

Supporting Information

Phase transfer directed synthesis of hollow zeolitic imidazolate frameworks-67 nanocages

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Experimental section

Synthesis of Cu₂O cubes

Cubic Cu₂O nanocrystals were obtained by the typical reduction method. In brief, 0.11 g CuSO₄ and 0.2 g PVP (K-30) were dissolved in 18 mL deionized water. Then, 1 mL water solution containing sodium citrate (0.218 g) and Na₂CO₃ (0.127 g) was dropwise added into the CuSO₄ solution, and the reaction was carried out at room temperature for 10 min with stirring. After that, 1 mL glucose (0.28 g) water solution was injected into the suspension, and the reduction was allowed for 2 h at 80 °C. Red colored Cu₂O cubes were obtained by centrifugation and dried for 24 h at 60 °C in vacuum after washed by ethanol.

Synthesis of Co(OH)₂ and ZIF-67 nanocages

In brief, 5 mg Cu₂O and 0.3 g PVP (K-30) were dissolved in the mixture of 5 mL ethanol and 5 mL deionized water. Then, 1.7 mg CoCl₂·2H₂O was added into the

suspension and stirred for 10 min. After that, 4 mL 1 M $\text{Na}_2\text{S}_2\text{O}_3$ water solution was dropwise added, and the etching process was carried out at room temperature for 10 min. $\text{Co}(\text{OH})_2$ nanoparticles were collected by centrifugation and re-dispersed in 2 mL methanol washed by ethanol. ZIF-67 nanocages were obtained by addition of 3 mL 2-methylimidazole (0.2 g) methanol into the $\text{Co}(\text{OH})_2$ suspension. The transformation was allowed from 12 to 48 h with the temperature ranging from 25 to 60 °C.

Synthesis of ZIF-67 by hydrothermal method

Typically, 5 mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 50 mmol 2-methylimidazole were dissolved in 60 and 40 mL methanol, respectively. Then, Co(II) methanol solution was dropwise added into the 2-methylimidazole solution at room temperature with stirring. After that, the suspension was allowed for 24 h in a 50 °C oven. The ZIF-67 nanocrystals were collected by centrifugation at 10,000 rpm for 10 min, and dried for 24 h at 80 °C after washed by methanol.

Characterization of nanocrystals

Morphology of the synthesized nanocrystals was characterized by high-resolution analytical transmission electron microscopy (TEM, Fei Tecnai G2 F20) and field emission scanning electron microscope (SEM, Hitachi S-4800). The crystalline structure of materials was characterized by powder X-ray diffraction (XRD, Rigaku D/MAX-2500, Japan). Determination of Co, Cu and S elements were conducted on the ICP-MS (Agilent 7700x). Thermogravimetric (TG) analysis were carried on a TG/DSC apparatus (Mettler Toledo, Switzerland) with a heating rate of

5 °C/min. N₂ adsorption was carried on the Micromeritics Tristar II 3020 at 77 K.

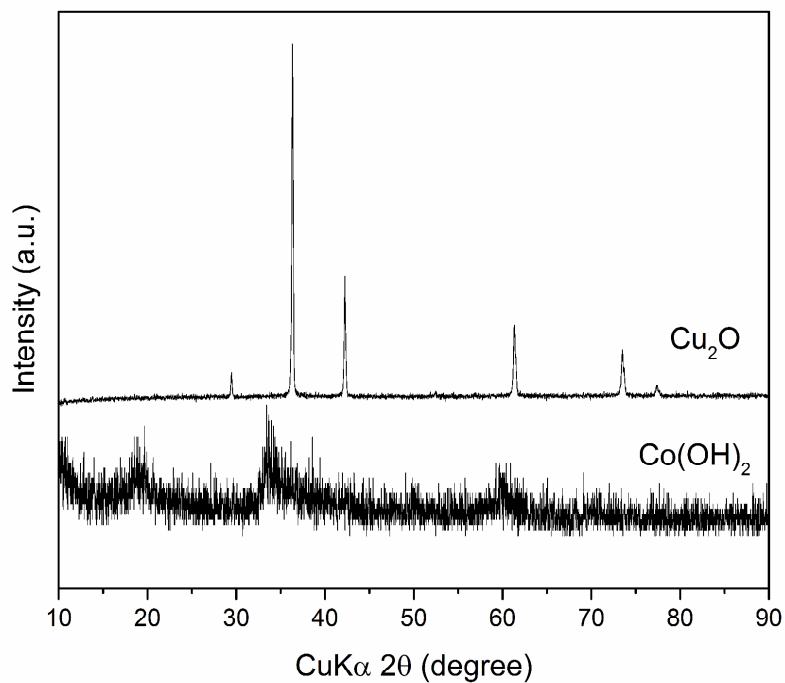


Figure S1. XRD analysis of Cu₂O before etching process and Co(OH)₂ formed after etching process.

