Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Controllable synthesis of urchin-like hierarchical superstructure MOFs with high catalytic activity and stability

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1. Experimental section

Materials

All chemicals, copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%), cobaltous nitrate hexahydrate ($Co(NO_3)_3 \cdot 6H_2O$), manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$), nano copper oxide (99.9%), micro cuprous oxide (99.9%), nano basic cupric carbonate (99.9%), N,N-dimethylformamide (DMF, 99.5%), ethanol(99.9%), 2-propanol (99.9%) and methanol (99.9%) was purchased from Sinopharm without further purification. 2,5-dihydroxyterephthalic acid (H_2DHTP, 98%), sodium borohydride ($NaBH_4$, 99.5%) was purchased from Aladdin without further purification.

Synthesis of nanosized metal oxide

Cu_2O nanocube was prepared by adding 60 mL aqueous solution containing 1.2 g $NaBH_4$ dropwise into a 0.08 M $Cu(NO_3)_2$ solution under vigorous stirring for 10 min. The black precipitate was washed with water four times and ethanol twice, following by being dried in a vacuum oven at 50 °C. The nanosize cobalt oxide and manganese oxide were prepared by changing the $Cu(NO_3)_2$ with relevant nitrite salt.

Nano cobalt oxide and manganese oxide were synthesized by replacing the $Cu(NO_3)_2$ solution with $Co(NO_3)_3$ and $Mn(NO_3)_2$ solution.

Conventional synthesis of MOFs using metal salts

Bulk Cu-MOF-74 was synthesized according to literature with some modification[1]. 360.9 mg $Cu(NO_3)_2 \cdot 3H_2O$ and 148.6 mg H_2DHTP was dissolved in 15 mL DMF. After stirring for 15min, the mixture was transferred into an autoclave and heated for 18h at 85 °C. Dark brown solid powders were collected from the bottom of the Teflon-lined autoclave and were washed with methanol six times. The final products were dried in a vacuum oven at 80 °C for 8h.

Bulk CoBTC was synthesized according to literature with some modification[2]. 727.5 mg Co $(NO_3)_2 \cdot 6H_2O$ and 265.5 mg H_3BTC was dissolved in a mixture of 5 mL DMF, 5 mL ethanol and 5 mL H_2O. After stirring for 15min, the mixture was transferred into an autoclave and heated for 20h at 80 °C. The final product was washed with methanol six times and dried in a vacuum oven at 80 °C for 8h.

Bulk MnBTC was synthesized by dissolving 251 mg $Mn(NO_3)_2 \cdot 6H_2O$ and 210 mg H_3BTC in a mixture of 3 mL DMF, 3 mL ethanol and 3 mL H_2O. After stirring for 15min, the mixture was transferred into an autoclave and heated for 24h at 120 °C. The final product was washed with methanol six times and dried in a vacuum oven at 80 °C for 8h.

Synthesis of MOFs using metal oxides

The general procedure to prepare Cu-MOF-74 with copper oxide consisted of adding a specific amount of copper complex depending on the selected molar ratio R (R = $[H_2DHTP]/[2Cu_2O]$, 0.75 , 1.25 and 2) dissolved in 10 mL H_2DHTP (0.1M) solution containing 8 mL DMF and 2mL 2-propanol. After stirring for 30min, the mixture was transferred into a stainless-steel autoclave and was heated at 85 °C for 18h. Dark brown solid powders were collected from the bottom of the

Teflon-lined autoclave and were washed with methanol six times. The final products were dried in a vacuum oven at 80 °C for 8h.

The general procedure to prepare Co-BTC with cobalt oxide consisted of mixing 31.3 mg as-prepared cobalt oxide with a specific amount of H_3BTC (32.8mg, 43.9mg and 65.6mg) in a mixed solution of 5 mL DMF, 5 mL ethanol and 5 mL H_2O. After stirring for 30min, the mixture was transferred into a stainless-steel autoclave and was heated at 85°C for 20h. The final product was washed with methanol six times and dried in a vacuum oven at 80 °C for 8h.

The general procedure to prepare Mn-BTC with manganese oxide consisted of mixing 88 mg as-prepared cobalt oxide with a specific amount of H_3BTC (210 mg, 280 mg and 350 mg) in a mixed solution of 3 mL DMF, 3 mL ethanol and 3 mL H_2O. After stirring for 30min, the mixture was transferred into a stainless-steel autoclave and was heated at 120°C for 24h. The final product was washed with methanol six times and dried in a vacuum oven at 80 °C for 8 h.

Characterization

The X-ray diffraction spectra (XRD) were conducted on an Empyrean X-ray Diffractometer (60 kV, 4 kW) under Cu Kα radiation (λ=0.15406 nm) with a scanning rate of 1 °/min. Scanning electron microscope images were obtained by a Zeiss Ultra Plus scanning electron microscopy. Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer Instruments STA 6000 Thermo Gravimetric Analyser with a heating rate of 5 °C from 30 to 800 °C under Air. The ICP-OES analysis was carried out on a Prodigy7 of LEEMAN LABS. Gas sorption isotherms were carried out on a Micromeritics TriStar II 3020. The N_2 sorption measurement was maintained at 77 K after degassing at 150 °C for 12 h. Total specific surface areas were calculated by the BET method. X-ray photoelectron spectra (XPS) were obtained by a Kratos Axis Ultra X-ray Photoelectron spectrometer with a monochromatic Al Kα (1486.6 eV) radiation at 150 W (15 kV, 10 mA). The binding energies were calibrated by the C 1s peak of adventitious carbon at 284.8 eV as a reference.

