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Smaller AgBr Nanoparticle Embedded in One-Dimensional Poly(vinyl pyrrolidone) Fibers

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A new series of AgBr/poly(vinyl pyrrolidone) (PVP) composite fibers have been prepared successfully by electrospinning technology and Sol-Gel method. This is a novel and simple approach. At first, we use Sol-Gel process to prepare thinner AgBr nanoparticles in the poly(vinyl pyrrolidone) solution and then the solution are electrospun to obtain AgBr/poly(vinyl pyrrolidone) composite nanofibers. The final products obtained were thoroughly characterized by transmission electron microscopy, scanning electron microscopy, X-ray diffraction patterns and X-ray photoemission spectroscopy.

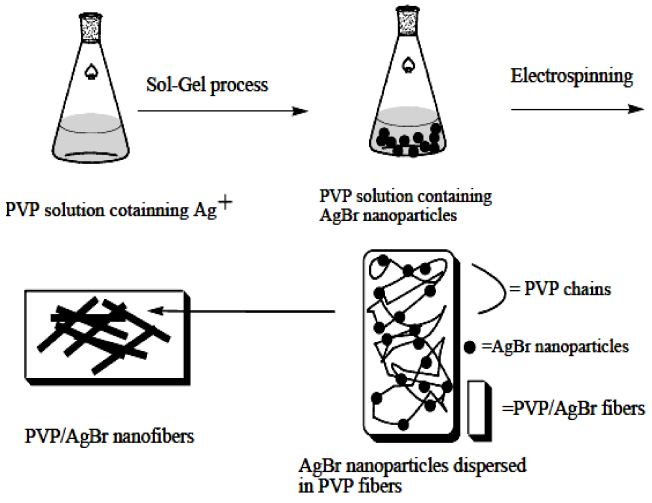
Key Words: AgBr nanoparticles, Poly(vinyl pyrrolidone), Composite nanofibers, Electrospinning.

INTRODUCTION

Organic-inorganic composite materials have been attracted substantial attention because of the possibility of combining the properties of organic and inorganic components[1-3]. Numerous studies have been performed on the preparation of new organic/inorganic hybrid materials and nanocomposites. The organic/inorganic nanocomposite is commonly used for polymers matrix containing dispersed inorganic nanoparticles with nanosize average particle[4-8].

Electrospinning is relatively simple and versatile method for producing polymer nanofibers. This process involves the production of continuous one-dimensional nanofibres by an electrostatically driven jet of polymer solution. In an electric field as strong as several kV, nanofibres are formed by the narrowing of the ejected jet stream as it undergoes increasing surface charge density due to the evaporation of the solvent. Directly collected as-spun fibres are usually randomly oriented[9-12]. However, it is feasible to achieve highly aligned polymer nanofibers by using mechanical or electrical methods as described earlier. Recently, many people study about preparation of inorganic/organics composite nanofibers using electrospinning technology. With the development of technology, many kinds of inorganic materials were introduced into polymer nanofiber matrixs. Xia's group have prepared metal oxides/polymer nanofibres with electrospi-nning method[13-15]. Wang's group has also reported the preparation of various inorganic nanoparticles dispersed in polymer nanofibres[16-18]. By electrospinning poly(vinyl alcohol) (PVA) solution containing a low concentration of gold nanoparticles, we successfully prepared Au/PVA composite fibres[19]. We presented a novel approach for the preparation of AgCl nanoparticles/polyacrylonitrile (PAN) firstly[20]. More recently, we prepared the nanofibers containing AgBr nanoparticles[21]. It obtained bigger size AgBr nanoparticles in the composite nanofibers.

In this paper, the hydrobromic acid acts as reagents and the obtained AgBr nanoparticle was small and well dispersed in the solution. We finally fabricated AgBr/poly(vinyl pyrrolidone) nanofibres by electrospinning. A series of test proved that the AgBr nanoparticles were uniformly dispersed in the poly(vinyl pyrrolidone) fibers (**Scheme-I**).



