Supporting Information

A template-free method for stable CuO hollow microspheres fabricated from metal organic framework (HKUST-1)

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Materials

All materials were purchased from Sigma-Aldrich and used as received without further purification.

Synthesis

Synthesis of HKUST-1 In a typical synthesis, 1.3576 g $Cu(NO_3)_2 \cdot 3H_2O$ and 0.8400 g benzene-1,3,5-tricarboxylic acid were dissolved in a mixture of N,N-dimethylformamide (15 ml), ethanol (15 ml) and deionized water (15 ml). After being stirred for 5 h, the precipitates were isolated by filtration, washed with mixed solvent of deionized water and ethanol for 3 times.

CuO microspheres The microshperes are obtained from pyrolysis of the as-prepared HKUST-1. The pyrolysis temperatures are based on the TGA results and set at 300 °C. In a typical process, 200 mg HKUST-1 was placed in a tube furnace. Before being heated, the furnace tube was flushed by the mixed gas of 2 vol. % O_2 balanced with helium at a speed of 35 mL/min to remove air. Then the furnace was heated to 300 °C at a rate of 10 °C min^{-1} and kept for different time. Finally, the product was taken out. The reactions conducted in pure N_2 and air are in the same process.

Characterization

The phase of the as-obtained samples was characterized by X-ray powder diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ=1.5406 Å). Morphological features were studied using field emission scanning electron microscope (FESEM, JEOL JSM-7600F). Internal structures of the samples were observed by transmission electron microscope (TEM, JEOL JEM-2010). Thermogravimetric analyses (TGA) were firstly performed on a Q500 TGA (TA Instruments) under nitrogen gas flow at 10 °C·min^{-1} from room temperature to 900 °C. Then it was conducted in pure air at 10 °C·min^{-1} from room temperature to 300 °C and kept at this temperature for 30 min. The IR spectrum was obtained on a Perkin-Elmer FT-IR spectrophotometer in the 400–2000 cm^{-1} region with a KBr pellet. Nitrogen adsorption isotherms of powder samples were measured with a Micromeritics ASAP 2020 adsorption apparatus at 77 K up to 1 bar. Before starting the adsorption measurements, each sample was activated by heating under vacuum at 373 K for 10 hours. The pore textural properties including Brunauer-Emmett-Teller (BET) surface area and pore size were obtained by analyzing nitrogen adsorption and desorption isotherms with Micromeritics ASAP 2020 built-in software.

Catalytic measurements

The catalytic activity of samples prepared for CO oxidation was tested in a fixed-bed flow reactor with 25 mg catalysts and with a gas flow mixed of CO (1.5 ml/min), O_2 (30 ml/min), and He (60 ml/min). The composition of the effluent gas was analyzed using a gas chromatograph (Agilent, 6890N) equipped with a Carbosieve SII column. After the test of catalytic activity, the fixed-bed was cooled down to 200 °C and kept for 24 h to measure the catalytic stability of samples.

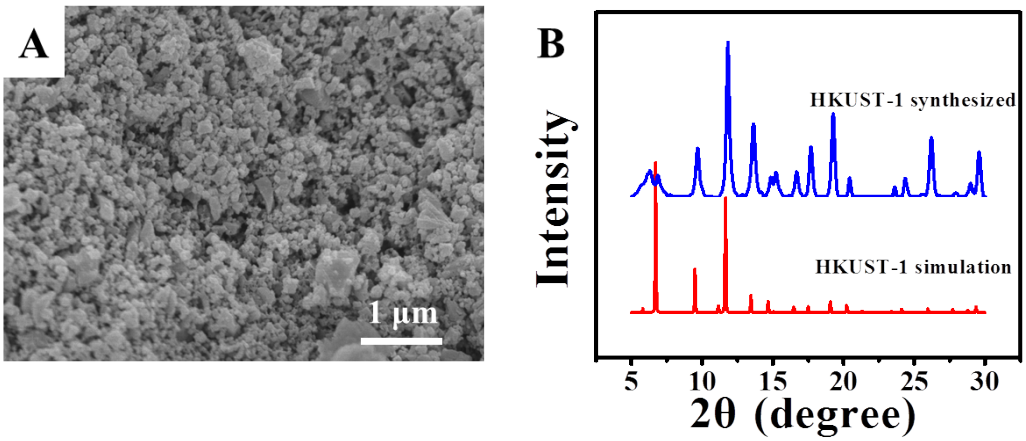

Figure S1 HKUST-1 with non-uniform morphology synthesized at ambient. A) the FESEM image of morphology; B) XRD patterns.