Catalyst activity evaluation

The prepared catalysts were evaluated in a fixed-bed quartz reactor (inner diameter: 9mm) equipped with a temperature-programming controller. In a typical run, 0.5g catalysts mixed with quartz sand (6g coarse SiO_2 particles and around 12g fine SiO_2 particle) were placed in the quartz reactor (bed height is 195mm) between two asbestos plugs and pretreated with N_2 at a flow rate of 400ml/min for 30 min at 150 °C to remove the moisture in the sample. After colling down to room temperature, mixed flue gas was injected from the top of the reactor at a flow rate of 1250 mL/min (the gas hourly spece velocity is 6045 h^{-1}), including 0.1% NO, 0.1% NH_3, 5% O_2 and N_2 as the balance gas. The temperature increased from 100 to 260 °C to measure the concentration of NO and NO_x, which was recorded with a portable Gas Analyzer (PG-300).In order to test the stability of the catalyst at operating temperature, the catalysts were reused for 5 times at 220°C for 30min during each run.

NO conversion was calculated by the following equation:

$$C_{NO}\% = \frac{[NOx]_{inlet} - [NOx]_{outlet}}{[NOx]_{inlet}} \times 100$$

2. Figures and Tables

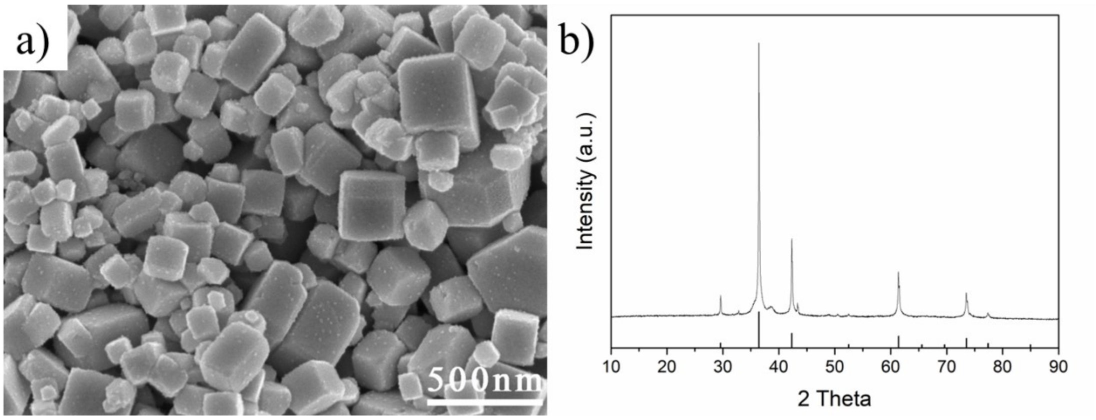

Figure S1. (a) SEM image and (b) XRD pattern (bottom column is peaks of simulated Cu_2O) of nanocube Cu_2O which was used for the synthesis of CuMOF-74-M, CuMOF-74-N and CuMOF-74-U.

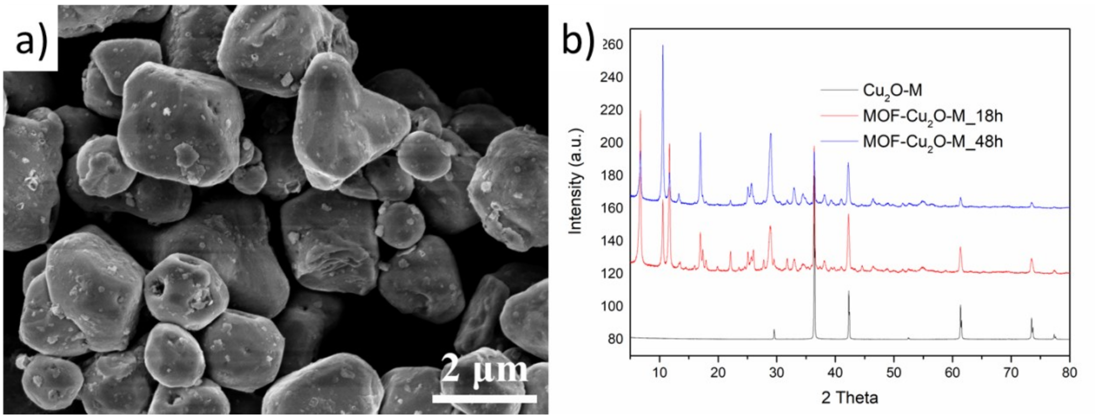

Figure S2. (a) SEM image of Cu_2O-M and (b) XRD patterns of Cu_2O-M and MOFs samples synthesis by Cu_2O-M with different reaction time.

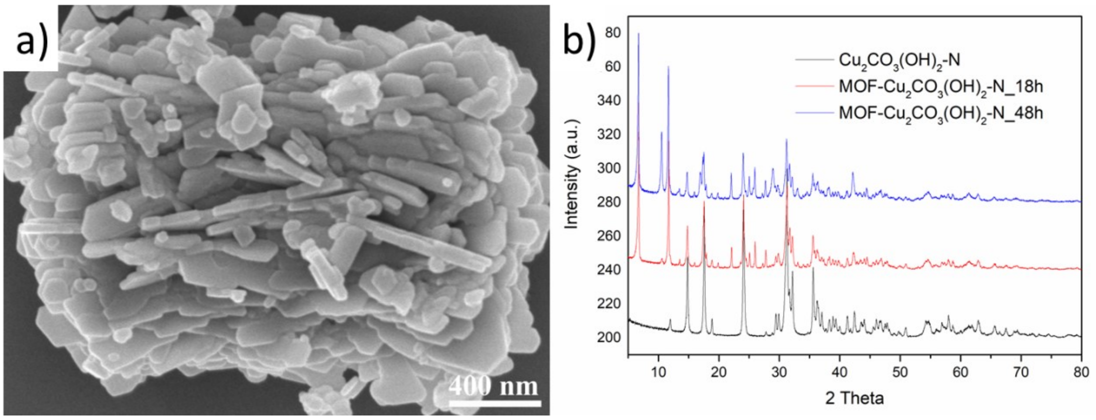

Figure S3. (a) SEM image of nanosized $Cu_2CO_3(OH)_2$ and (b) XRD patterns of $Cu_2CO_3(OH)_2$ and MOFs samples synthesis by $Cu_2CO_3(OH)_2$ with different reaction time.

