Preparation of Atactic Poly(vinyl alcohol)/Silver Composite Nanofibers by Electrospinning and Their Characterization

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ABSTRACT: Poly(vinyl alcohol) (PVA)/silver composite nanofibers were successfully prepared by the electrospinning method. Water-based colloidal silver in a PVA solution was directly mixed without any chemical or structural modifications into PVA polymer fibers to form organic–inorganic composite nanofibers. The ratio of silver colloidal solution to PVA played an important role in the formation of the PVA/silver composite nanofibers. We prepared two different atactic PVA/silver nanocomposites with number-average degrees of polymerization of 1700 and 4000 through electrospinning with various processing parameters, such as initial polymer concentration, amount of silver colloidal solution, applied voltage, and tip-to-collector distance. The PVA/silver composite nanofibers were characterized by field emission scanning electron microscopy and transmission electron microscopy (TEM). TEM images showed that silver nanoparticles with an average diameter of 30–50 nm were obtained and were well distributed in the PVA nanofibers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2883–2891, 2010

Key words: degree of polymerization (DP); fibers; nanocomposites; nanotechnology; water-soluble polymers

INTRODUCTION

Polymer/inorganic nanoparticle composites have been the focus of extensive research efforts in the past decade.[1–6] The introduction of inorganic nanoparticles into the polymer matrix has proven to be an effective and low-cost method for improving the performance of existing polymer materials.[1–3,6] The synergistic properties produced by the addition of inorganic nanoparticles include improved modulus and dimensional stability, lower thermal expansion coefficient and gas permeability, higher swelling resistance, and enhanced ionic conductivity.[7–10] When nanometer-sized particles are applied, these benefits can be achieved at very low loading levels as a result of their unusually large specific surface area.

During the past few decades, silver nanoparticles and silver compounds have attracted considerable interest because of their application in areas such as electromagnetic interference shielding, antibiotic medical devices, and surface-enhanced Raman scattering.[11–15] It is well known that silver is superior to other nanostructured metal particles for many reason, including electrical conductivity,[16] antimicrobial effects,[17] optical properties,[18] and oxidative catalysis.[19] Many methods (e.g., chemical reduction, a polyol process, and a radiolytic method)[20,21] have been developed for the synthesis of silver nanoparticles. These methods are expected to result in very narrow particle size distributions and particles of uniform shape. However, several components used in these syntheses, which include stabilizers and reducing agents such as such as poly(vinyl pyrrolidone) and NaBH$_4$, are possible health hazards.[22]

The preparation of metal nanoparticles dispersed in polymer nanofibers has drawn great attention because this kind of nanocomposite combines the unique properties of metal nanoparticles with the outstanding characteristics of nanofibers. Ultrafine nanofibers prepared by the electrospinning of a polymer solution have been studied extensively because of their unique properties, including a high surface-area-to-volume ratio and high porosity. Ultrafine fibers containing silver nanoparticles exhibit much stronger antimicrobial activity than conventional microfibers because of their higher surface-area-to-volume ratio. Because of the high surface-area-to-volume ratio of the electrospun fibers and the high porosity on the submicrometer length scale of the obtained nonwoven mat, proposed applications for these materials are in areas such as

nanofiber-reinforced composites, nanofiber-based supports for enzymes and catalysts, and nanofibrous membranes to be used in many biomedical applications,[23–26] including drug delivery, wound healing, and scaffolding for tissue engineering. Lin and Yang[27] first reported the electrospinning of ultrafine polyacrylonitrile (PAN) fibers containing silver nanoparticles. In their study, Lin and Yang[27] prepared a PAN/silver nitrate (AgNO$_3$) solution in N,N-dimethylformamide, reduced the Ag$^+$ ions by adding hydrazine hydroxide, and then poured the solution into an excess of acetone to precipitate PAN-protected Ag nanoparticles. These methods are expected to result in very narrow particle size distributions and particles of uniform shape. However, several components used in the preparation of nanofibers, which include stabilizers and reducing agents such as N,N-dimethylformamide and hydrazine hydroxide, are possible health hazards. Until now, diverse types of polymer/inorganic nanoparticle nanocomposite fibers and inorganic fibers have been successfully obtained via electrospinning.

