

The facile preparation of mixed-valence metal-organic frameworks through reduction

*Yunshi Wang, Cen Chen, and Liying Zhang**

Address: Department of Chemistry, College of Sciences, Northeastern University,
Shenyang 110819, P. R. China

E-mail: zhangliying@mail.neu.edu.cn

Experimental

Materials: Copper(II) nitrate trihydrate, 1,3,5-benzenetricarboxylic acid (BTC), hydrazine hydrate aqueous solution ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, 85%), N,N-dimethylformamide (DMF), hydrochloric acid (HCl), methanol (MeOH), and ethanol (EtOH) were all purchased from Sinopharm Chemical Reagent Co. Ltd. Amyl acetate, benzyl azide and phenylacetylene were sourced from Macklin. Pure water was obtained from Shenyang Wahaha Group Co. Ltd. All reagents and solvents were employed without additional purification.

Preparation of small-size HKUST-1 (S): 3.5 g copper(II) nitrate trihydrate and 1.75 g BTC were separately dissolved in 100 mL MeOH. The two solutions were mixed and stirred at room temperature for 2 h. The resulting blue precipitates were washed with MeOH for three times and dried under vacuum at 85 °C for 10 h.

Preparation of large-size HKUST-1 (B): 628 mg copper(II) nitrate trihydrate and 273 mg BTC were dissolved in a mixed solvent of 5 mL DMF and 5 mL EtOH. The solution was sonicated for 20 min. Then 5 mL H_2O was added to the mixture and about 70 μL 12 mol/L HCl were added until the solution turned clear blue. The mixture solution was heated to 85 °C for 24 h. After being washed with DMF and EtOH for three times, the obtained blue crystals were filtered and dried under vacuum at 120 °C for 10 h.

Reduction process: 50 mg HKUST-1 (S or B) was dissolved in 10 mL EtOH at room temperature. Hydrazine hydrate was added to reduce HKUST-1 for 2 h. Subsequently, the reduction products were filtered and washed with EtOH, then vacuum dried at 60 °C for 12 h. The volume of hydrazine hydrate was 50 μL and 100 μL , and the reduction products were designed as S50 and S100 from S, and B50 and B100 from B, respectively.

Catalytic Test: The Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC) was catalyzed by the reduction products and HKUST-1 (S and B). 10 mg catalyst was added to a Schlenk tube, 4 mL ethanol as solvent and 1 mmol amyl acetate as internal standard. Then 1 mmol benzyl azide and 2 mmol phenylacetylene were added as reactants. The reaction mixture was stirred at 80 °C for 3 h. After reaction, the yield of products was determined by gas chromatography (GC). ^1H NMR spectroscopy was used to confirm the structure of the product.

Characterization: Scanning electron microscopy (SEM) images was acquired using a Hitachi SU8010. X-ray diffraction (XRD) was captured on a Shimadzu XRD-6000. Fourier transform infrared (FT-IR) spectroscopy was recorded with a Bruker Vertex 70. X-ray photoelectron spectroscopy (XPS) spectra was recorded with a Thermo Scientific K-Alpha. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA-2050 thermobalance under N_2 atmosphere with heating rate of 10 °C/min from room temperature to 600 °C. The N_2 adsorption-desorption isotherms was determined by Micromeritics

ASAP 2020 system at 77 K. Gas chromatography (GC) was performed on a SP-3420A. ^1H nuclear magnetic resonance (^1H NMR) spectra was obtained using a Bruker Ascend TM 600 MHz.

