Surface Functionalization of Polymer Nanofibers by Silver Sputter Coating

Q. F. Wei,[1] H. Ye,[1] D. Y. Hou,[2] H. B. Wang,[1] W. D. Gao[1]

[1]*CTTR, Southern Yangtze University, Wuxi 214122, People's Republic of China*
[2]*Anhui University of Technology and Science, Wuhu 241000, People's Republic of China*

ABSTRACT: The surface properties of polymer nanofibers are of importance in many applications. In this study, the electrospun polyamide nanofibers were used as substrates for creating functional coating on the nanofiber surfaces. A direct current (DC) sputter coating was used to deposit functional silver nanofilm onto the nanofibers. Atomic force microscopy (AFM) and environmental scanning electron microscopy (ESEM) were employed to study the topography and chemical composition of the nanofibers, respectively. The AFM results indicate a significant difference in the morphology of the nanofibers before and after the sputter coating. The observations by AFM also show the change in the morphology of the nanofibers with coating time. A full energy dispersive X-ray analysis (EDX) mounted on the ESEM was also used to detect the elemental composition of the functional nanofibers. EDX examination reveals the change in the chemical compositions of the nanofiber surfaces. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2384–2388, 2006

Key words: nanolayers; surfaces; AFM; sputtering; silver; ESEM

INTRODUCTION

Nanofibers have great potential for a wide range of applications because of a very large surface area. A number of applications of such polymer nanofibers are being explored, including composites, filtration, biomaterials, and many other applications.[1]

Among various processing techniques, electrospinning is widely used to produce polymer nanofibers.[2] This process involves the application of a strong electric field to a polymer solution. If electrostatic forces overcome the surface tension of a polymer solution a charged jet is ejected and moves toward a grounded electrode. The electronspun nanofibers can be collected on a substrate located on the counter electrode.[3]

For a variety of applications, it is desirable to produce such nanofibers with well-defined surface properties. Fibers with specific surface properties are also of interest in many technical applications, as the surface features affect wettability, adsorption, and adhesion of the fibers.[4] However, the surfaces of nanofibers are often not ideal for a particular application. Many techniques have been developed to modify the surface properties of polymer or polymer fibers.[5–7] In all of these, sputter coating[8] is one of the most promising techniques to make functional nanofibers.

The ability to deposit well-controlled coatings on nanofibers would expand the applications of nanofibers, based on changes to both the physical and chemical properties of the nanofibers. Silver exhibits good optical, electrical, and biocompatibility properties, and in recent years, it has been used in a variety of applications ranging from optical material to wound dressings.[9,10] In this study, the electrospun polyamide nanofibers were modified with silver by a DC sputter coating for protective applications. Atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), and energy dispersive X-ray analysis (EDX) were employed to study the topography and chemical composition of the fibers.

EXPERIMENTAL

Materials

Polyamide 6 was obtained from BASF and used as received. The polymer solution concentration of 10 wt % were prepared by dissolving the polymer in formic acid. The solution was spun from a 50 mL syringe with a needle of 0.3 mm diameter. Upon applying a high voltage (15 kV), a fluid jet was ejected from the capillary. As the jet accelerated toward a grounded collector, the solvent evaporated and charged polymer fibers were deposited on an aluminum foil and dried in a vacuum oven at room temperature for 24 h to remove the residual solvent.
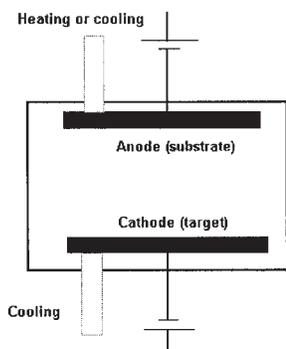
Figure 1 A DC sputter coating system.