Water-based colloidal silver, a dispersion of tiny silver particles in water, is in a form that is commonly used for disinfectant purposes. The ultimate colloidal silver suspension would be at the molecular level. It has been suggested that the smaller the silver particles are, the more stable and effective the colloidal suspension is. Aggregates of the metal colloid tend to coagulate, which makes them unstable and difficult to use. This problem can be largely overcome by transferring the metal nanoparticles onto a solid polymer substrate. Poly(vinyl alcohol) (PVA) could be considered as a good host material for metals and semiconductors because of its good thermostability and chemical resistance.[22] It is expected that PVA nanofibers are a good candidate for nanofiber mats exhibiting good mechanical properties.[28,29] Hong et al.[28] reported that antimicrobial PVA nanofibers containing Ag nanoparticles were prepared by the electrospinning of PVA/AgNO$_3$ aqueous solutions followed by a short heat treatment, and their antimicrobial activity was investigated for wound-dressing applications. After the short heat treatment, the Ag$^+$ ions therein were reduced to produce a large number of Ag nanoparticles. In another previous study,[29] for the preparation of PVA nanofibers containing Ag nanoparticles for use in antimicrobial applications, the following two methods were investigated. In the first method, the reduction of Ag$^+$ ions in PVA/AgNO$_3$ aqueous solutions was attempted by their refluxing without any chemical reducing agents, and then, the resulting PVA solutions containing Ag nanoparticles were directly electrospun. In the second method, Ag nanoparticles were generated by annealing of the PVA nanofibers electrospun from PVA/AgNO$_3$

aqueous solutions. It was reported that PVA could be a reducing agent and a stabilizer of the Ag nanoparticles.

In this study, PVA/silver composite nanofibers containing silver nanoparticles were electrospun from a PVA solution with small amounts of a water-based silver colloidal solution. Particularly, we prepared two different atactic poly(vinyl alcohol) (a-PVA)/silver nanocomposites with number-average degree of polymerization (P_n) values of 1700 and 4000 through electrospinning with various processing parameters, such as initial polymer concentration, amount of silver colloidal solution, applied voltage, and tip-to-collector distance (TCD). Conventionally, the PVA solution and silver colloidal solution were mechanically mixed to form composites. This method did not require any tedious postprocessing, such as the precipitation–redissolution and photoreduction procedures used in other investigations, or any external reducing agents. The variations in the morphology of these composite nanofibers were investigated under various preparation conditions.

EXPERIMENTAL

Materials

a-PVA with a P_n of 1700 and a degree of saponification (DS) of 99.9% was purchased from DC Chemical Co., Ltd. (Seoul, Korea). To synthesize high-molecular-weight a-PVA with a P_n of 4000 and a DS of 99.9%, a vinyl acetate was suspension polymerized in water at 40°C with 2,2′-azobis(2,4-dimethylvaleronitrile) as an initiator followed by subsequent saponification.[30] Water-based nanocolloidal silver was supplied from Miji Tech Co., Ltd. (Ansan, Korea). The initial concentration of water-based colloidal silver (AGS-WP001) was 10000 ppm. The diameter of the silver nanoparticles in the colloidal solution was 30–50 nm.

Electrospinning setup

To prepare the PVA/silver composite nanofibers, various concentrations of a-PVA aqueous solution with small amounts of silver colloidal solution (0.0, 0.2, 0.5, and 1.0 wt % to the amount of PVA) were electrospun. PVA was dissolved in water at 90°C for 2 h and maintained for 30 min to ensure homogenization. The concentration of the PVA aqueous solution was varied from 3 to 9 wt %. To prepare homogeneous polymer solutions containing silver nanoparticles, silver colloidal solutions at 0.2, 0.5, and 1.0 wt % PVA were mixed with the PVA solution at 60°C for 30 min. Figure 1 shows the schematic representation of the electrospinning
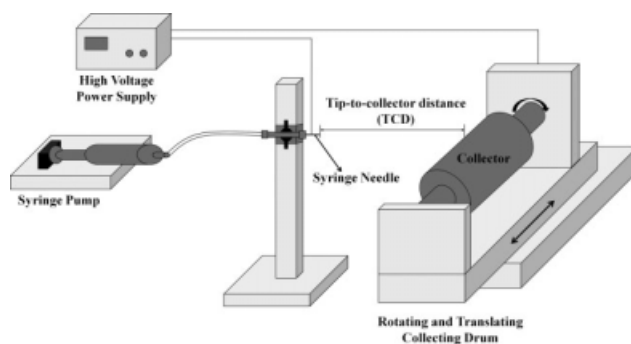
Figure 1 Experimental setup device for the electrospinning process in this study.

apparatus. The electrospinning setup consisted of a syringe and needle (i.d. = 0.95 mm), an aluminum collecting drum, and a high-voltage supply (Dongyang, Co., Daegu, Korea). Table I lists the electrospinning conditions for the PVA/silver composite nanofibers. All electrospinning procedures were carried out at room temperature.

Characterization

The viscosity of the PVA/silver composites solutions were measured by a digital viscometer (DV-I+, Brookfield Co., Middleboro, MA) at room temperature. The morphologies and compositions of the PVA/silver composite nanofibers were analyzed by field emission scanning electron microscopy (SEM; Hitachi S-4200, Hitachi Co., Ltd., Tokyo, Japan) after gold coating. The average diameters of the PVA/silver composite nanofibers were determined by analysis of the SEM images with a custom code image analysis program. The viscosity of the spinning solution and the average diameters of the PVA/silver composite nanofibers are listed in Table II. Transmission electron microscopy (TEM) images were obtained with a Philips CM 200 (Eindhoven, Netherlands) with samples deposited on carbon-coated copper grids.