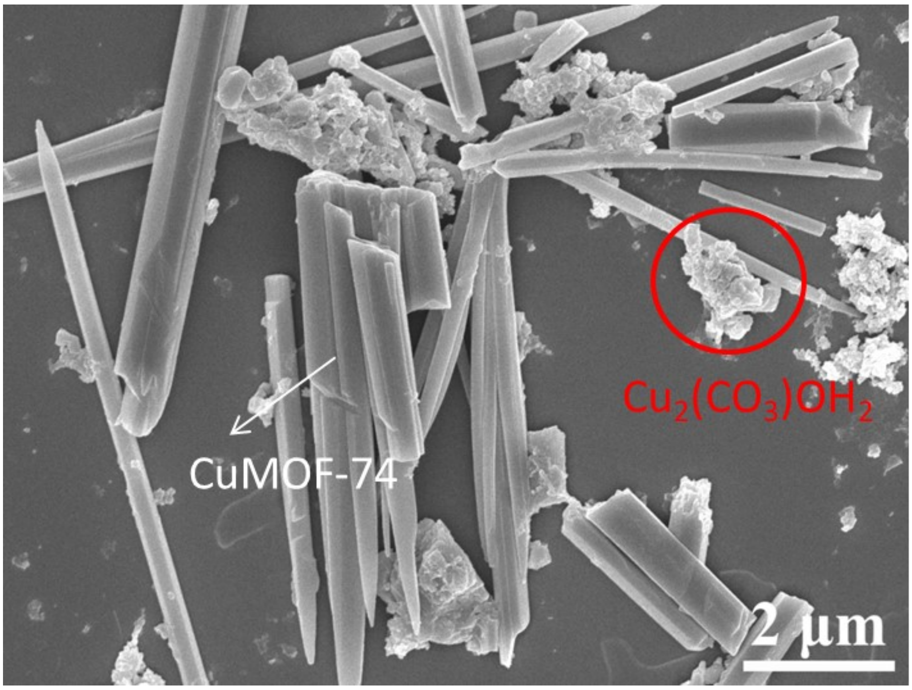

Figure S4. SEM image of MOF-$Cu_2CO_3(OH)_2$_18 h shows that the $Cu_2CO_3(OH)_2$ is not fully converted to CuMOF-74.

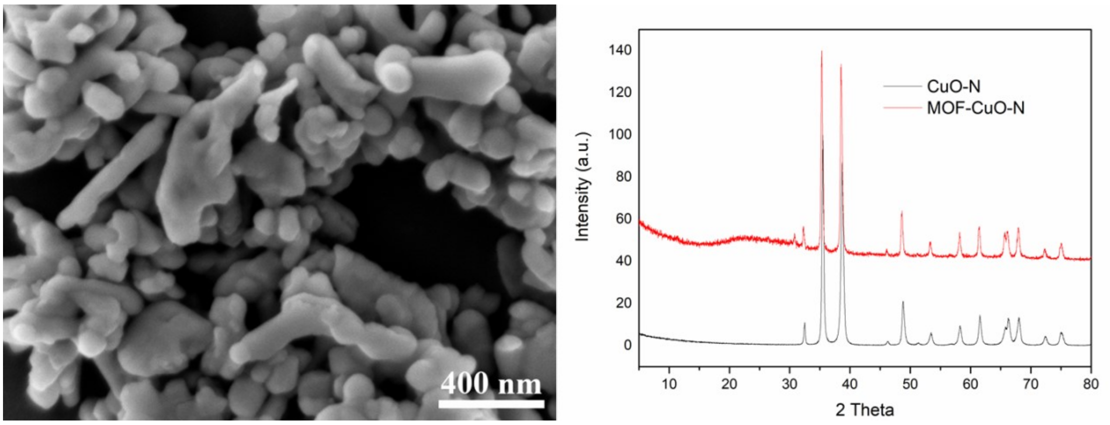

Figure S5. (a) SEM image of nanosized CuO (CuO-N) and (b) XRD patterns of CuO-N and MOFs samples synthesis by CuO-N after reaction for 48 h.

