Electronic Supplementary information

Metal-organic frameworks derived porous CuO/Cu₂O composite

hollow octahedrons as high performance anode materials for sodium

ion batteries †

Xiaojie Zhang, Wei Qin, Dongsheng Li, Dong Yan, Bingwen Hu, Zhuo Sun, Likun Pan*

Engineering Research Center for Nanophotonics & Advanced Instrument, Ministry of Education, Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, China. E-mail: lkpan@phy.ecnu.edu.cn; Fax: +86 21 62234321; Tel: +86 21 62234132.

Experimental Section

Preparation

Synthesis of Cu-based metal-organic frameworks (Cu-MOFs)

All chemicals were of analytical grade and used without further purification. The Cu-MOFs were prepared as reported previously.^{1, 2} In a typical procedure, 7.2 mmol copper nitrate (Cu(NO₃)₂·3H₂O) was dissolved in 36 ml deionized water and 8.0 mmol benzene-1,3,5-tricarboxylic acid (C₆H₃(COOH)₃) was dissolved in 36 ml ethanol, and then the copper nitrate solution was transferred into the tricarboxylic acid solution. The mixture solution was transferred into a Teflon-lined stainless autoclave. The autoclave was sealed and heated at 120 °C for 12 h, and then cooled to room temperature. The precipitation was retrieved by centrifugation and washed with water and absolute ethanol for several times to remove the residues, and then dried at 80 °C

under vacuum overnight.

Preparation of porous CuO/Cu₂O composite hollow octahedrons

The porous CuO/Cu₂O composite hollow octahedron (CHO) was prepared through a two-step calcination route. Specifically, Cu-MOFs were first pyrolyzed at 300 °C at a rate of 5 °C min⁻¹ for 30 min under nitrogen gas flow. After that, the nitrogen gas flowing was switched off and the furnace was still kept at different temperatures (300 °C, 350 °C and 400 °C) for another 120 min in a flowing air. Finally, the product was taken out and its color was found to be changed from blue to black. The CHO samples obtained from pyrolysis of the Cu-MOFs at 300 °C, 350 °C and 400 °C were named as CHO-1, CHO-2 and CHO-3, respectively.

Characterizations

The morphology and structure of the samples were characterized by X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) measurement with Cu K α radiation (V = 30 kV, I = 25 mA, λ = 1.5418 Å), field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010). The X-ray photoelectron spectroscopy (XPS) analysis was carried out on Kratos Axis Ultra using a monochromatic Al K α radiation and the binding energies were calibrated with that of C1s at 284.8 eV as the reference. Thermogravimetric (TG) analysis was carried out using a Shimadzu-50 thermoanalyser under air flow at 10 °C min⁻¹ in a temperature range of 30-700 °C. The specific surface area, pore volume and mean pore diameter were evaluated with

an ASAP 2020 Accelerated Surface Area and Porosimetry System (Norcross, GA) based on the Brunauer-Emmet-Teller (BET) multipoint method.

Electrochemical measurements

Electrochemical characterizations were carried out in two electrode coin-cell configurations. For preparing working electrode, the CHO samples as active materials, Super-P carbon black as conductive agent and carboxymethyl cellulose as binder were mixed in deionized water with a weight ratio of 70:20:10 to form a homogenously slurry and coated on a copper foil followed by drying at 120 °C overnight in vacuum oven. Coin type cells (CR2032) were assembled in a glove box (MB-10-compact, MBRAUN) under Ar atmosphere, with oxygen and water contents less than 0.5 ppm, where sodium metal foil and Whatman glass fiber membrane were used as the counter electrode and separator, respectively. The electrolyte was 1 M NaClO₄ solution in ethylene carbonate and propylene carbonate (1:1, w/w) with the addition of 5 wt% fluoroethylene carbonate. Galvanostatic charge-discharge test was conducted on a LAND2001A battery test system in a voltage range of 0.005-3 V at a current density of 50 mA g⁻¹ unless otherwise specified. Cyclic voltammetry was performed using an electrochemical workstation (AUTOLAB PGSTAT302N) in a voltage range of 0.005-3 V at a scan rate of 0.2 mV s⁻¹ at room temperature. Electrochemical impedance spectroscopy measurement was carried out on the same electrochemical workstation in a frequency range of 0.01 Hz to 100 kHz, and the applied bias voltage and ac amplitude were set at the open circuit voltage of the cells and 5 mV, respectively.



Fig. S1 FESEM image of Cu-MOFs.



Fig. S2 XRD pattern of Cu-MOFs.



Fig. S3 TG curve of Cu-MOFs in air.

As shown in Fig. S3, the weight loss in the first step from room temperature to \sim 130 °C is mainly due to the loss of water molecules from the porous framework of MOFs. A second sharp weight loss of \sim 35% occurs between 270 °C and 300 °C resulting from the decomposition and oxidation of the organic groups.



Fig. S4 XPS spectra of CHO samples.



Fig. S5 Selected area electron diffraction pattern of CHO-1.



Fig. S6 FESEM images of (a) CHO-2 and (b) CHO-3.



Fig. S7 N_2 adsorption/desorption isotherms at 77 K for CHO samples. Inset depicts the corresponding pore size distributions.

samples.							
Samples	Specific surface	Pore volume/	Mean pore				
	area/m ² g ⁻¹	$cm^3 g^{-1}$	diameter/nm				
CHO-1	10.65	1.45	25.34				
CHO-2	3.57	0.74	20.73				
CHO-3	2.39	0.64	16.49				

Table S1 Specific surface areas, pore volumes and mean pore diameters of CHO



Fig. S8 Discharge/charge curves at 1st, 2nd and 10th cycles of (a) CHO-3, (b) CHO-2 and (c) CHO-1 at a current density of 50 mA g⁻¹.



Fig. S9 (a), (b) and (c) Nyquist plots of CHO-1, CHO-2 and CHO-3 electrodes at different temperatures. The inset of (a) shows the corresponding equivalent circuit model. R_i, R_f, R_{ct}, Z_W and CPE denote internal resistance of the test battery, resistance of SEI layer, charge transfer resistance, Warburg impedance and constant phase element, respectively. (d) Corresponding Arrhenius plots of -ln(T/R_{ct}) versus 1000/T.

Table S2 Fitted values of R _{ct} for CHO electrodes at different temperatures.						
	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
Samples	R_{ct}/Ω	R_{ct}/Ω	R_{ct}/Ω	R_{ct}/Ω	R_{ct}/Ω	$R_{ct}\!/\Omega$
CHO-1	55.3	47.7	31.6	28.5	15.8	12.1
CHO-2	72.9	53.7	46.3	35.1	30.4	26.1
CHO-3	102.9	81.8	60.5	44.1	33.0	28.3

References

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2. S. Chui, S. Lo, J. Charmant, A. Orpen and I. Williams, Science, 1999, 283, 1148.