Supporting Information for:

Controllable Formation of Meso- and Macropores within Metal-Organic Framework Crystals via Citric Acid Modulator

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Supplemental Experimental section

Preparation of submicrometer-sized Cu_2O cubes

Submicrometer-sized Cu_2O cubes were synthesized according to a published procedure[1]. Typically, 4.0 mL of 0.1 M $CuCl_2$ and 8.0 mL of 1.0 M NaOH solution were added into 382 mL deionized water (18.3 MΩ) and kept stirring. Then, 3.48 g of sodium dodecyl sulfate powder was added. After the white powder was dissolved thoroughly, 6.0 mL of 0.20 M $NH_2OH \cdot HCl$ was mixed with the solution. The solution was aged for 17 hours at room temperature. The resultant Cu_2O cubes were collected by discarding the supernatant, washed with ethanol three times and dispersed in 8.0 mL of ethanol for subsequent use.

Preparation of octahedral HP-HKUST-1 particles from submicrometer-sized Cu_2O cubes

The procedure was similar to that from Cu_2O nanowires except that the Cu_2O nanowires were replaced by Cu_2O cubes (about 10mg) and the amount of H_3BTC ethanol solution (0.16 M) was increased to 6.24 mL.

Preparation of Cu-CA complex

3.0 mL, 0.16 M CA ethanol solution was mixed with 3.0 mL ethanol Cu_2O nanowires dispersion (about 4 mg Cu_2O). Then, the mixture was diluted to 12 mL with ethanol and kept at 30°C until the yellow solution changed into blue (about 2 days). The fibrous Cu-CA complex was obtained by centrifugation and washed by ethanol for three times.

Supplemental Figures

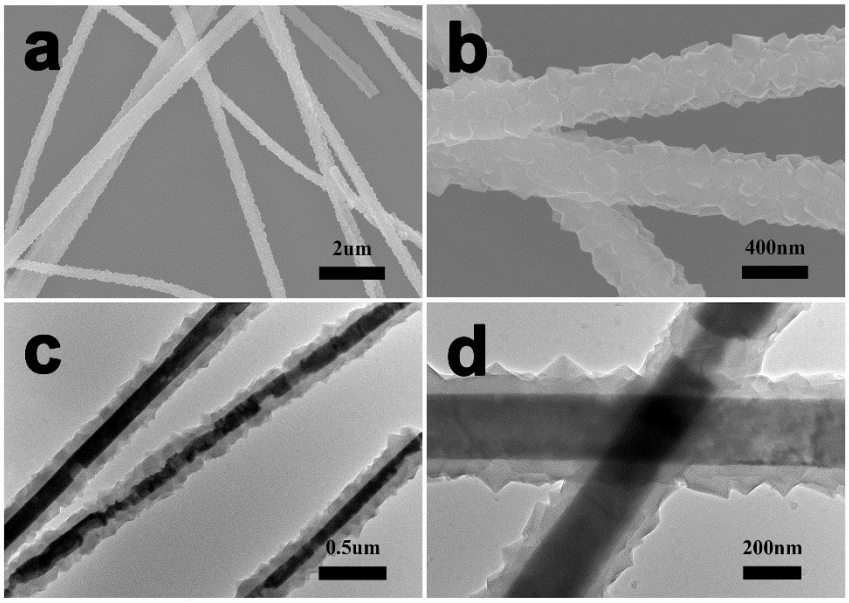


Figure S1 FESEM images (a,b) and TEM images (c,d) of Cu_2O@HKUST-1 core@shell cable-like nanostructures formed with the absence of CA.