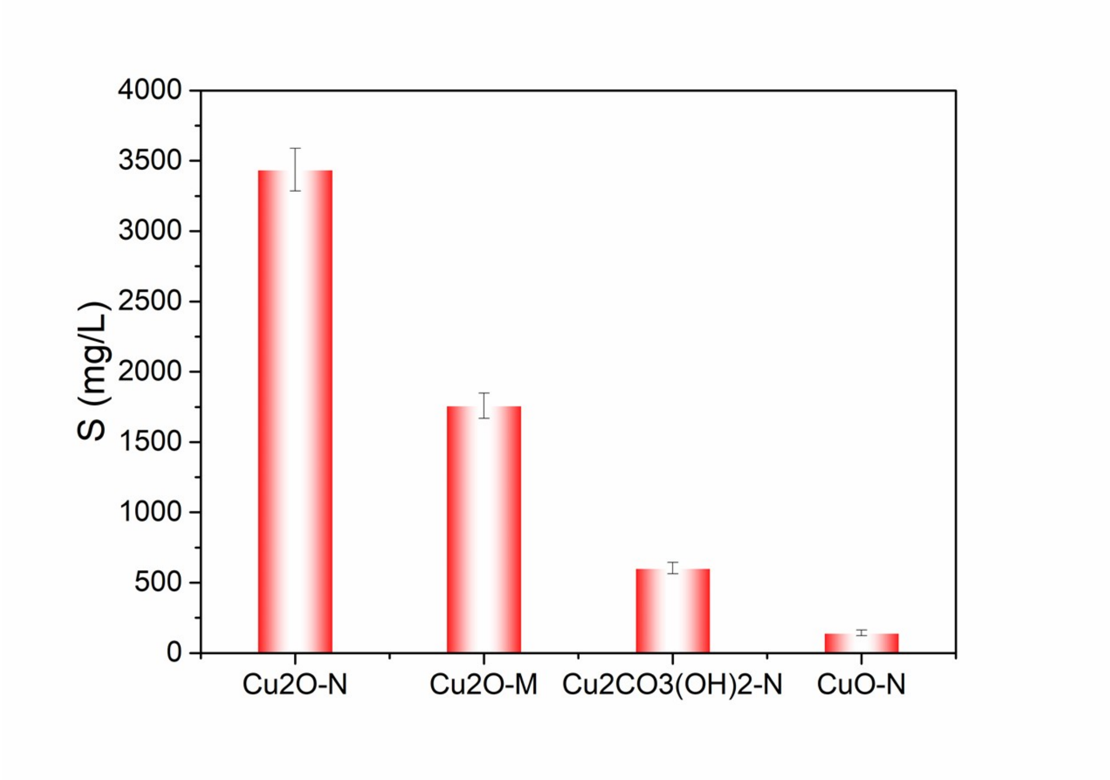

Figure S6. ICP results shown the solubility of Cu_2O-N, Cu_2O-M, $Cu_2CO_3(OH)_2$-N and CuO-N

