



## Research paper

# Microstructure and electrochemical properties of polyacrylonitrile-based carbon micro- and nanofibers fabricated by centrifugal spinning



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## ABSTRACT

Carbon nanofibers were prepared by using centrifugal spinning with polyacrylonitrile as precursor. The microstructure and electrochemical properties of prepared samples were investigated by using scanning electron microscopy and electrochemical workstation, respectively. The results showed that the distribution of fiber diameter showed a normal law. The carbon fibers present good cycle stability at low scan rate. Moreover, the integral area of cyclic voltammetry curve reaches the maximum when the mass ratio of PAN/PMMA is 20:3. The specific capacitance of it is 102 F/g and 84 F/g, in case of the current density at 0.1 A/g and 0.2 A/g, respectively.

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## 1. Introduction

Due to their high specific surface area, long fiber length and superior mechanical properties, nanofibers have potential applications in filtration, medical treatment, textile, composite materials, etc. As regard to the fabrication process of nanofibers, there are phase separation, synthesis by using template, self-assembly and electrospinning [1–4]. Except the electrospinning method, other fabrication processes mentioned above have little applications due to the complexity of the fiber formation process and the limited material selection. Because of its simple principle and wide selection of materials, electrospinning has become an excellent method to prepare nanofibers. Although the electrospinning is very popular and powerful, it is not the ideal method for producing nanofibers in some respects. Firstly, the mass production of fiber is limited by its low efficiency. Secondly, the electrical conductivity of solution and the surrounding environment have higher requirements. Moreover, electrospinning needs a high electric field and the inevitable solvent, which will lead to a waste of production and safety issues. Therefore, advanced technology should be developed to overcome the disadvantages of electrospinning. Centrifugal spinning, the derived forspinning and pressurized gyration which developed very quickly in recent years, were reported to be successful in the production of micro and nano scale fibers, by using the solution of varies polymers such as poly ethylene oxide,

etc. [5–9]. In the current literatures, a centrifugal spinning system has been developed to facilitate the large-scale and low-cost production of fibers with diameters ranging from micro- to nano-scale [10]. The centrifugal spinning set-up is mainly composed of a vessel with many small holes for forming fibers as rotating at a high speed. This centrifugal spinning system is simple as well capable of eliminating the limitations of electrospinning.

During centrifugal spinning, a polymer solution is put into the vessel, which is rotated at high speeds. When the rotational speed reaches a critical value, the centrifugal force overcomes the surface tension of the solution and ejects a liquid jet from each small hole. The jet then undergoes a stretching process, accompanied by rapid evaporation of the solvent, and is eventually deposited on the collectors forming dried nanofibers. Since the centrifugal spinning process does not use high-voltage electric field, it alleviates the related safety concern. In addition, the high rotational speed allows fast and scalable fiber fabrication, which can dramatically improve the production rate by two to three orders of magnitude and reduce the production cost when compared with the electrospinning process [11,12]. Moreover, the centrifugal spinning process enables the fabrication of nanofibers from polymer solutions with much higher concentrations than the electrospinning process, which also reduces the production cost by using less solvent.

Polyacrylonitrile (PAN) is a well-known polymer with good stability and mechanical properties. PAN nanofibers can be potentially applied into multiple fields including tissue engineering, sensing, composites, battery separators, and precursors for producing carbon nanofibers. Among the various applications, the most

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important role of PAN nanofibers is the precursor for producing carbon nanofibers due to its high carbon yield and flexibility for tailoring the structures of resultant carbon nanofibers [13]. Therefore, the mass production of high-quality PAN nanofibers is urgently demanded. Recently, PAN-based carbon nanofibers containing graphene nanoplatelets were prepared through an improved centrifugal spinning by Wu et al. [14]. The effect of additive concentration of graphene nanoplatelets on the microstructure, morphology and electrical properties of PAN-based carbon fibers were investigated in that work. In this study, we used PAN with additives of Polymethylmethacrylate (PMMA) as precursor to prepare PAN/PMMA fibers by centrifugal spinning, and then prepared carbon fibers by pre-oxidation and carbonization. The aim of the addition of PMMA, a pore-forming agent, is to increase the specific surface area and thus improve the electrochemical properties such as the specific capacitance of charge/discharge process. This work is promising helpful to the applications of carbon nanofibers in the field of super capacitor, battery and energy storage devices. Moreover, centrifugal spinning is a kind of fabrication process of carbon nanofibers with low cost and high efficiency.

The composition and microstructure of prepared nanofibers were investigated X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and specific surface area test. The electrochemical properties of the samples were characterized by electrochemical workstation, including cyclic voltammetry and constant current charge/discharge test.

## 2. Experimental

PAN (homopolymer, Mw = 150000) purchased from Beijing Bailingwei Technology Co. Ltd was chosen as the precursor. N,N-dimethylformamide (DMF) was selected as the solvent to dissolve PAN. PMMA purchased from TCI Chemical Industrial Development Co. Ltd. was added as additive. Polyvinylidene fluoride (PVDF) purchased from Beijing Bailingwei Technology Co. Ltd was used to prepare electrode plates.

