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Fabrication of the silver/polypyrrole/polyacrylonitrile composite nanofibrous mats

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ABSTRACT

The $AgNO_3$/polyacrylonitrile hybrid nanofibers were prepared by using electrospinning technique, then the hybrid fibers of $AgNO_3$/polyacrylonitrile were treated with pyrrole in the boiling toluene medium, finally, the silver/polypyrrole/polyacrylonitrile composite fibrous mats were obtained. The scanning electron microscopy, transmission electron microscopy, X-ray diffraction and Raman spectra were used to characterize the obtained silver/polypyrrole/polyacrylonitrile composite fibrous mats. And the results indicated that the morphologies of the composite fibers were influenced by the content of $AgNO_3$ in the $AgNO_3$/polyacrylonitrile fibers. The silver/polypyrrole composite dispersed in the fibrous mats exhibited core-shell structure, and the conductivity of the optimum silver/polypyrrole/polyacrylonitrile composite fibrous mats is relatively high.

1. Introduction

Polypyrrole (PPy), one of the most important conducting polymers, has been attracted much attention for its potential applications in batteries, supercapacitors, microwave shielding, sensors and actuators [1–6]. Recently, many efforts have been focused on the preparation of metal nanoparticle/conducting polymer (CP) composites including metal nanoparticles embedded in a CP matrix, metal/CP coaxial nanocables and metal/CP coreshell nanoparticles [7–10]. In most previous reports, metal/CP composite nanostructures have mainly been prepared by polymerization monomer moieties in the presence of metal nanoparticles [7–9] or through a template guided synthesis approach [10] in which the metal salts and monomer are used as oxidizer and reducer, respectively.

On the other hand, electrospinning technique has been recognized as an efficient method to manufacture nanoscale fibrous structures [11,12]. The fibrous mats such as organic, inorganic and organic–inorganic hybrid nanofibrous mats (such as Ag/PAN) with a large surface-area-to-volume ratio have been fabricated by eletrospinning technique because of their potential application in such fields as drug delivery, tissue scaffold and sensors [11–16]. Furthermore, the soluble conducting polymers such as pristine polyaniline and its derivatives [17] have been fabricated into nanofibers by electrospinning. Recently, the PPy fibrous mats have also been prepared through the method of combining electrospinning and vapor phase polymerization [18].

In this paper we describe the fabrication of the composite nanofibers of Ag/PPy/polyacrylonitrile (PAN). The conductivities and the evolution of the morphologies of the composite mats have also been investigated.

2. Experimental procedure

$AgNO_3$ (99.8%) was purchased from Beijing Chemical Plant. Pyrrole monomer (Chinese Army Medical Institute) was distilled under reduced pressure and stored below 0°C before use. PAN (M_W = 86000) was obtained from Aldrich, and all other reagents were reagent grade.

Different amount of $AgNO_3$ was dissolved in the solution of PAN (90mg) in dimethylformamide (1.0ml) under stirring. Then the mixture was transferred into a plastic pipette with the inner diameter of ~ 1mm. The potential for electrospinning was kept at ~ 13.7kV, and the resulted fibers were collected on a sheet of grounded aluminum foil placed 12cm below the plastic pipette tip. The contents of $AgNO_3$ in the $AgNO_3$/PAN hybrid fibrous mats were 10, 36, 52, 62 and 69% when the electrospinning solutions contain 10, 50, 100, 150 and 200mg $AgNO_3$, respectively.

The $AgNO_3$/PAN mats were peeled off the aluminum foil and put into the boiling mixture of 50μl pyrrole and 20ml toluene. Then the pyrrole was oxidized by silver ions, yielding PPy and elemental Ag simultaneously [20]. After having being kept for boiling 15min, the mixture was then cooled automatically to room temperature. After being washed three times by methanol, the black fibrous mats were collected and dried under vacuum for 24h.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs images were recorded on a JEOL-JSM-6700F and H-600-2 (Hitachi, Japan) microscopic analyzer, respectively. Raman spectra were recorded on a RM 2000 microscopic

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confocal Raman spectrometer by employing a 633nm laser beam. XRD patterns were measured by a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation). The electrical conductivity was measured by the four-probe method.