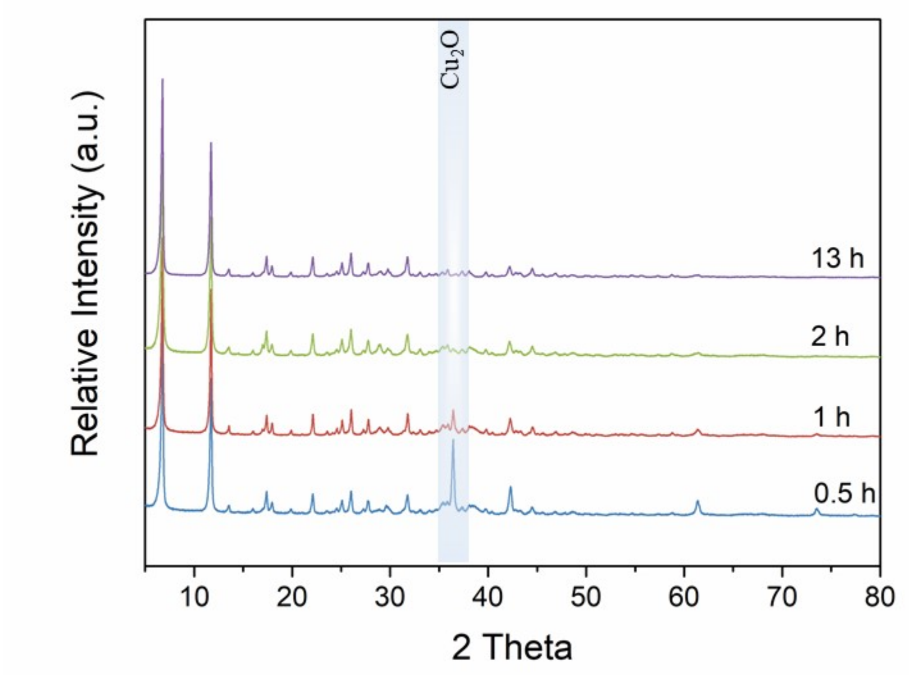

Figure S7. XRD patterns of CuMOF-74 after reaction for different time

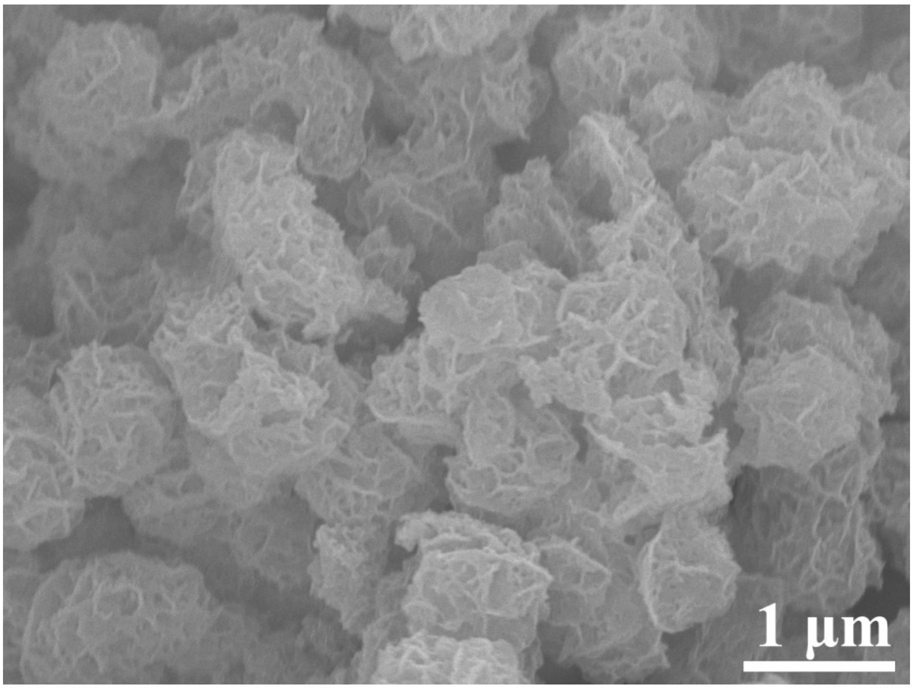

Figure S8. SEM image of Co-ONS

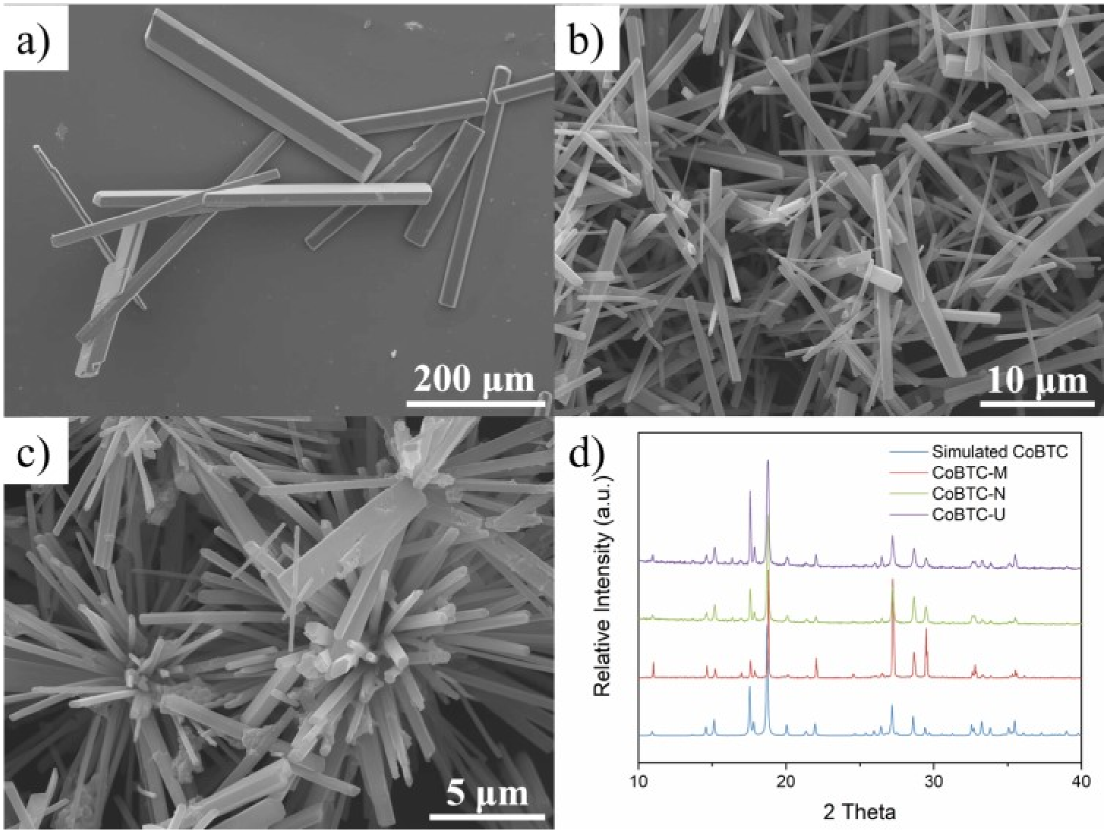

Figure S9. The SEM images of (a) microrod CoBTC (CoBTC-M), (b) nanorod CoBTC (CoBTC-N), and (c) urchin-shaped CoBTC (CoBTC-U). (d) The XRD patterns of the as-prepared CoBTC samples.

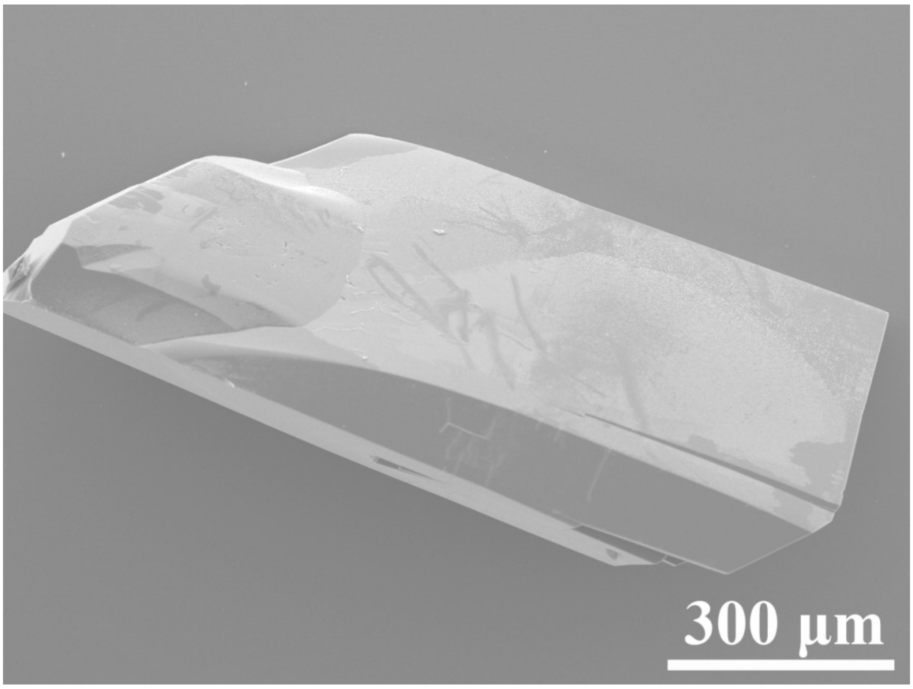

Figure S10. SEM image of bulk CoBTC (CoBTC-B) synthesized by using cobalt nitrate as metal source.

