Supporting information

Nitrogen doped hierarchical porous carbon for supercapacitors and zinc ion hybrid capacitors

Jun Ni[a], Weijian Chen[a], Xinyang Zhang[a], Hui Xu[a], Minghui Zhang*[b], Xiaoliang Wu*[a]

[a]*College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, 26 Hexing Road, Harbin 150040, P. R. China*

[b]*School of Pharmacy, Health Science Center, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China*

**Address correspondence to wuxiaoliang90@163.com; minghuizhang@xjtu.edu.cn*

1.1 Materials

Urea, Potassium bicarbonate, Agar，Potassium hydroxide (KOH), Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), Hydrochloric acid (HCl), Polytetrafluoroethylene (PTFE) and Ethanol were analytical-grade and obtained from Sinopharm Chemical Reagent, Co., Ltd (Shanghai, China). Zinc foil (thickness of 300 μm) and Glass fiber separator (Whatman, 0.5 mm) were purchased from Qingyuan Metal Material Co., Ltd (Guangdong, China). All raw materials were used directly as purchased without further purification. The water used in the experiments was freshly deionized.

1.2 Structural characterizations

The microstructures were measured by scanning/transmission electron microscope (SEM JEOL JSM-7500F, TEM JEM-2800F). Powder X-ray diffractometer (XRD) was used to characterize the crystal structures. X-ray photoelectron spectroscopy (XPS) measurement (Thermo Scientific K-Alpha) was used to detect the surface chemical state of the obtained samples. Nitrogen adsorption/desorption measurement was used to detect the specific surface area by the multi-point Brunauer-Emmett-Teller (BET) way and the pore size distribution was estimated by density functional theory (DFT).

1.3 Assembling three-electrode system

The carbon sample (75 wt%), carbon black (20 wt%), and polytetrafluoroethylene (PTFE) binder (5 wt%) were mixed homogeneously to form a slurry and then pasted onto the nickel foam (1×1 cm^2, current collector) with a mass loading of about 3.0 mg cm^{-2} (thickness of about 35 μm), followed by drying at 60 °C for 12 h to obtain the working electrodes. In 6 M KOH solution, the electrochemical performance of the NPC electrode was tested by a CHI 660E electrochemical workstation using a three-electrode configuration of opposing electrode (using a platinum plate),

reference electrode (Hg/HgO electrode), and working electrode.

1.4 Assembling symmetric supercapacitor

The electrochemical performance of the synthesized carbon materials was also evaluated in symmetrical device using two-electrode system in 2 M $ZnSO_4$ solution. All measurements were tested by electrochemical workstation (CHI 660E).

1.5 Assembling Zinc-ion hybrid supercapacitor

The mass ratio contains 80 wt% hierarchical porous carbon, 10 wt% conductive carbon black and 5 wt% polytetrafluoroethylene (PTFE), and then mixed and ground with ethanol to form a uniform slurry with no particles on the surface. After coating on the stainless steel mesh, the loaded activated carbon is about 3 mg cm^{-2}. The electrode was vacuum dried overnight at 60 °C. To fabricate ZIHC, the prepared carbon electrode was used as the cathode, the zinc foil was used as the anode, and the Wattman glass fiber was used as the separator. The aqueous 2 M $ZnSO_4$ was used as the electrolyte.

1.6 Electrochemical measurement

1.6.1 Three-electrode system

The electrochemical performance of the three-electrode system (platinum plate for the counter electrode and Hg/HgO electrode for the reference electrode) was investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) on a CHI660E electrochemistry workstation (Chenhua, Shanghai, China) at room temperature. The CV curves of the three-electrode system were tested in the voltage range from -1 to 0 V at a scan rate of 2-100 mV s^{-1}. GCD curves were tested at current densities ranging from 0.5 to 20 A g^{-1}. EIS measurements were made in the frequency range of 0.01 Hz to 1 MHz.

The gravimetric specific capacitance (C) was computed by the formulas:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where I (A) is the constant discharging current, Δt (s)is discharge time, ΔV (V) is the potential region, *m(g)* is the mass of active materials.

1.6.2 symmetric supercapacitor

Likewise, by testing the two-electrode system, we can calculate the gravimetric specific capacitances via

$$C = \frac{4I\Delta t}{m_t V} \tag{2}$$

where I (A) refers to the discharge current, Δt (s) is the discharge time, m_t (g) is the total mass of the porous carbon material for two electrodes and V (v) is the potential change.