RESULTS AND DISCUSSION

To prepare fine and even PVA nanofibers containing silver nanoparticles, we performed a series of experiments, varying the processing parameters, including the concentration of the PVA solution with a small amount of silver colloidal solution, applied voltage,

TCD, and the molecular weight of PVA. The electrospinning process could be sustained in a variety of modes characterized by the shape of surface from which the liquid jet originated. It has been verified experimentally that the shape of the initiating drop can be changed with spinning conditions (voltage, viscosity, feed rate).[31]

Microscopic fiber diameter distribution studies for evaluating the optimum electrospinning conditions of various polymer systems have been conducted by several researchers. Demir et al.[32] reported the effects of these parameters on the electrospinning behavior of elastomeric polyurethane copolymer using microscopic methods, including optical microscopy, SEM, and atomic force microscopy. The effects of the electrospinning parameters on the morphological change, especially the beaded structure of the nanofiber, were studied by Fong et al.[33] Morphological studies were also performed by Deitzel et al.,[34] Sukigara et al.,[35] Pawlowski et al.,[36] and Ohgo et al.[37] They used SEM as their main characterization method in numerous studies to determine the optical electric field, solution concentration, and TCD for PVA electrospun fibers with regard to fiber diameter and morphology. In the literature, at optimum electrospinning conditions for PVA, nanofabrics with average diameters of 250 and 300 nm were successfully produced. The average diameter of the PVA nanoweb was slightly decreased with increasing electric potential and with decreasing TCD and solution concentration.[38]

The dispersion and particle size of the silver nanoparticles in our water-based silver colloidal solution were examined with TEM photographs, as shown in Figure 2. The nanoparticles had a diameter of less than 30–50 nm without aggregation.

The morphologies of the as-prepared electrospun PVA/silver composite nanofibers with PVA with a P_n of 1700 with different amounts of silver colloidal solution (0.0, 0.2, 0.5, and 1.0 wt % of the amount of PVA) are shown in Figure 3. The color of the PVA nanofiber containing silver nanoparticles gradually changed to light yellow to the naked eye after a certain initial time period; this indicated that silver ions in the fine PVA fibers were slowly photoreduced and aggregated into silver nanoparticles in a general laboratory environment.[39] The concentration of PVA solution was 7 wt %, and electrospinning was carried out at an applied voltage and TCD of 20 kV

TABLE I
Electrospinning Conditions for This Study

P_n	DS (%)	Solvent	Concentration (wt %)	Amount of silver colloidal solution (wt %)	Applied voltage (kV)	TCD (cm)
1700	99.9	Water	7, 9	0.0, 0.2, 0.5 1.0	20–25	10–30
4000	99.9	Water	3, 4	0.0, 0.2, 0.5, 1.0	20–30	7–11

TABLE II
Viscosity Data of the PVA/Silver Composite Spinning Solutions and Average Diameters of the PVA/Silver Nanocomposites

P_n	PVA concentration (wt %)	Amount of silver colloidal solution (wt %)	Viscosity (cp)	Average diameter (nm)
1700	7	0.0	176	115
		0.2	216	346
		0.5	196	226
		1.0	172	183
	9	0.0	263	338
		0.2	417	482
		0.5	357	313
		1.0	283	208
4000	3	0.0	64	431
		0.2	72	547
		0.5	60	395
		1.0	56	353
	4	0.0	160	742
		0.2	391	1365
		0.5	287	835
		1.0	167	560

and 10 cm, respectively. Although all of the samples appeared to show relatively smooth surface morphologies in the SEM images, we also found that the bead-on-string morphologies were observed prominently in all of the webs [except Fig. 3(c)]; this resulted from the low viscoelastic force in comparison with Coulombic repulsion force.[31] Particularly, as shown in Figure 3(c), the formation of a uniform fiber structure with finer fibers appeared, whereas the other images showed several beads on the fiber. In these cases, the critical concentration of silver colloidal solution was expected to be 0.5 wt %. It is well known that the formation of beads generally indicates a system with a viscosity too low to offset the surface tension. Drew et al.[40] reported the electrospinning of poly(ethylene oxide) fibers containing titanium dioxide (TiO_2) nanoparticles. In their study,

