# Electronic Supplementary Information

## Nitrogen-rich hierarchical porous hollow carbon nanofibers for high-performance supercapacitor electrodes

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**Experimental details**

Polyvinylpyrrolidone (PVP; Mw = 30,000) and polyacrylonitrile (PAN; Mw = 130,000) were purchased from Sinopharm Chemical Reagent Co. 40 wt.% of PVP was dissolved in N, N-dimethylformamide (DMF) as a core precursor. 9 wt.% of PAN and 4.5 wt.% of PVP were dissolved in DMF as a shell precursor. The solutions were stirred at 65 °C for 12 h. A concentric nozzle with inner and outer diameter of 0.5 and 1.5 mm was used to carry out concentric electrospinning. The condition of electrospinning was set up as follows: the applied voltage was 22 kV, the tip-to-collector distance was 20 cm, and the flow rates of inner and outer polymer solution were 0.6 and 1 mL $h^{-1}$.

In order to keep the nonwoven web structure during the washing process, two stainless steel nets were used to clamp the obtained precursor nanofibers. The samples were ultrasonically washed by deionized water for three times to remove PVP. After vacuum filtration, the nonwoven web was dipped into 30 wt.% KCl/$K_2CO_3$ solution (KCl : $K_2CO_3$ = 9) and then was filtrated again by vacuum. The mass ratio of activator/PAN is ~2 after drying. Subsequently, the fibers were stabilized by heating to 250 °C at a rate of 5 °C $min^{-1}$ in air, and maintaining for 2 h. Then, the

stabilized fibers were transferred to a quartz tube (ID = 9 cm) and heated to 800 °C at a rate of 5 °C $min^{-1}$ in nitrogen (Flow rate: 200 sccm) for 1 h. Finally, the samples were washed and dried under vacuum. For comparison, samples directly carbonized and carbonized with only KCl were also prepared and named as HCNFs and HCNFs-KCl.

Scanning electron microscopy (SEM, LEO1530) and transmission electron microscopy (TEM, Tecnai G20, 200 kV) were used to characterize the samples. $N_2$ sorption isotherms were measured by using a volume adsorption apparatus (autosorb-1) at 77 K. The total pore volumes were estimated from single point adsorption ($P/P_0$= 0.995), the specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, the micropore surface area and micropore volume were determined by t-plot method, and pore size distributions (PSD) were derived from density functional theory (DFT). PHI Quantera Imaging X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemistry.

A three-electrode system tests were carried out in 6.0 M KOH aqueous solution with electrode active material mass of 2 mg, a reference electrode of Hg/HgO and Pt wire counter electrode. The electrochemical performance was determined by cyclic voltammetry (CV), electrochemical impendence spectroscopy (EIS) and galvanostatic charge/discharge cycling (GC) tests with a potential window ranging from -1 to 0 V (vs. Hg/ HgO). CV and EIS tests were conducted in VSP-300 electrochemical interface. CV curves were obtained at various scan rates from 5.0-1000 mV $s^{-1}$ and EIS tests were performed by sweeping with an AC-amplitude of 10 mV at the frequency from 50 mHz to 40 kHz. The galvanostatic charge-discharge capacitance measurements was conducted on an Arbin-BT2000 test station with different current densities from 0.2 to 50 A $g^{-1}$.