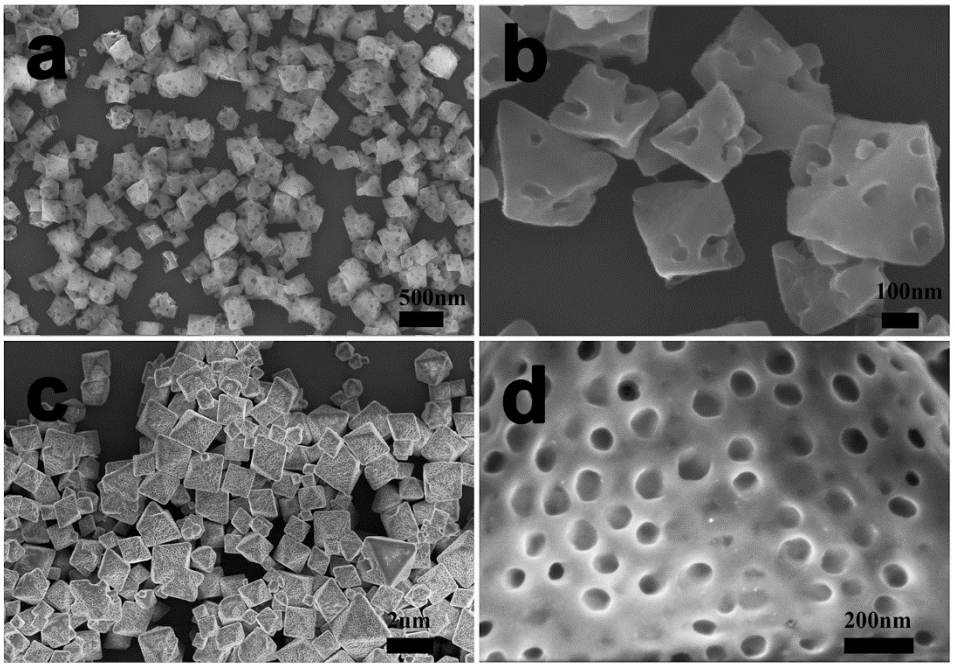


Figure S2 Supplemental FESEM images for product **1** (a, b) and **2** (c,d).

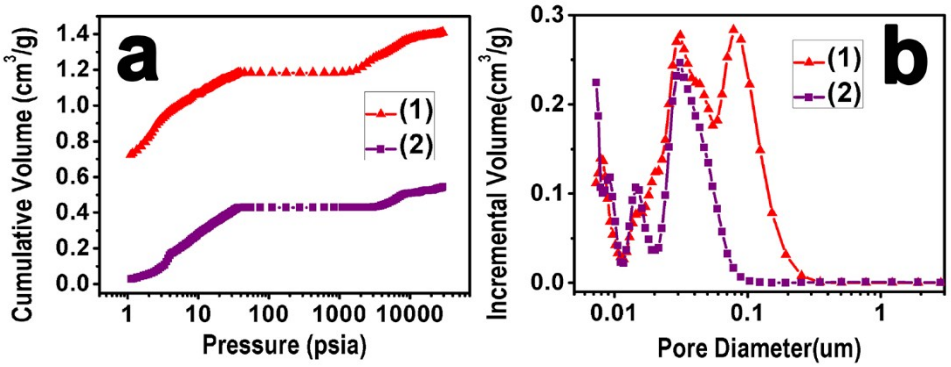


Figure S3 The Hg intrusion cumulative curves (a) and the pore size distribution curves measured by Hg intrusion porosimetry (b) for product **1** and **2**.

