Supporting information for

Hierarchically macro-meso-microporous metal-organic framework for photocatalytic oxidation

Yufei Sha,[a, b] Jianling Zhang,*[a, b, c] Dongxing Tan,[a, b] Fanyu Zhang,[a, b] Xiuyan Cheng,[a, b] Xiuniang Tan,[a, b] Bingxing Zhang,[a, b] Buxing Han,[a, b, c] Lirong Zheng,[d] Jing Zhang,[d]

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R.China.

[b]School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, P.R.China.

[c]Physical Science Laboratory, Huairou National Comprehensive Science Center, Beijing 101400, P.R.China.

[d]Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P.R.China.

*Corresponding author e-mail: zhangjl@iccas.ac.cn

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Experimental

Materials.

Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, 99%), 2,2'-bipyridine-5,5'-dicarboxylic acid (bpydc, 97%), 4-chlorobenzylamine (98%), 4-fluorobenzylamine (97%) were supplied by Beijing Innochem Science & Technology Co., Ltd. Benzylamine (99%) and 4-methylbenzylamine (98%) were provided by Acros. CO_2 (> 99.95%) was purchased from Beijing Analysis Instrument Factory. N,N-dimethylformamide (DMF, A. R. grade), methyl sulfoxide (DMSO, A. R. grade) and ethanol (A. R. grade) were produced by Beijing Chemical Works. All chemicals were used directly without additional purification.

Synthesis of Zn-bpydc.

Typically, $Zn(OAc)_2 \cdot 2H_2O$ (0.4 mmol) and bpydc (0.1 mmol) were added into 5 mL DMF, which was loaded in a stainless steel autoclave (30 mL). CO_2 was charged into the autoclave under stirring until the desired pressure was reached. The mixture was magnetically stirred at 35 °C for 24 h. Then CO_2 was released and the solid product was obtained after centrifugation, washing with DMF and ethanol and drying at 25 °C under vacuum for 12 h.

Characterizations.

The morphologies of the obtained materials were characterized by scanning electron microscope (SEM, HITACHI S-4800), transmission electron microscope (TEM, JEOL-1011). X-ray diffraction (XRD) was carried out via a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) was performed on VG Scientific ESCALab220i-XL spectrometer using Al Ka radiation. Fourier transform infrared (FT-IR) spectra were obtained using a Bruker Tensor 27 spectrometer. Ultraviolet visible diffused reflectance spectrum (UV-Vis DRS, UV-2600, SHIMADZU) was recorded within the wavelength range of 220-800 nm, and $BaSO_4$ was used as the reference material. The porosity properties of samples were derived from N_2 adsorption-desorption isotherms at 77 K using an autosorb-iQ system. X-ray absorption fine structure (XAFS) measurement for Zn K-edge was carried out at room temperature at 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. The raw data of XAFS were processed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6. Data were processed with k^3-weighting and a Rbkg value of 1.0. Normalized XANES data were obtained directly from the Athena program of the IFEFFIT package.

Electrochemical measurements.

Photoelectrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China), using a standard three-electrode system. The photocatalyst-coated ITO glass, graphite electrode (i.d. = 0.4 mm) and Ag/AgCl with 3.5 M KCl served as the working electrode, counter electrode and reference electrode, respectively. For the preparation of working electrodes, 10 mg of Zn-bpydc photocatalyst was dispersed into 200 µL ethanol solution containing 20 µL of 5 wt.% Nafion. After ultrasonicated for 30 min, the suspension (200 µL) was coated onto the surface of an ITO glass (1.5 cm^2) with a uniform and similar thickness. The progress was measured in 0.5 M Na_2SO_4 solution, using a full spectrum 300 W Xe lamp as light source.

Photocatalytic oxidation of amines.