Scheme-I Scheme of the procedure used to prepare the AgBr/poly(vinyl pyrrolidone) nanofibers

EXPERIMENTAL

Poly(vinyl pyrrolidone) (PVP, m.w. = 1,300,000) was provided by Xiamen Sanland Chemicals Co. Limited (China). Silver nitrate ($AgNO_3$) was purchased from Sinopharm Medicine Holding Shenyang Co., Ltd. (China). Hydrochloric acid (HCl, 36 %) and ethanol were supplied by Beijing Chemicals Co. (China). In all the experiments, the chemicals were analytical grade and water was high purity water.

Preparation of poly(vinyl pyrrolidone)/AgBr composite nanofibres using elelctrospinning method: Poly(vinyl pyrrolidone) (0.8 g) was dissolved in 9.2 g ethanol/water (8/2) at room temperature. And then, 0.122, 0.061 and 0.041 g $AgNO_3$ were added to the solution under stirring, respectively. The above three solutions were stirred in the dark at 0 ºC for *ca.* 12 h and different ratios of poly(vinyl pyrrolidone) monomer/$AgNO_3$ [10:1 20:1 and 30:1 for 8 wt. % of poly(vinyl pyrrolidone)] homogeneous solution was formed. The above solutions were put into a 25 mL flask, respectively. An appropriate amount of hydrobromic acid was added to the solutions with rapid stirring. Poly(vinyl pyrrolidone)/AgBr composite sols were obtained. In the test, the pure poly(vinyl pyrrolidone) fibers, which were electrospun from 8 wt % concentration of poly(vinyl pyrrolidone) solution are labeled as sample A. The molar ratio of the AgBr to monomer of poly(vinyl pyrrolidone) in samples B, C and D was calculated to be 1:10, 1:20 and 1:30, respectively. The voltage used for electrospinning was 15 kV and the collection distance was 15 cm. The temperature of electrospinning was controlled at 20 ºC.

Characterization of AgBr/poly(vinyl pyrrolidone) nanocomposite: The morphologies of the AgBr/poly(vinyl pyrrolidone) composite nanofibers were observed by field-emission scanning electron microscopy (SEM, FEI XL30 ESEM). The morphologies of the AgBr were observed by a Hitachi S-570 transmission electron microscopy (TEM) operation at 200 kV. The chemical composition of the products was characterized by X-ray photoemission spectroscopy, X-ray photoemission spectroscopy using a VG-Scientific ESCALAB 250 spectrometer with a monochromatic AlK_α xray source at 1486.6 eV. A piece of AgBr/poly(vinyl pyrrolidone) nanofibre film was stuck on an Al sheet to determine the XRD pattern at a scanning rate of 4º min^{-1}, using a DXP-18AHF diffractometer with CuK_α radiation ($\lambda = 0.154\ 178$ nm). FTIR spectra were taken with a thermo nicolet nexus spectrometer and transmission spectra of the samples were obtained by forming fibers film.

RESULTS AND DISCUSSION

Fig. 1 shows the scanning electron microscopic images of the as-prepared AgBr/poly(vinyl pyrrolidone) composite nanofibers. It is known that the content of inorganic nanoparticles is a key factor determining the morphology and the diameter of the electrospinning products, which has been discussed in our previous report. Increasing the concentration of AgBr nanoparticles in poly(vinyl pyrrolidone) solution, the diameter of nanofibers can be thinned. In this study, 8 wt % of poly(vinyl pyrrolidone) in ethanol/water (8/2) solvents was chosen and meanwhile, to study the adding of AgBr was how to affect poly(vinyl pyrrolidone) fibers produced. Fig. 1 shows the scanning electron microscopy images of 8 wt % of poly(vinyl pyrrolidone) before and after adding various ratio of AgBr nanoparticles. It was found that before adding the AgBr nanoparticles, the electrospun fibers were straight and smooth. The average diameter of poly(vinyl pyrrolidone) fibers is about 1 mm, however, after introducing various ratio of AgBr nanoparticles into the poly(vinyl pyrrolidone) solutions, scanning electron microscopy images clearly showed that there were the thinner fibers. These images indicate that the diameter of the poly(vinyl pyrrolidone) fiber is significantly affected by the AgBr nanoparticles content of the polymer solution used for electrospinning. The molar ratio of the AgBr to monomer of poly(vinyl pyrrolidone) in samples were1:30, 1:20 and 1:10, respectively. The average diameter of the AgBr/poly(vinyl pyrrolidone) composite nanofibres was reduced to 424, 368 and 286 nm (Fig. 1A-C), respectively.

