

Nitrogen/Oxygen co-doped mesoporous carbon octahedrons for high-performance potassium-ion battery

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Materials and methods

1. Materials Synthesis

Synthesis of the metal-organic frameworks (Cu-BTC): All chemicals are analytical grade, and were used without any further purification. The Cu-BTC precursor was synthesized according the previous research. The typical experiment was carried out as follows. 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 50 ml absolute methanol under ultrasonication, respectively. After that, the solution was mixed under agitated string for a while and kept at room temperature for 12h. the precipitation was retrieved by centrifugation and washed with methanol several times. Finally, the blue powder of Cu-BTC was dried in a vacuum at 60 °C.

The synthesis of the nitrogen/oxygen co-doped mesoporous carbon octhedrons (MCOs): the precursor was annealed under N₂ atmosphere at 600 °C for 2 h to prepare Cu/C composites. Then the composites were treated with 10 wt% nitric acid at 60 °C for 24 hours to obtain nitrogen doped carbon materials for activation. As for the activation, 500 mg powder after HNO₃

treating was dispersed in 50 ml 3M aqueous KOH solution and stirred for 6 hours. The extra KOH solution was removed by centrifugation, and then the mixture was dried at 60 °C for 24 hours. The dry mixture was heated at 800 °C for 2 hours under N₂ atmosphere. After cooling down to room temperature, the sample was repeatedly washed by deionized water until a pH value of 7 was reached. Finally, the sample was dried at 60 °C for 24 hours to get MCOs.

2. Characterization

The power X-ray diffraction (XRD) patterns of all samples were recorded with an X-ray diffractometer (Japan Rigaku D/MAX- γ A) equipped with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$) over the 2θ range of 20-80°. Field emission scanning electron microscopy (FE-SEM) images were collected on a JEOL JSM-6700 M scanning electron microscope. Transmission electron microscope (TEM) images were taken on Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV, and high-resolution transmission electron microscope (HRTEM) (jeol-2011) was operated at an acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K (Micromeritics ASAP 2020) using the Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size were calculated according to the Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. Thermogravimetric analysis (TGA) was carried out using a Shimadzu-50 thermoanalyser under nitrogen flow. XPS measurements were performed on a VGESCALAB MK II X-ray photoelectron spectrometer with an MgK α excitation source (1253.6 eV).

3. Electrochemical Measurement

The electrochemical behavior of the MCOs were performed using CR2032 coin-type cells with potassium serving as the counter electrode and the reference electrode. To prepare a working

electrode, the as-synthesized active material (MCOs, 80 wt%), conductive material (acetylene black, 10 wt%), and the polymer binder (PVDF, 10 wt%) were mixed in N-methyl-2-pyrrolidone. The mixture was subsequently brush coated on copper foil and then dried at 80 °C for 12 h. The electrolyte used in the cells was 1.00 M KPF_6 in ethylene carbonate and diethyl carbonate (EC/DEC = 1:1). The cells were assembled in an argon-filled glove box with both the moisture and the oxygen content below 1 ppm (Mikrouna, Super (1220/750/900)). Cyclic voltammograms (CV) were obtained on a CHI760E electrochemical workstation. The electrode capacity was measured using the galvanostatic discharge/charge method and employing a battery test system (Neware CT-3008W) with a voltage range between 0.01 and 3.0 V.

4. Computational Methods

All the calculations were based on density functional theory with spin unrestricted by using the Vienna ab-initio simulation package (VASP)^[1]. The generalized gradient approximation (GGA) with the function of Perdew-Becke-Ernzerhof (PBE) was employed to describe the electron interaction energy of exchange correlation^[2,3]. The projector augmented wave was applied to describe the electron-ion interaction and the plane-wave energy cutoff was set to 400 eV. All structures were optimized with a convergence criterion of 1×10^{-5} eV for the energy and 0.01 eV/Å for the forces. Brillouin zone sampling was employed using a Monkhorst-Packing grid with $3 \times 3 \times 1$. And $5 \times 5 \times 1$ K-point grid was used to calculate the density of states (DOS). The insertion energy is defined as the following Equation:

$$\Delta E = [E_2 - (E_1 + \mu_K)]$$

where E_1 and E_2 are the total energies of the system before and after introducing potassium atoms, respectively, and μ_K is the chemical potential of potassium bulk. A

positive ΔE indicates an endothermic and unstable K insertion reaction while a negative ΔE suggests an exothermic and stable reaction.

Table S1. The insertion energy of different structure.

Structure	pure O doped carbon	pure N doped carbon	N and O co-doped carbon
Insertion energy/eV	-1.28	-1.86	-1.90

References

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- [2] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [3] J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982.