In a typical experiment, the Zn-bpydc (10 mg) was dispersed in 5 mL DMF, followed by the addition of 0.5 mmol amine. The reaction mixture was stirred under air atmosphere in a 100 mL round-bottom flask for 15 min. Then the flask was sealed with a rubber plug and stirred at 25 °C in a water bath. A full spectrum 300 W Xe lamp was used as light source. After a required reaction time, the Zn-bpydc was removed from the solution by centrifugation and the liquid mixture was analyzed by ^{1}H NMR using DMSO-d_6 as the internal standard. The turnover frequency (TOF) values were calculated as the moles of products divided by the mass of photocatalyst and the reaction time.

Results and Discussion

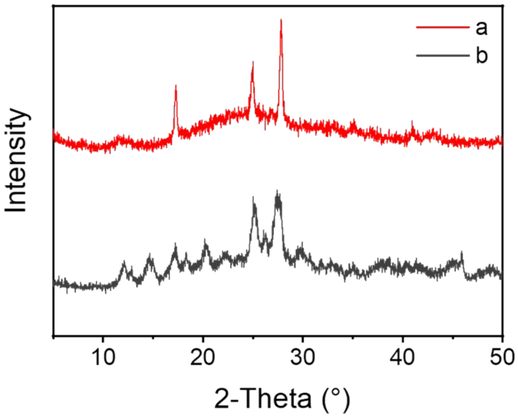

Fig. S1 XRD patterns of the Zn-bpydc synthesized in CO_2-expanded DMF at 4.5 MPa (a) and reported in literature (b).

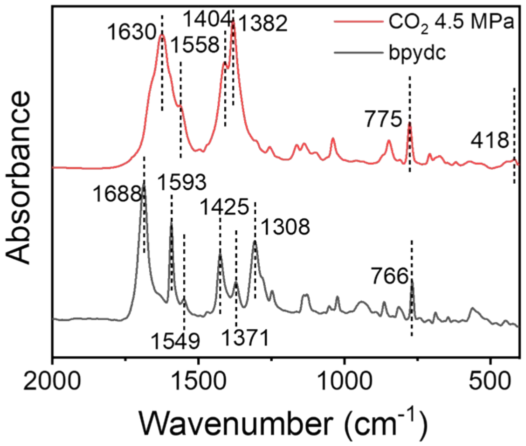

Fig. S2 FT-IR spectra of the Zn-bpydc synthesized in CO$_2$-expanded DMF at 4.5 MPa and bpydc.

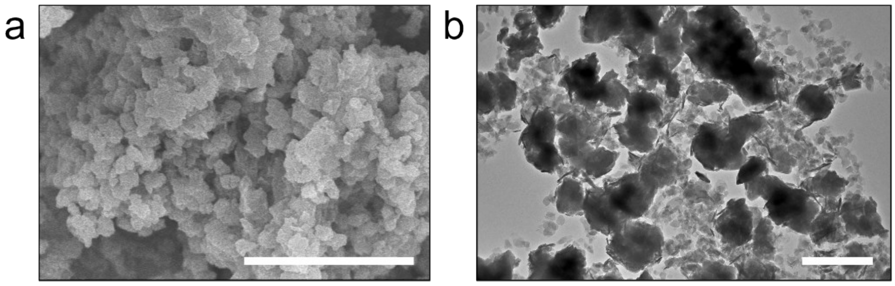

Fig. S3 SEM (a) and TEM (b) images of the sample synthesized in pure DMF. Scale bars: 5 µm in (a), 1 µm in (b).

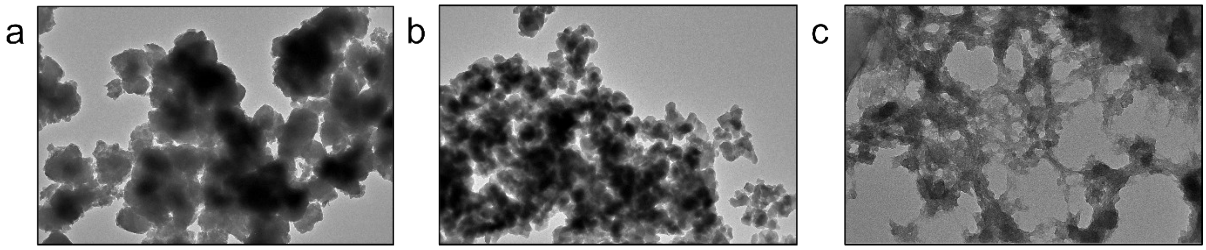

Fig. S4 TEM images of the samples synthesized in CO_2-expanded DMF at different pressures. (a) 1.5 MPa, (b) 3.0 MPa, (c) 6.5 MPa. Scale bars, 500 nm in (a), 500 nm in (b), 200 nm in (c).