Moreover, the specific energy (E, W h kg^{-1}) was calculated via the equation

$$E = \frac{CV^2}{2} \tag{3}$$

where C (F g^{-1}) represents the specific capacitance and V refers to the potential change. The specific power (P, W kg^{-1}) can also be obtained with the following formula:

$$P = \frac{E}{\Delta t} \tag{4}$$

where E is the energy density and Δt refers to the discharge time.

1.6.3 Zinc-ion hybrid capacitors

The electrochemical performance of zinc ion capacitors was investigated by using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) at room temperature on a CHI660E electrochemical workstation (Chenhua,

Shanghai, China) battery testing system (CT-4008, Neware). CV tests were performed on zinc-ion capacitors in the voltage range of 0.2 to 1.8 V at a sweep rate of 2-100 mV s^{-1}. GCD curves were tested at current densities ranging from 0.1 to 10 A g^{-1}. EIS measurements were made in the frequency range of 0.01 Hz to 1 MHz.

The gravimetric specific capacitance (C') was computed by the formulas:

$$C' = \frac{I\Delta t}{3.6m} \tag{5}$$

where I (A) is the current density, Δt (s) is discharge time, $m(g)$ is the mass of active materials.

The energy density and the power density of the devices were computed by the formulas:

$$E = 0.5C'\Delta V \tag{6}$$

$$P = \frac{3600 \times E}{\Delta t} \tag{7}$$

Where E (Wh kg^{-1}) is the energy density, P (W kg^{-1}) is the power density, C' (mAh g^{-1}) is the specific capacitance of the ZIHCs, ΔV (V) is the operating voltage window of the ZIHCs, and Δt (s) is the discharge time.

Fig. S1 (a) SEM image of NPC-500. (b) SEM image of NPC-700.

Table S1 The atomic percentage of C, N and O of carbon materials from the XPS results.

Samples	C at.%	N at.%	O at.%
NPC-500	78.96	6.22	14.82
NPC-600	84.05	5.30	10.65
NPC-700	85.67	4.32	10.02

Table S2 Corresponding to the change of group percentage content of C, N and O elements in the XPS diagram.

	C at.%				N at.%				O at.%		
	C-C	**C-N**	**C-O**	**C=O**	**N-6**	**N-5**	**N-Q**	**N-O**	**C=O**	**C-O**	**O-C=O**
NPC-500	67.47	14.59	9.33	8.61	66.84	22.02	7.87	3.27	71.50	24.43	4.07
NPC-600	76.05	11.98	7.75	4.22	66.27	22.90	5.48	5.35	78.52	18.74	2.74
NPC-700	69.04	15.88	7.30	7.78	66.47	14.51	10.39	8.63	59.38	28.70	11.92

Fig. S2 (a) Contact angle of NPC-500. (b) Contact angle of NPC-600. (c) Contact angle of NPC-700.

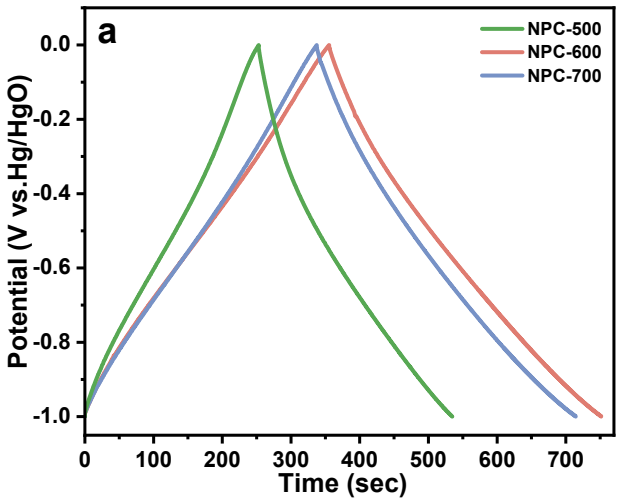

Fig. S3 (a) GCD curves of NPC samples at 1 A g^{-1}.