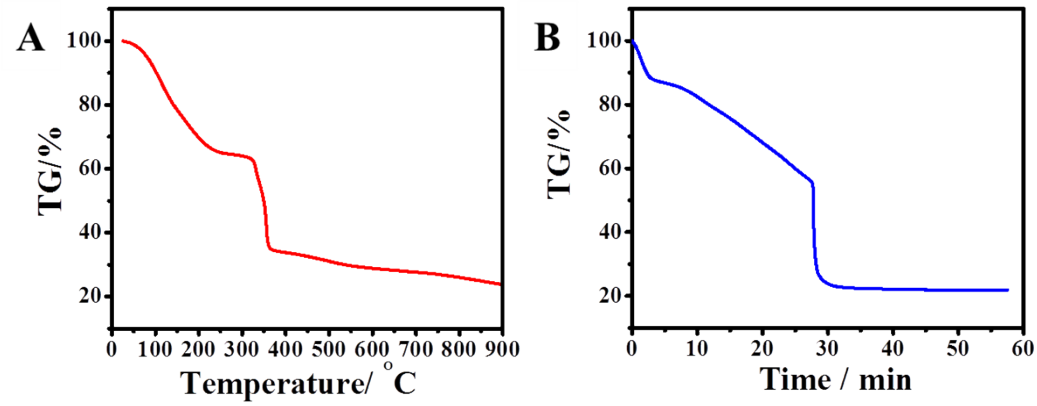

Figure S2 Thermogravimetric analysis (TGA) curve of as-prepared HKUST-1 in pure N_2 (A) and in pure air at 300 °C for 30 min (B).

