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A Non-Woven Network of Porous Nitrogen-doping Carbon Nanofibers as a Binder-free Electrode for Supercapacitors



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ABSTRACT

A non-woven network of porous nitrogen-doping carbon nanofibers (PNCNFs) is prepared by electrospinning of polyacrylonitrile (PAN)/polyvinylpyrrolidone (PVP), followed by stabilization and carbonization. The specific surface areas, porosity and nitrogen content of PNCNFs can be easily controlled by adjusting the content ratio of PVP to PAN. The non-woven PNCNFs based network provides abundant interface sites and hierarchical porosity for solvated ions. In a three-electrode configuration, PNCNFs-2-3 provides a high specific capacitance of 198 Fg^{-1} at 1 Ag^{-1} in 6 M KOH. A two-electrode configuration supercapacitor using PNCNFs-2-3 delivers 148 Fg^{-1} capacitance at 1 Ag^{-1} as well as excellent cycling stability.

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1. Introduction

Supercapacitors (SCs), one of the most promising energy storage devices, have been widely investigated due to their higher power density and quick charge-discharge rate as well as long lifespan

[1–8]. To enhanced the energy density and power density, various materials including porous carbon, transition metal oxides and conducting polymers have been used as electrode active materials [9–13]. Among them, porous carbon, such as activated carbon [14], carbon nanofibers [15], carbon nanotubes [16], graphene [17], hollow carbon nanowires [18] are the most promising materials for SCs due to their lower cost, excellent chemical stability and high surface area [16,19–22].

It is known that energy storage mechanism of carbon materials for SCs are based on electrochemical double layer capacitors (EDLCs). The capacitance of EDLCs depends strongly on the accessible specific surface area at electrode/electrolyte interface and the transport kinetics of solvated ions [23]. It is therefore an ongoing challenge to design a porous carbon with high specific surface, suitable pore size distributions and high electrical conductivity for ideal electrodes [9,17,24,25]. Kim et al. [25]

demonstrated that the optimized pore size distribution in nanosize is one of key factors to enhance the electrochemical performance of carbon materials. Recently, various strategies have been tried to make porous carbon nanofibers using SiO₂ [26], CaCO₃ [19], PMMA [27,28] as templates, or KOH [29], CO₂ [30] as activation agents. It was found that accessible N-containing species (N-6, N-Q) would provide chemically active sites to improve the electrochemical performance of SCs [31]. For instance, Zeng et al. reported a fabrication of nitrogen-doped porous carbon nanofibers from polyacrylonitrile (PAN) via electrospinning using PMMA and SiO₂ as templates, which provided a specific capacitance of 198 Fg^{-1} at 1 Ag^{-1} in two-electrode configuration in 6 M KOH electrolyte [32]. Xu et al. prepared a kind of nitrogen-doped hollow activated carbon nanofibers from PAN via coaxial electrospinning and NH₃ activation, which showed a high specific capacitance of 197 Fg^{-1} at 0.2 Ag^{-1} current density in 6 M KOH [33]. Recently, Fan et al. prepared nitrogen doping carbon nanofibers through a co-eletrospinning of PAN/PVP/SiO₂ blended solution, followed by pyrolysis and SiO₂ removal. The as-obtained CNFs displayed a high pseudocapacitance $(120\,F\,g^{-1}~at~0.2\,A\,g^{-1})$ in a two electrode device with 1 M H₂SO₄ aqueous solution [26]. Although PAN was widely used to produce carbon nanofibers owing to high carbon vield and continuous fibrous structure [34], PAN-based CNFs are usually resulted in skin-core structure which possess a nonporous structure [35,36]. In addition, either SiO₂ template or NH₃ activation for making porosity, additional re-treatment is needed.

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However, there has been no report on a facile synthesis to realize N-doping and porous structure at the same time yet. It is known that polyvinylpyrrolidone (PVP) is used as a soft template to generate porosity, for PVP can be easily removed by water [37]. And PVP can serve as nitrogen precursor due to its nitrogen enriched molecular [38,39]. Consequently, both PAN and PVP can serve as nitrogen sources for the generation of nitrogen-doping CNFs.