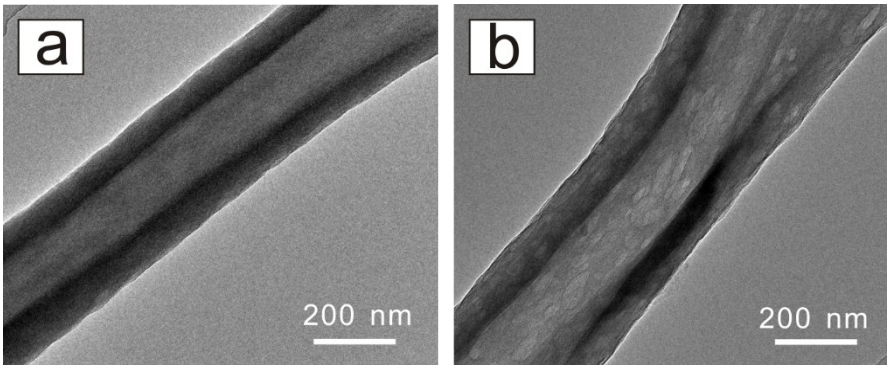


**Fig. S1** TEM images of (a) HCNFs and (b) HCNFs-KCl.

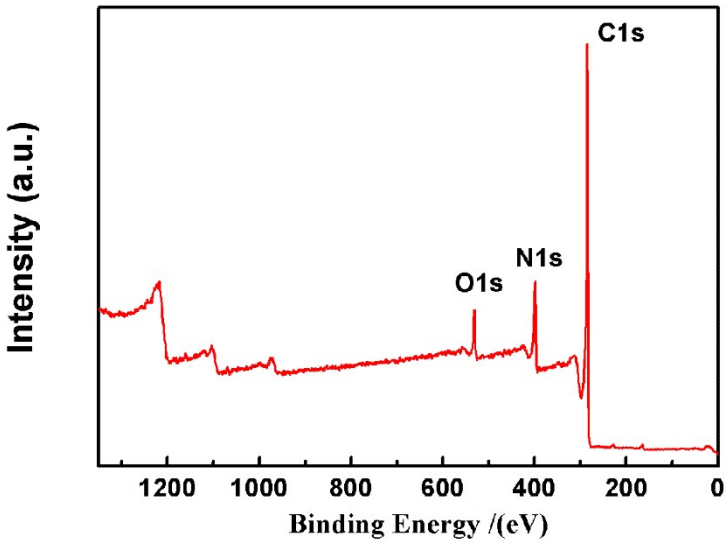


**Fig. S2** XPS survey spectrum of HPCNFs

**Table S1**

Nitrogen content of activated carbon materials.

| Precursor | Carbonization temperature/ °C | Nitrogen content/% | Reference |
|---|---|---|---|
| **PPy** | 700 | 7.2 | *ACS Nano*, 2012, **6,** 7092. |
| **Rice** | 700 | 6.2 | *J. Mater. Chem. A*, 2014, **2,** 3317. |
| **PPy** | 850 | 6.0 | *J. Mater. Chem. A*, 2015, **3**， 2914. |
| **Dicyandiamide** | 600 | 13.1 | *Adv. Funct. Mater.*, 2013, **23,** 2322. |
| **Ethylenediaminetetraacetic acid** | 700 | 7.7 | *Electrochim. Acta*, 2013, **98,** 176. |
| **Ethylenediamine** | 600 | 5.0 | *Chem. Mater.*, 2014, **26,** 2820. |
| **Melamine** | 900 | 7.0 | *Chem. Eur. J.*, 2014, **20,** 564. |
| **PPy** | 650 | 10.25 | *Adv. Mater.*, 2012, **24,** 2047. |
| **PPy** | 650 | 8.8 | *Nanoscale,* 2014, **6,** 1384. |

| | | | |
|---|---|---|---|
| **PAN** | 800 | 14.4 | This work |

**Table S2**

Details of XPS spectrum

| | Element content, wt% | | | Content of different type N, wt% | | | |
|---|---|---|---|---|---|---|---|
| | C | N | O | [a]N6-O | [b]N6 | [c]N-Q | [d]N5 |
| HPCNFs | 81.2 | 14.4 | 4.4 | 3.0 | 4.9 | 5.6 | 0.9 |

[a] Oxidized pyridinic-N

[b] Pyridinic-N

[c] Quaternary-N

[d] Pyrrolic-N

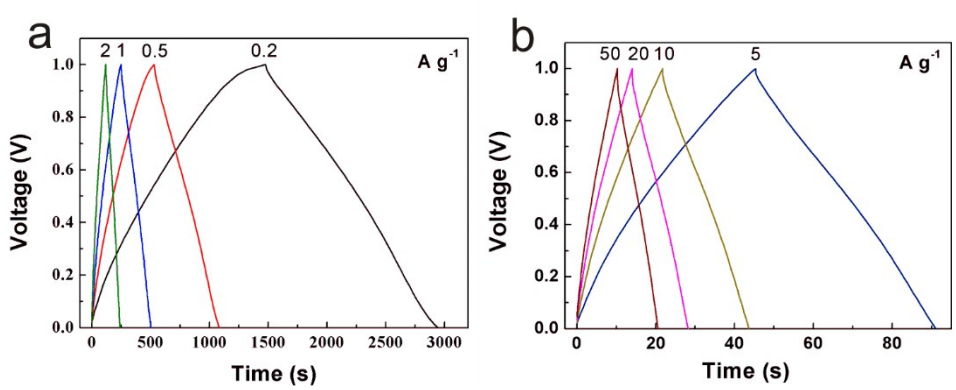


**Fig. S3** GCD curves recorded from 0.2 to 50 A $g^{-1}$

**Table S3**

Maximum capacitances of porous carbon nanofiber materials.