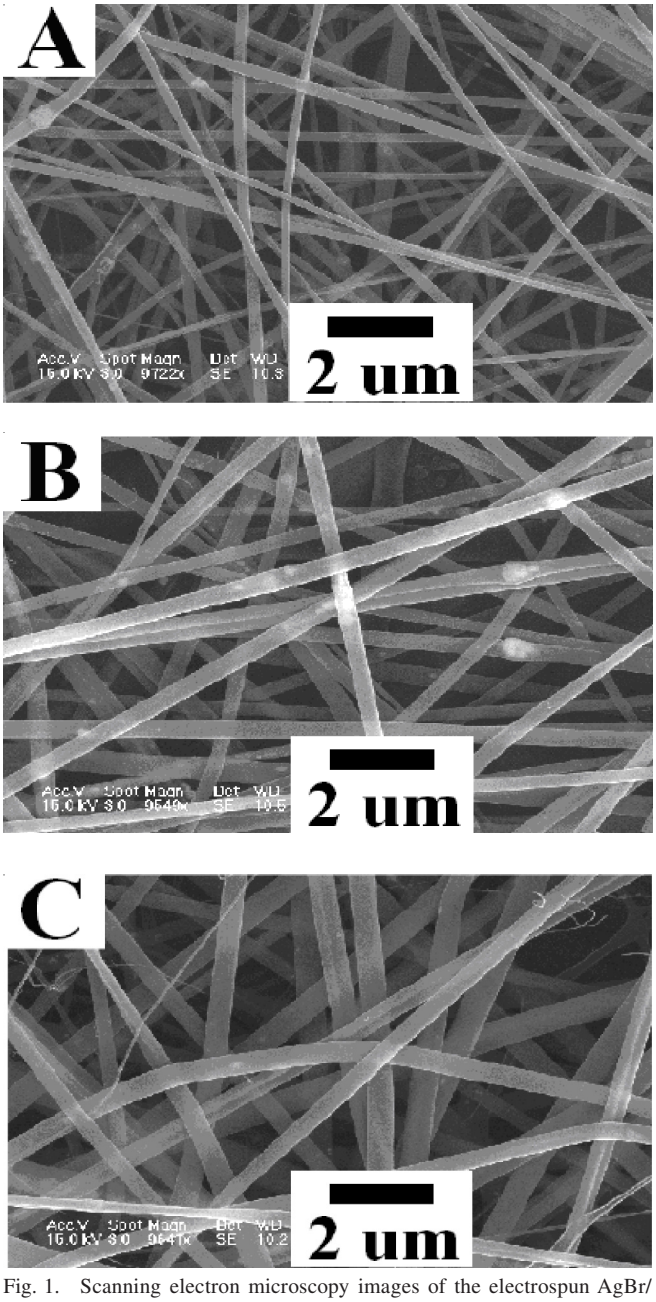


Fig. 1. Scanning electron microscopy images of the electrospun AgBr/poly(vinyl pyrrolidone) composite fibres, the molar ratio of AgBr to VP is 1:10(A), 1:20 (B) and 1:30 (C)

To investigate the existence and morphology of nanoparticles in the composite nanofibers, transmission electron microscopy (TEM) was conducted to observe the composite nanofibers. The transmission electron microscopic images of the AgBr/poly(vinyl pyrrolidone) (1/30) AgBr/poly(vinyl pyrrolidone) (1/20) and AgBr/poly(vinyl pyrrolidone) (1/10) composite nanofibers are shown in Fig. 2A-C. The dark spots in the nanofibres are AgBr nanoparticles. Measuring the AgBr nanoparticles sizes from transmission electron microscopic images reveals that the average diameter of the AgBr nanoparticles is 30.2 nm in Fig. 2A, the average diameter of the AgBr nanoparticles is 32.6 nm in Fig. 2B and the average diameter of the silver bromide nanoparticles is 38.4 nm.