3. Results and discussion

When the hybrid $AgNO_3$/PAN fibers contain 0, 10, 36, 52, 62 and 69% $AgNO_3$, the average diameters of the hybrid fibers are 245, 180, 214, 230, 280 and 292nm, respectively (see supporting materials). Similar to the literature [13], low $AgNO_3$ content can decrease the diameters of the hybrid fibers. However, when the $AgNO_3$ concentration increases further, the diameters of the hybrid fibers increase because of the high content of the solute in the electrospinning solution. The typical SEM image of $AgNO_3$/PAN fibers (62% $AgNO_3$) is shown in (Fig. 1A), the fibers exhibit a smooth surface although the content of $AgNO_3$ is as high as 62%. There are many gaps distributed in the mats. The other hybrid fibers containing different amounts of $AgNO_3$ exhibit the similar morphologies to Fig. 1A. When the content of $AgNO_3$ in the hybrid fibers is as low as 10%, there are few particles observed on the surfaces of Ag/PPy/PAN fibers whose average diameter are 300nm (Fig. 1B), and the surface of the fibers is almost smooth. However, there are a large number of particles with a relatively narrow distribution dispersed on the surface of Ag/PPy/PAN fibers (~ 350nm) prepared from $AgNO_3$/PAN fibers containing 36% $AgNO_3$ (Fig. 1C). When the content of $AgNO_3$ reaches to 52%, the particles with the diameters of 50–100nm (Fig. 1D) are observed on the fibers (~ 390nm) surfaces. As the content of $AgNO_3$ increases to 62%, besides the further increase of the fibers average diameters (590nm) and the particles sizes, the gaps distributed in the mats are filled partly by the formed PPy (Fig. 1E). By increasing the content of $AgNO_3$ to 69% further, the fibers average diameters reach to 750nm and the pores distributed in the mats almost disappear because of the more formed PPy, and there are large clusters (> 300nm) dispersed on the mats surface. From the EDX spectrum inserted in Fig. 1F, we find that the large clusters are compose of silver, carbon and nitrogen. The silver particles are formed when $AgNO_3$/PAN fibers are treated with pyrrole monomer, which, at the same time is oxidized to form PPy. So the diameters of Ag/PPy/PAN fibers become larger than that of $AgNO_3$/PAN fibers.

As shown in TEM images, there are nanoparticles with average diameters of ~ 13nm and relatively narrow distribution (Fig. 2A) dispersed in the Ag/PPy/PAN fibers prepared from $AgNO_3$/PAN fibers containing 10% $AgNO_3$. When the content of $AgNO_3$ reaches to 36%, the diameters of the formed nanoparticles reach to about 38nm (Fig. 2B). In Ag/PPy/PAN fibers prepared from $AgNO_3$/PAN fibers (52% $AgNO_3$), the distribution of Ag particles becomes wider, and the size of the particles reaches to ~ 75nm (Fig. 2C). Furthermore, we find that Ag particles are coated with a shell of PPy with an average thickness of 20nm. By increasing the content of $AgNO_3$ (62%) further, the particles with a wide distribution and large size (50 ~ 150nm) are