| Precursor | Synthetic methodology | Electrolyte | C/(F $g^{-1}$) | Reference |
|---|---|---|---|---|
| **PMMA/GO** | Electrospinning | 6 M KOH | 128 | *Electrochim. Acta.*, 2012, **75,** 325. |
| **PAN** | Electrospinning | 1 M $H_2SO_4$ | 210 | *J. Power Sources*, 2013, **235,** 289. |
| **PAN/PVP/TPA** | Electrospinning | 1 M $H_2SO_4$ | 225 | *Nano Energy*, 2015, **15,** 66. |
| **PVA** | Electrospinning | 6 M KOH | 256 | *Carbon*, 2013, **51,** 290. |
| **Resole-type Phenolic resin** | Electrospinning | 6 M KOH | 171 | *Mater. Lett.*, 2012, **76,** 214. |
| **PAN/GO** | Electrospinning | 6 M KOH | 263 | *J. Power Sources*, 2013, **222,** 410. |
| **PAN/GO** | Electrospinning | 6 M KOH | 197 | *J. Power Sources*, 2012, **199,** 373. |
| **Bacterial Cellulose** | Pyrolysis | 2 M $H_2SO_4$ | 204 | *Adv. Funct. Mater.*, 2014, **24,** 5104. |
| **DCDA** | Hard-templating /soft-templating | 1 M $H_2SO_4$ | 264 | *J. Mater. Chem. A*, 2013, **1,** 8488. |
| **PAN/PVP** | Concentric electrospinning | 6 M KOH | 293 | This work |

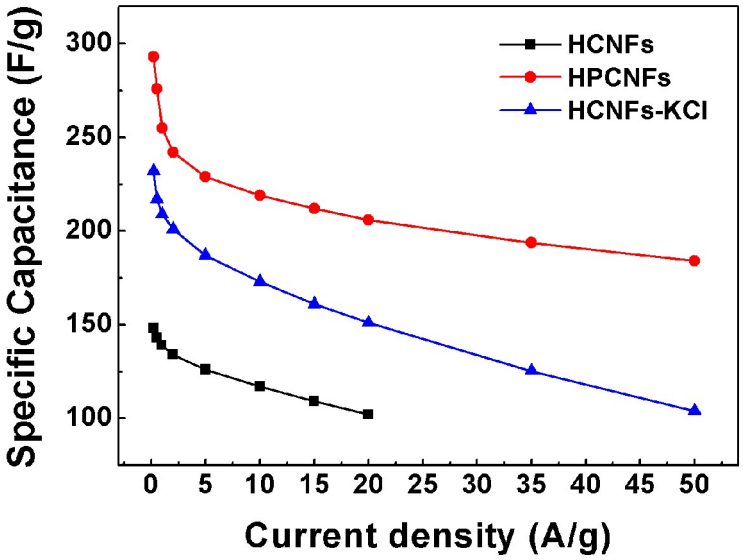


**Fig. S4** rate performances of HCNFs, HPCNFs and HCNFs-KCl

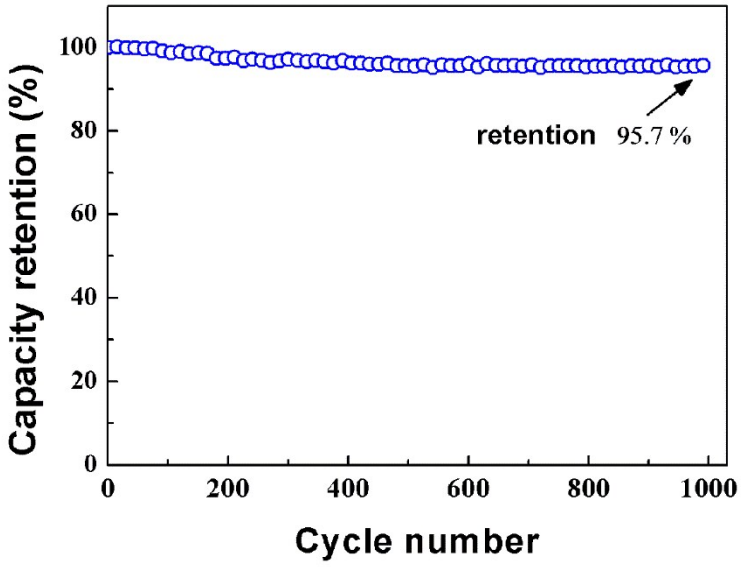


**Fig. S5** cycling stability of HPCNFs at 5 A $g^{-1}$