

A MOF Nanoparticle@Carbon Aerogel Integrated Photothermal Catalytic Microreactor for CO₂ Utilization

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Experimental section

Chemicals. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), potassium hydroxide (KOH) and 1,3,5-Benzenetricarboxylic acid (H_3BTC) were purchased from Energy Chemical (Shanghai). Carboxyl methyl cellulose (CMC) were purchased from Macklin Biochemical (Shanghai). Tetrabutylammonium bromide (TBAB) and styrene oxide were purchased from Sigma-Aldrich. 1, 4-dioxane and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in this work was deionized water. All chemicals used in this work were analytical grade and without further purification.

Fabrication of $\text{Cu}(\text{OH})_2@$ CMC aerogel. 56.1 mg KOH 330 mg was dissolved in 25 mL H_2O , and 124 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 5 mL H_2O . The $\text{Cu}(\text{OH})_2$ colloidal solution can be obtained by adding the CuSO_4 solution to the stirred KOH solution drop by drop. Then 495 mg CMC was dissolved in above $\text{Cu}(\text{OH})_2$ colloidal solution with stirring for 8 h to obtain the homogeneous mixed colloidal solution. And the $\text{Cu}(\text{OH})_2@$ CMC aerogel was formed after freeze-drying.

Fabrication of carbon aerogel ($\text{CuO}@$ CA). The $\text{Cu}(\text{OH})_2@$ CMC aerogels were subsequently annealed at 400 °C for 2 h under Ar atmosphere to obtain the carbon aerogel ($\text{CuO}@$ CA).

Fabrication of n-MOF@CA carbon aerogel. 14.5 mg ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 8.4 mg H_3BTC was dissolved in 1 mL mixed solvent of DMF and CH_3OH (V:V = 1:1). Then, the mixture is dripped and wetted onto the obtained $\text{CuO}@$ CA ($\sim 1 \text{ cm}^3$). And the carbon

aerogel with mixture subsequently was moved to the heating table at 120 °C, with the evaporation of the solvent, the carbon aerogel was dried to obtain n-MOF@CA carbon aerogel.

Catalytic ability of n-MOF@CA for CO₂ cycloaddition reaction. The n-MOF@CA was wetted by the mixture of 1.31 mmol styrene oxide and 0.1 mmol TBAB. And the n-MOF@CA was placed into a quartz vessel equipped with CO₂ atmosphere (1 atm). Then, the cycloaddition reaction system was irradiated with a Xe lamp for 12 h. After the reaction, the reactant was washed by 1,4-dioxane and analyzed by gas chromatography method.

Characterizations. Morphologies of samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi SU8010). The crystallographic information was analyzed by X-ray diffraction (XRD, PANalytical Empyrean) equipped with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The specific surface area was calculated by using the Brunauer-Emmett-Teller (BET, Micromeritics ASAP2020). The organic groups in the nanoporous metallic networks were characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70). Thermogravimetric analysis (TGA) was carried out with a thermobalance (TGA-2050, TA Instruments) under N₂ from room temperature to 600 °C with a temperature ramp of 10 °C min⁻¹.

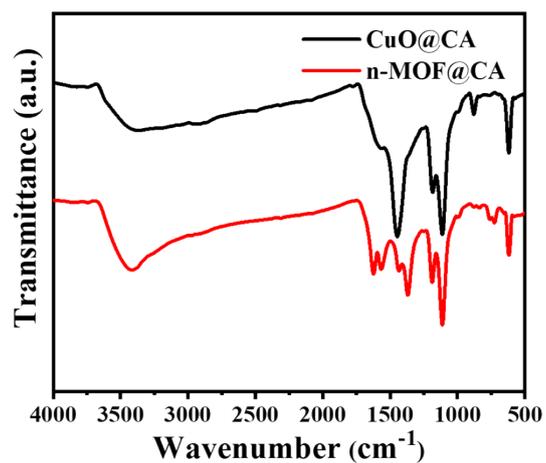


Fig. S1 FT-IR spectra of CuO@CA and n-MOF@CA.