the addition of TiO_2 particles resulted in a larger fiber diameter and a greater occurrence of beads than that observed from a spinning solution of the same polymer concentration without added particles. Because the addition of nanoparticles induced these apparently contradictory effects, we conceived that the nanoparticles tended to aggregate and cause beading, even though the particles increased the solution viscosity. Thus, it is conceivable that the formation of beads and changes in the fiber structure were, at least partially, caused by the aggregation of the nanoparticles in the solution. At a higher concentration (i.e., 9 wt %), smooth fibers without beads were observed. When the amounts of silver colloidal solution were 0.2, 0.5, and 1.0 wt % in the PVA with a P_n of 1700, the average diameters of the PVA/silver composite nanofibers were 482, 313, and 208 nm,
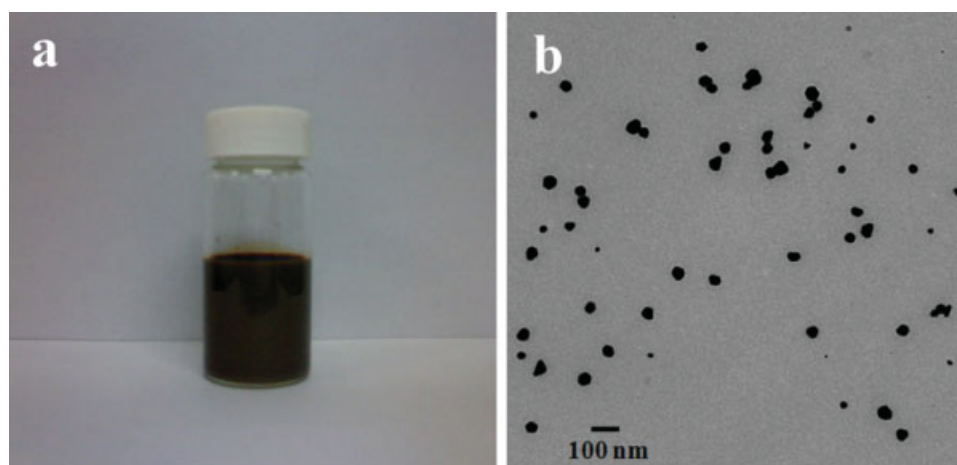

Figure 2 (a) Picture of the water-based silver colloidal solution and (b) TEM images of silver nanoparticles in a water-based silver colloidal solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
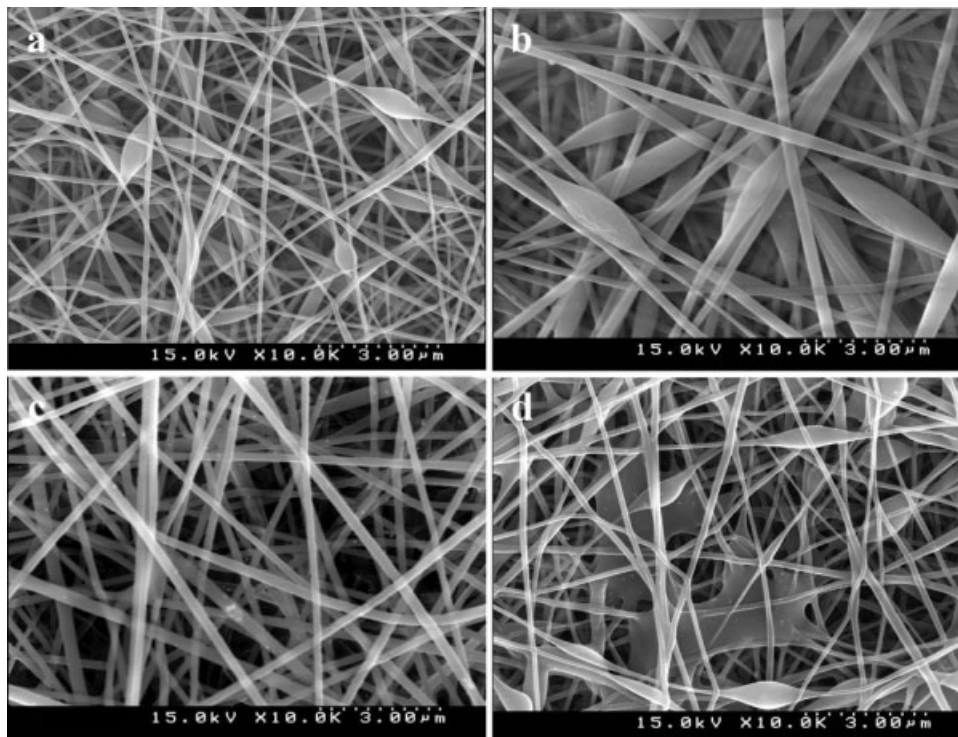
Figure 3 SEM photographs of PVA/silver composite nanofibers having a P_n of 1700 electrospun from a 7 wt % PVA solution with different amounts of the silver colloidal solution: (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The applied voltage and TCD were 20 kV and 10 cm, respectively.
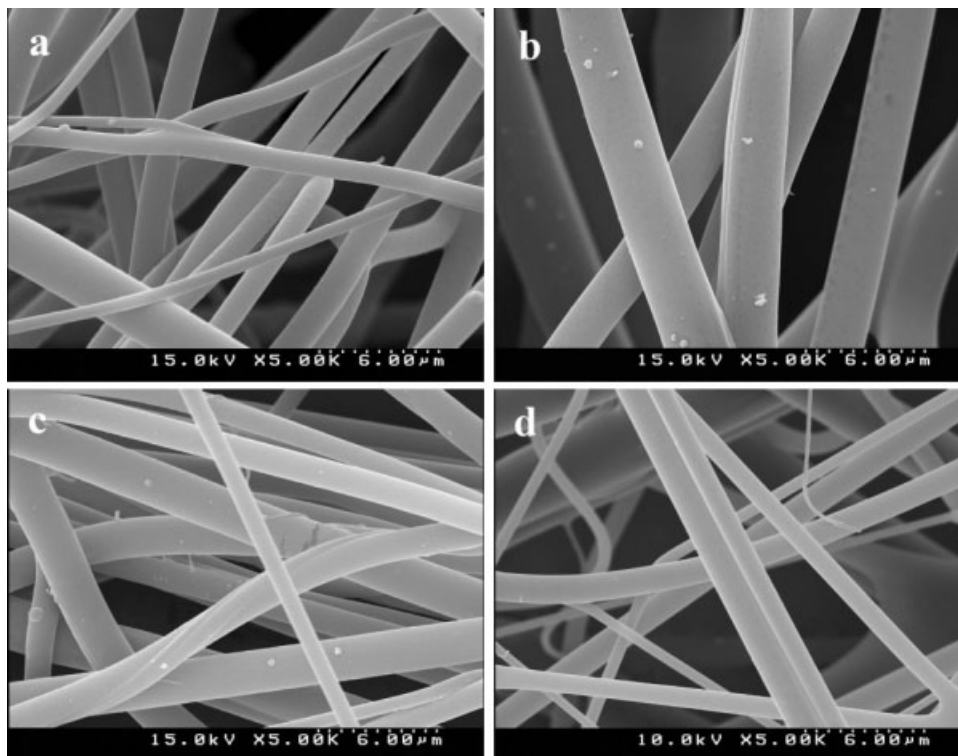