In this work, we present a facile method to prepare a nonwoven network of porous nitrogen-doped carbon nanofibers (PNCNFs) *via* electrospinning technique. PAN is used as carbon precursor while PVP serve as nitrogen enriched precursor and porogen. More importantly, the non-woven CNFs network can be directly used as electrode for supercapacitors without any binder. We have systematically discussed the effects of PVP content on the microstructure and electrochemical performance of PNCNFs. Electrochemical performances of the symmetric device based on three-electrode and two-electrode configurations using PNCNFs as binder-free electrode are studied, respectively.

2. Materials

2.1. Synthesis of PNCNFs

For the preparation of spinning solutions, analytical pure N, N-dimethyl-Formamide (DMF) was used as the solvent. PVP was added to the 6 wt.% PAN/DMF solutions and then stirred vigorously at 250 rpm for 1 day at 298 K to obtain a homogeneous solutions. The PAN/PVP content ratio in the spinning solutions was as follows: 100/150, 100/170, 100/240 in wt./wt., respectively, from which the electrospun nanofibers were labeled as NF-2-3. NF-3-5, and NF-3-7, correspondingly. And the final carbon fibers were marked as PNCNFs-2-3, PNCNFs-3-5 and PNCNFs-3-7, respectively. The electrospinning device in the present study was a horizontal type (Model DFS-L-01) produced by Beijing Tech-Nova technology co. Ltd. The solution was placed in a 5 mL syringe having a capillary tip with the diameter of 1 mm. The electrospun nanofibers were collected on a rotating disk covered with an aluminum foil and the rotating speed of the collector was 700 rpm. The applied voltage was 20 kV, the flow rate of solution was 1.5 mL h^{-1} , and the roation distance between the tip and the collector was 20 cm. All spinning were carried out at 27 ± 2 °C and a relative humidity of less than 40%. The as-spun nanofibers were then dried in vacuum at 80 °C for 8 h. Stabilization of the as-spun nanofibers was carried out by heating the samples in air at a rate of 2 °C min⁻¹ and kept at 300 °C for 3 h. The nanofibers were further heated up and carbonized at 850 °C for 3 h in nitrogen with a flow rate of 300 mLmin⁻¹. As a result, PNCNFs were generated. In addition, the phenolic resin based CNFs (PR-CNFs) was prepared as described previously [40].

2.2. Characterizations

The morphology of samples was characterized by field emission scanning electron microscope (FEINova 400 Nano SEM). Raman spectra were examined on micro-Raman spectroscope (LabRAM HR Evolution) using 532 nm incident radiation. X-ray diffraction (XRD) patterns were obtained from DMSX-2500 PC X-ray spectrometer with Cu K α radiation (λ = 1.5406 Å) at a scanning speed of 4° min⁻¹. The elemental composition of carbon nanofibers was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Thermo Fisher Scientifix). The specific surface area and the pore structure of samples were performed by nitrogen adsorption measurements (Belsorp Mini) at 77 K. The specific surface area and the pore size distribution were determined based on the non-local density functional theory (NL-DFT).

2.3. Electrochemical measurements

Both three-electrode and two-electrode configuration were used to measure the electrochemical performance of PNCNFs and PR-CNFs for supercapacitors. For a three-electrode configuration, the working electrodes were prepared by cutting CNFs into square pieces (area: $1*1 \text{ cm}^2$, weight: ~1.5 mg), which were pressed on the nickel foam current collectors. In the three-electrode configuration, 6 M KOH was used as the electrolyte, platinum foil and Hg/HgCl₂ were used as the counter and reference electrode, respectively. Cyclic voltammograms (CV) at various scan rates and galvanostatic charge/discharge (GCD) at different current densities



Fig. 1. Schematic of fabrication process for PNCNFs.

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