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\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, 99%), cobaltous nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O), manganese(II) nitrate tetrahydrate (Mn(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O), 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\textsubscript{2}DHTP, 98%), sodium borohydride (NaBH\textsubscript{4}, 99.5%) was purchased from Aladdin without further purification.

Synthesis of nanosized metal oxide
Cu\textsubscript{2}O nanocube was prepared by adding 60 mL aqueous solution containing 1.2 g NaBH\textsubscript{4} dropwise into a 0.08 M Cu(NO\textsubscript{3})\textsubscript{2} solution under vigorous stirring for 10 min. The black precipitate was washed with water four times and ethanol twice, followed by being dried in a vacuum oven at 50 °C. The nanosize cobalt oxide and manganese oxide were prepared by changing the Cu(NO\textsubscript{3})\textsubscript{2} with relevant nitrite salt.

Nano cobalt oxide and manganese oxide were synthesized by replacing the Cu(NO\textsubscript{3})\textsubscript{2} solution with Co(NO\textsubscript{3})\textsubscript{3} and Mn(NO\textsubscript{3})\textsubscript{2} solution.

Conventional synthesis of MOFs using metal salts
Bulk Cu-MOF-74 was synthesized according to literature with some modification\textsuperscript{1}. 360.9 mg Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O and 148.6 mg H\textsubscript{2}DHTP 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\textsuperscript{2}. 727.5 mg Co(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O and 265.5 mg H\textsubscript{3}BTC was dissolved in a mixture of 5 mL DMF, 5 mL ethanol and 5 mL H\textsubscript{2}O. 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\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 210 mg H\textsubscript{3}BTC in a mixture of 3 mL DMF, 3 mL ethanol and 3 mL H\textsubscript{2}O. 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\textsubscript{2}DHTP]/[2Cu\textsubscript{2}O], 0.75 , 1.25 and 2) dissolved in 10 mL H\textsubscript{2}DHTP (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$_3$BTC (32.8mg, 43.9mg and 65.6mg) in a mixed solution of 5 mL DMF, 5 mL ethanol and 5 mL H$_2$O. 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$_3$BTC (210 mg, 280 mg and 350 mg) in a mixed solution of 3 mL DMF, 3 mL ethanol and 3 mL H$_2$O. 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 8h.

**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:

$$C_{NO\%} = \frac{[NOx]_{\text{inlet}} - [NOx]_{\text{outlet}}}{[NOx]_{\text{inlet}}} \times 100$$
2. Figures and Tables

Figure S1. (a) SEM image and (b) XRD pattern (bottom column is peaks of simulated Cu$_2$O) of nanocube Cu$_2$O which was used for the synthesis of CuMOF-74-M, CuMOF-74-N and CuMOF-74-U.

Figure S2. (a) SEM image of Cu$_2$O-M and (b) XRD patterns of Cu$_2$O-M and MOFs samples synthesis by Cu$_2$O-M with different reaction time.

Figure S3. (a) SEM image of nanosized Cu$_2$CO$_3$(OH)$_2$ and (b) XRD patterns of Cu$_2$CO$_3$(OH)$_2$ and MOFs samples synthesis by Cu$_2$CO$_3$(OH)$_2$ with different reaction time.
Figure S4. SEM image of MOF-Cu$_2$CO$_3$(OH)$_2$$_{18}$ h shows that the Cu$_2$CO$_3$(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$_2$O-N, Cu$_2$O-M, Cu$_2$CO$_3$(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\textsubscript{2} sorption of fresh CuMOF-74 and CuMOF-74 after 5 cycles SCR test

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<th>Sample ID</th>
<th>Volume in pores &lt;1.269nm (cm\textsuperscript{3}/g)</th>
<th>Total volume in pores &lt;172nm (cm\textsuperscript{3}/g)</th>
<th>Proportion of micropore volume (%)</th>
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3. References