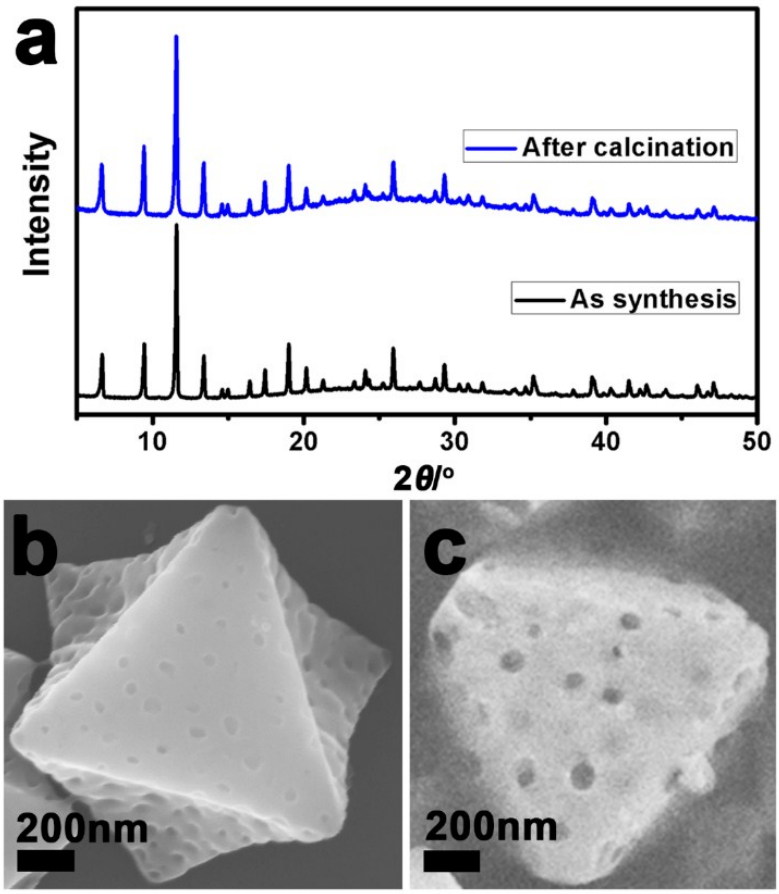


Figure S4 (a) PXRD patterns and FESEM images of HP-HKUST-1 micrometer particles: (b) as synthesis; (c) after calcination at 260°C for 5 hours in nitrogen atmosphere.

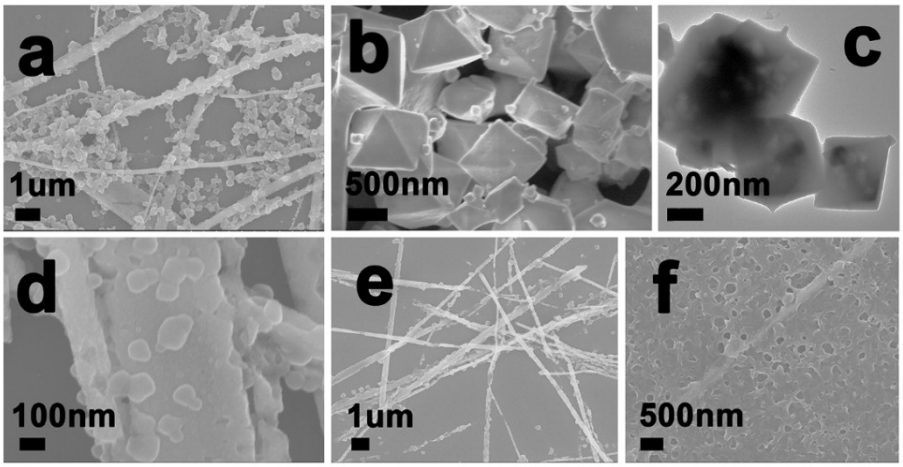


Figure S5 FESEM images obtained by monitoring the growth process of HP-HKUST-1 sub-micrometer particles modulated by a less amount of CA (0.24mL, 0.16 M CA solution) at the reaction time of (a) 4h, and (b) 16h, respectively. (c) TEM images of products modulated by a less amount of CA (0.24mL, 0.16 M CA solution) at the reaction time of 16h. FESEM images obtained by monitoring the growth process of HP-HKUST-1 micrometer particles modulated by a little more amount of CA (0.36mL, 0.16 M CA solution) at the reaction time of (d) 8h, (e, f) 14h, respectively.