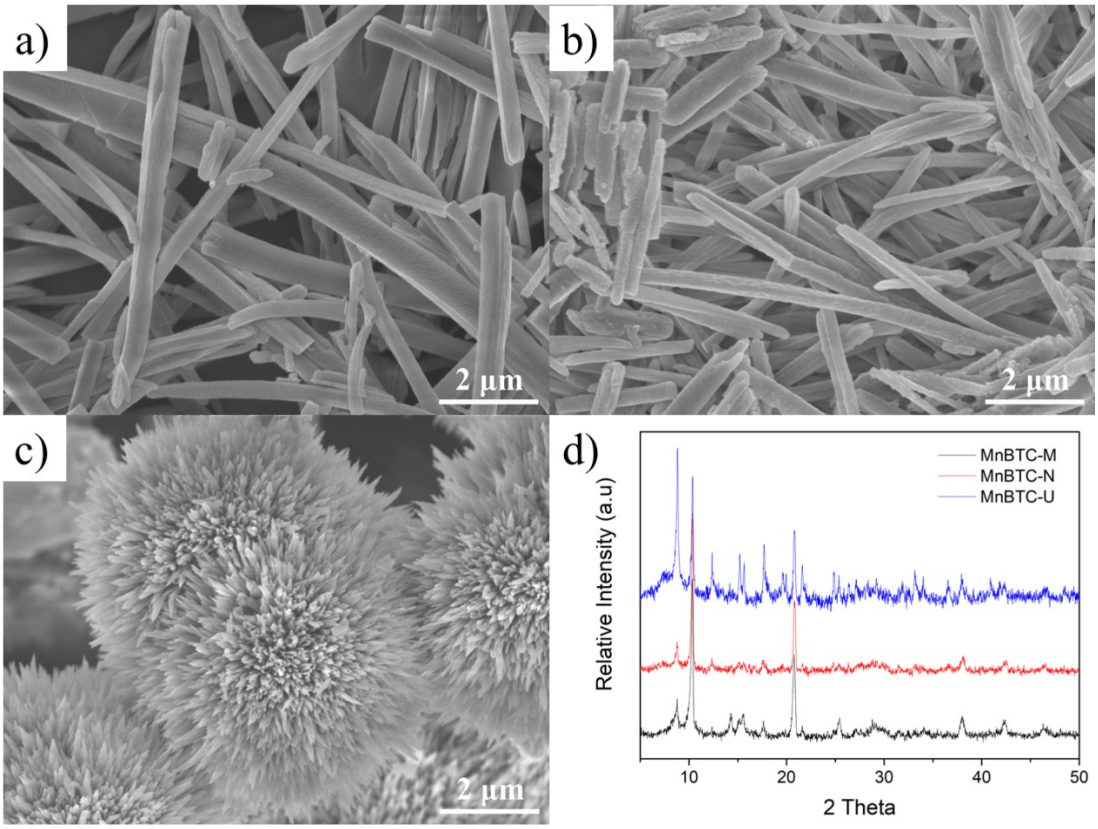

Figure S11. SEM images of (a) micro rod MnBTC (MnBTC-M), (b) nanorod MnBTC (MnBTC-N) and urchin-like MnBTC (MnBTC-U) and (d) the XRD patterns of as-prepared MnBTC.