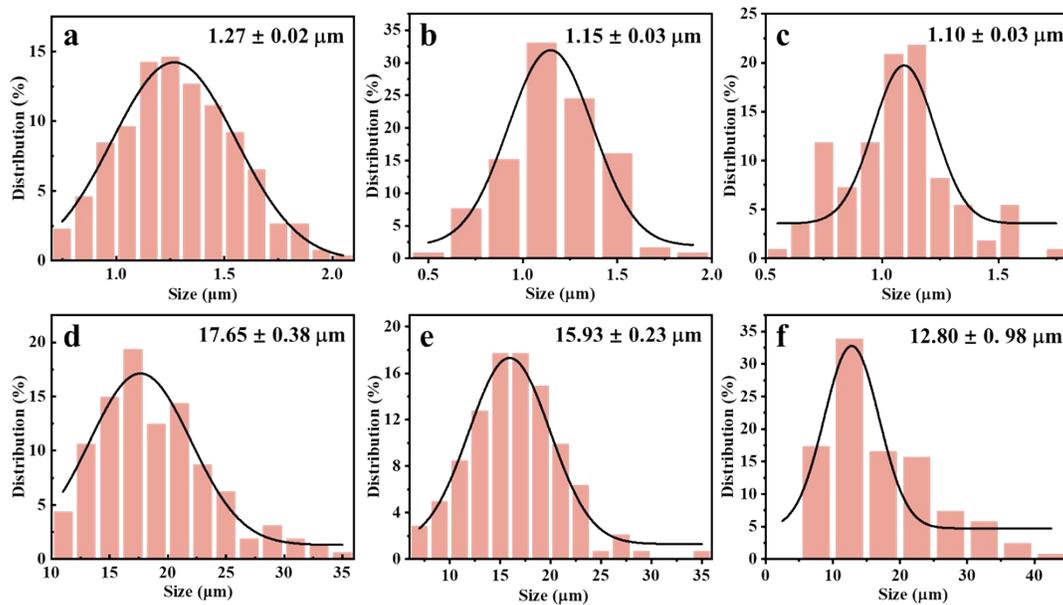


Figure S1. Histograms of lateral dimension distribution of (a) S, (b) S50, (c) S100, (d) B, (e) B50 and (f) B100.

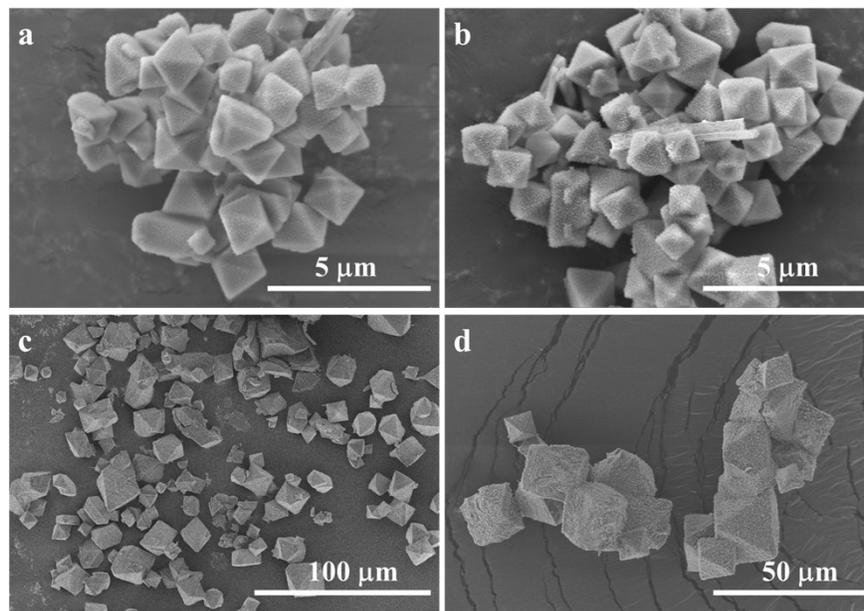


Figure S2. SEM images of (a) S50, (b) S100, (c) B50 and (d) B100.