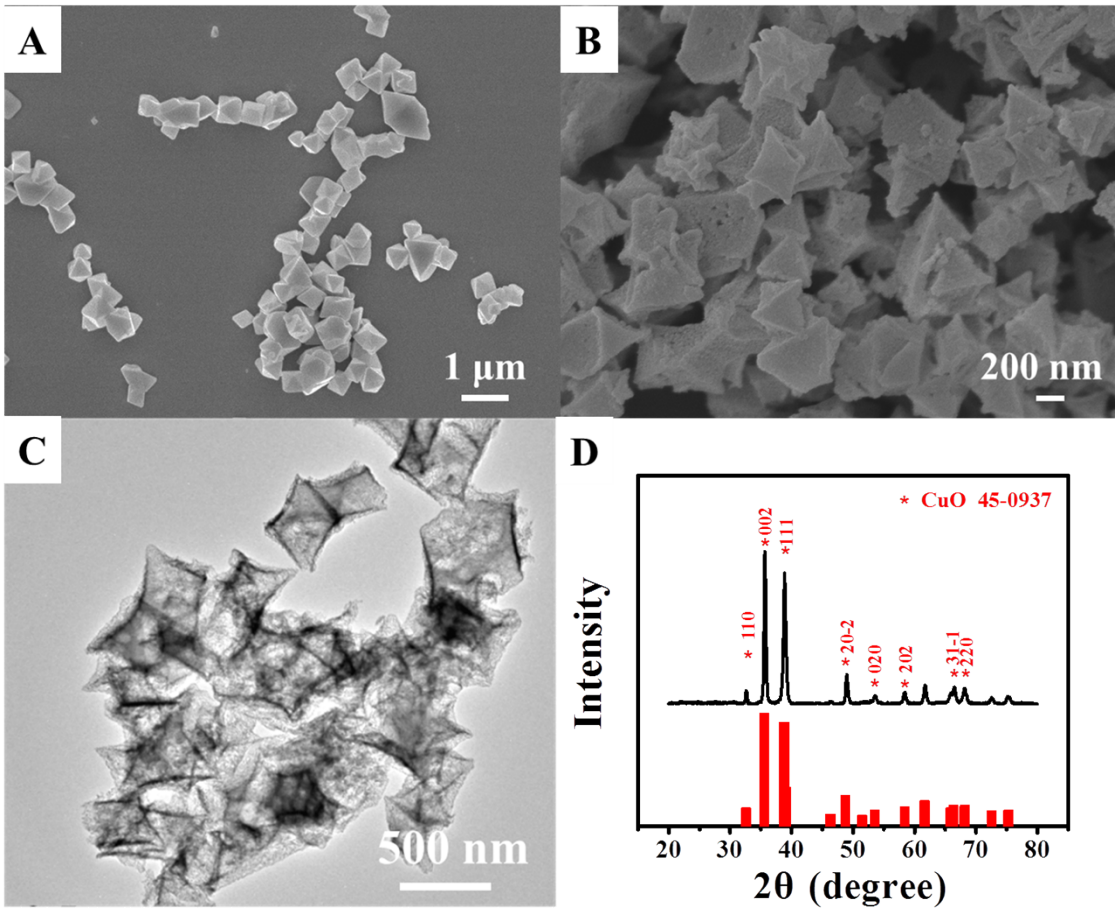

Figure S3 FESEM images of octahedral HKUST-1 synthesized (A) and CuO hollow octahedra obtained from calcination of HKUST-1 (B), TEM image (C) and XRD pattern (D) of CuO hollow octahedra.

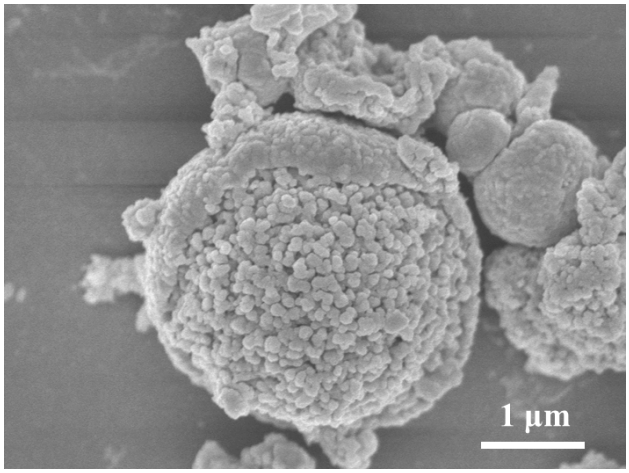

Figure S4 FESEM image of product after oxidation in 2 % (v/v) O_2/He at 300 ^oC for 4 h.

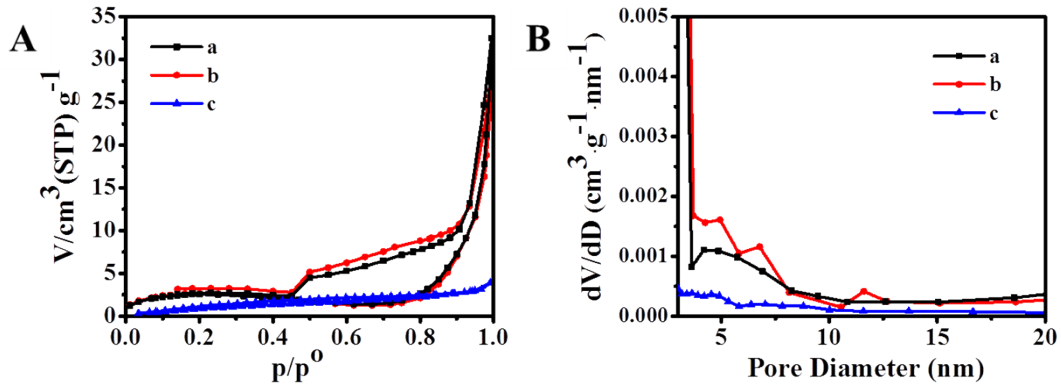

Figure S5 N_2 Adsorption–desorption isotherms (A) and Pore size distributions (B) of CuO hollow microspheres for (a) 3 h, (b) 4 h and (c) CuO hollow octahedra.