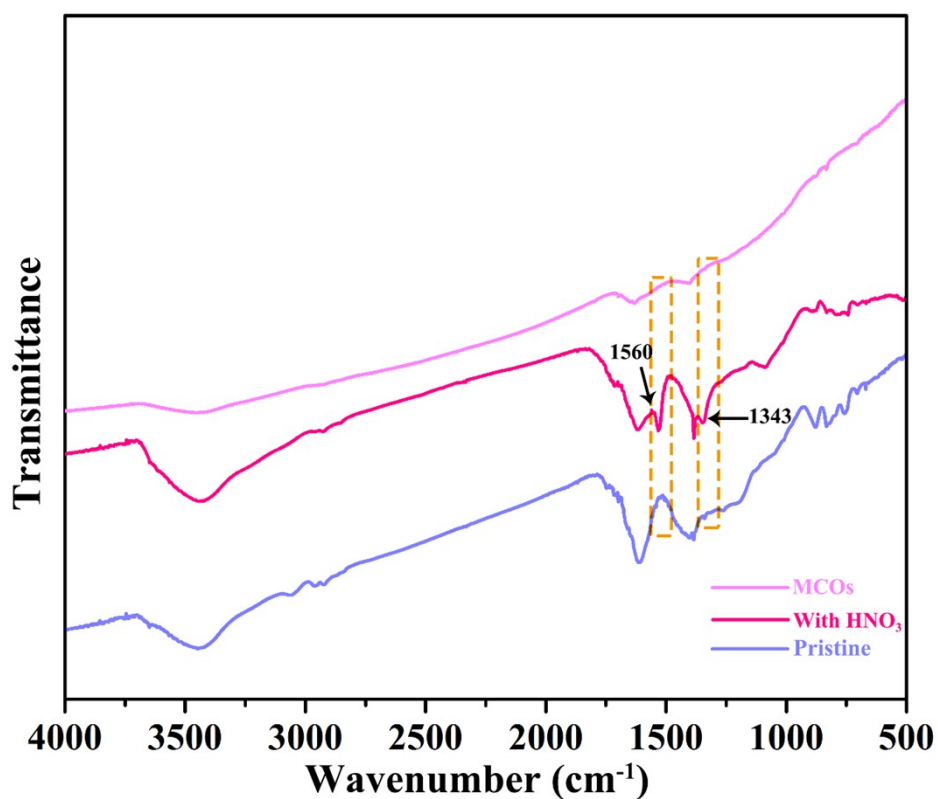


Figure S1. FT-IR spectrum of the pristine Cu/C composites (after carbonization), after HNO₃ washing and MCOs

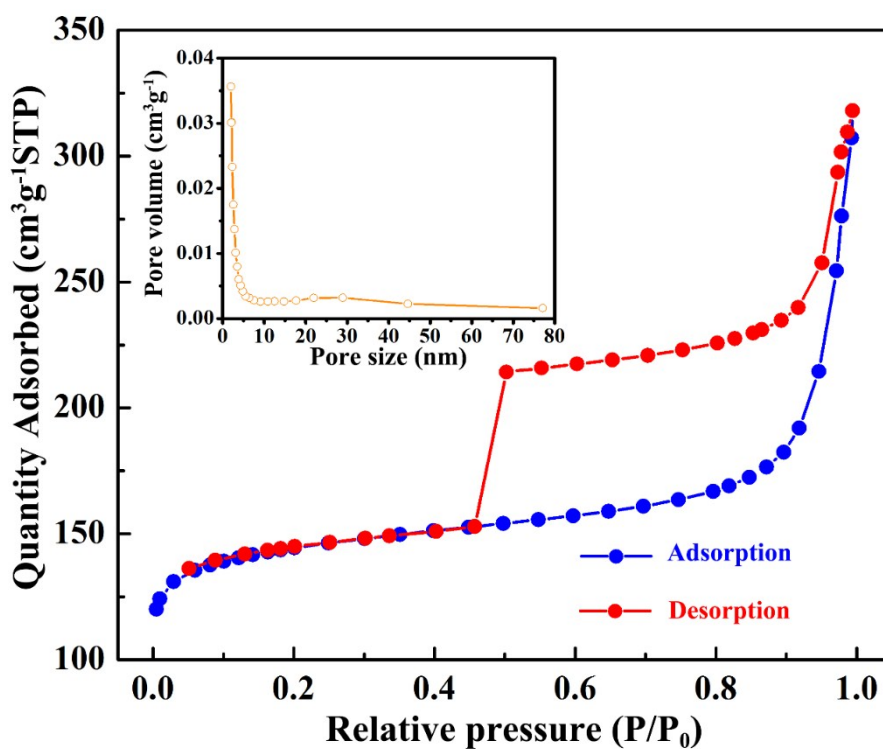


Figure S2. Nitrogen adsorption-desorption isotherm (inset: pore size distribution) for MCOs without etching

