



# Nitrogen-enriched porous carbon nanofiber networks for binder-free supercapacitors obtained by using a reactive surfactant as a porogen



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## ABSTRACT

We present a novel approach to fabricate nitrogen-enriched porous carbon nanofiber networks based on electrospinning from a poly(acrylonitrile) (PAN) solution containing allyl polyethylene glycol (APEG), followed by a thermal treatment. During the pre-oxidation process, the APEG can react with the diene systems formed by the PAN elimination reaction via a Diels-Alder addition. The grafted APEG acts as a porogen, increasing the number and enlarging the size of the micropores, and also increases the nitrogen-doping level in the carbon nanofibers. When used as a binder-free electrode for supercapacitors, the nitrogen-enriched porous carbon nanofiber films can exhibit a specific capacitance of up to  $302 \text{ F g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ , retaining 94.6% of their capacitance after 2000 cycles. A power density of  $10 \text{ kW kg}^{-1}$  with an energy density of  $5.2 \text{ Wh kg}^{-1}$  can be achieved in an aqueous solution. The excellent electrochemical performance of the nanofiber films is attributed to their high specific surface area ( $753 \text{ m}^2 \text{ g}^{-1}$ ) and high nitrogen content (5.44%).

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## 1. Introduction

In the past few decades, supercapacitors have received considerable attention due to their high specific power, long cyclic life and excellent discharge rate capability [1,2]. To realize a high power density, the electrode materials must exhibit an excellent conductivity and a rapid ion-transport capability [3]. Carbon materials such as porous carbon, carbon nanofibers, carbon nanotubes, and graphene are able to meet these requirements and are considered to be the most promising supercapacitor material [4–8]. Since the specific surface area (SSA) of electrode materials has a major influence on the performance of electric double-layer capacitors (EDLC), increasing the SSA and the pore volume of carbon materials is the most common approach to improve the performance of supercapacitors [4,7,9,10]. For example, Zhao et al. used mesoporous carbon spheres prepared via a dual-template strategy as electrode materials for supercapacitors, which showed a high specific capacitance of  $208 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  in a 2.0 M aqueous  $\text{H}_2\text{SO}_4$  solution [11]. Puthusseri et al. reported on the fabrication of 3D interconnected microporous carbon sheets from polymer potassium salt utilizing a single step pyrolysis process, which showed a specific capacitance of  $255 \text{ F g}^{-1}$  at a current density of  $0.5 \text{ A g}^{-1}$  [12]. Another approach to enhance the

capacitance of carbon electrodes is the incorporation of heteroatoms, such as oxygen, nitrogen and boron, to achieve so-called pseudocapacitance [13–15]. Nitrogen-doped carbon materials have attracted much attention because doping with nitrogen can simultaneously improve the conductivity and the pseudocapacitance [16–19]. Furthermore, the application of carbon-based nanocomposites as electrode materials for electrochemical energy storage has been proposed in order to increase the gravimetric capacitance [20,21]. In general, the preparation of electrodes is a relatively complicated process, and polytetrafluoroethylene (PTFE) is typically used as a binder. However, PTFE may block the transport of electrons, resulting in a decay of the rate capacity [22,23]. Hence, the next generation of supercapacitors is expected to be based on binder-free electrode materials [24–26].

Electrospinning followed by stabilization and carbonization is a common method to produce carbon nanofibers films, which can then be used as binder-free electrode materials for the fabrication of supercapacitors or lithium-ion batteries [27]. Poly(acrylonitrile) (PAN) and poly(vinylpyrrolidone) (PVP) are typically used as precursors to synthesize nitrogen-doped carbon nanofibers [28–31]. In order to improve the porosity of the nanofiber films, KOH is generally introduced into the spinning solution as an activating agent to increase the fiber film's SSA. For example, Ma et al. reported on the fabrication of microporous carbon nanofibers ( $597 \text{ m}^2 \text{ g}^{-1}$ ) with a specific capacitance of  $256 \text{ F g}^{-1}$  at a current density of  $0.2 \text{ A g}^{-1}$  [32]. Physical activation using  $\text{CO}_2$  can also result in a more homogeneous development of porosity. Ra et al.

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reported that a CO<sub>2</sub>-treated carbon nanofiber electrode showed a maximum specific capacitance of 240 F g<sup>-1</sup> in a 6 M aqueous KOH solution [33]. However, these treatments reduce the amount of nitrogen in the material, which might result in a reduction of the pseudocapacitance [16,18]. Therefore, increasing the SSA of carbon materials while maintaining their nitrogen content is still considered a challenge. Recently, Zhong et al. reported on the preparation of nitrogen-enriched porous carbon through a direct pyrolysis of poly(acrylonitrile)-co-poly (n-butylacrylate) (PBA-co-PAN). They found that a hierarchical pore structure can be formed by preserving the initial phase-separated nanostructure after carbonization [34]. According to a detailed analysis of the pre-oxidation mechanism of PAN [35,36], a Diels-Alder reaction of the diene structures with macromolecular dienophiles is believed to occur, resulting in the formation of substituted cyclohexenes.