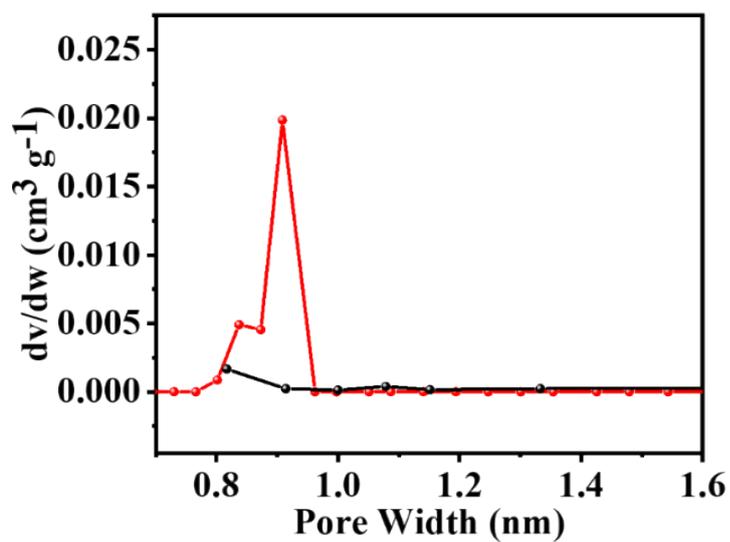


Fig. S2 The pore-size distribution curves of CuO@CA and n-MOF@CA.

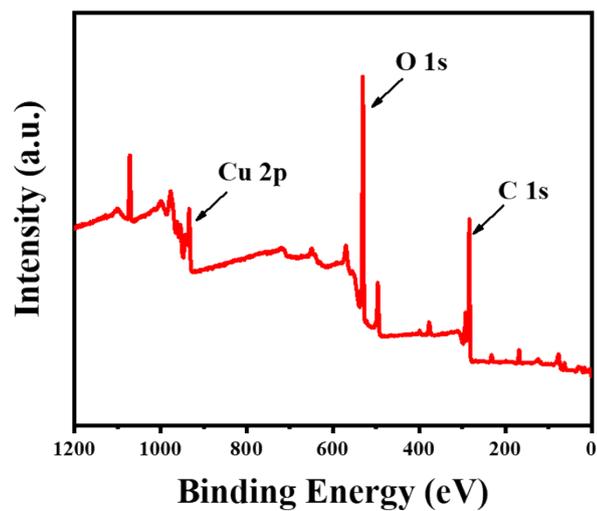


Figure S3. The XPS analysis of n-MOF@CA.

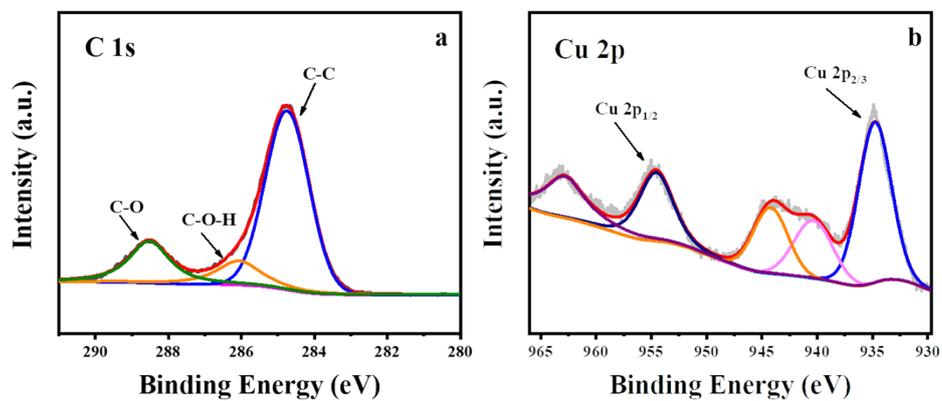


Fig. S4 The high resolution XPS spectra of n-MOF@CA at (a) C region and (b) Cu region.

