

Preparation and characterization of electrospun Ag/polyacrylonitrile composite nanofibers

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(Received 19 October 2010 • accepted 12 January 2011)

Abstract—Novel composite nanofibers consisting of Ag nanoparticles and polyacrylonitrile (PAN) were fabricated successfully. The Raman properties of these Ag/PAN nanofibers were studied at low temperatures, which showed good Raman characteristics. In the process, a PAN solution containing Ag ions was directly electrospun to obtain nanofiber films containing Ag ions, and the Ag ions of resulting composite nanofibers were reduced to Ag nanoparticles in N_2H_4OH aqueous solution. Then, we treated Ag/PAN composite nanofibers at 100 °C, 200 °C, 400 and 600 °C, respectively. The Ag/PAN nanocomposite film was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) patterns and surface-enhanced Raman scattering (SERS) spectroscopy.

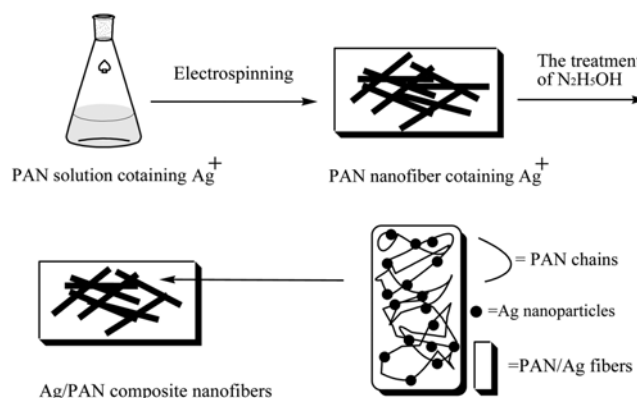
Key words: Polyacrylonitrile (PAN), Electrospinning, Nanofibers, Ag Nanoparticles, Raman Spectroscopy

INTRODUCTION

In recent years, ultrafine polymer fibers prepared by electrospinning a polymer solution have drawn great attention because of their unique properties, such as high surface area-to-volume and length-to-diameter ratios [1-4]. When a strong electrostatic force was applied to the capillary containing a polymer solution, a charged solution was ejected from the capillary and deposited as a nonwoven fibrous mat on a template serving as the ground for the electric charges. With the addition of various materials, functional ultrafine fibers exhibit more novel properties than conventional polymer fibers [5-9].

Electrospinning has been considered to be a simple and effective technique for manufacturing polymer fibers, inorganic fibers, and composite fibers. Especially, the incorporation of inorganic nanoparticles and nanofibers produces functional nanofibers having optical, electrical, or magnetic properties. Different composite nanofibers containing inorganic nanoparticles in the polymers matrix have been obtained by this method. Silver, because of its great surface activity and catalysis, has different applications in catalysts, photographic emulsions and surface-enhanced Raman scattering activity [10-14]. Since silver has highly electric capability and steady chemical property, silver powders in nanograde are often used as electrical dopes, adhesives and stuffing of electrical membranes. For a long time, more and more people have devoted themselves to research on nanomaterials [15-17]. In 2004, silver nanoparticles were first introduced into nanofibers to prepare Ag/PAN composite nanofibers by electrospinning [18], which was paid attention extensively. Subsequently, people adopted many similar methods to prepare Ag/PVA and Ag/CA fibers [19,20].

In this study, on the basis of previous work, we report the product of dispersed Ag nanoparticles in PAN nanofiber matrices by using a simple method (see Scheme 1). The composites contained two materials: AgNs (noble metal nanoparticle), and PAN (polymer).



Scheme 1. Scheme of the procedure used to prepare the Ag/PAN composite nanofibers.

The composite nanofiber showed good Raman characteristics.

EXPERIMENTAL

1. Materials

N, N-dimethylformamide (DMF), hydrazinium hydroxide, and silver nitrate (analytical grade) were supplied from Beijing Chemical Agent Co. (China). Polyacrylonitrile (PAN, Mw=80,000) was obtained from Jilin Carbon Group (China). All chemicals were used without further purification.

2. Preparation of PAN Solution Containing Ag Ions

In the preparation, 2.4 g PAN was dissolved in 17.6 g DMF to make a solution with concentration of 10 wt%, and the polymer solution was rapidly stirred for 48 h at room temperature. Then, the solution was cooled to 0 °C, and 0.8 g $AgNO_3$ was added to the above solution. The solution containing silver salt was stirred for 24 h at this temperature. Thus, the electrospinning solution was obtained.

3. Preparation of PAN/ $AgNO_3$ Composite Nanofibers by Electrospinning

The $AgNO_3$ /PAN solution was loaded into glass capillary with a

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diameter of 1 mm, and the electrospinning equipment was assembled as in the previous study. The voltage used for electrospinning was 10 kV, and the collection distance was 15 cm. The temperature of electrospinning was controlled at room temperature.