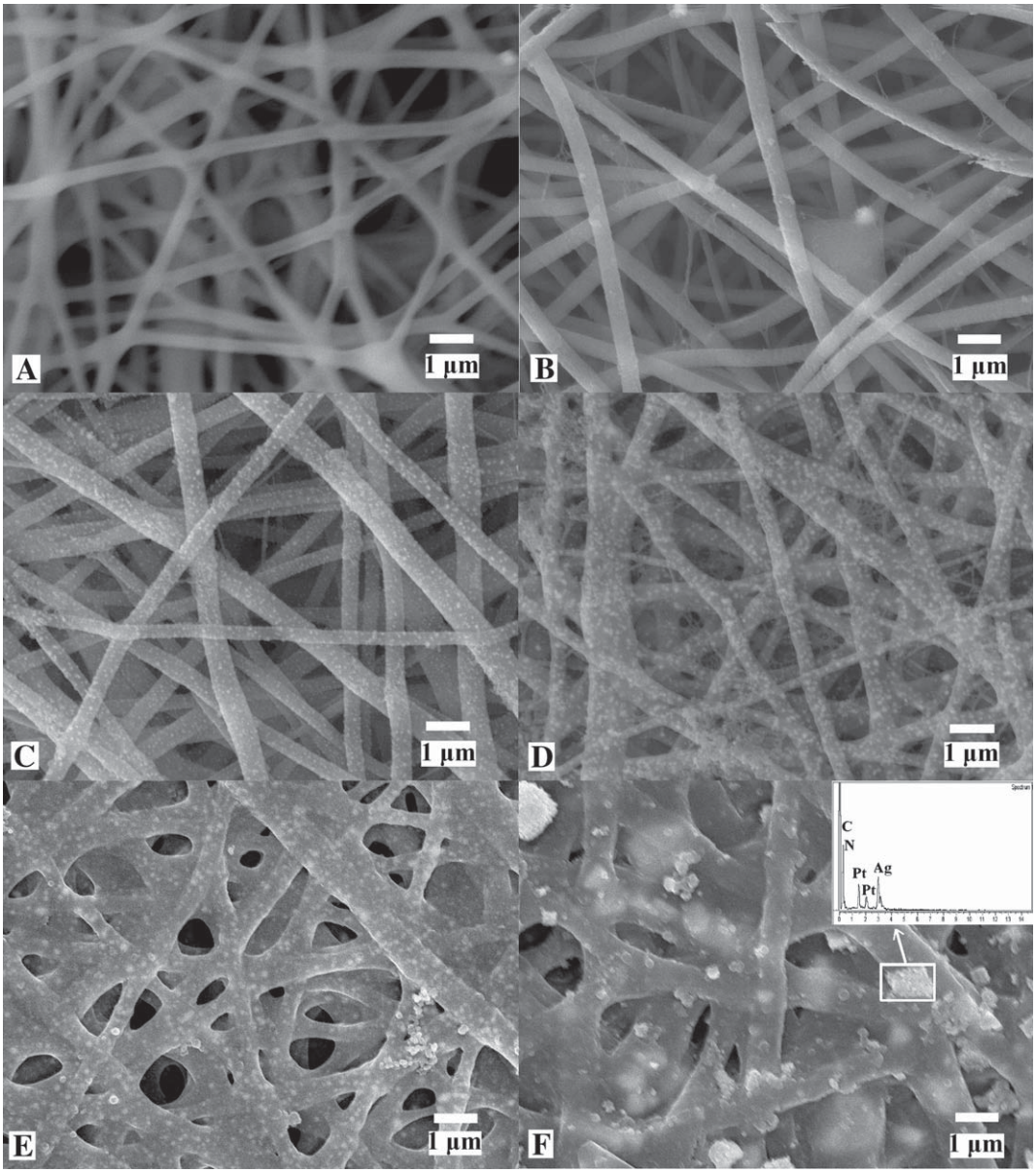

Fig. 1. SEM images of (A) the $AgNO_3$/PAN hybrid mats containing 62% $AgNO_3$, and the Ag/PPy/PAN fibrous mats prepared from $AgNO_3$/PAN fibrous mats containing (B) 10, (C) 36, (D) 52, (E) 62 and (F) 69% $AgNO_3$, respectively.

