Electronic Supplementary Information

Electrospun metal-organic framework derived hierarchical carbon nanofibers with high performance for supercapacitor

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Materials and Methods:

Materials: Zn (NO$_3$)$_2$·6H$_2$O, 2-methylimidazole (2-MeIM), Polyacrylonitrile (PAN, MW=150000) were obtained from Sigma-Aldrich. N,N-dimethylformamide (DMF, ≥99.9%), anhydrous ethanol were all purchased from Nanjing Chemical Reagent Co., Ltd. and used without further purification. Deionized (DI) water was used in all experiments.

Synthesis of ZIF-8 cubic nanocrystals. ZIF-8 cubic nanocrystals were synthesized according to the previous reported method with modifications.$^{41}$ 10.8 g 2-MeIM was dissolved in 100 mL of DI water; 5.0 mL of 0.01 M CTAB was added into the 2-MeIM solution with stirring for 5 min. Then Zn (NO$_3$)$_2$·6H$_2$O (0.7g) in 100 mL of water was added into the above solution with stirring for another 5 min. The mixture was let at room temperature for 3 h. The white product was collected by centrifugation (8000 r/min, 10 min) and washed thoroughly with water and anhydrous ethanol for three times. Finally, the powder was dried under vacuum for 4 h at 80 °C.

Synthesis of NCPF. In a typical synthesis, 0.6 g ZIF-8 powder was added into 5 mL DMF with sonication until it was well dispersed. Then, 0.8 g PAN was added into the solution with stirring at 65 °C for 4h to obtain the electrospinning precursor. The electrospinning process was carried out by applying a high positive voltage (10.4 kV) with a collecting distance 15 cm. The injection speed was fixed at 0.08 mm min$^{-1}$. The obtained fibers were peeled off from the collector directly to the following heat-treatment. It was first stabilized at 240 °C for 1 h and then carbonized and at 800
°C for 3 h in N₂ atmosphere with a ramp rate of 5 °C min⁻¹.

Synthesis of PAN-C and ZIF-8-NPC. ZIF-8-NPC was prepared from directly carbonized ZIF-8 powder. PAN fibers were prepared without adding ZIF-8 in the precursor solution, following with same and pyrolysis as above.

Characterization: The morphology of the samples was investigated by STEM (Tecnai G2 F30 S-TWIN), TEM (FEI T20), SEM (FEI 250). The XPS (X-ray photoelectron spectroscopy) spectra were obtained by using a PHI Quantera II ESCA System with Al Kα radiation at 1486.8 V. N₂ adsorption and desorption isotherms were measured using Micromeritics ASAP-2020 at liquid nitrogen temperature (77 K). The composition was examined by XRD instrument (BRUKER D8, Cu Kα) at 40 kV and 40 mA (λ=1.5418 Å). The conductivities of ZIF-8-derived NPC, PAN-C, and NPCF were investigated by four-probe method with the help of a SDT-4 digital electrometer (Guangzhou, China.).

Electrochemical measurements: All the electrochemical measurements were carried out using a Chenhua electrochemical workstation (CHI660E, Shanghai, China). The three electrode method was applied with 1 M H₂SO₄ as the electrolyte solution, platinum wire as the counter electrode, Ag/AgCl as the reference electrode, glassy carbon as the working electrode. The working electrodes were prepared as follows: 5 mg samples was mixed with 0.5 mL DI water and isopropanol. Then 10 μL suspension solution was dropped onto the glass carbon electrode with a diameter of 3 mm. After drying, a Nafion solution (0.5 wt % in isopropanol) was coated on the sample as the binder. The CV (cyclic voltammetry) and GCD (galvanostatic charge-discharge) tests were measured at various scan rates and current densities. The EIS (electrochemistry impedance) measurements were carried out in the frequency range from 0.05 Hz to 100 kHz with 5 mV ac amplitude.

Fig. S1 (a) ZIF-8 NPs/PAN/DMF solution (right) and ZIF-8 NPs DMF solution (left); (b) A digital pictures of ZIF-8/PAN and NPCF films.

Fig. S2 (a) XRD patterns of ZIF-8, ZIF-8/PAN; (b) IR spectra of ZIF-8, PAN, ZIF-8/PAN.

Fig. S3 SEM images of PAN and PAN-C
Fig. S4 N₂ sorption isotherms of (a) ZIF-8-NPC, (b) NPCF.

Table S1 Textural parameters and proportion of carbon, nitrogen, oxide calculated by XPS of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface Area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>C content (%)</th>
<th>N content (%)</th>
<th>O content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8-NPC</td>
<td>989.0</td>
<td>0.39</td>
<td>76.6</td>
<td>18.6</td>
<td>4.8</td>
</tr>
<tr>
<td>NPCF</td>
<td>314.7</td>
<td>0.33</td>
<td>86.7</td>
<td>8.3</td>
<td>5.0</td>
</tr>
<tr>
<td>PAN-C</td>
<td>183.1</td>
<td>0.25</td>
<td>85.9</td>
<td>10.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Fig. S5 TG curves of ZIF-8, PAN/ZIF-8, PAN.
Fig. S6 (a) XPS survey spectrum; (b) High resolution N 1s of NPCF.

Fig. S7 CV curves and galvanostatic charge-discharge curves of (a and b) PAN-C, (c and d) ZIF-8-NPC
**Figure S8** Equivalent circuit of ZIF-NPC, PAN-C and NPCF.

R1 is the equivalent internal resistance, including resistance of the electrolyte and the internal resistance of the electrode. C2 is double-layer capacitance, Ws is the finite-length Warburg diffusion element, R2 is charge transfer resistance, and C1 is the faradic capacitance.\textsuperscript{S2}

Fig. S9 TEM of (a) NPCF-0.2 and (b) NPCF-0.4

Fig. S10 galvanostatic charge-discharge curves of NPCF-0.2, NPCF-0.4, NPCF-0.6 at 1 A g⁻¹