Figure 4 SEM photographs of PVA/silver composite nanofibers having a P_n of 4000 electrospun from a 4 wt % PVA solution with different amounts of the silver colloidal solution: (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The applied voltage and TCD were 25 kV and 9 cm, respectively.
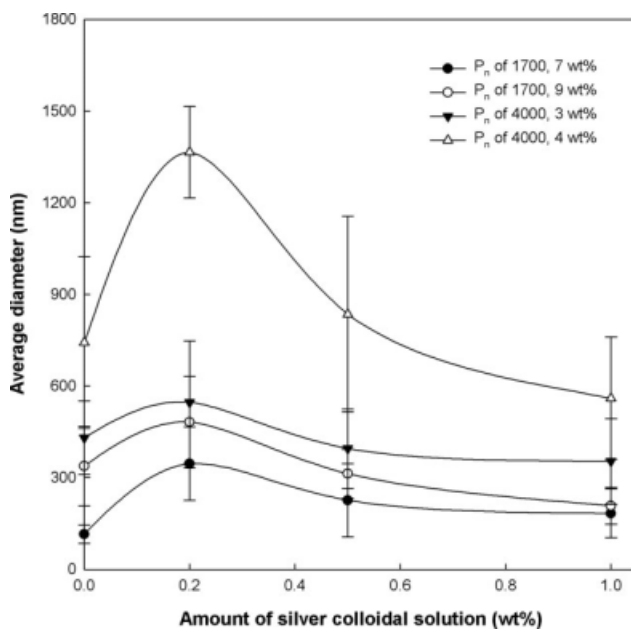
Figure 5 Average diameters of the PVA/silver composite nanofibers as functions of different P_n values of PVA and the amount of silver colloidal solution added.