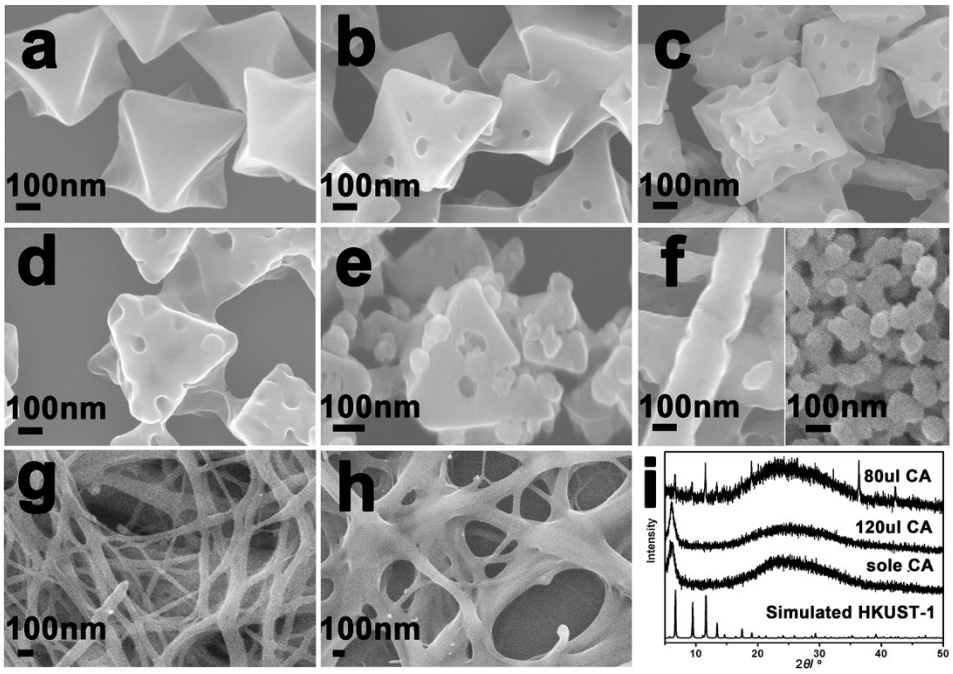


Figure S6. FESEM of the final products with different CA amounts of (a) 0.12mL, (b) 0.18mL, (c) 0.21mL, (d) 0.24mL, (e) 0.36mL, (f) 0.48mL, (g) 0.72mL, 0.16M CA/EtOH solution added into the reaction solution. (h) FESEM of the products obtained from the reaction of Cu_2O only with CA. (i) PXRD patterns of samples obtained from 0.48mL, 0.72mL, 0.16M CA addition and only the CA.

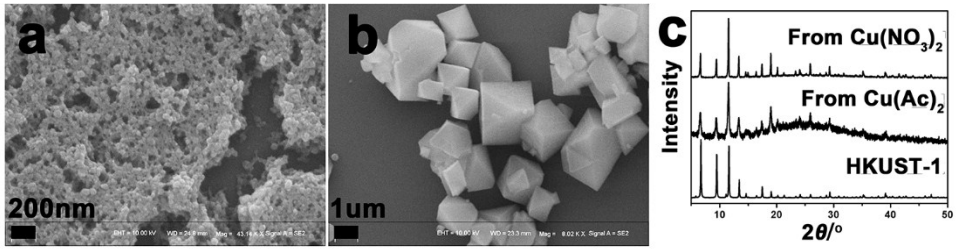


Figure S7 FESEM of (a) spherical particles obtained from $Cu(Ac)_2$ and (b) octahedrons with smooth surfaces obtained from $Cu(NO_3)_2$. (c) PXRD patterns of these two samples.

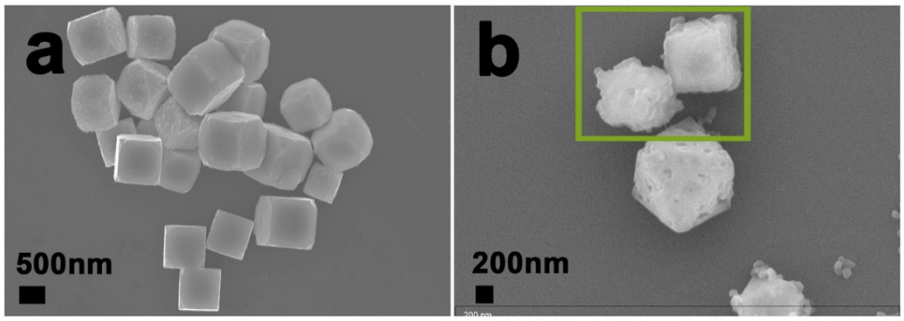


Figure S8 FESEM of (a) Cu_2O Cubes and (b) HP-HKUST-1 crystals obtained from Cu_2O Cubes, the Cubes particles with rough surfaces located in the lime rectangular frame (b) is the unreacted Cu_2O.