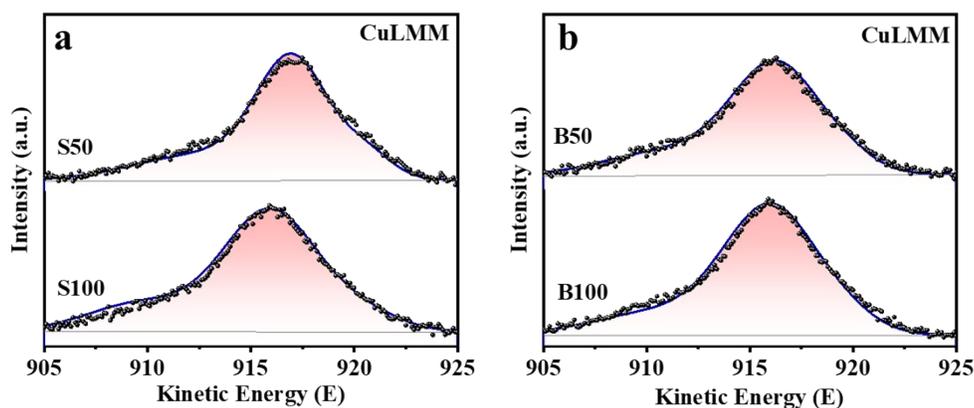


Figure S3. Cu LMM spectra of (a) S50 and S100 and (b) B50 and B100.

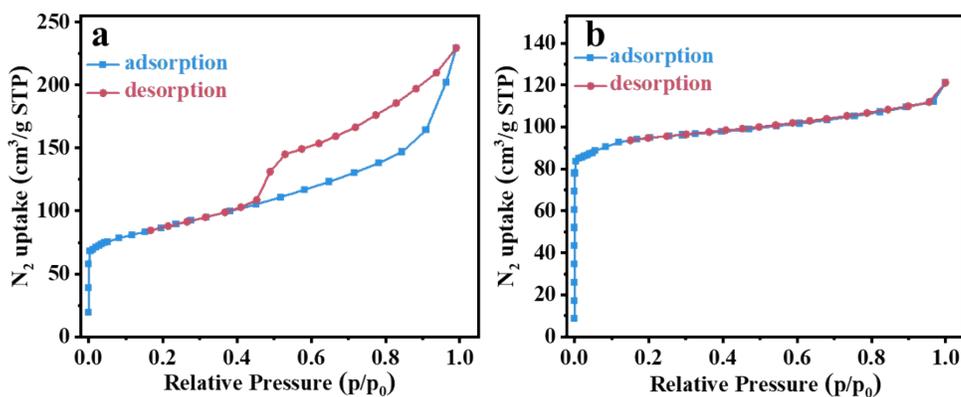


Figure S4. N₂ absorption/desorption isotherms of (a) S and (b) B.

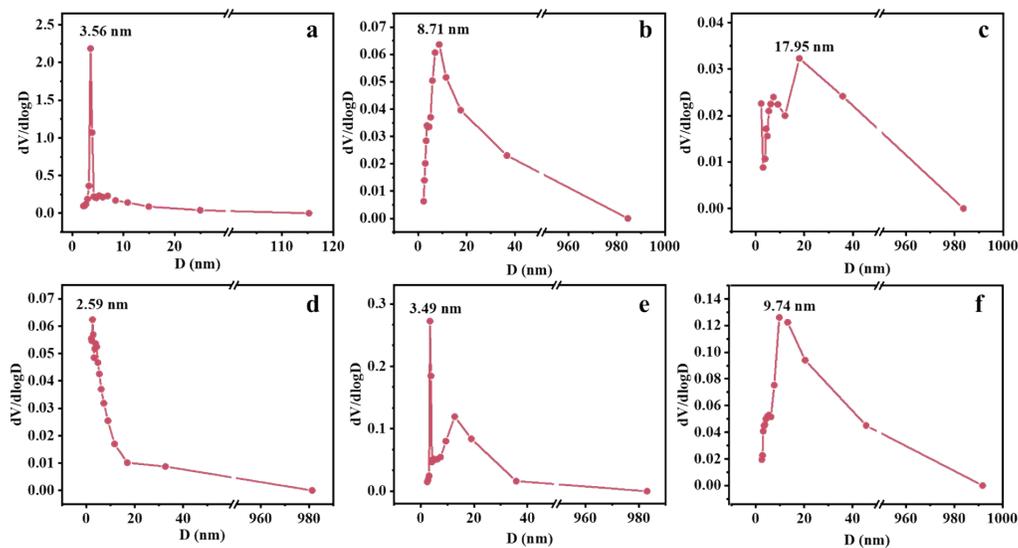


Figure S5. Pore size distribution curves of (a) S, (b) S50, (c) S100, (d) B, (e) B50 and (f) B100.

