

Supporting information

MOFs-templated formation of porous CuO hollow octahedrons for lithium-ion battery anode materials

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S1

Experimental details

Synthesis of Cu-btc MOFs. All chemicals were of analytical grade and used without further purification. In a typical procedure, 1.82 g copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 0.875 g benzene-1,3,5-tricarboxylic acid ($\text{C}_6\text{H}_3(\text{COOH})_3$) were dissolved in a 50 ml absolute methanol under ultrasonication, respectively. After that, the copper nitrate solution was transferred into the tricarboxylic acid solution. The mixture solution was kept at room temperature for 2 h until MOF precipitation finished. The precipitation was retrieved by centrifugation and washed with methanol for two times. At last, the blue powder of Cu-btc MOFs was dried in vacuum at room temperature.

Preparation of the CuO hollow octahedrons. At first, a glass vessel containing the powder of Cu-btc MOFs was placed in a tube furnace. Before being heated, the furnace tube was flushed twice by high-purity nitrogen gas to remove oxygen. The furnace was then heated to 300 °C at a rate of 10 °C min⁻¹ and maintained at this temperature for 30 min under nitrogen gas flow. After that, the nitrogen gas flowing was switched off and the furnace was still kept at this temperature for another 60 min in flowing air. Finally, the product was taken out and it was found that the color changed from blue to black.

Materials Characterization. The crystal phase of the prepared samples was characterized by X-ray powder diffractometer (Bruker D8 Advance) with Cu K α radiation ($\lambda=1.5406$ Å). Morphological features and internal structures of the samples were studied using field emission scanning electron microscope (FESEM, JEOL JSM-7600F) and transmission electron microscope (HRTEM, JEOL JEM-2100F), respectively. The thermogravimetric analysis (TGA) was carried out by using a Shimadzu-60 thermogravimetric analyzer under air flow at 10 °C min⁻¹ from room temperature to 600 °C. The nitrogen adsorption-desorption isotherm was measured using a Quantachrome Instruments Autosorb AS-6B equipment.

Electrochemical Measurements. To fabricate the cathode of a coin cell battery, the sample of CuO octahedron was mixed with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 in N-methyl-2 pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil, dried at 120 °C for 12 h, and then punched into round plates with diameter of 10.0 mm as the cathode electrodes. Finally, the prepared cathode, a Celgard 2400 separator (diameter of 16.0 mm), a lithium anode, electrolyte of 1M LiPF₆ in EC-DEC-EMC (1:1:1 vol %), and the other components of the coin-type cell were assembled into a coin cell (CR2032) in an argon filled glove box. The coin cells prepared were examined at various charge-discharge currents between 0.01-3.0 V. Cyclic voltammetry (CV) was collected using an Autolab PGSTAT30 Electrochemical Workstation. Electrochemical impedance spectroscopy (EIS) was performed using Solartron SI 1260 Impedance/Gain-Phase Analyser. The sinusoidal excitation voltage applied to the cells was 10 mV with a frequency range of between 1MHz and 10 mHz.

S2

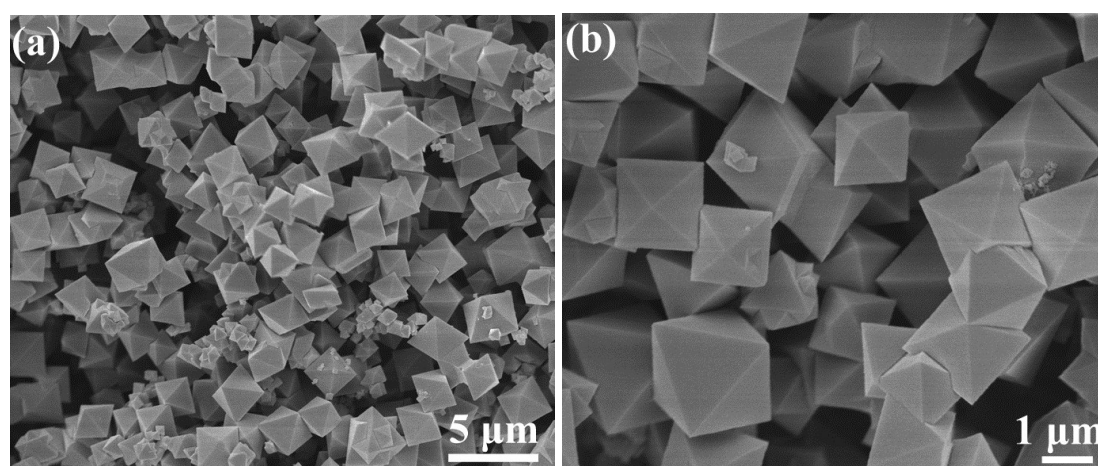


Figure S2 (a) Low- and (b) high-magnified FESEM images of Cu-btc MOFs.