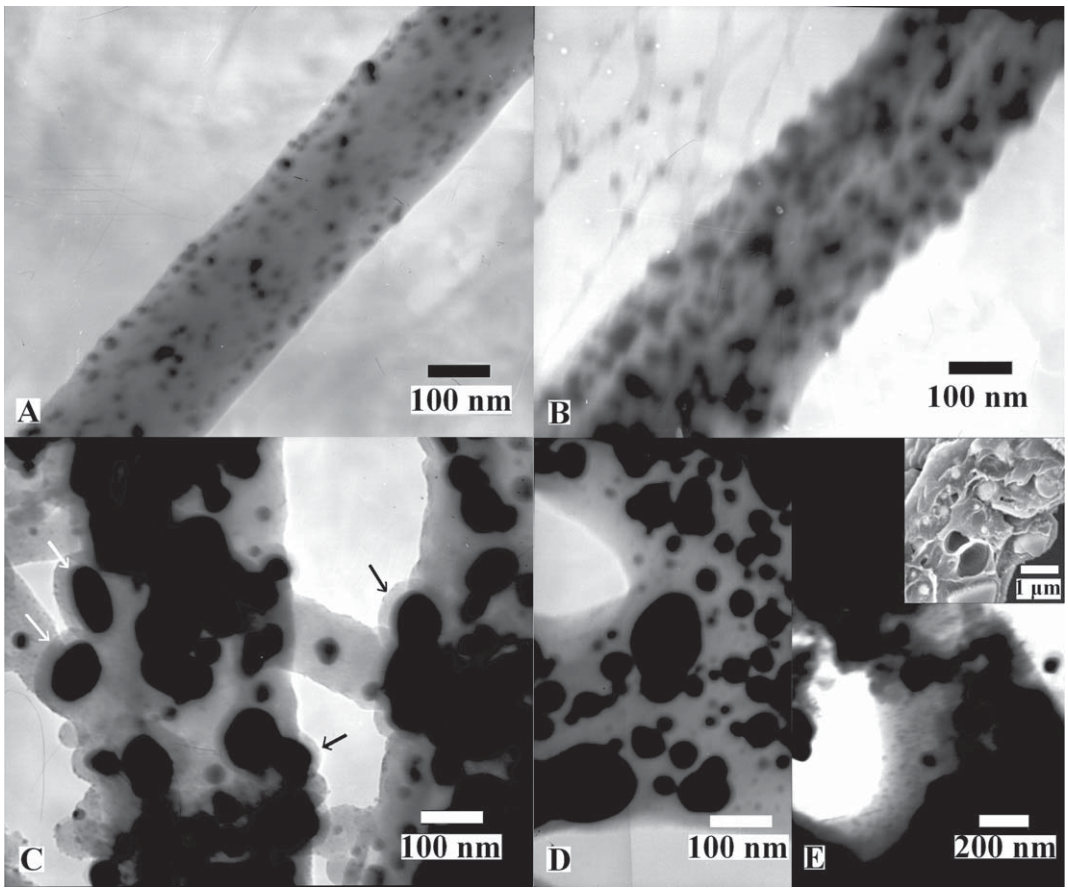

Fig. 2. TEM images of the Ag/PPy/PAN fibrous mats prepared from $AgNO_3$/PAN mats in which the content of $AgNO_3$ is (A) 10, (B) 36, (C) 52, (D) 62 and (E) 69% (inserted image: SEM image of the cross section), respectively.

dispersed in the matrix of PAN and PPy (Fig. 2D). Finally, some particles congregate into larger clusters (> 300nm) (Fig. 2E), in which the $AgNO_3$/PAN fibers contain 69% $AgNO_3$.

The XRD patterns are shown in Fig. 3. The broad diffraction peak at ~ 17.3° is related to the orthorhombic PAN (110) reflection [19], and the other diffraction peaks at about 38.2°, 44.4°, 64.6° and 77.5° are related to (111), (200), (220) and (311) planes of the standard cubic phases of silver, respectively. There is only Ag (111) diffraction peak observed in the Ag/PPy/PAN composite prepared from $AgNO_3$/PAN fibers containing 10% $AgNO_3$ (Fig. 3b) because of the small size and low content of Ag particles. This result is consistent with the results of the TEM and SEM.

The conductivities of Ag/PPy/PAN composite fibrous mats are measured and the results are shown in Fig. 4A. The optimum conductivity is found to be ~ 1.3×10^{-3} S cm^{-1} for Ag/PPy/PAN composite fibrous mats prepared form $AgNO_3$/PAN containing 52% $AgNO_3$. It is noticeable that the optimum conductivity for Ag/PPy/PAN composite fibrous mats is about 1000 times of that for Ag/PPy core-shell composite (10^{-6} S cm^{-1}) reported by previous literature [20]. The reason may contribute to the organic reaction medium or the fibrous structure of composite in our paper.