Table S1. The specific surface area of the reduction products.

Sample name	S	S50	S100	B	B50	B100
Specific surface area (m ² /g)	315.8	11.0	7.5	360.5	94.5	17.1

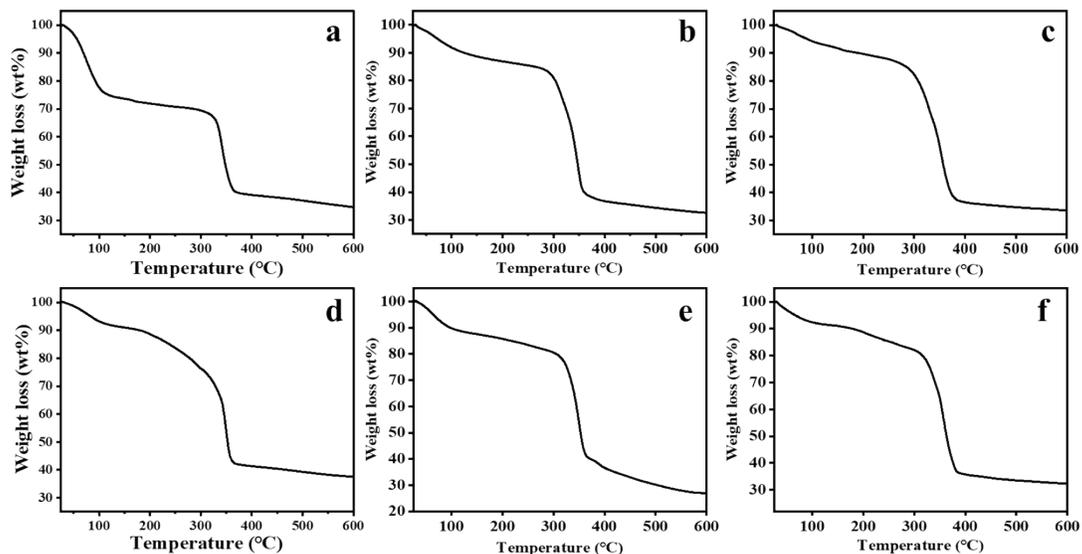


Figure S6. The TGA curves of (a) S, (b) S50, (c) S100, (d) B, (e) B50 and (f) B100.