respectively. It is clear that the charge density increased with the addition of silver nanoparticles in the solution; thus the ejected jets had stronger elongation forces in the electric field. These tendencies were also observed in the cases of high-molecular-weight PVA/silver nanocomposite fibers with a P_n of 4000, as presented in Figure 4. The concentration of the base PVA solution was 4 wt % with different amounts of silver colloidal solution and with the electrospinning carried out a fixed electrostatic field strength and TCD of 25 kV and 9 cm, respectively. When the amounts of silver colloidal solution were 0.2, 0.5, and 1.0 wt % in the PVA with a P_n of 4000, the average diameters of the PVA/silver composite nanofibers were 1365, 835, and 560 nm, respectively, and the interfiber space increased significantly. The effects of the molecular weight of PVA and the amount of silver colloidal solution on the average diameters of the PVA/silver composite nanofibers are shown in Figure 5. At high molecular weight, a broad distribution of fibers with a significant number of large fibers was observed in the structure, as shown in Figure 4. The degree of splaying in these large fibers may not have been as extensive as the fibers shown in Figures 3 and 6. This behavior may have arisen as a result of the surface tension difference between various solutions. It has been established that the surface tension of PVA solutions is proportional to the degree of polymerization. In addition, the relaxation of the polymeric chain becomes more difficult as the molecular weight increases, and the jet splitting and splaying process are not as effective. As a result, the fiber diameter increases with increasing molecular weight.[38]
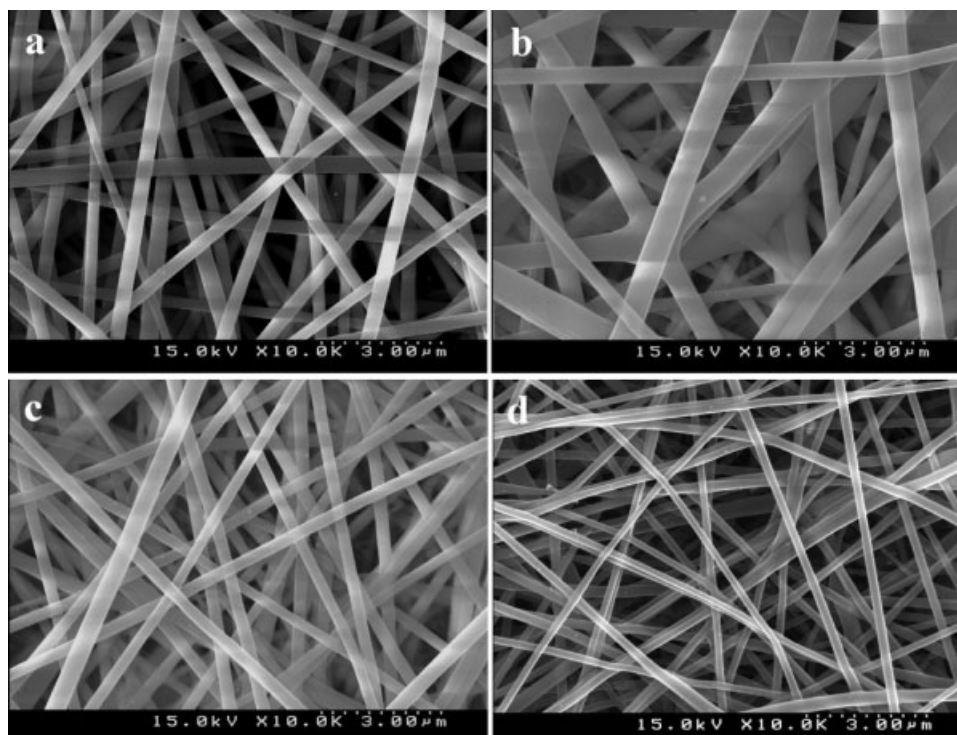