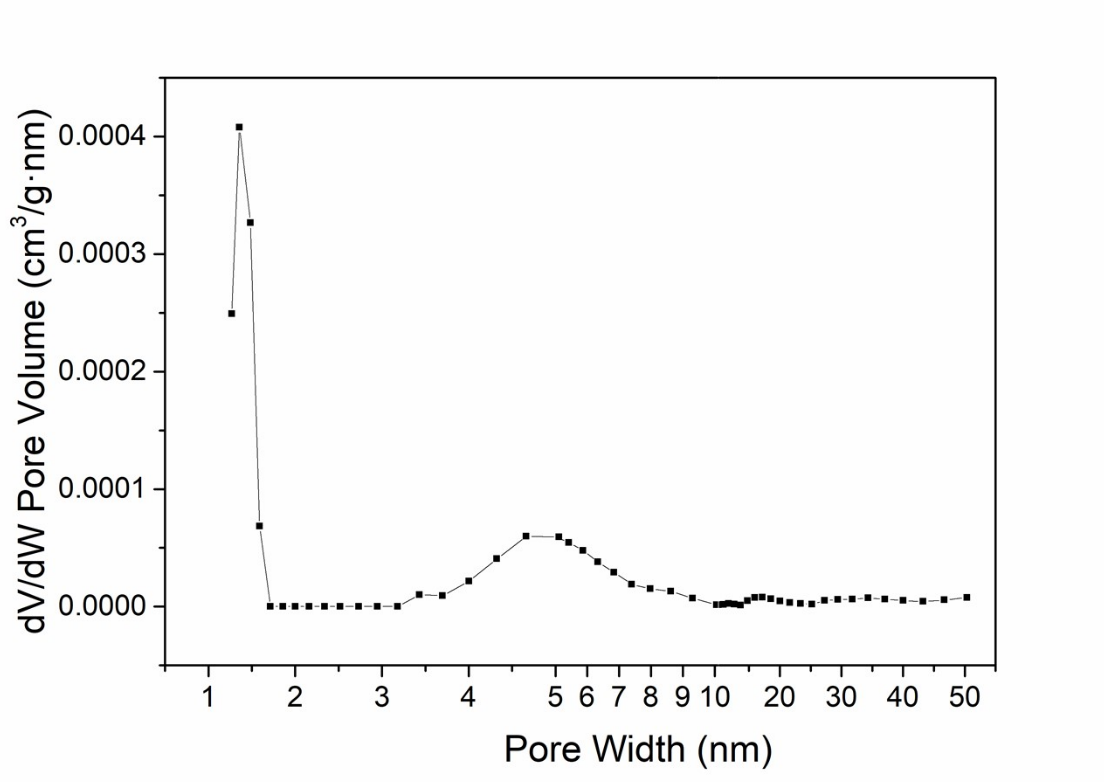

Figure S12. Pore size distribution of CuMOF-74-U calculated by N_2-DFT model.

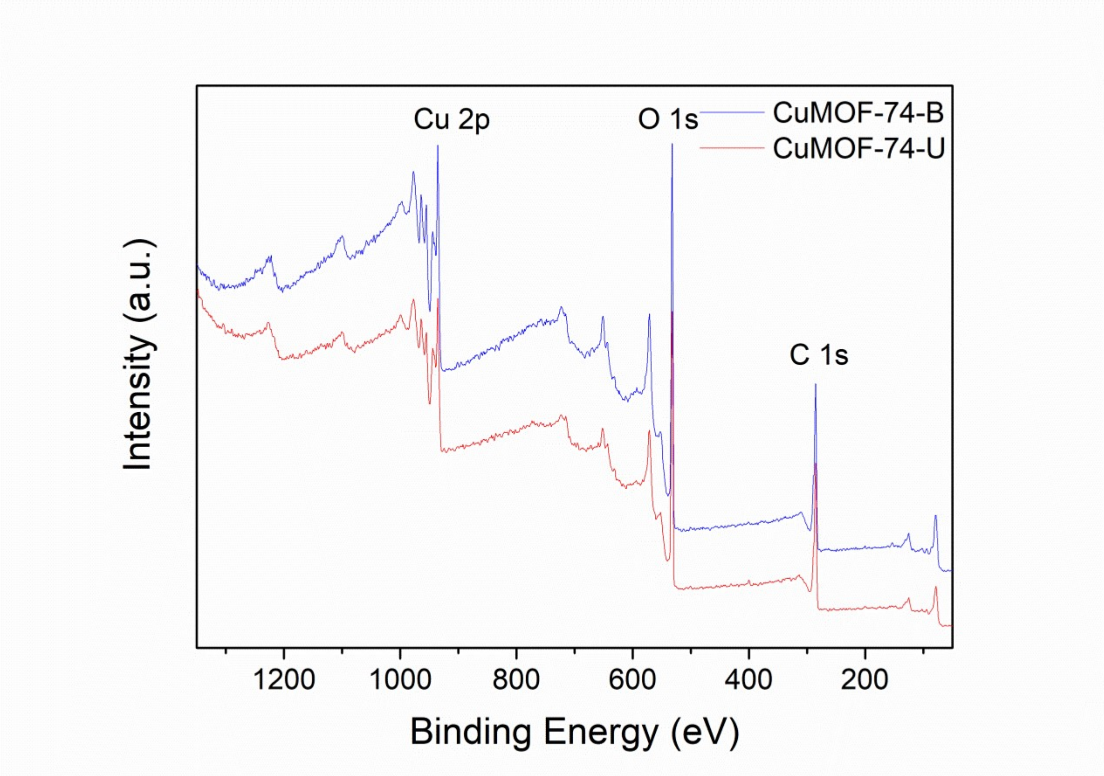

Figure S13. Survey XPS of CuMOF-74-B and CuMOF-74-U.

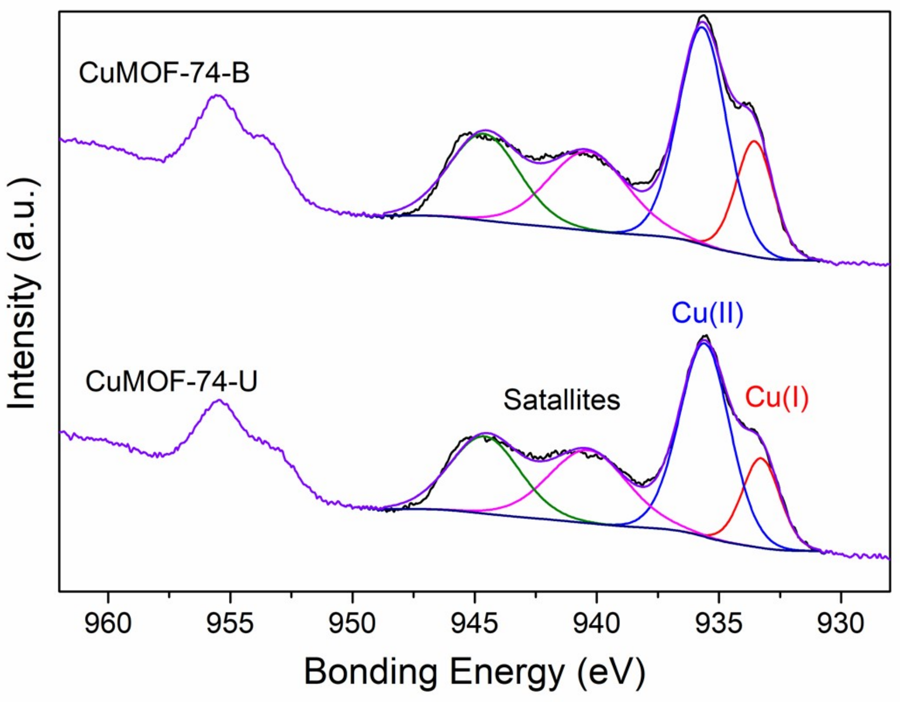

Figure S14. High-resolution XPS of CuMOF-74-B and CuMOF-74-U;