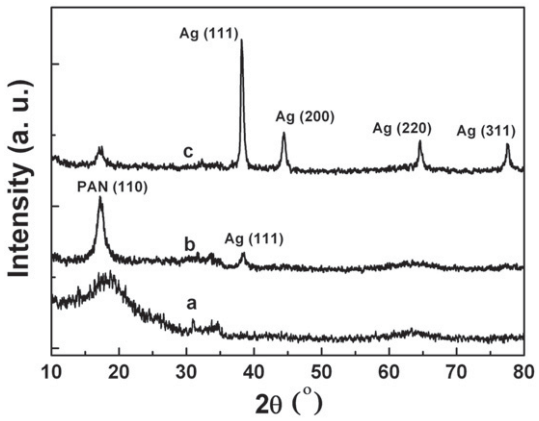

Fig. 3. The XRD patterns of (a) pure PAN and the Ag/PPy/PAN composite fibrous mats prepared from $AgNO_3$/PAN hybrid fibers containing (b) 10%, and (c) 52% $AgNO_3$.

No characteristic Raman bands of PPy are observed in the sample prepared from $AgNO_3$/PAN fibers containing 10% $AgNO_3$ because of the low content of PPy (Fig. 4B–a). With the increase of the content of $AgNO_3$, the bands corresponding to PPy appear, according to the literature [21–24], the band at ~1622 and 1592 cm^{-1} is attributed to the C=C bond stretching of the oxidized species and neutral species of PPy, respectively. The band at 1416, 1326 and 1260 cm^{-1} is corresponding to the antisymmetric C–N stretching, the ring stretching and the antisymmetric C–H in plane bending of PPy, respectively. The double band at approximate to 1092 cm^{-1} and 1048 cm^{-1} are assigned to the C–H in-plane deformation and the band at about 932 cm^{-1} is assigned to ring deformation of PPy. Furthermore, the Ag/PPy/PAN fibers prepared from $AgNO_3$/PAN fibers containing 52% $AgNO_3$ exhibit stronger Raman scattering (Fig. 4B–c) than other samples. Therefore, it is reasonable to conclude that Ag/PPy/PAN composite fibrous mats have been successfully fabricated.

4. Conclusions

The Ag/PPy/PAN composite fibrous mats have been fabricated. The Ag/PPy core-shell particles structure is observed clearly in the optimum Ag/PPy/PAN composite fibers prepared from $AgNO_3$/PAN (52%$AgNO_3$), which exhibits higher conductivity and stronger Raman scattering intensity than other composite fibers. The size of the Ag particles and the conductivities of the composite fibrous mats are influenced by the content of $AgNO_3$ in the $AgNO_3$/PAN fibers. These composite fibrous materials may be applied in microwave shielding or sensor fields.

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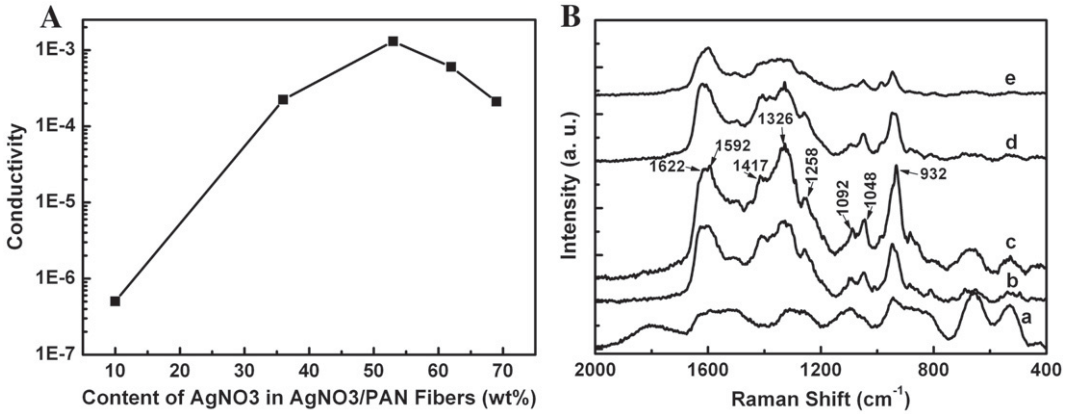

Fig. 4. (A) The plot of the conductivities (logarithmic scale) of Ag/PPy/PAN fibrous mats versus the content of $AgNO_3$ in $AgNO_3$/PAN; (B) The Raman spectra of the Ag/PPy/PAN fibrous mats prepared from $AgNO_3$/PAN fibers containing (a) 10, (b) 36, (c) 52, (d) 62 and (e) 69% $AgNO_3$, respectively.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2008.05.054.

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