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Preparation and characterization of PVC-based carbon nanofibers with barrel-like graphite granules by electrospinning

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ABSTRACT

PVC-based carbon nanofibers with graphitic nanoparticles were fabricated by an electrospinning–carbonization technique and characterized by SEM, (HR)TEM and XRD. The hydrogen storage capability of the resultant nanofibers was evaluated using the volumetric method. The results show that the PVC-based carbon nanofibers obtained from the electrospun PVC/$NiCl_2$ nanofibers consist of both amorphous carbon and a well-grown graphite layered sphere with a diameter of 35 nm. It is clear that the iodine treatment is essential for retaining a fibrous shape during the carbonization, and Ni is beneficial to the growth of graphitization at low temperatures. The hydrogen storage capacity of the PVC-based carbon nanofibers obtained at 1000 °C is 0.30 wt%, suggesting that the resultant nanofibers are a potential energy storage material.

1. Introduction

Since the discovery of carbon filaments formed by the interaction of ethylene and silica at 1200–1300 °C, carbon nanofibers have attracted much attention [1]. Carbon nanofibers have been investigated in many fields such as electrode materials [2,3], catalyst supports [4] and gas storage [5,6] due to their unique physical and chemical properties. Of particular interest, carbon nanofibers with graphite structure which exhibit a large portion of open edges and unique stacking are expected to have better performances in these fields.

Carbon nanofibers are mainly prepared by catalytic chemical vapor deposition (CCVD) using CO or hydrocarbons as a carbon source under a hydrogen atmosphere [7]. Recently, researchers have been increasingly interested in electrospinning, which is employed to prepare ultrafine polymer fibers ranging from tens to a few hundreds of nanometers in diameter. The most outstanding features of this technique are its simplicity, low cost, and high yield [8,9] as well as its lack of the flammable and explosive hydrocarbon gases commonly used in CCVD.

Polymers such as polybenzimidazole (PBI), poly(vinyl alcohol) (PVA), and polyacrylonitrile (PAN) have already been employed to prepare carbon fibers. Among them, PAN is the most common precursor for carbon fibers because of its good spinnability and high carbon yield. However, its high cost constrains its practical use. Poly(vinyl chloride) (PVC) and its waste are alternative, relatively inexpensive precursors. Qiao et al. [10] obtained PVC-based activated carbon fibers with a diameter of 10 to 25 μm by melt spinning combined with carbonization and activation technology. However, it is well known that the size and shape of materials are crucial factors for controlling the properties such as gas storage, electrical transport, magnetic properties [11].

In this study, PVC-based carbon nanofibers (50–100 nm in diameter) containing graphitic nanoparticles (approximately 35 nm in diameter) were synthesized by an electrospinning–carbonization method. The hydrogen storage of the obtained material was investigated, and the effects of $NiCl_2$ and iodine pretreatment on the formation of graphitic nanofibers were discussed.

2. Experimental

Preparation: To prepare the solution of PVC/$NiCl_2 \cdot 6H_2O$ (PVC/Ni), 1.4 g PVC (M_W: 78,000–81,000; theoretical chlorine content: 56.8%) and 0.056 g $NiCl_2 \cdot 6H_2O$ were dissolved in 18.6 mL *N*,*N*-dimethylformamide (DMF) with 0.1 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and stirred at 50 °C for 5 h. The solution was cooled to ambient temperature and added to a syringe with metal needle

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(diameter of 0.8 mm). The distance between the cathode and the anode was fixed at 15 cm, and a voltage of 25 kV was provided by a high-voltage power supply. The ejection rate of the solution from the syringe was controlled at 0.6 mL/h by a syringe pump (TS2-60). The electrospun PVC/Ni composite fibers were collected using aluminum foil at 35 °C in air and dried in a vacuum oven at 50 °C for 8 h. The obtained nanofibers were then exposed to iodine vapor at 80 °C for 48 h prior to carbonization at 1000 °C for 15 min with a heating rate of 2 °C/min under nitrogen atmosphere.

Characterization: The morphology and structure of the prepared carbon nanofibers were investigated using a field emission scanning electron microscope (FESEM, JEOL, JSM-7500F) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010), respectively. The samples were sputtered with golden for SEM analysis, whereas dispersed in ethanol and loaded on a TEM copper grid for TEM testing. The phase and crystallinity of the carbon nanofibers were identified by X-ray diffraction analysis (XRD, Philips, X'Pert Pro MPD) using Cu $K\alpha$ radiation within the range of $2\theta=5$–80°. N_2 adsorption–desorption experiments were carried out with a surface area analyzer (Ankersmid, Belsorp-max) at liquid nitrogen temperature (77 K). The hydrogen storage capacity of the carbon nanofibers was evaluated on a hydrogen storage analyzer (Hiden, HTP1-V) at 298 K. The purity of the hydrogen gas used was 99.999%. The pressure ranges from 0 to 95 bar.