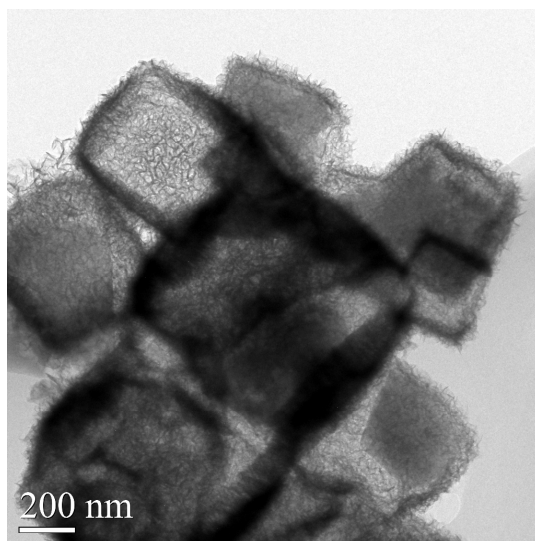


Figure S2. TEM image of cubic Co(OH)₂ nanocages formed by coordinating etching

and precipitation process.

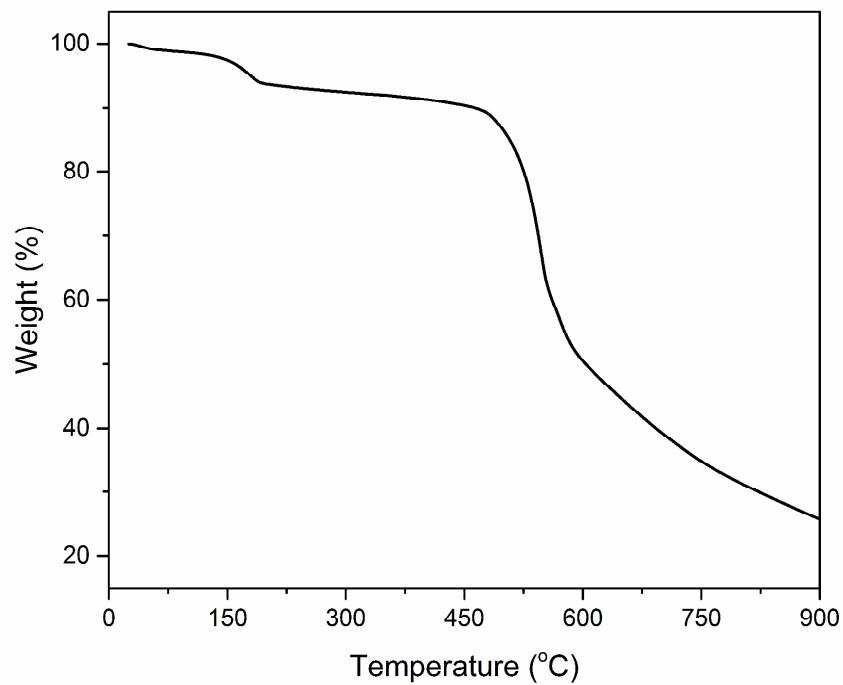


Figure S3. TG of synthesized cubic ZIF-67 nanocages

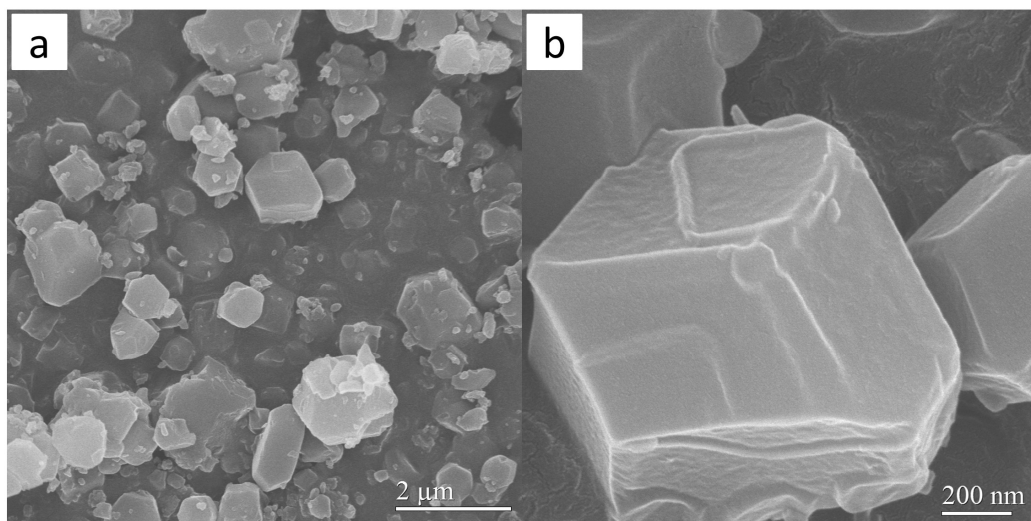


Figure S4. SEM images of ZIF-67 by hydrothermal method.