S3

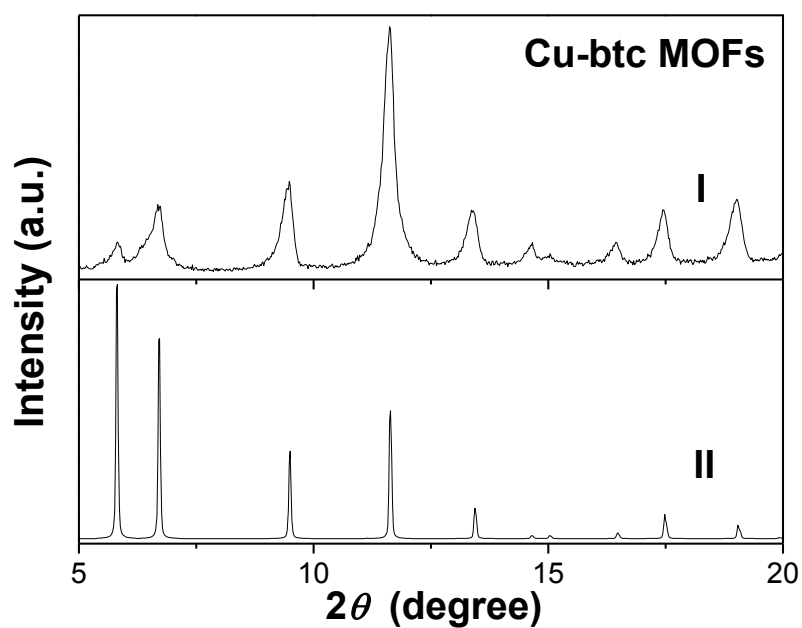


Figure S3. (I) Experimental and (II) simulated XRD patterns of Cu-btc MOFs.

S4

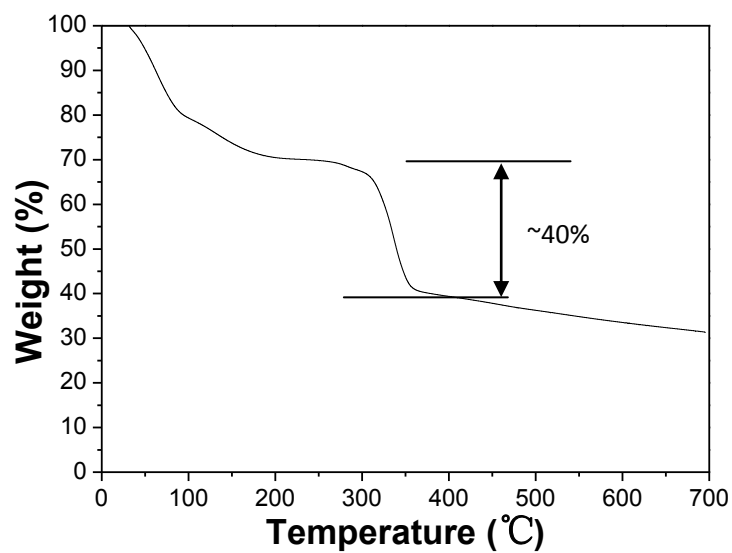


Figure S4. Thermogravimetric analysis (TGA) curve of as-prepared Cu-btc MOFs under nitrogen atmosphere with a ramp of $10^{\circ}\text{C min}^{-1}$.