Figure 6 SEM photographs of PVA/silver composite nanofibers having a P_n of 1700 electrospun from a 9 wt % PVA solution with different amounts of the silver colloidal solution: (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 wt %. The applied voltage and TCD were 25 kV and 30 cm, respectively.
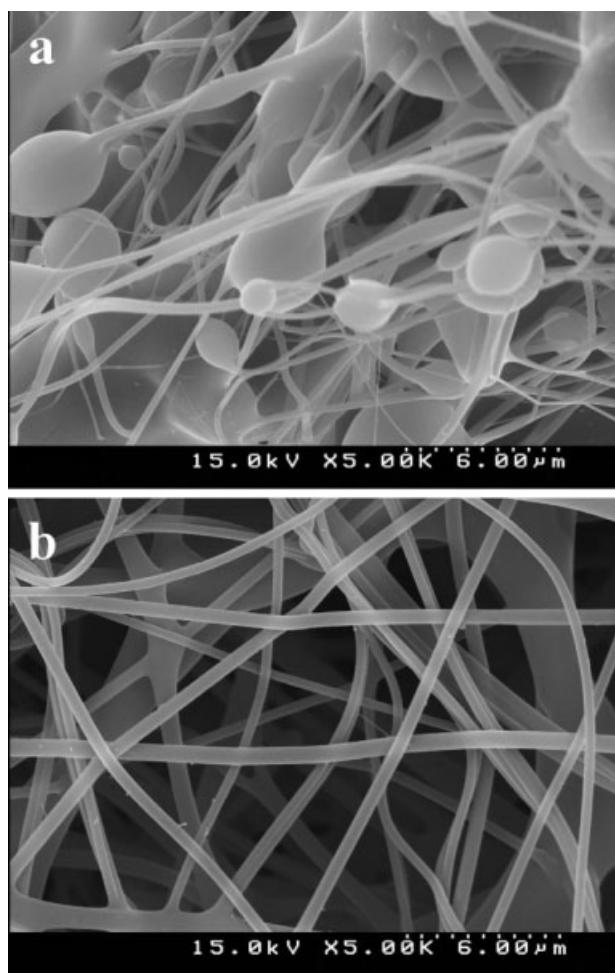
fiber thickness was systematically investigated by the electrospinning of the nanocomposite solutions at 20, 25, and 30 kV. Figure 8 shows the effects of the applied voltage in the morphological changes of the fibers electrospun from PVA with a P_n of 4000 at
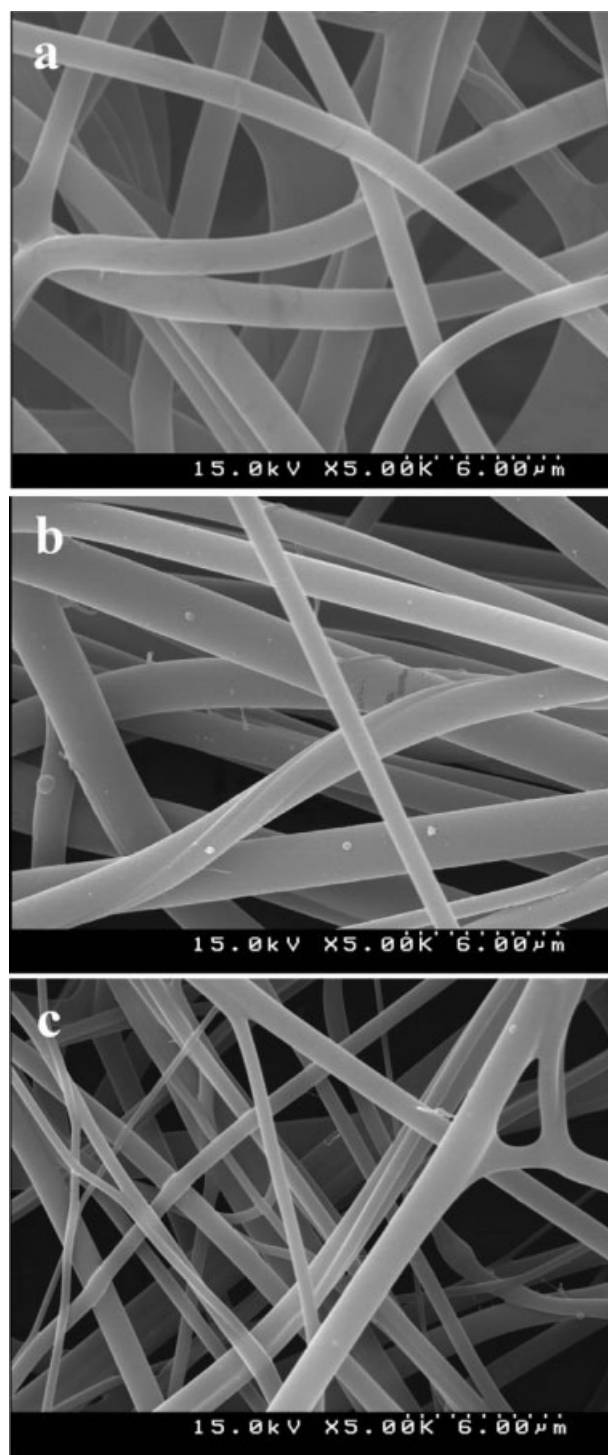

Figure 7 SEM photographs of PVA/silver composite nanofibers having a P_n of 1700 electrospun from a 7 wt % PVA solution with 0.5 wt % silver colloidal solution and a TCD of 10 cm at different applied voltages: (a) 15 and (b) 30 kV.

The spinning voltage had a significant effect on the fiber structure and diameter. The electrostatic force gradually increased with increasing applied voltage. When the applied voltage was increased, the jet velocity increased, and the solution was removed from the tip more quickly. An applied voltage lower than 15 kV did not produce uniform fibers because a 15 kV potential was not enough to overcome the surface tension. Therefore, electrospinning at 15 kV resulted in more mushroom-shaped bead defects, as shown in Figure 7(a), than fibers. As the applied voltage increased to 25 or 30 kV, the surface tension behavior was no longer dominant over the fiber shape. At higher voltages, such as 30 kV, the fiber diameter was decreased because of the simultaneous stretching effect of the charged fibers. During the travel of the fibers toward the collector, the higher voltage allowed the fiber to stretch more, and this resulted in thin fibers [Fig. 7(b)]. The stretching effect of the electrostatic voltage on the