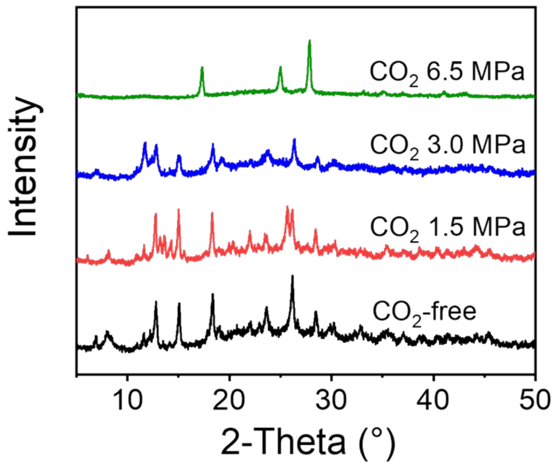

Fig. S5 XRD patterns of the samples synthesized in pure DMF and CO_2-expanded DMF at different pressures.

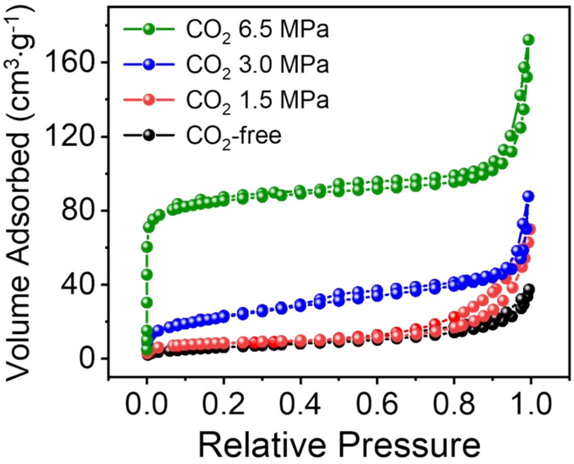

Fig. S6 N_2 adsorption-desorption isotherms of the samples synthesized in CO_2-expanded DMF at different pressures.

Table S1 Catalytic performances of various photocatalysts in the photocatalytic oxidation of benzylamine.

Entry	Catalysts	Conditions	Conv. (%)	Sel. (%)	TOF (umol·g^{-1}·h^{-1})	Ref.
1	Zn-bpydc (4.5 MPa)	25 °C, air, 4 h, benzylamine 0.5 mmol, Zn-bpydc 10 mg, DMF 5 mL, 300 W Xe lamp.	99.7	> 99	6231	This work
2	TiO_2	RT, air, 9 h, benzylamine 0.1 mmol, catalyst 10 mg, CH_3CN 5 mL, 100 W Hg lamp (> 300 nm)	99	85	472	[1]
3	HNb_3O_8	25 °C, air, 6 h, benzylamine 0.25 mmol, catalyst 10 mg, CH_3CN 1.5 mL, visible light.	95	99	1959	[2]
4	Cd(dcbpy)	25 °C, air, 7 h, benzylamine 0.48 mmol, catalyst 10 mg, DMF 5 mL, 300 W Xe lamp	99.1	> 99	3398	[3]
5	$Ru(bpy)_3$@MIL-125	RT, air, 3 h, benzylamine 0.1 mmol, catalyst 5 mg, CH_3CN 3 mL, visible light (> 440 nm).	> 99	> 99	3333	[4]
6	PCN-222	RT, air, 1 h, benzylamine 0.1 mmol, catalyst 5 mg, CH_3CN 3 mL, Xe lamp (> 420 nm)	100	100	10000	[5]

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