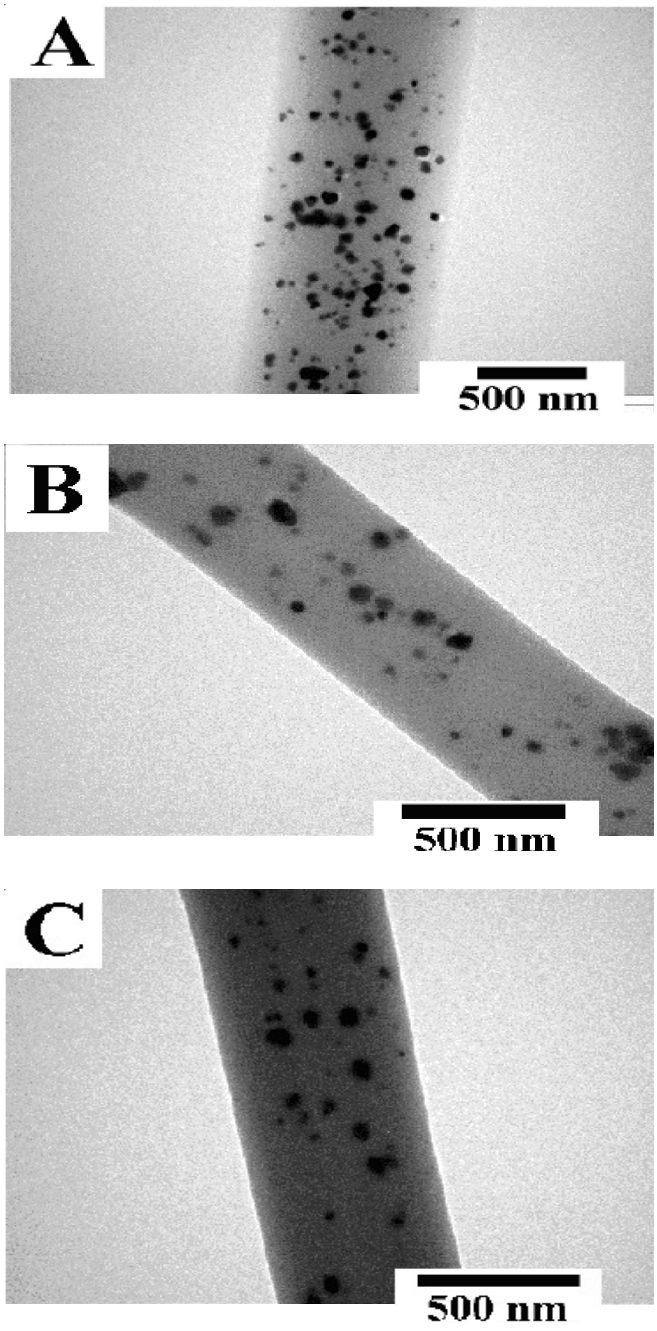


Fig. 2 Transmission electron microscopy images of the electrospun AgBr/poly(vinyl pyrrolidone) composite fibres the molar ratio of AgBr to VP is 1:10 (A), 1:20(B), 1:30(B)