4. Preparation of Ag/PAN Composite Nanofibers

Ag/PAN composite nanofibers were prepared by reducing PAN nanofibers containing AgNO_3 in $\text{N}_2\text{H}_5\text{OH}$ aqueous solution. 1 ml $\text{N}_2\text{H}_5\text{OH}$ and 200 ml triple distilled water were mixed in a 500 ml beaker, and a piece of PAN/ AgNO_3 nanofibrous film was put into the solution in the beaker. The color of fiber film changed from colorless to yellow, which indicated that the silver ions were reduced to silver in PAN nanofibrous film. 20 minutes later, the film was taken out and washed in distilled water, then dried in a vacuum oven. The pure PAN nanofiber film was also prepared using the similar procedure as described above.

5. The Treatment of Ag/PAN Composite Nanofiber at Various Temperatures

The Ag/PAN nanofiber membrane was put into electric cooker in which there was a quartz tube and highly pure nitrogen was added to replace the air. The flux of nitrogen was controlled in 20 ml/h and treated at 100 °C, 200 °C, 400 °C and 600 °C, respectively. Four hours later, the temperature was lowered to room temperature under nitrogen.

6. Characterization

The nanofiber images were taken by scanning electron microscopy (SEM). The SEM measurements were performed on an XL30 ESEM FEI scanning electron microscope. The Ag/PAN nanofibrous films were collected on a 1 cm² aluminum sheets to determine X-ray diffraction (XRD) patterns by a DXP-18AHF diffrac-

tometer and the scanning rate was controlled at 4° min⁻¹. Raman spectra were recorded with a Bruker IFS 100 Fourier transform Raman spectrometer equipped with an air-cooled Nd:YAG laser source (514.5 nm), an output power of 30-200 mW and a Ge detector cooled by liquid nitrogen.

RESULTS AND DISCUSSIONS

Fig. 1 shows the SEM micrographs of the Ag/PAN fibers treated at different temperatures. From the picture we could see that nanofiber membranes shrank gradually with increase in temperature. The fibers bent and twisted partly, and were not linear in structure. As seen from the change of the fibrous diameters, at 0 °C, the average diameter of Ag/PAN nanofibers was about 350 nm. At 100 °C, the diameter of fibers increased a little and was 380 nm. At 200 °C, the fibrous diameter increased to 410 nm. It decreased to about 340 nm and 300 nm, respectively, at 400 °C and 600 °C. 400 °C ago, it was seen from the fibrous surface which was covered by a large number of silver nanoparticles and the fibrous surface was very rough. At 400 °C, there were a few silver nanoparticles on the fibrous surface; there were no silver nanoparticles at 600 °C.

How the dimension and morphology of the fibers changed can be explained as follows: at 200 °C ago, PAN was not carbonized basically or incompletely. There was a large amount of CN^- in the surface of the fibers. This CN^- reacted with silver nanoparticles so that silver particles covered the surface of the fibers compactly. With the increase of the temperature, silver particles agglomerated partly and made the diameter of the fibers increase notably. 400 °C later, because the PAN fibers were transformed to carbon fibers gradually, the contact with silver particles decreased, and meanwhile, N and H elements were transformed to the gas gradually, such as NH_3 , HCN and so on. As a result, silver particles were lost gradually and the diameter of the fibers decreased notably.

Fig. 2 shows the experimental results of X-ray of Ag/PAN nanofibers treated at different temperatures. We could see that there was a diffractive peak where 2θ was 16.9, which corresponded with PAN

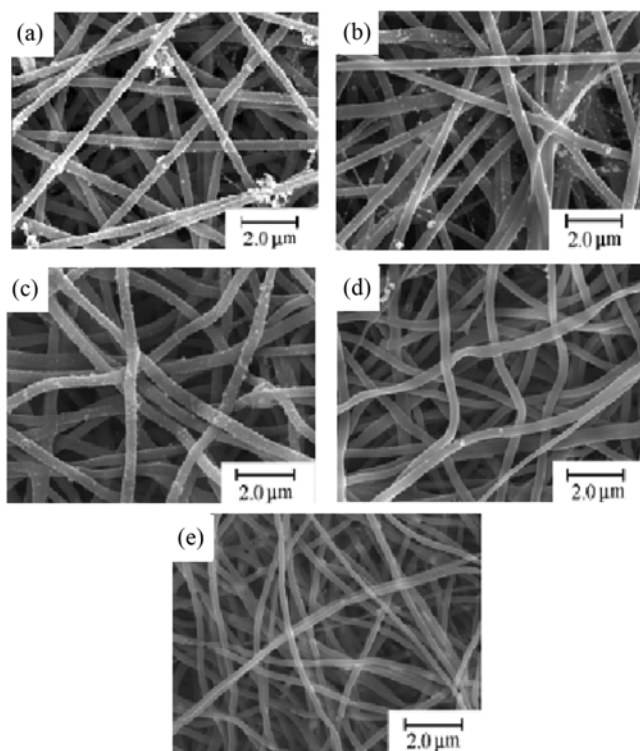


Fig. 1. SEM images of Ag/PAN nanofibers treated at different temperatures: (A) 0 °C, (B) 100 °C, (C) 200 °C, (D) 400 °C, and (E) 600 °C.