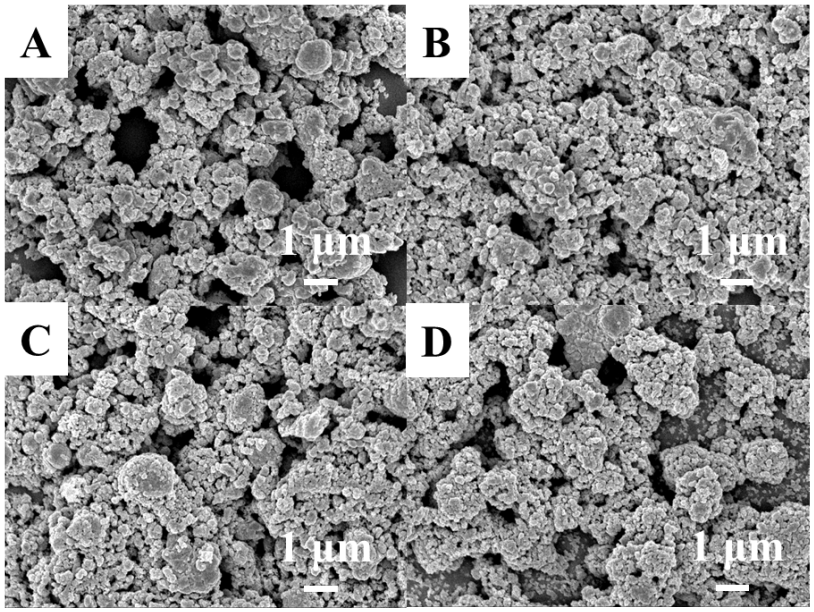

Figure S6 FESEM images of products after calcination in pure He at 300 °C for A) 1 h; B) 2 h; C) 3 h; D) 4 h.

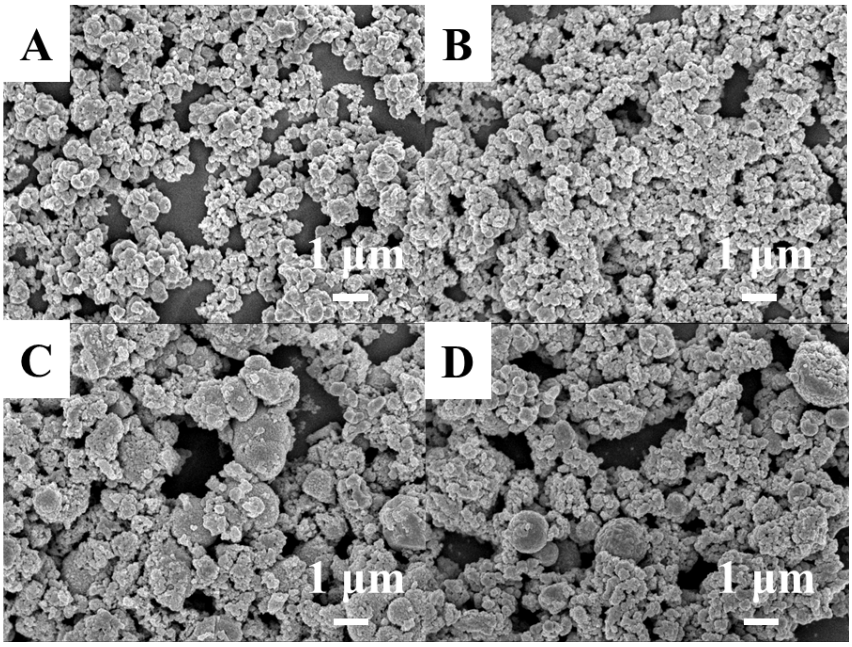

Figure S7 FESEM images of products after calcination in pure air at 300 °C for A) 1 h; B) 2 h; C) 3 h; D) 4 h.