3. Results and discussion

SEM: Fig. 1 depicts the SEM images for various electrospun PVC nanofiber mats and their carbonized nanofibers. It is clear that both electrospun PVC nanofibers and PVC/Ni nanofibers possess a smooth surface with a diameter range of 80–140 nm, whereas the nanofibers obtained via carbonization present an inhomogeneous surface with a grainy, porous structure. The carbonized materials obtained from PVC/Ni nanofibers without iodine pretreatment exhibit a sheet-like structure due to the melting of PVC/Ni nanofibers. In the presence of iodine, the carbonized materials present a fibrous structure with a diameter range of 50–100 nm, suggesting that iodine is a good thermal stabilizer for PVC. It is known that the decomposition temperature of PVC is higher than the melting point. The presence of iodine transforms PVC into conjugated polyenes via dehydrochlorination at temperatures below the melting point of PVC [12,13].

TEM: Fig. 2a–c show the (HR)TEM images of the carbonized PVC/Ni nanofibers with iodine pretreatment. The carbonized PVC/Ni nanofibers consist of both amorphous carbon and well-grown graphite layered nanospheres. The graphite layered spheres are similar to the barrel-like carbon nanoparticles reported by Perkson et al. [14]. The barrel-like nanoparticles are approximately 35 nm in diameter (Fig. 2c), which is in accordance with the diameter of the granules observed in SEM images (Fig. 1c and d). A layer lattice image of the (0 0 2) face of a graphite crystal can be observed in Fig. 2c. According to a selected area electron diffraction pattern (Fig. 2d), the interspace of the graphite (0 0 2) crystal face is approximately 0.34 nm. The results reveal that the PVC/Ni nanofibers pretreated with iodine can form barrel-like graphite nanoparticles dispersed in amorphous carbon fibers during carbonization. Danno et al. [12] reported that the amorphous phase of PVC was predominantly dehydrochlorinated. The presence of iodine causes the dehydrochlorination of the amorphous part of PVC nanofibers at temperatures below the PVC melting point. As a result, the dehydrochlorinated materials retain their nanofiber shape. Moreover, the crystalline part of the PVC nanofibers melts into graphite nanoparticles during carbonization. However, the

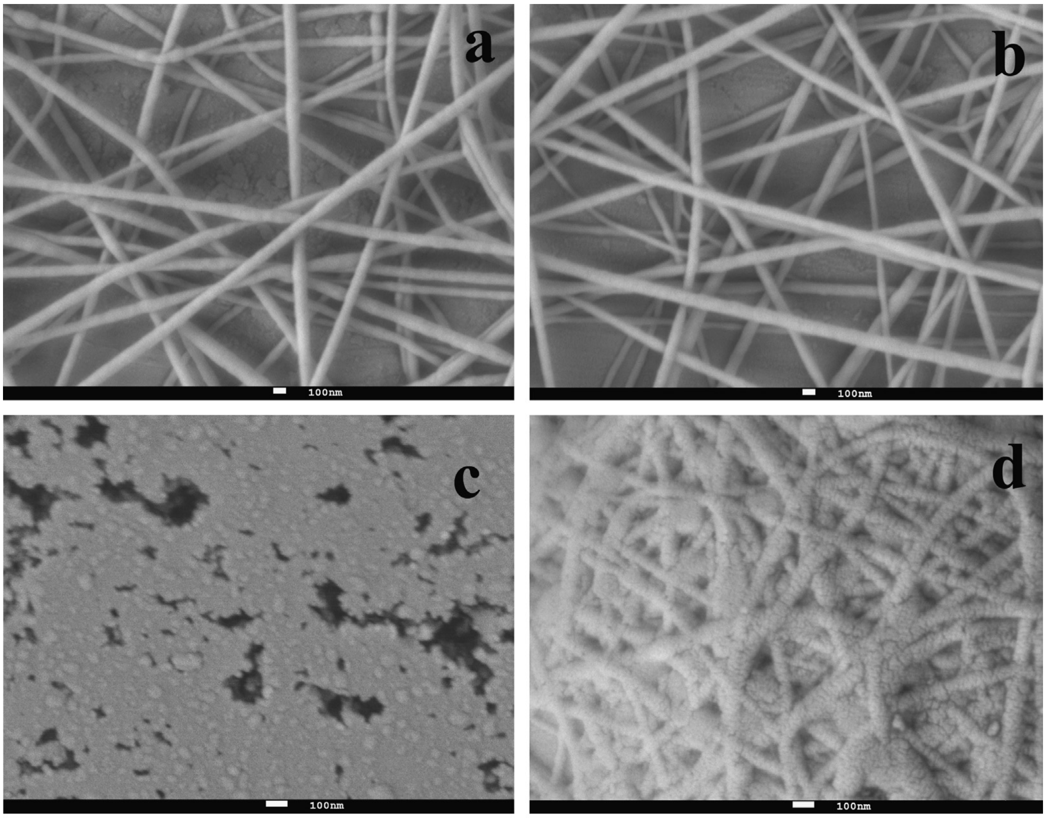

Fig. 1. SEM images of the PVC nanofibers and nanofibers obtained after carbonization in nitrogen atmosphere: (a) PVC nanofiber mats, (b) PVC/Ni nanofiber mats, (c) carbonized PVC/Ni nanofibers without iodine pretreatment, and (d) carbonized PVC/Ni nanofibers with iodine pretreatment.