Fig. 2 shows the XRD curve for various fiber samples. As shown in Fig. 2(a), it was pure poly(vinyl pyrrolidone) nanofibers, there existed a broad peak around 2θ that the value is 21.55º, corresponding to the peak of poly(vinyl pyrrolidone) crystalline. And then, this peak was also observed in Fig. 2(b-d). From Fig. 3(b), crystalline peak of poly(vinyl pyrrolidone) appeared at 21.55º. At the same time, others six peaks appeared with the reflection peaks around 2θ = 26.6º, 30.9º, 44.3º, 55.0º, 64.6º and 73.3º among 10º and 80º. These data could be indexed to the cubic face-center of AgBr (JCPDS card). When the content of AgBr nanoparticles was increased to 1/20 (Fig. 3c) and 1/10 (Fig. 3d), the reflection peaks intensity of AgBr decreased. The results proved that the cubic face-center of AgBr nanoparticles was dispersed in polymer nanofiber matrix.

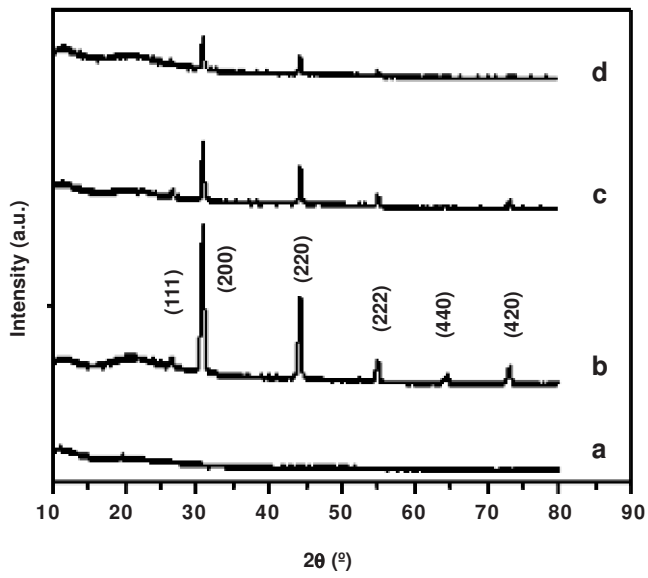


Fig. 3. XRD patterns of AgBr/poly(vinyl pyrrolidone) composite fibres: pure poly(vinyl pyrrolidone) (a), the molar ratio of AgBr to VP is 1:30 (b), 1:20 (c) and 1:10(d)

To study the existence of some elements in the AgBr/poly-(vinyl pyrrolidone) nanofibers, X-ray photoelectron spectroscopy (XPS) (Fig. 4) was performed to determine the sort of their surface composition. In Fig. 4a, Peak I at 368.6 eV and Peak II at 374. 6 eV correspond to Ag 3d3/2 and Ag 3d5/2, respectively. The peak at 68.7 eV (Fig. 4b) corresponds to Br 2p transitions. All of the observed binding energy values for Ag 3d and Br 2p were in accordance with the reported data[22]. The results indicated that AgBr nanoparticles were dispersed in polymer nanofiber matrix.

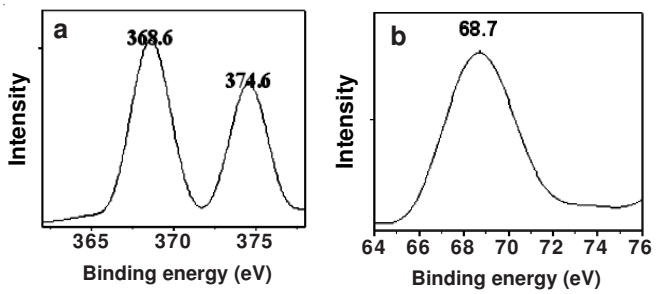


Fig. 4. XPS data on the electrospun AgBr/poly(vinyl pyrrolidone) (1/10) composite fibres. (a) Ag 3d; (b) Br 2p

Conclusion

In this study, the AgBr/poly(vinyl pyrrolidone) composite nanofibers generated by sol-gel method followed by electrospinning technology. XRD and transmission electron microscopy measurements revealed that AgBr nanoparticles are in nanometer size domain.

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