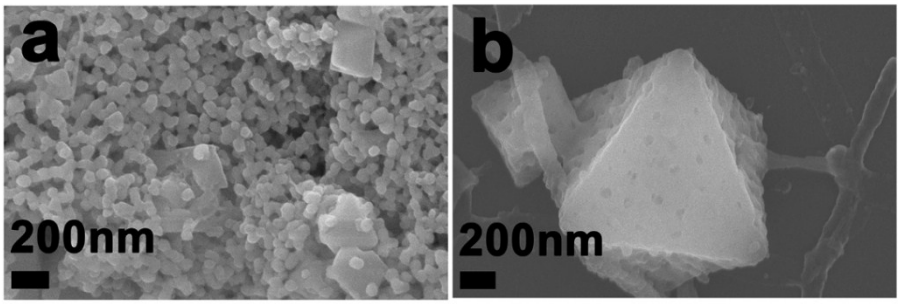


Figure S9 FESEM images of (a) spherical particles and (b) heterogeneous porous octahedrons obtained with addition of 0.48mL, 0.16M CA solution in the absence and existence of DMA, respectively.

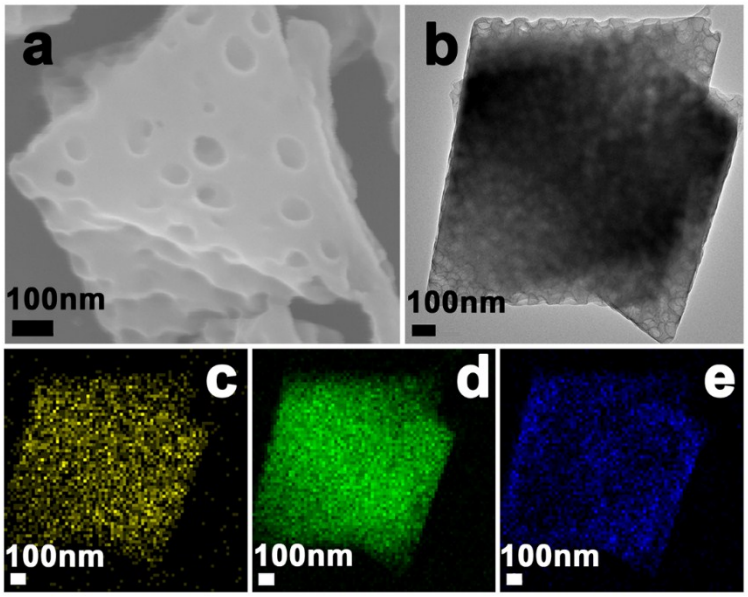


Figure S10 (a) FESEM image and (b) TEM image of HPMo/HP-HKUST-1micrometer particles; (c-e) elemental maps of P, Cu, and Mo concentrations in the HPMo/HP-HKUST-1 micrometer particles.

