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# Nitrogen-doped hollow activated carbon nanofibers as high performance supercapacitor electrodes

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ABSTRACT

Nitrogen-doped hollow activated carbon nanofibers (HACNFs) have been prepared by the concentric electrospinning and the following $NH_3$ activation. The as-obtained samples were directly used as supercapacitor electrode without binders and conductive additives. Owing to the unique hollow architecture and high N-doping level (8.2%), the HACNFs exhibit a high specific capacitance of 197 F $g^{-1}$ at 0.2 A $g^{-1}$, which is 1.33 times than that of the solid electrospun nanofibers activated in the same condition. The samples also possess a superior rate capability of 72.1% (143 F $g^{-1}$) at 20 A $g^{-1}$ and long-term cycling stability with a retention of 98.6% after 1000 cycles at 5 A $g^{-1}$ in 6 M KOH.

## 1. Introduction

Owing to their high energy and power density as well as long cycle life, supercapacitors (SCs) have become promising energy storage technologies for applications like hybrid electric vehicles, portable electronic devices, and uninterrupted power supplies [1,2]. Porous carbon materials are nowadays the most widely used electrode materials for supercapacitors. And great efforts have been made to improve the specific capacitance while maintaining the high rate capability [3–5]. Carbon nanofibers (CNFs) prepared via electrospinning could be promising candidates due to their controllable specific surface area (SSA), unique one dimensional nanostructure, high electrical conductivity [6,7], and especially the free-standing properties [8]. However, the low SSA and poor wettability in aqueous solution are still the bottlenecks limiting their wide applications [9–11].

To date, vigorous works have been focused on enhancing the porosities of ACNFs for improving the capacitive performance [7,12]. Concentric electrospinning is an effective approach to obtain unique hollow core/porous shell carbon nanofibers [13]. Compared with conventional electrospun fibers, the extra inner surface and mesoporous tubes can increase the SSA and pore volumes [14,15], which is very beneficial for enhancing the capacitive performance.

Herein, we report an efficient method to prepare N-doped hollow activated carbon nanofibers (HACNFs) *via* the concentric electrospinning of polyvinylpyrrolidone (PVP) as a core precursor and polyacrylonitrile (PAN) as shell precursor. This method is advantageous in facile removing the recyclable PVP just by water-washing instead of being sacrificed by heat treatment. Furthermore, high content of N-doping can be achieved in a short time under the following $NH_3$ activation [3]. More importantly, the free-standing HACNFs film can be directly used as electrode materials for high-performance SCs without binders and conductive additives.

## 2. Experimental

### 2.1. Preparation of the HACNFs

As illustrated in Fig. 1a, the precursor nanofibers were prepared by the concentric electrospinning technology with a concentric nozzle, of which the inner and outer diameter are 0.5 and 1.5 mm. 40 wt.% of PVP (Mw = 30,000) and 10 wt.% of PAN (Mw = 130,000) were separately dissolved in N, N-dimethylformamide (DMF) by magnetic stirring at 65 °C for 12 h. 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 (PVP) and outer (PAN) polymer solution were 0.6 and 1 mL $h^{-1}$. The obtained precursor nanofibers were washed with deionized water at 50 °C for three times to completely remove

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PVP. After being dried under vacuum, the fibers were stabilized at 250 °C in air for 2 h. Subsequently, the stabilized fibers were transferred to a quartz tube and heated to 800 °C at a rate of 5 °C $min^{-1}$ in $N_2$. Once the temperature reached 800 °C, the gas was switched to $NH_3$ for activation and N-doping. During the period of cooldown, the gas was switched to $N_2$ again. To study the influence of the $NH_3$ activation on the product, the activation time was set at 2 h and 1 h, and the corresponding products were respectively named as HACNF-2h and HACNF-1h. For comparison, a sample was carbonized for 2 h at 800 °C in $N_2$ and was denoted as HCNF. In addition, the common solid PAN electrospun nanofibers activated in $NH_3$ at 800 °C for 2 h (named as ACNF-2h) were also prepared for comparison.

### 2.2. Materials characterization and electrochemical evaluation

The morphologies of the samples were observed by scanning electron microscopy (SEM, LEO1530) and transmission electron microscopy (TEM, Tecnai G20, 200 kV). $N_2$ adsorption/desorption isotherms were measured by a volume adsorption apparatus (autosorb-1) at 77 K. BET method, density functional theory (DFT) and t-plot method were used to determine the SSA, the pore size distributions (PSD) and the micropore volumes, respectively. The surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS, PHI Quantera Imaging).

The electrochemical measurement was carried out using a three-electrode cell with a reference electrode of Hg/HgO and a counter electrode of Pt wire in 6 M KOH. The working electrodes were prepared by direct pressing the sample (2–3 mg) between two nickel foams without binders and conductive additives. Cyclic voltammetry (CV) tests and galvanostatic charge/discharge cycling (GCD) tests were separately carried out on a VSP300 electrochemical workstation and an Arbin-BT2000 test station.