In this paper, we present a simple approach to prepare carbon nanofiber films using a reactive surfactant (Allyl polyethylene glycol, APEG) as the porogen, as illustrated in Fig. 1. We found that the carbon nanofibers produced with APEG possess a higher SSA and nitrogen content. The porous carbon films were then used to fabricate capacitors, which showed a high specific capacitance, a good rate capacity, and excellent cyclability.

## 2. Experimental

### 2.1. Chemicals

PAN (Mw = 150,000) was purchased from Aldrich Chemical Company Inc. APEG was supplied by Yangzhou Chenhua New Materials CO., LTD. The dimethylformamide (DMF) and other reagents used in this paper are of analytical grade and were used as-received without further purification.

### 2.2. Sample preparation

DMF solutions containing 14 wt% PAN and a certain concentration of APEG were prepared at 60 °C through ultrasonic stirring for at least 2 h. Afterwards, the polymeric solution was transferred into a 5 mL syringe with a stainless steel needle with an inner diameter of 0.6 mm. A voltage of 15 kV was applied to the positively charged capillary, and a tip to collector distance of 15 cm was maintained during the electrospinning process. Under these conditions, both pure PAN fiber films and PAN/APEG fiber films were formed. The prepared PAN/APEG fiber films were then placed in an electric furnace, annealed to 200 °C in air and kept at this temperature for 6 h. As a last step, the films were exposed to another annealing process in a N<sub>2</sub> atmosphere with the temperature increased by 3 °C min<sup>-1</sup>, and finally kept at a temperature of 800, 850 or 900 °C for another 2 h, with the final products denoted as PA-800, PA-850 and PA-900, respectively. The pure PAN fiber films were

exposed to the same sequential annealing process with a final temperature of 850 °C, and the sample was labeled P-850.

### 2.3. Characterization

The morphology of the as-prepared nanofibers was analyzed by field emission scanning electron microscopy (FESEM, JSM6700F). High-resolution transmission electron microscopy (HRTEM) and an elemental mapping utilizing scanning transmission electron microscopy energy dispersive X-ray spectroscopy (STEM-EDS) were performed on a JEOL-2100 electron microscope. The elemental composition of the carbon nanofibers was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher) using a monochromatic Al K $\alpha$  X-ray source. The SSA and the pore size distribution (PSD) were determined based on the BET equations and non-local density functional theory (NL-DFT) using a Micromeritics ASAP 2020 instrument. Powder X-ray diffraction (XRD) was conducted on a D8 Bruker X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm). In addition, Raman spectra were recorded on a confocal Raman microspectrometer (RM1000, Renishaw) equipped with a 514.5 nm Ar-ion laser.

For the electrochemical investigations, two-electrode cells were built using the carbon nanofiber film samples as electrode material. Before assembly, two pieces of carbon nanofibers films were first attached to two nickel foams. The electrochemical properties were determined in a 6 mol L<sup>-1</sup> aqueous KOH solution using a CHI660E electrochemical workstation. The cyclic voltammetry (CV) measurements were performed varying the scan rate from 10 mV s<sup>-1</sup> to 200 mV s<sup>-1</sup>, and the galvanostatic charge-discharge (GCD) tests were carried out for a voltage between 0 and 1 V at current densities in the range from 0.2 A g<sup>-1</sup> to 40 A g<sup>-1</sup>. The Nyquist plots were obtained in the frequency range from 100 kHz to 0.1 Hz with a 5 mV AC amplitude.

The specific capacitance ( $C_s$ ), the energy density ( $E$ ) and the power density ( $P$ ) of these cells were calculated using the following equations [37]:

$$C_s = \frac{2 \times I \Delta t}{m \Delta V} \quad (1)$$

$$E = \frac{C_s \Delta V^2}{2 \times 3.6} \quad (2)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (3)$$

where  $I$  (A) is the discharge current,  $\Delta t$  (s) is the discharge time,  $m$  (g) is the mass of the carbon films in a single working electrode, and

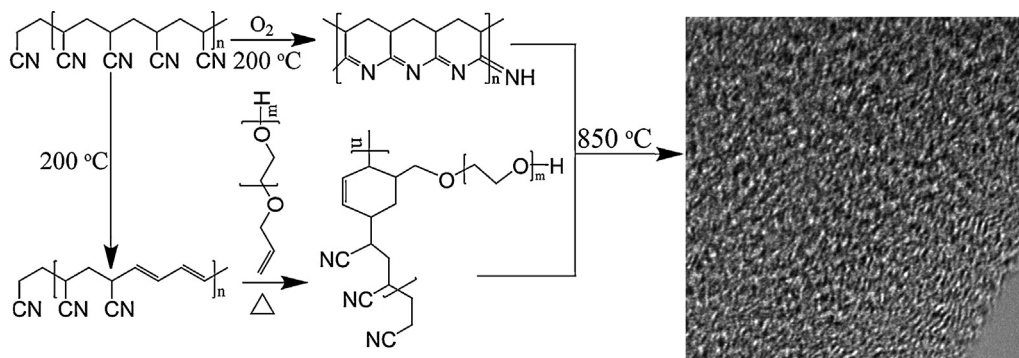


Fig. 1. Schematic illustration of the carbon nanofiber film fabrication process at 850 °C.

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