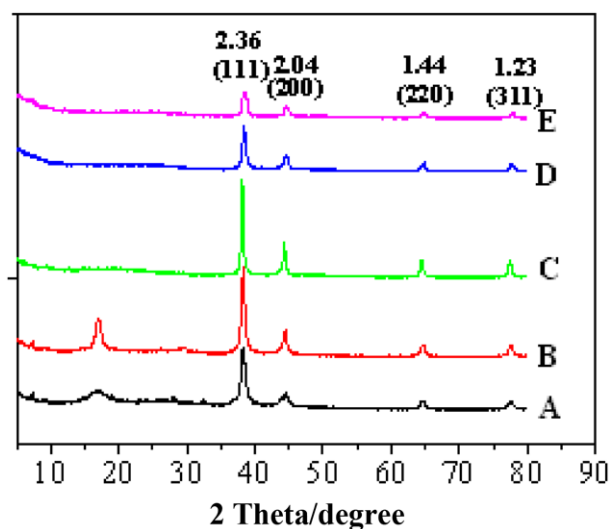


Fig. 2. XRD pattern of Ag/PAN nanofibers treated at different temperatures: (A) 0 °C, (B) 100 °C, (C) 200 °C, (D) 400 °C, and (E) 600 °C.

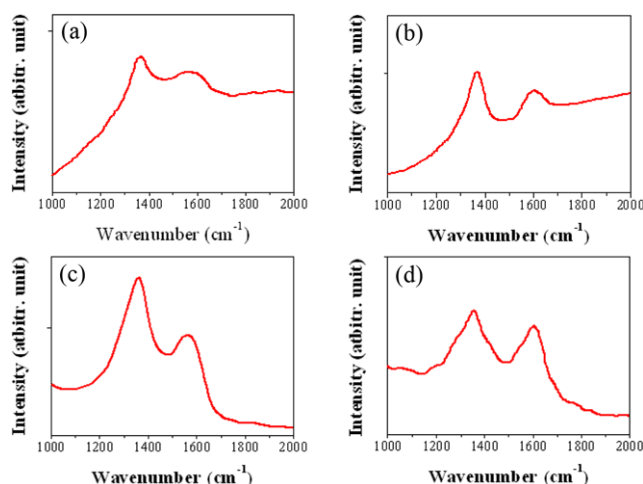


Fig. 3. SERS spectrum pattern of Ag/PAN nanofibers treated at different temperatures: (A) 100 °C, (B) 200 °C, (C) 400 °C, and (D) 600 °C.

crystal. As temperature increased, four other diffractive peaks were observed between 2θ was 30 to 80; the numerical values were 36.2, 44.3, 64.4, and 77.4 respectively. Their corresponding d values were 2.36, 2.04, 1.44, and 1.23 respectively. Compared with the International Center of Diffraction Data card of silver crystal, silver nanoparticles we obtained were cubic face-centered. These numerical values corresponded with (110), (200), (220), (311) diffractive surfaces respectively. The fact that d values remained steady in the range of 0–600 °C showed the crystal structure of silver nanoparticle did not change.

Silver nanoparticles had an important effect on surface-enhanced Raman spectra because of their special characters. They made the matter that had weak Raman signal gain the strong Raman signal to finish catching and transferring signals. Carbon fibers can provide information on crystalline perfection of graphite-based materials. Single-crystal graphite shows two bands at $1,360\text{ cm}^{-1}$ (D peak) and $1,580\text{ cm}^{-1}$ (G peak) from $1,000\text{ cm}^{-1}$ to $2,000\text{ cm}^{-1}$. Santiago-Aviles et al. researched Raman spectra of PAN-based carbon fiber, and they observed two peaks after PAN nanofibers were treated with vacuum calcination. In this study, we treated Ag/PAN composite nanofibers at 100 °C, 200 °C, 400 °C and 600 °C, respectively. The results showed that there were two Raman spectra peaks at $1,360\text{ cm}^{-1}$ and $1,568\text{ cm}^{-1}$ in Fig. 3. These spectra were exactly identical to the reported Raman spectra of PAN-based carbon fiber. The graphite were very weak because the fibers were hardly carbonized when the temperature was 100 °C, 200 °C and 400 °C, which may be attributed to the existence of silver nanoparticles.

CONCLUSION

Ag/PAN nanofibers were treated at low temperatures by combining electrospinning with the process of fiber carbonization. When the temperature was lower than 200 °C, with the increasing of temperature, the diameter of fibers increased and silver nanoparticles on the surface of fibers gradually agglomerated. When the temperature was higher than 200 °C, with the increasing of temperature, the diameter of fibers decreased and the silver nanoparticles on the surface of fibers gradually decreased. Ag/PAN nanofibers that were treated at low temperatures showed the Raman characteristic.

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