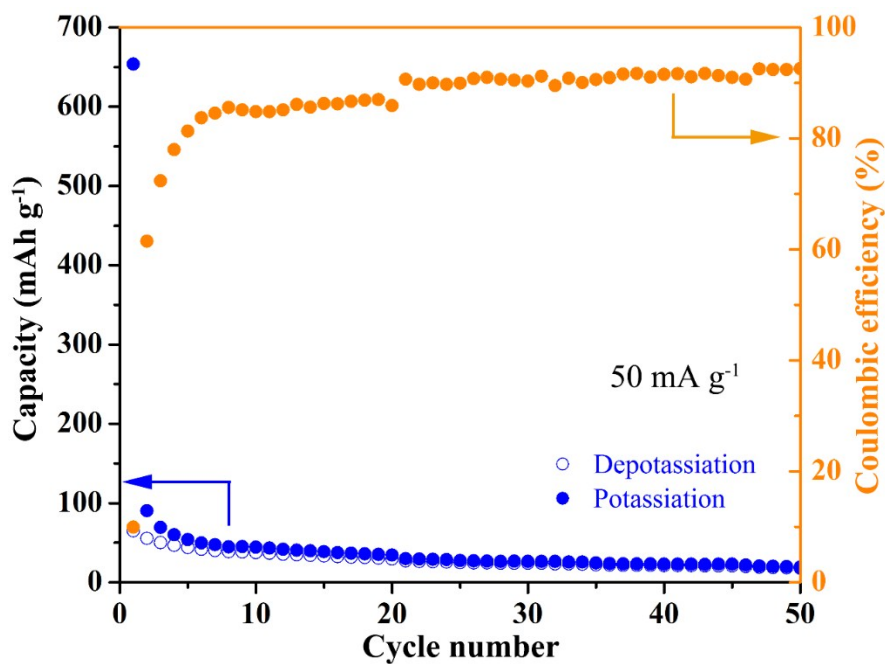


Figure S3. cycling performance of MCOs without etching at a current density of 50 mA g⁻¹

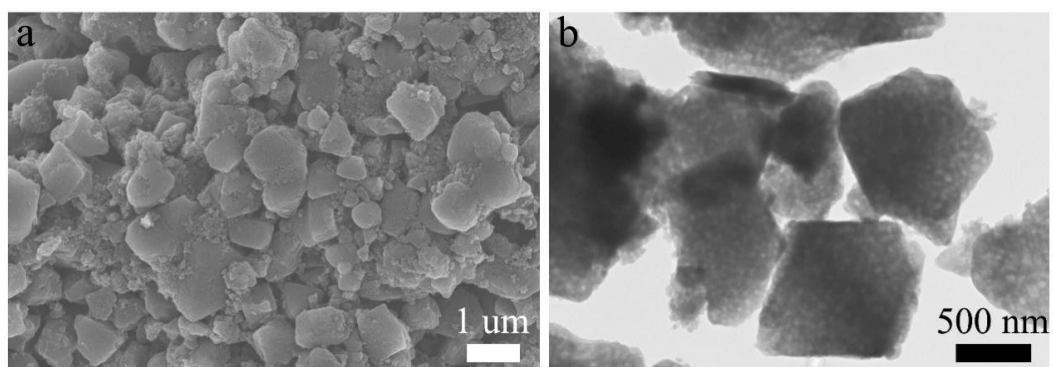


Figure S4. a) SEM and b) TEM images of MCO after 3000 cycles at 2 A g^{-1}

Table S2. The comparison of K-storage performance between MCOs and other carbonaceous materials.

Name	Current density (mA g^{-1})	Charge capacity (mA h g^{-1})	Cycle number	Reference
Hard carbon	28	216	100	Ref 9
PCMs	50	226.6	100	Ref 12
OMC	50	257.4	100	Ref 13
Nanofiber	25	248	100	Ref 14
graphite	200	100	100	Ref 26
Soft carbon	100	249	100	Ref 27
Graphene	100	210	100	Ref 28
NONPHC	50	230.6	100	Ref 29
MCOs	50/100	364/240	50/100	This work
	1000/2000	100/80	1300/3000	This work