S5

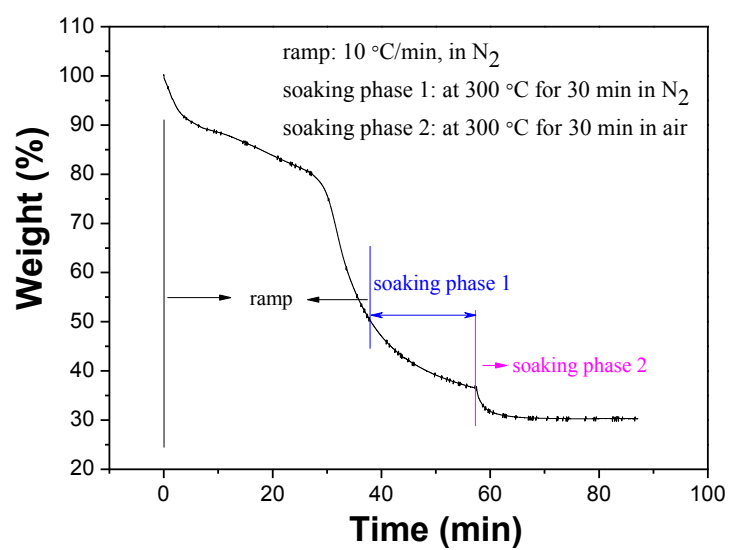


Figure S5. Thermogravimetric analysis (TGA) curve of as-prepared Cu-btc MOFs under the heating treatment.

S6

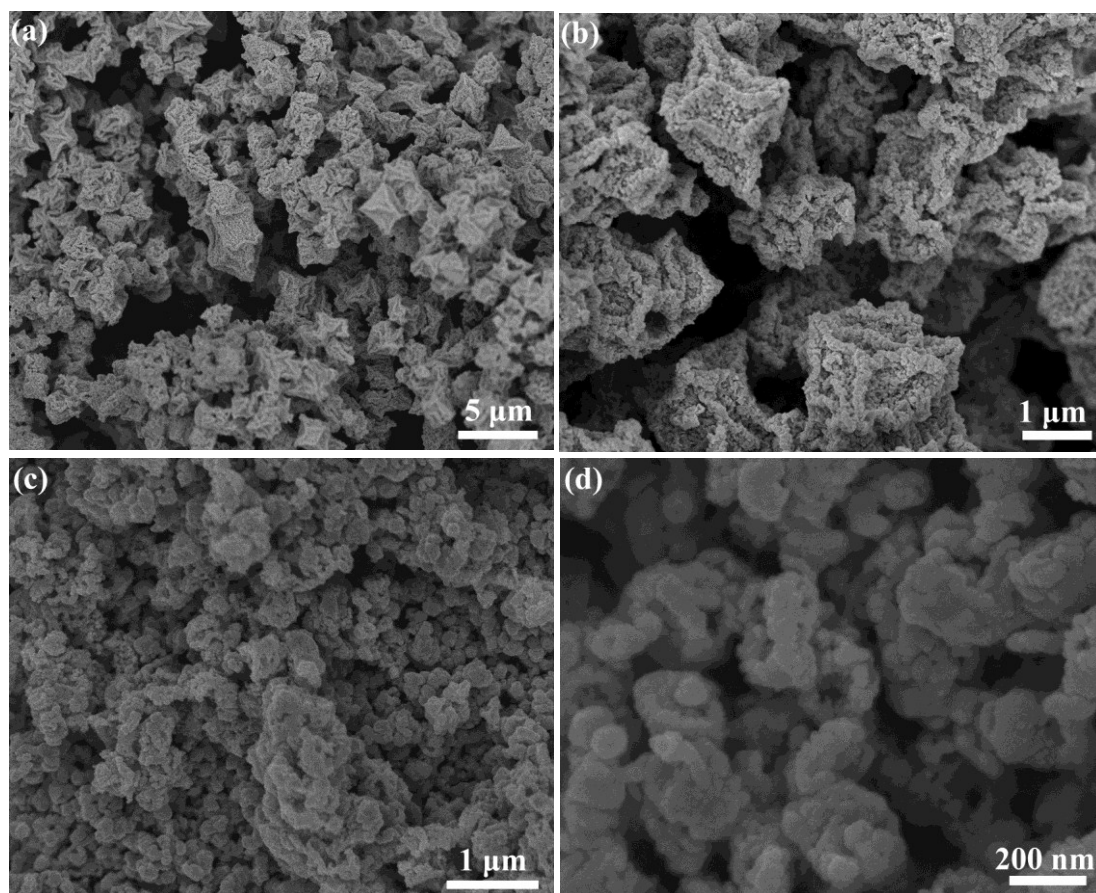


Figure S6. (a) Low- and (b) high-magnified FESEM images of products obtained after heating Cu-btc MOFs at 350 °C; (c) low- and (d) high-magnified FESEM images of products obtained after heating Cu-btc MOFs at 400 °C.