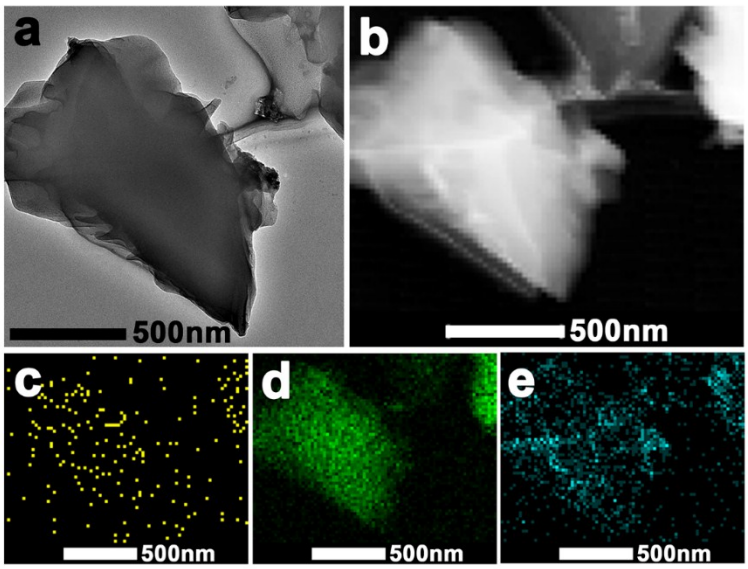


Figure S11 (a) TEM image and (b) HAADF-STEM image of HPMo/HP-HKUST-1 fragment; (c-e) elemental maps of P, Cu, and Mo concentrations in the HPMo/HP-HKUST-1 fragment.

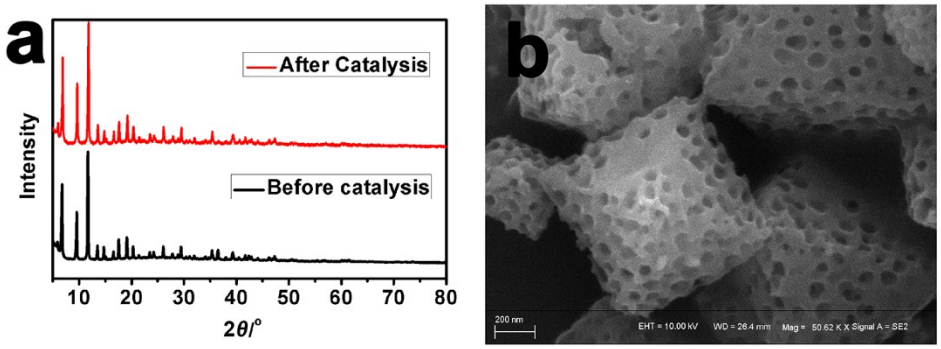
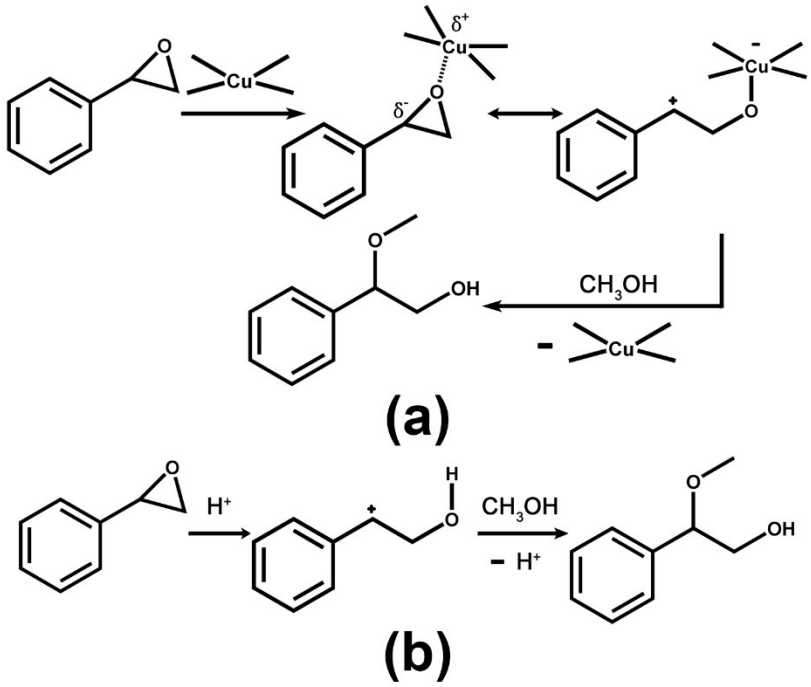


Figure S12 (a) PXRD pattern and FESEM image of HPMo/HP-HKUST-1 micrometer particles after catalysis.



Scheme S1 Proposed mechanisms for the ring opening of styrene oxide with MeOH catalyzed by HKUST-1 (a) and heteropoly acid (b), respectively.

Reference:

1. J. Ho and M. H. Huang, *J. Phys. Chem. C*, 2009, 113, 14159-14164.