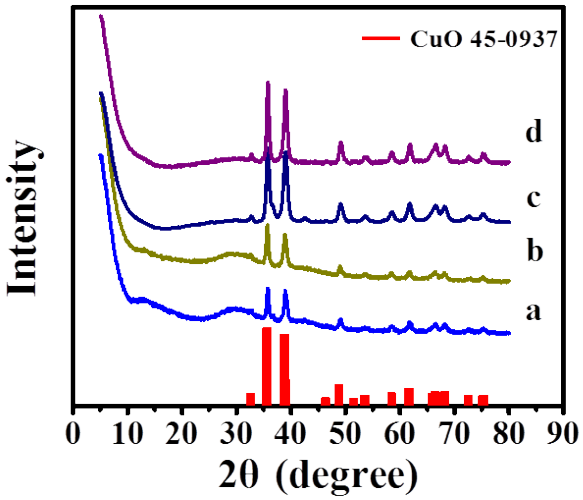

Figure S8 XRD patterns of products after calcination in pure air at 300 °C for a) 1 h; b) 2 h; c) 3 h; d) 4 h.

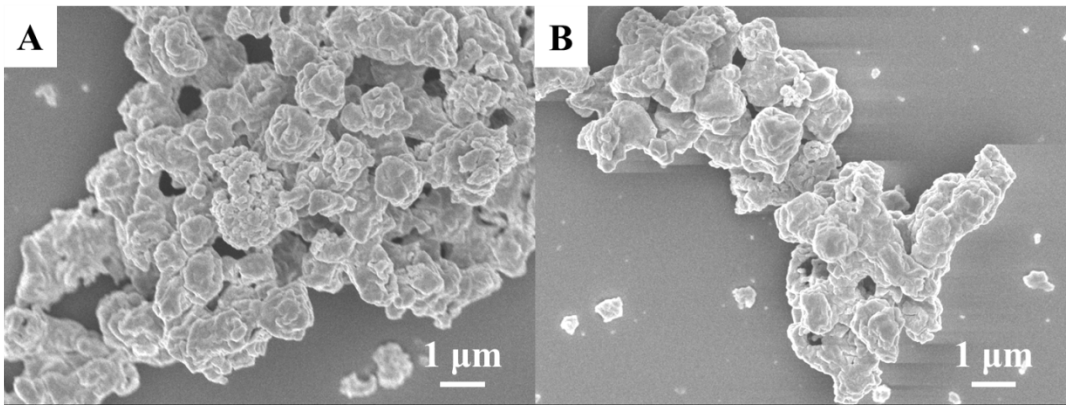

Figure S9 FESEM images of CuO hollow octahedra after 24 h catalytic reaction (A) and heat treatment in pure N_2 at 500 ^oC for 1 h (B).