The PAN solution was prepared with a concentration of 10 wt% in DMF, and then divided into five parts. The five PAN solutions were added additives to fabricate spinning solutions with different concentrations of PMMA 0, 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, respectively. The prepared five spinning solutions were placed on the magnetic mixer, stirring 12 h to clarify the solution for a complete resolution. The prepared PAN/PMMA solution was placed in a spinning vessel, and then ejected from the small holes on the wall of vessel with a high rotating speed thus the composite fiber formed in case of evaporation of solvent DMF meanwhile. The formed PAN/PMMA fibers with different concentration of PMMA 0, 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt% were labeled as samples A, B, C, D, and E, respectively. The PAN/PMMA fiber was infiltrated with acetone for more than half an hour, and formed a porous fiber based on a fact that PMMA is soluble in acetone while PAN can't be dissolved in acetone. Then, the fibers were placed in an oven to dry for 30 min at 80 °C. The dried fibers are heated to 280 with a rate of 2 °C/min and maintain 1 h at the final temperature for pre-oxidation. The pre-oxidation sample was heated to 800 °C and kept 2 h for carbonization in argon atmosphere [15,16]. The microstructure of the pre-oxidized and carbonized samples were analyzed by SEM. The specific surface area of the CNFs was evaluated by physical adsorption of nitrogen at 77 K in a volumetric adsorption system (Quantachrome ASIQM0002-4) using the Brunauer–Emmett–Teller (BET) equation.

In order to test the electrochemical performance of the sample, the electrode sheet which can be tested was prepared. Main operation steps are as follows: (1) The foam nickel cut into 1 cm×3 cm

piece was put into ethanol, and then placed in ultrasonic cleaning machine for cleaning; (2) The carbon fiber, conductive carbon black, graphite and PVDF were mixed according to the mass ratio of 8:0.5:0.5:1. The 1- methyl -2 was added as adhesive to make the solution mixed evenly in the quartz crucible; (3) The Na<sub>2</sub>SO<sub>4</sub> solution of 0.5 mol/L and the saturated KCl solution were used for testing. Electrochemical tests used three electrode systems: cathode material as the working electrode, blank nickel plate as the counter electrode and saturated calomel electrode as the reference electrode. The test was carried out with an electrochemical workstation typed CHI1604B.

## 3. Results and discussion

### 3.1. XRD analysis of carbon fibers

Fig. 1 shows a typical XRD pattern of carbon fiber sample D which was selected for the crystalline investigation. It can be seen that there are two distinct characteristic peaks at 26 deg (002) and 44.5 deg (101) [17]. Compared with the XRD standard card (#75-1621), the carbon fiber can be identified as an amorphous carbon structure.

### 3.2. FTIR analysis of the micro- and nanofibers

Fig. 2 presents the FTIR patterns of sample D before and after carbonization. In Fig. 2b, it can be seen that C–C bond and C=C bond stretching vibration appeared in nearby 1200 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>, respectively. This result showed that there are only C–C bond and C=C bond inside carbon fiber. Moreover, it was indicated that C–H, N–H, and C=O bonds in the PAN/PMMA fibers had already disappeared after carbonization process [18].

### 3.3. Morphology and diameter distribution of the fibers

The results of SEM are important because the diameter of fibers and the distribution of fiber size can be observed. Moreover, by using the result of SEM images and calculation software the distribution histogram of fiber diameter can be drawn, thus the relationship between the solution concentration and fiber morphology as well diameter can be obtained.

Fig. 3 shows the SEM micrographs and diameter distribution of PAN/PMMA composite fibers samples (before carbonization) with different concentration of PMMA. The morphology of fibers can be observed in SEM micrographs clearly, and the arrangement

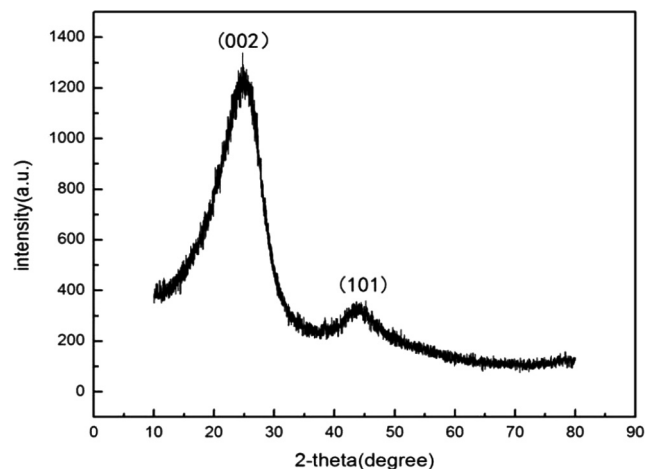


Fig. 1. The XRD patterns of sample D after carbonization.

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