Figure 8 SEM photographs of PVA/silver composite nanofibers having a P_n of 4000 electrospun from a 4 wt % PVA solution with 0.5 wt % silver colloidal solution and a TCD of 9 cm at different applied voltages: (a) 20, (b) 25, and (c) 30 kV.
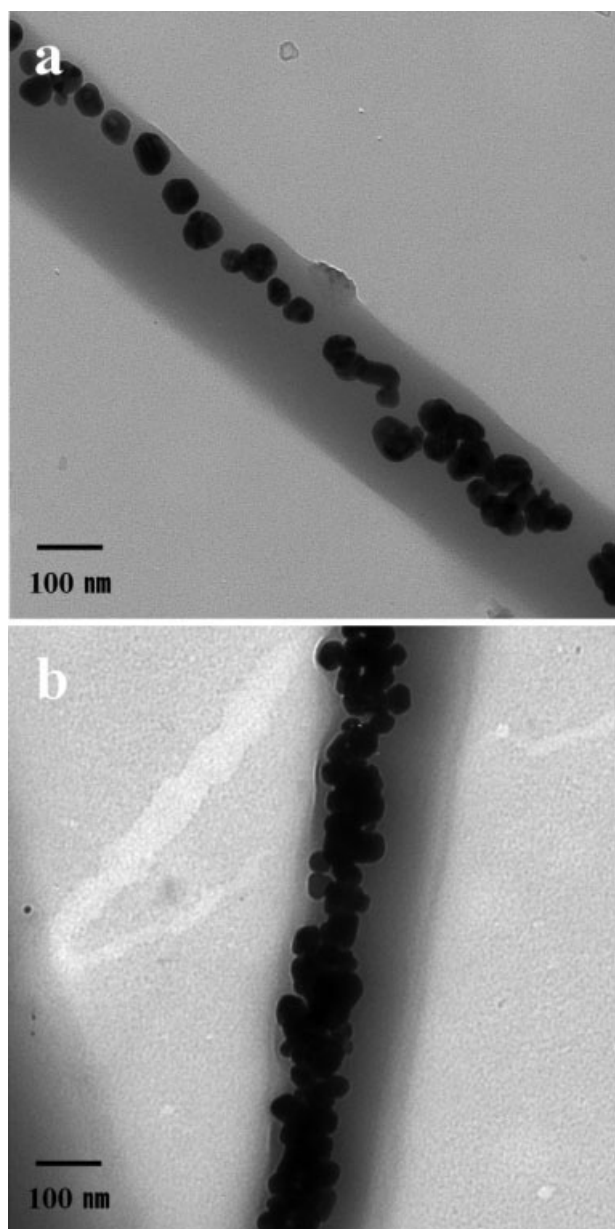
Figure 9 TEM images of PVA/silver composite nanofibers having a P_n of 1700 electrospun from a 9 wt % PVA solution with different amounts of the silver colloidal solution: (a) 0.2 and (b) 1.0 wt %. The applied voltage and TCD were 25 kV and 10 cm, respectively.

a concentration and TCD of 4 wt % and 9 cm, respectively. With increasing applied voltage, the PVA/silver composite nanofibers became thinner. At an applied voltage of 30 kV, however, the formation of a branched or spitted fiber structure [Fig. 8(c)] was observed because of the excessively increased voltage to break the ideal droplet. It is known that split fibers are formed by the separation of a primary jet into two smaller jets. Splitting occurs in the web, which is formed from the skin of jet. The repul-

sion of the charges on the skin create a lateral force on the web to split. The molecules in the electrospun fibers are usually oriented along the fiber axis; this causes the web to be relatively weak in the lateral direction.[41] From these results, we supposed that the optimum voltage applied during the electrospinning of the PVA/silver nanocomposites was 25 kV.

Figure 9 shows the TEM images of ultrafine PVA/silver composite nanofibers electrospun from PVA with a P_n of 1700 at a 9 wt % PVA solution with various amounts of silver colloidal solution. The numbers of silver nanoparticles in the ultrafine composite nanofibers increased as the amount of silver colloidal solution increased. The silver nanoparticles were all sphere-shaped and evenly distributed in the PVA nanofibers in Figure 9(a); other TEM images showed that the silver nanoparticles were more heavily dispersed in the PVA nanofibers, as shown in Figure 9(b). The numbers of silver nanoparticles in PVA/silver composite nanofibers increased as the amount of silver colloidal solution increased. These results indicate that the silver nanoparticles were well incorporated into the PVA nanofibers.

CONCLUSIONS

PVA/silver composite nanofibers were successfully prepared via the electrospinning technique. A simple method was introduced for the preparation of organic–inorganic composite nanofibers that consisted of PVA and silver nanoparticles through the direct mixing of water-based colloidal silver and PVA solutions in the absence of any tedious postprocessing, such as the precipitation–redissolution and photoreduction procedures used by others investigations, or any external reducing agents. TEM images showed that the dense silver nanoparticles were all spherical in shape with an average diameter of approximately 30–50 nm and were separated from each other and evenly dispersed in the PVA fibers. This new technique of nanocomposite production opens a variety of industrial applications. In particular, it may be greatly useful to perform the electrospinning of PVA/silver nanocomposites without the application of stabilizers and reducing agents to a reduction of Ag^+ ion in polymer nanofibers. In the near future, we will report on the preparation of stereoregular PVA/silver composite nanofibers.

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