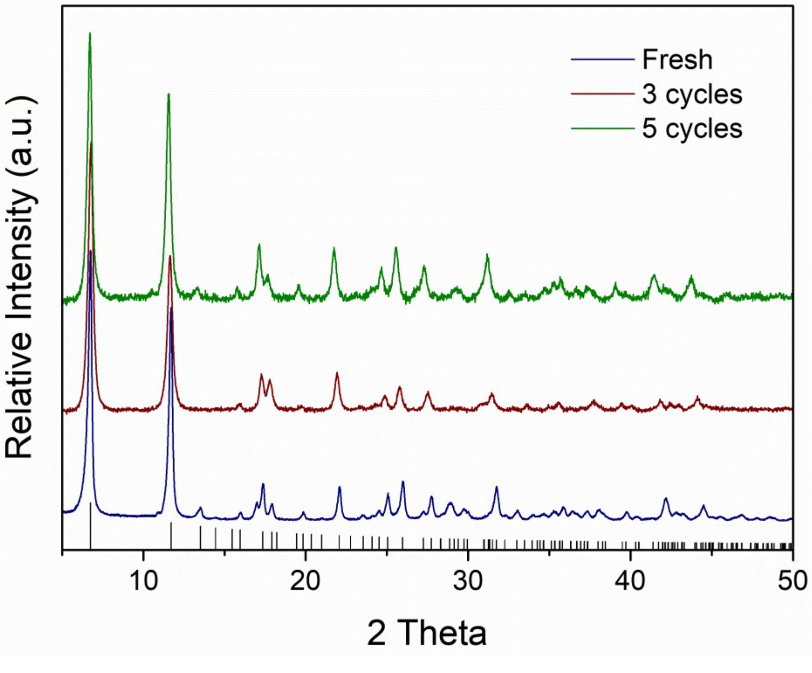

Figure S15. XRD patterns of CuMOF-74-U after catalytic activity test.

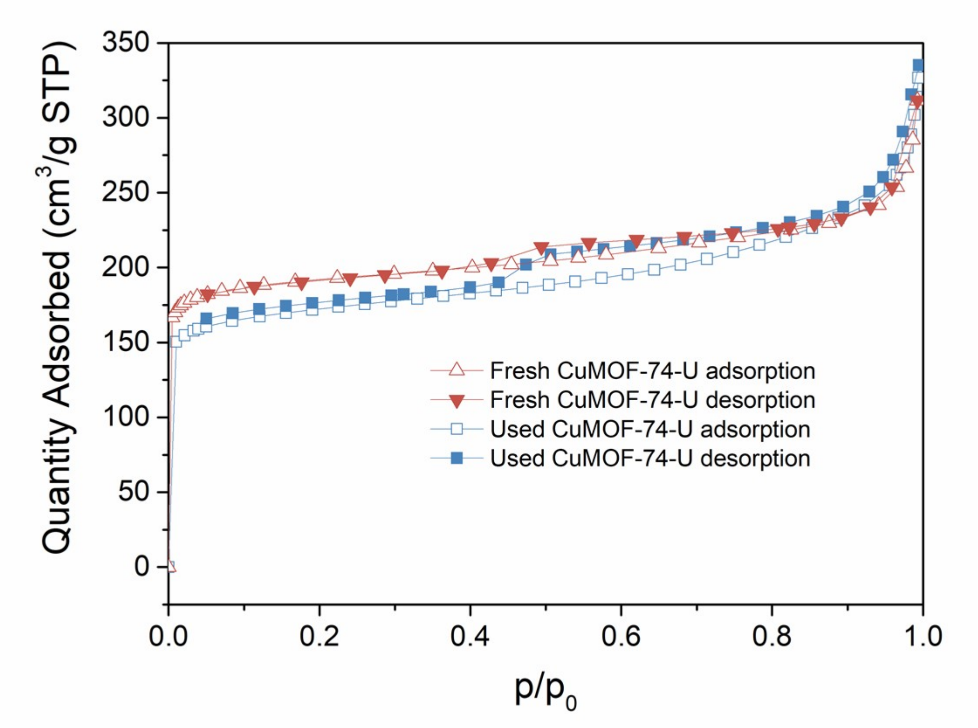

Figure S16. N_2 sorption of fresh CuMOF-74 and CuMOF-74 after 5 cycles SCR test

Table S1 Pore structure parameters of CuMOF-74-M, CuMOF-74-N and CuMOF-74-U calculated by N_2-DFT model

Sample ID	Volume in pores <1.269nm (cm^3/g)	Total volume in pores <172nm (cm^3/g)	Proportion of micropore volume (%)
CuMOF-74-M	0.406	0.406	100
CuMOF-74-N	0.337	0.339	99.3
CuMOF-74-U	0.222	0.335	66.2

3. References

1. I. Luz, A. Loiudice, D. T. Sun, W. L. Queen and R. Buonsanti, *Chem. Mater.*, 2016, **28**, 3839-3849.
2. H. Li, J. Wan, Y. Ma, Y. Wang, X. Chen and Z. Guan, *J. Hazard. Mater.*, 2016, **318**, 154-163.