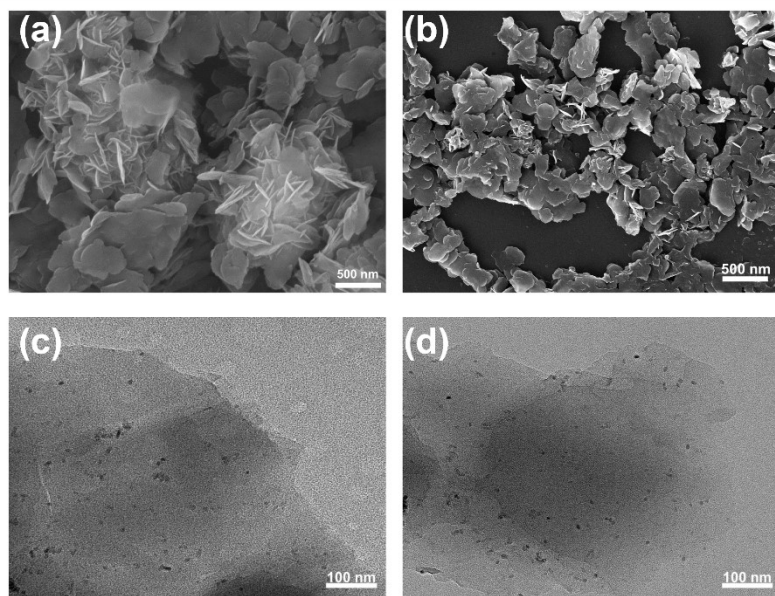


Figure S8. SEM and TEM images of Al-MOF@TiO<sub>2</sub> before and after the CO<sub>2</sub> photoreduction reaction. (a) and (c) SEM and TEM image of Al-MOF@TiO<sub>2</sub> before CO<sub>2</sub> photoreduction reaction; (d) and (e) SEM and TEM image of Al-MOF@TiO<sub>2</sub> after CO<sub>2</sub> photoreduction reaction.



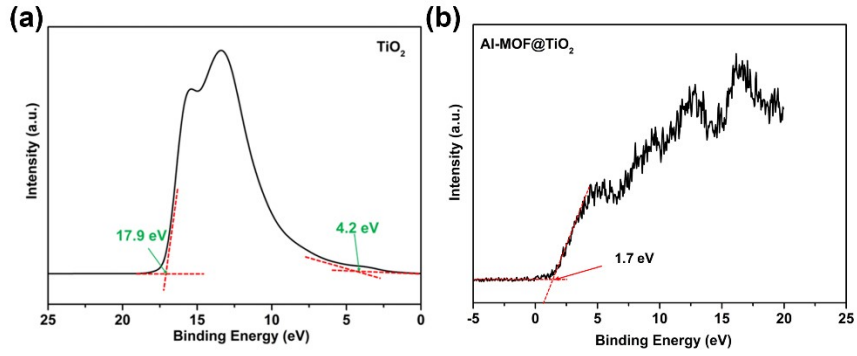


Figure S9. (a) UPS spectra of TiO<sub>2</sub>; (b) XPS valence band (VB) spectrum of Al-MOF.

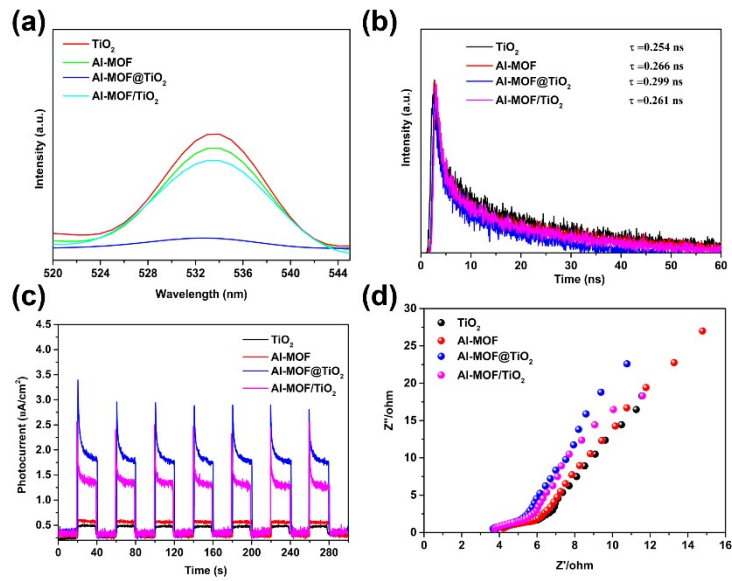


Figure S10. (a) photoluminescence spectroscopy (PL); (b) time-resolved photoluminescence; (c) spectroscopy photocurrent measurements and (d) electrochemical impedance spectroscopy test.

Table S1 The energy band information of TiO<sub>2</sub> and Al-MOF.

Sample	Band Gap (eV)	VB (eV)	CB (eV)
TiO <sub>2</sub>	3.10	2.67	-0.43
Al-MOF	2.68	1.7	-0.98

[1] L. Que, Z. Lan, W. Wu, J. Wu, J. Lin, M. Huang, Journal of Power Sources. 268 (2014) 670-676.