S7

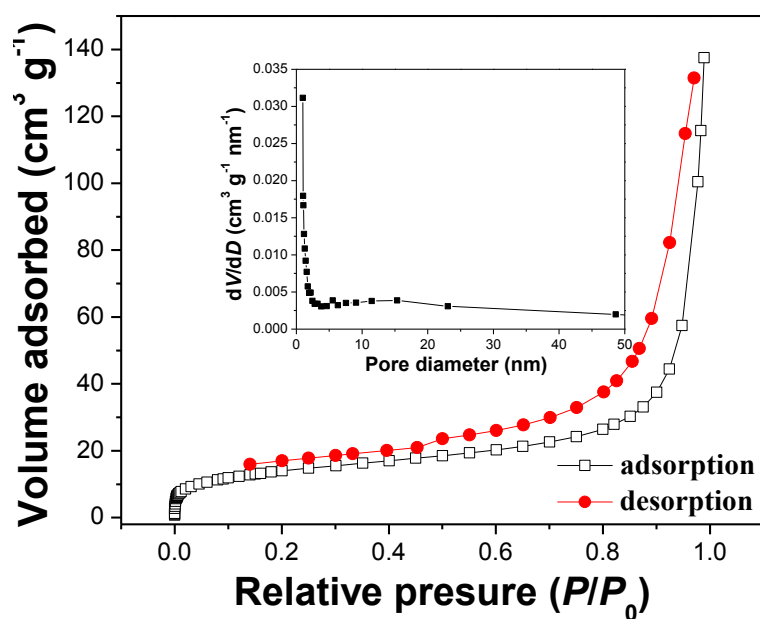


Figure S7. N₂ adsorption/desorption isotherm curve of the CuO hollow octahedrons with the inset showing the distribution of the pore sizes.

S8

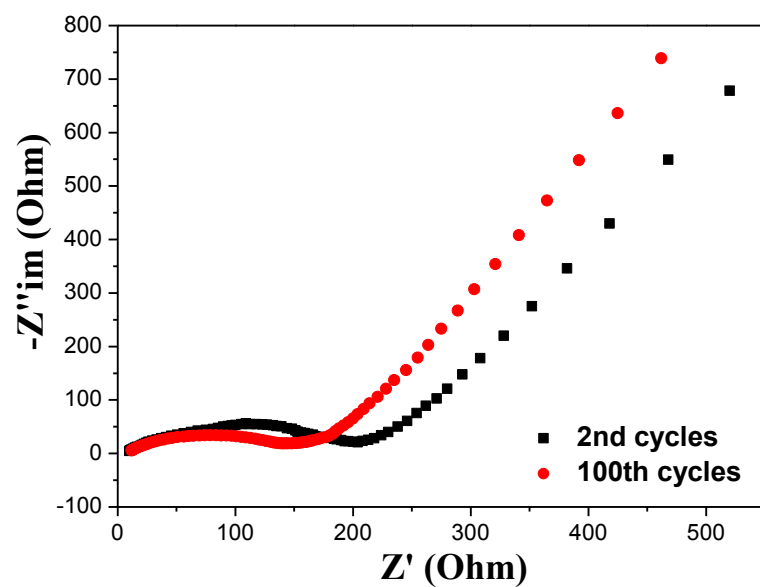


Figure S8. Electrochemical impedance spectra (EIS) of CuO octahedrons after discharge-charge cycles.

S9

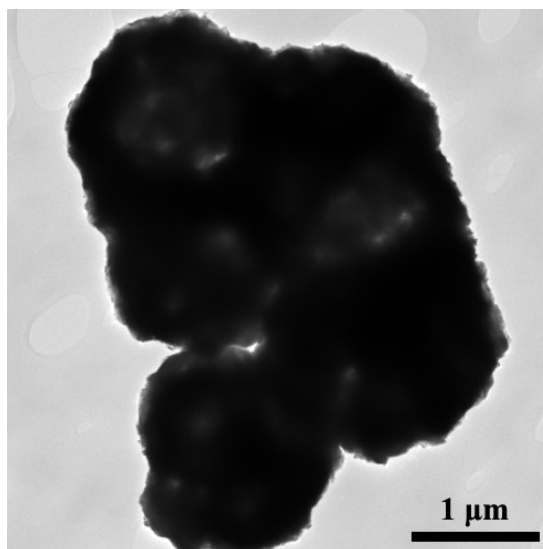


Figure S9. The TEM image of the electrode after 100 cycles