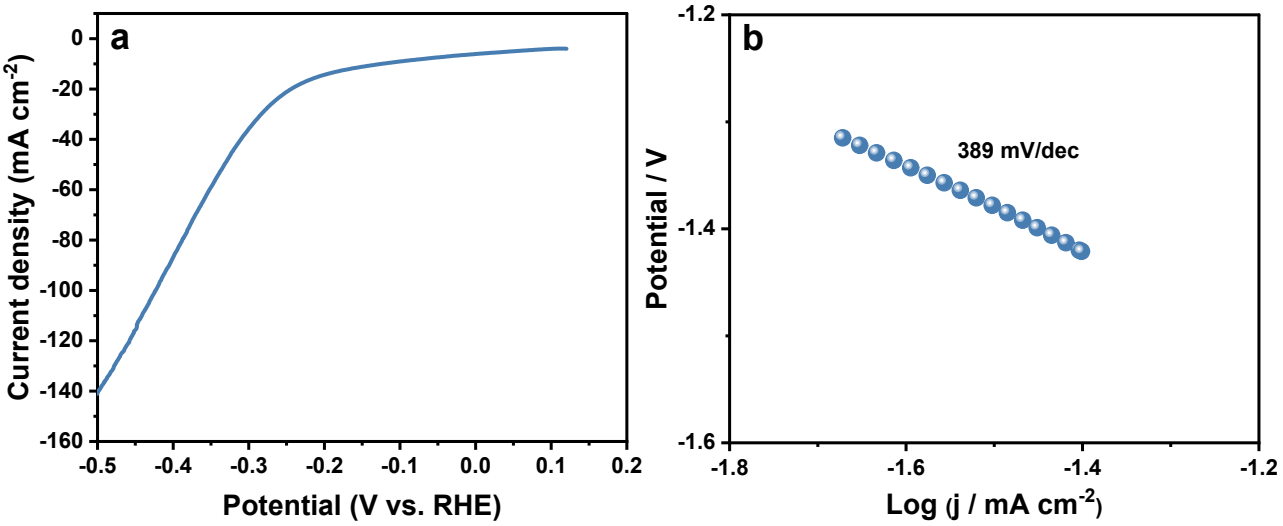

Fig. S4 (a) Linear Sweep Voltammetry of NPC-600. (b) Hydrogen Evolution Reaction.

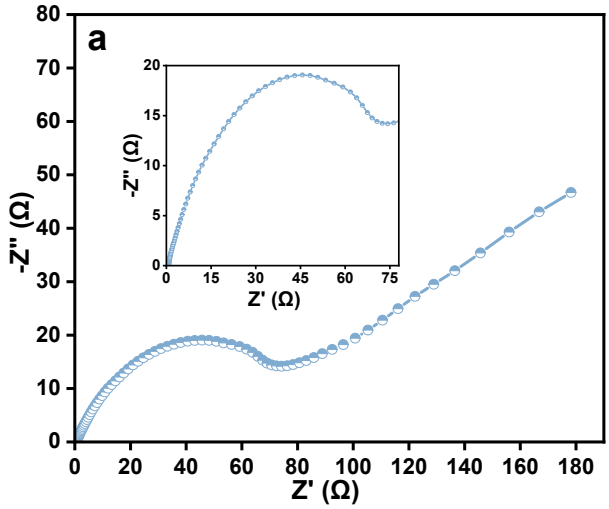

Fig. S5 (a) Nyquist plots of the Zn//$ZnSO_4$//NPC hybrid capacitor.

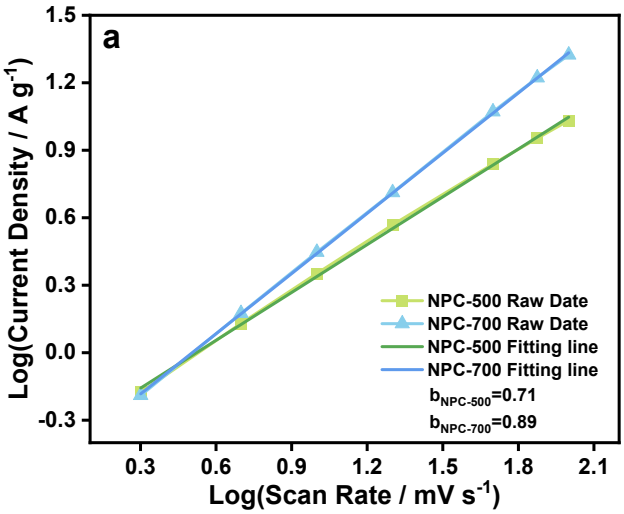

Fig. S6 (a) The b values of NPC-500 and NPC-700 obtained from the linear relationship between log*(i)* and log*(v)*.

Fig. S7 Capacitance and diffusion-controlled contribution at different scanning rate.