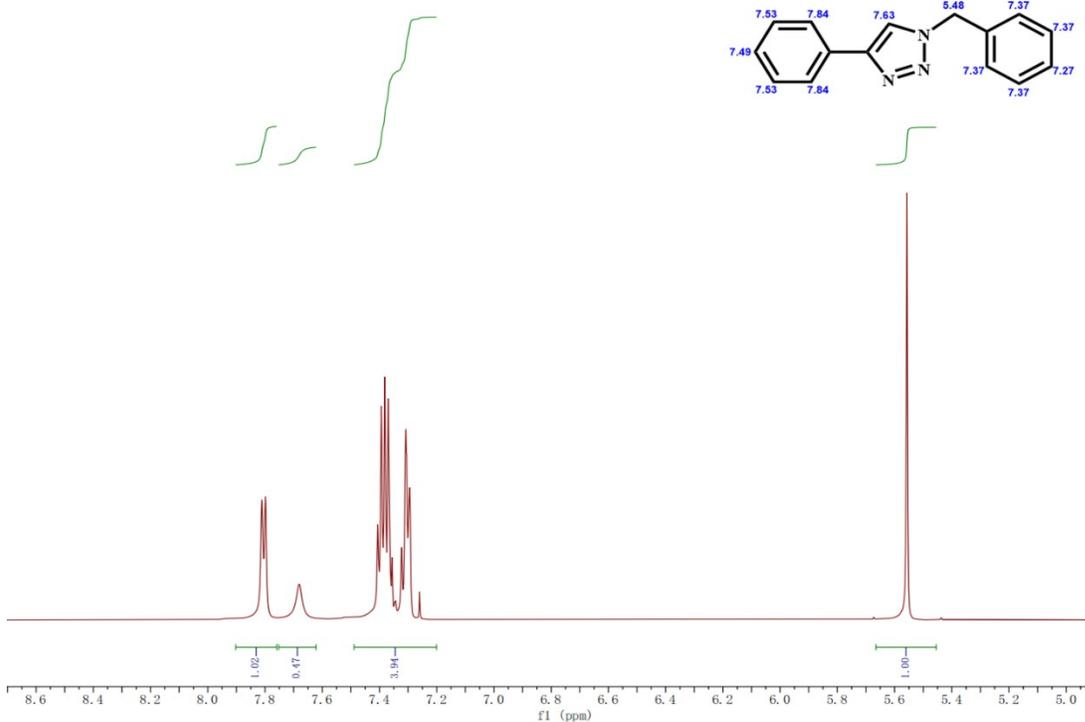


Figure S7. ¹H NMR spectrum of the product 1-benzyl-4-phenyl-1H-1,2,3-triazole.

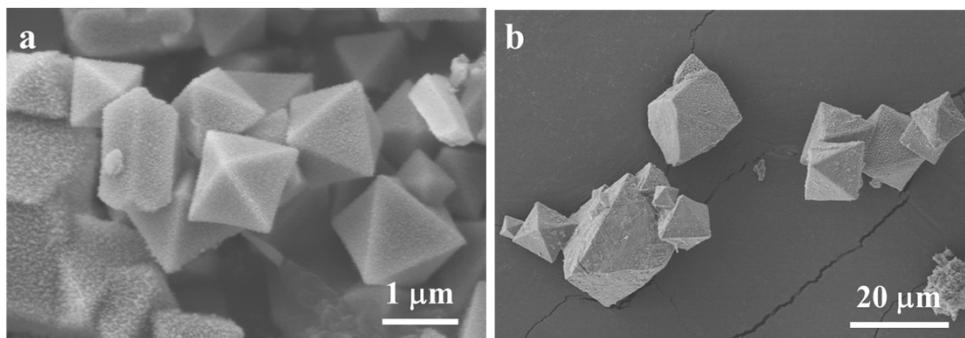


Figure S8. SEM images of (a) S50 and (b) B100 after catalytic reaction.

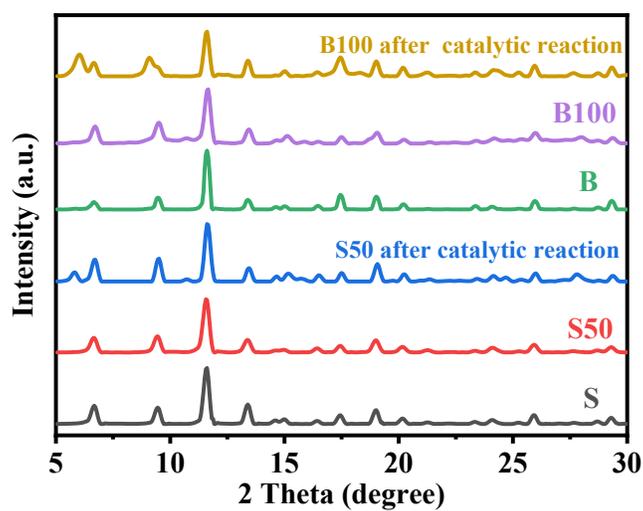


Figure S9. XRD patterns of S, S50, S50 after catalytic reaction, B, B100 and B100 after catalytic reaction.