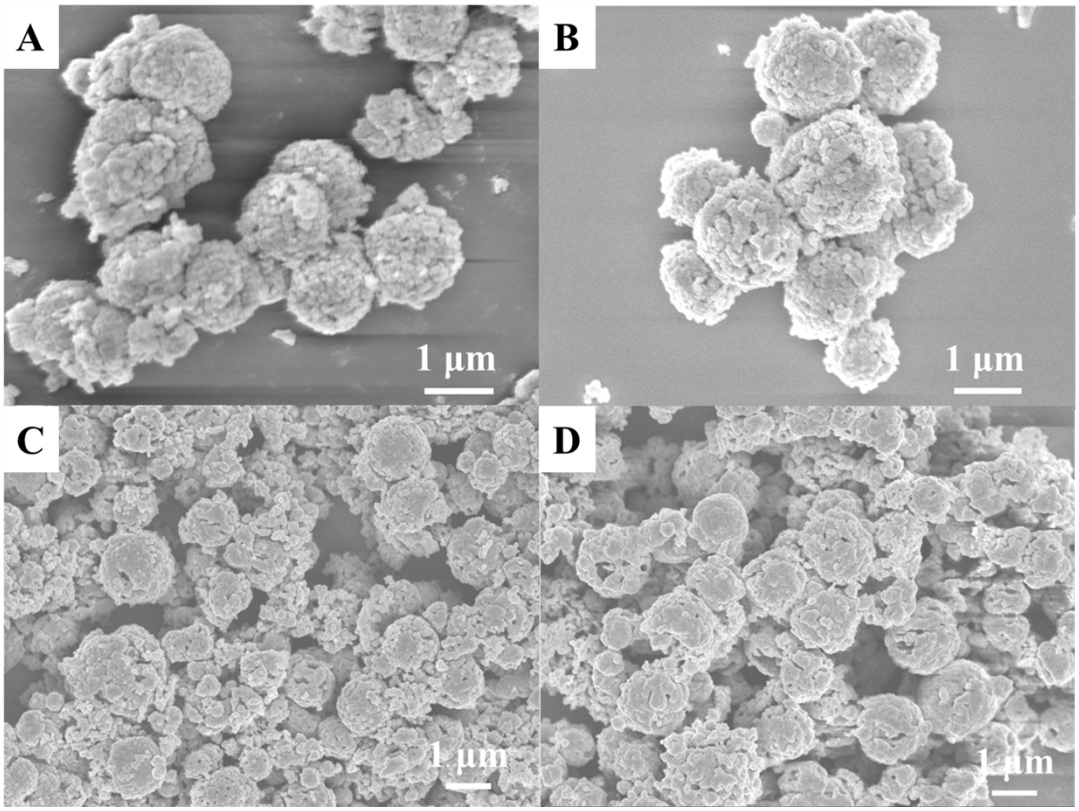

Figure S10 FESEM images of samples after 24 h catalytic reaction (A, B) and heat treatment in pure N_2 at 500 ^oC for 5 h (C, D): CuO hollow microspheres obtained after oxidation in 2 % (v/v) O_2/He (A, C) for 3 h; (B, D) for 4 h.

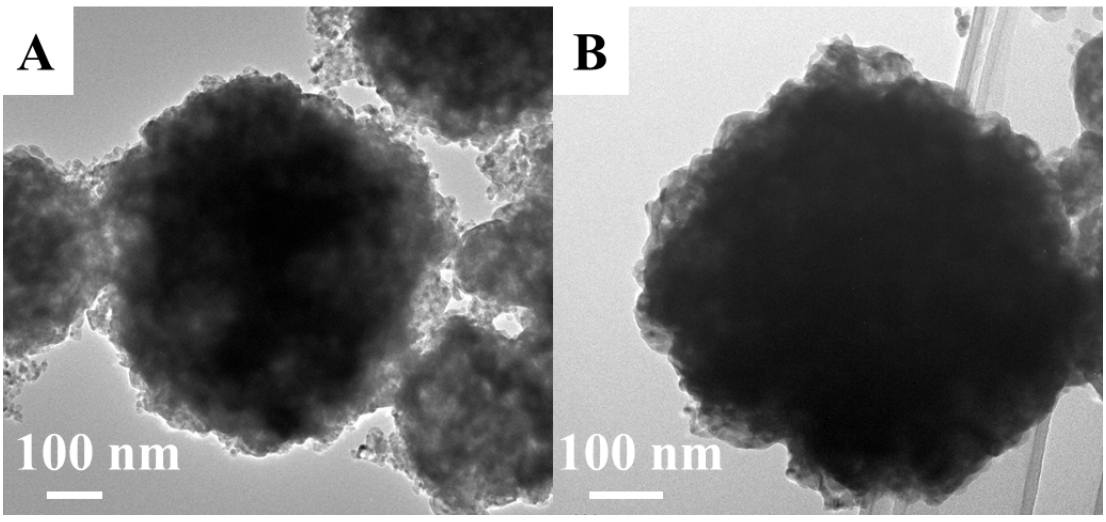

Figure S11 TEM images of CuO hollow microspheres after 24 h catalytic reaction (A) and heat treatment in pure N_2 at 500 ^oC for 5 h (B): CuO hollow microspheres was obtained after oxidation in 2 % (v/v) O_2/He for 3 h.