# **Supporting Information**

# Porous Copper/Zinc Bimetallic Oxides Derived from MOFs for Efficient Photocatalytic Reduction of CO<sub>2</sub> to Methanol

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### 1. Experimental Section

**Materials.** Copper acetate monohydrate, zinc acetate dihydrate were supplied by Sinopharm Chemical Reagent Co., Ltd. triethylamine (A.R. Grade), N,N-Dimethylformamide (A.R. Grade) and acetone (A.R. Grade) were obtained from Beijing Chemical Works. Deionized water was provided by Beijing Analysis Instrument Factory. Sodium sulfate( $\geq$  99.5%) and benzene-1,3,5-tricarboxylic acid( $\geq$  99.5%) were provided by Beijing J&K Chemicals Reagent Co., Ltd. N<sub>2</sub> (99.999%) and CO<sub>2</sub> (99.999%) were provided by Beijing Analysis Instrument Factory. Dimethyl sulfoxide-d6 (DMSO-d6, 99.8 atom % D, with 0.03%(V/V) TMS) was bought from Innochem Reagent Co., Ltd. All drugs were used directly without any required additional separation and purification.

**Synthesis of Cu/Zn-bimetal MOF.** A series of CuO with different zinc contents were synthesized by varying the dosage of copper acetate monohydrate and zinc acetate dihydrate used, while the other experimental conditions were the same. 0.4 mmol copper acetate monohydrate, 0.6 mmol zinc acetate dihydrate and 1 mmol benzene-1,3,5-tricarboxylic acid were added into 200 mL dimethylformamide keep stirring. After reaction for 3 d, the solid was separated by centrifugation, washed three times with dimethylformamide and ethanol and dried in a vacuum oven at 60 °C for 24 h. A series of MOF with different zinc contents were synthesized by the same procedure with Cu/Zn ratio of 6/4, 5/5, 4/6 and 2/8.

**Synthesis of bimetallic oxide with different zinc contents:** The ceramic ark containing 1.0g of MOF was placed in a muffle furnace and calcined in air for 1 hour. The heating procedure is as follows: the heating rate is maintained at 5 °C/min for 25 min to reach 150 °C and stay for 1.0 h to remove the left dimethylformamide. Then the heating rate is maintained at 3 °C/min for 70 min to reach 35 °C and stay for 1.0 h. After the above process, it was naturally cooled to room temperature directly to obtain the prepared sample, which was a gray-black powdery solid, and the color gradually became lighter with the increase of zinc oxide content.

**Characterizations.** X-ray diffraction (XRD) was determined by a Rigaku D/max-2500 (Tokyo, Japan) diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at 40 kV and 200 mA. The morphologies of samples were observed on scanning electron microscope (SEM, HITACHI S-4800, Tokyo, Chiyoda District, Japan), transmission electron microscope (TEM, JEOL JEM-1011, Tokyo, Shoshima city, Japan) and High resolution transmission electron

microscope (JEOL JEM-2100F) were also captured. The element contents of zinc was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, VISTA-MPX, Varian, California, USA).

Photocatalytic reduction of CO<sub>2</sub> to methanol. Photocatalytic CO<sub>2</sub> reduction experiment was carried out in a round bottomed flask. 10 mg of catalyst, 6 ml DMF, 2 ml triethylamine, and 2 ml water were added to a round bottom flask, and ultrasound treatment was performed for 10 s to form a mixed solution. Before the test, 0.5 h's supply of nitrogen gas was pumped into the flask to expel the air, followed by a half hour's supply of high-purity CO<sub>2</sub> gas to ensure that the entire test was conducted in a CO<sub>2</sub> atmosphere. The electrochemical measurement was implemented in a three-electrode system at electrochemical workstation (CHI660E, Chenhua Instrument, Shanghai, China) with the photocatalyst-coated indium-tin oxide (ITO) as the working electrode, an Ag/AgCl with 3.5 M KCl as a reference electrode and Pt net (1×1 cm) as the counter electrode. The illumination source adopted in photocurrent ON/OFF cycles was a 300 W Xe lamp with full spectrum. A 0.5 M Na<sub>2</sub>SO4 solution (pH = 6.8) was applied as electrolyte. To prepare the catalyst ink, 3 mg of the photocatalyst and 10 µL of 5 % Nafion 117 solution, as conducting binder, were introduced into 200 µL of ethanol and sonicated for 1 h. Then the catalyst ink was dropped on the surface of an ITO plate (1×1 cm) to prepare the working electrodes. All the potentials were recorded versus RHE. For the faradaic efficiency analysis, gas products were detected by gas chromatograph (GC, Agilent7890D, Palo alto, California, USA), which was equipped with FID and TCD detectors using argon as internal standard. The liquid product was analyzed by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy (Bruker Avance III 400 HD, Billerica, Massachusetts, USA). All experiments were performed at room temperature and atmospheric pressure.

Photocatalyst	Rate of Methanol Formation (µmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Ref.
CZ350	3710	This work
CNT/NiO/Fe <sub>2</sub> O <sub>3</sub>	2191	Ref.[1]
ZnFe <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	139	Ref.[2]
ZnFe <sub>2</sub> O <sub>4</sub> /TiO <sub>2</sub>	141	Ref.[3]
Bi2MoO6 quantum dots/rGO	84.8	Ref.[4]
Ag/ZnMn2O4	122	Ref.[5]
CeO <sub>2</sub> -N-G Cu <sup>2+</sup>	507	Ref.[6]
$Cs_2[Mo_6Br_{14}]$	278.3	Ref.[7]
rGO-CuO116	52	Ref.[8]
1%Cu-3%In2O3-TiO2	68	Ref.[9]
Cu <sub>2</sub> O/SiC	39	Ref.[10]

Table S1. A comparison of photocatalytic activity of CZ350 with other materials reported in the literature.



**Figure S1.** High-resolution XPS spectra of Zn 2p (a), Cu 2p (b) in the CZ350 catalyst.

### References

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