## 3. Results and discussions

The typical SEM and TEM images of the prepared samples are shown in Fig. 1. All concentric electrospun fibers exhibit very similar continuous fibrous morphologies (Fig. 1b–d)with an outer and a inner fiber diameter of ~300 nm and ~150 nm, respectively (Fig. 1e). We can also observe plenty of swells randomly distributed in the fibrous network, which could be generated by the instability of electrospinning (Fig. 1f). These open swells can serve as effective entrances where electrolyte ions can quickly transfer to inner surface of the fibers at high charge/discharge rates. In contrast, the ACNF-2h sample shows a solid nanofibrous morphology with a similar fiber diameter of ~300 nm (Fig. 1g).

$N_2$ adsorption measurements have been taken to estimate the texture properties of the prepared samples. As shown in Fig. 2a, the hollow CNFs exhibit typical pseudo-type I isotherm with obvious hysteresis loops at high relative pressure, which should be caused by the hollow structure. The inset in Fig. 2a shows the corresponding PSD curves. All samples show developed micropores and the hollow fibers also show obvious mesopore peaks at 3 and 4.5 nm. The detailed porosity parameters are summarized in Table 1. From HCNF to HACNF-1h, enormous increase of SSA values from 380 $m^2\ g^{-1}$ to 655 $m^2\ g^{-1}$ can be observed, whereas the value of HACNF-2h just increases 50 $m^2\ g^{-1}$ compared with HACNF-1h.This suggests that over long time of $NH_3$ activation at 800 °C would not effectively enhance the microporosity. Meanwhile, with the activation time increasing, the total pore volumes of the hollow fibers gradually increase from 0.284 to 0.497 $cm^3\ g^{-1}$. For comparison, the ACNF-2h sample shows lower SSA value of 603 $m^2\ g^{-1}$ and total volume of 0.309 $cm^3\ g^{-1}$.

Since the surface functionalities play an important role in determining the electrochemical performance, XPS tests have been taken. Fig. 2b–e show the N1s spectra of HCNF, HACNF-1h, HACNF-2h and ACNF-2h. According to previous reports, the N1s spectra can be divided into four different types of N-doping: quaternary-N (401.0 eV), pyridinic-N (398.5 eV), oxidized pyridinic-N (403.2 eV) and pyrrolic-N (399.9 eV) [16,17]. The peak intensity of pyridinic-N has a remarkable increase relative to quaternary-N's peak intensity when the activation time increases.

Nitrogen-doping has been widely used to optimize the electrochemical properties of carbonaceous electrode materials. The nitrogen-doping not only can contribute some pseudocapacitance

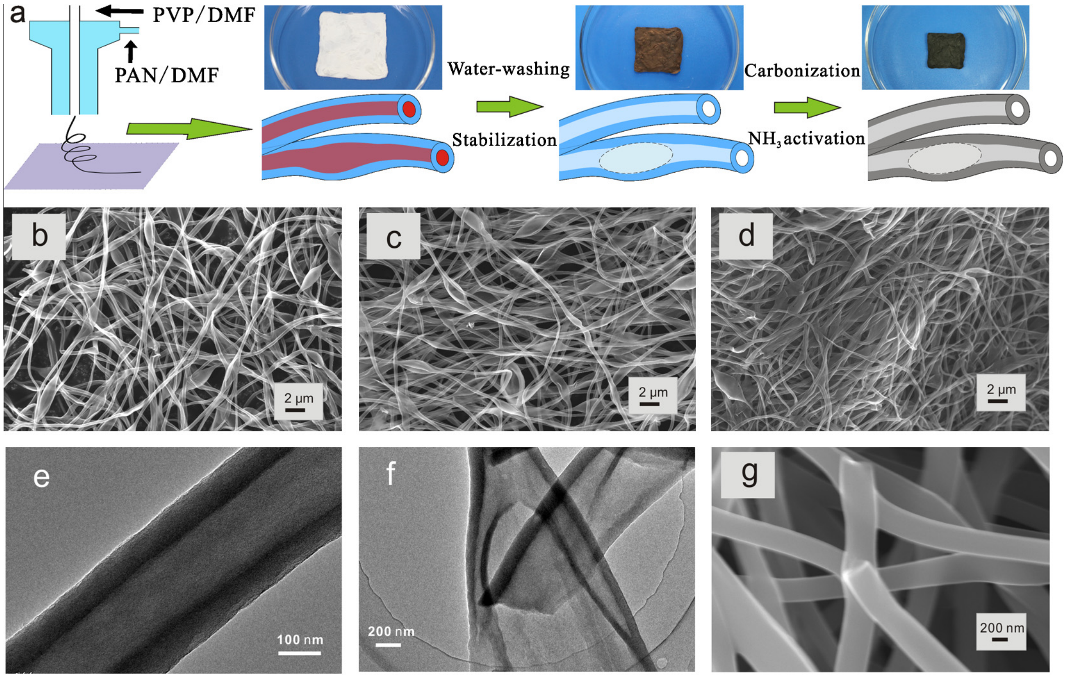

**Fig. 1.** (a) Schematic illustration of the fabricating process, (b–d, g) SEM images of HCNF, HACNF-1h, HACNF-2h, and ACNF-2h, (e, f) TEM images of HACNF-2h.