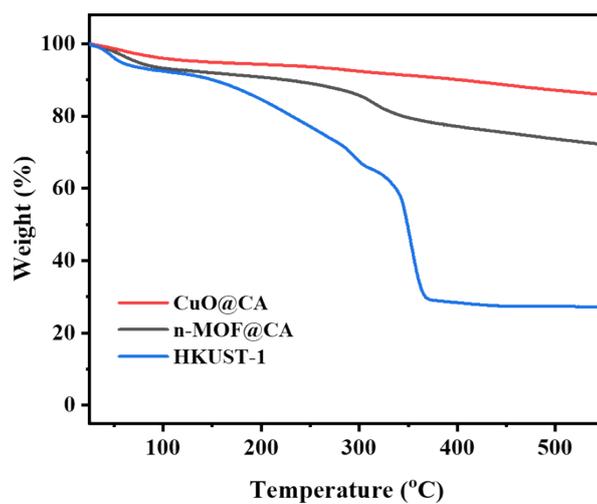


Fig. S5 The TGA curves of HKUST-1, CuO@CA and n-MOF@CA.

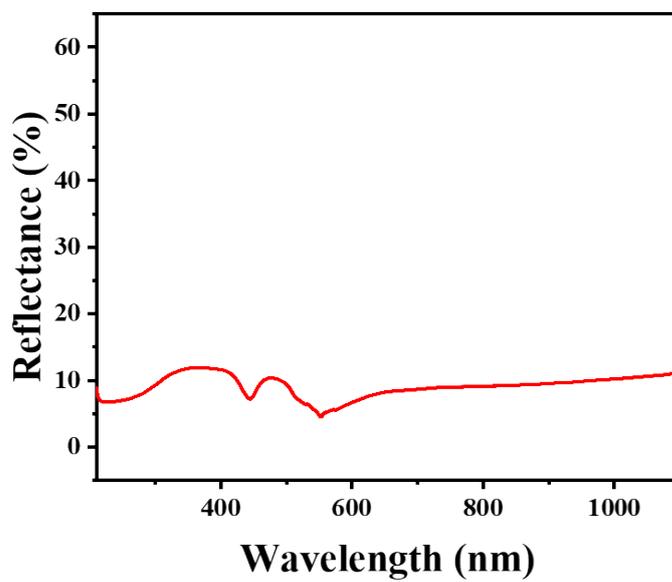


Fig. S6 Reflection spectrum of n-MOF@CA.

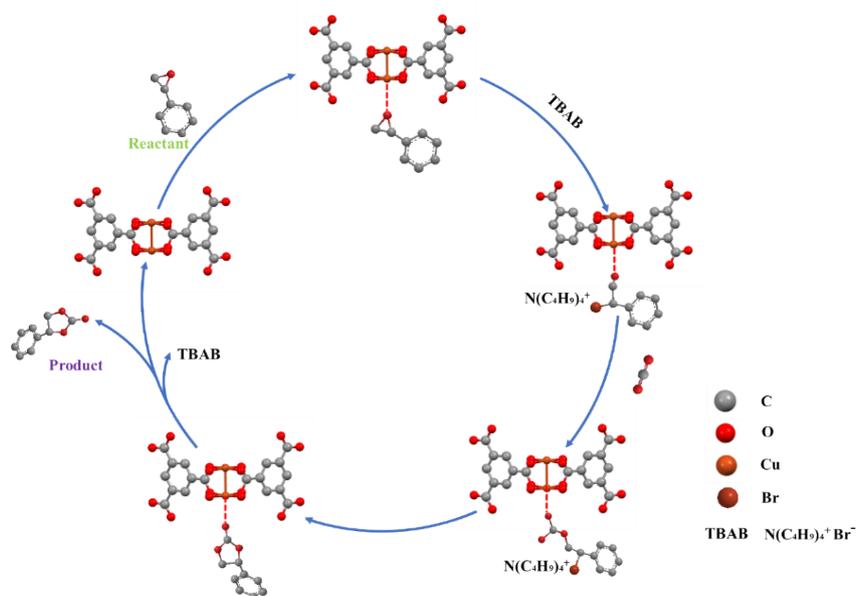


Fig. S7 Possible catalytic mechanism for CO₂ cycloaddition reaction by n-MOF@CA.