A direct current (DC) sputter coating system was used to deposit a functional film on the nanofiber surface (Fig. 1). A high-purity silver target was mounted on the cathode, and argon was used as the bombardment gas. The deposition conditions were set at the current of 20 mA and the vacuum chamber pressure of 0.1 Torr. The deposition was performed for 1 and 10 min, respectively.
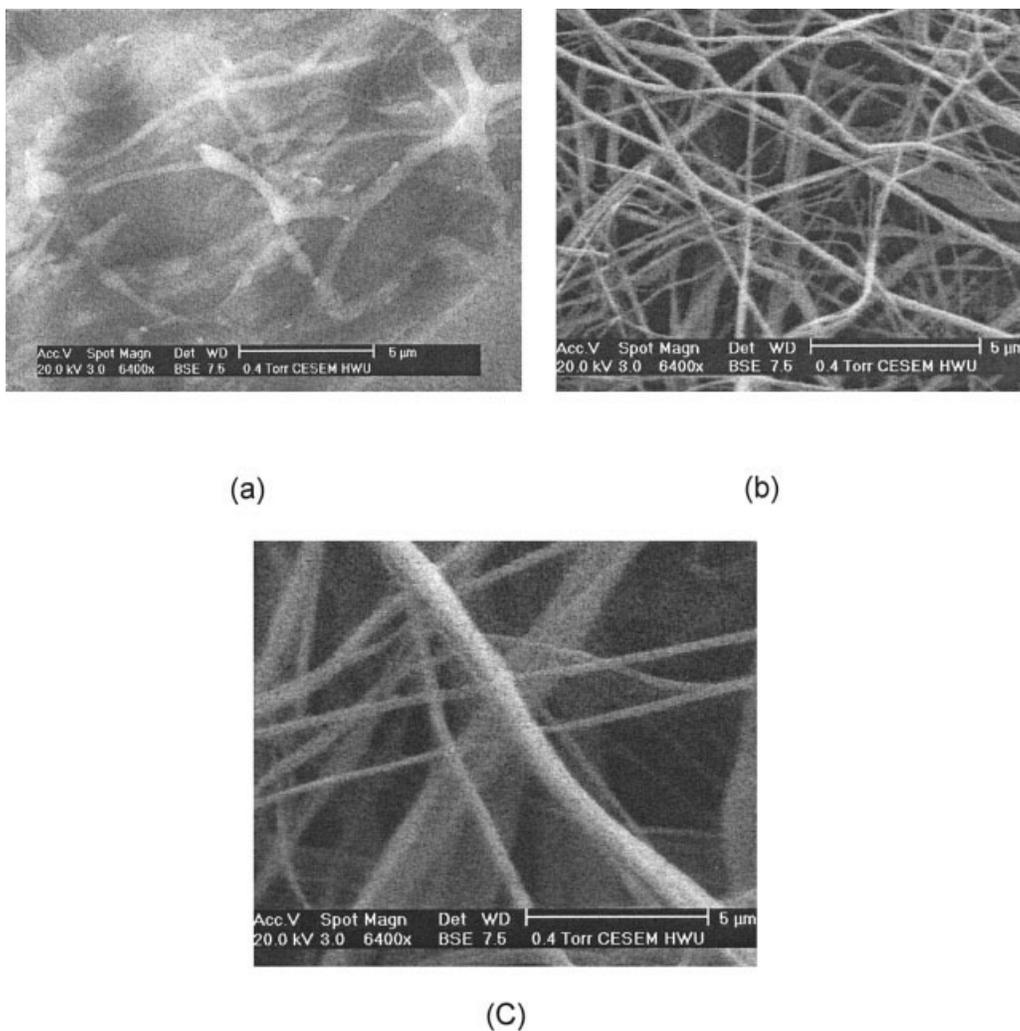
Surface characterization
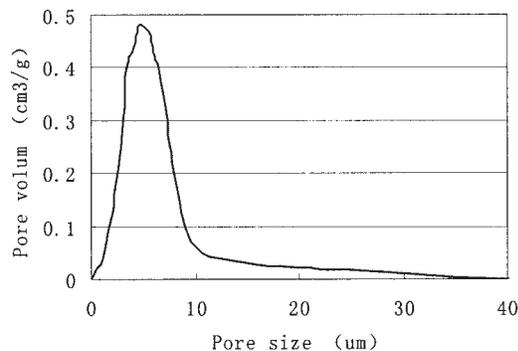
ESEM characterization

ESEM is able to image uncoated and hydrated samples by means of a differential pumping system and a gaseous secondary electron detector. ESEM offers full functionality in the three modes of operation: high vacuum, low vacuum, and ESEM mode. A low vacuum mode is suitable for the examination of uncoated nonconductive samples. ESEM mode allows very high chamber pressures up to 20 Torr.[11]

The Philips XL30 ESEM-FEG was used to examine the surface characteristics. Images were taken at 20 kV and 0.5 Torr.

The pore structure of the material was also analyzed using Poresizer 9320.

Figure 2 ESEM images of PA nanofibers: (a) uncoated, (b) coated for 1 min, and (c) coated for 10 min.

Figure 3 Pore distribution of the PA6 nanofibers.

AFM characterization

A Topometrix TMX 2000 Explorer (TM Microscopes) atomic force microscope (AFM) was employed to image the morphology of the nanofibers. Scanning was carried out in contact mode AFM[12] with a silicon nitride cantilever with a nominal spring constant of 0.03 N/m. All images were obtained at ambient conditions.

EDX analysis

The Philips XL30 ESEM-FEG equipped with a Phoenix EDX system was used to examine the chemical compositions of the sputter coated nanofibers. EDX is available in all modes in the ESEM and all elements down to boron can be detected, including the light elements, such as carbon, nitrogen, and oxygen.[13] In the EDX analysis, an accelerating voltage of 20 kV with accounting time of 100 s was applied.

Resistance measurement

The surface resistance of the sputter coated nanofiber web was measured using a 2-probe resistance meter. The measurements were performed at room tempera-
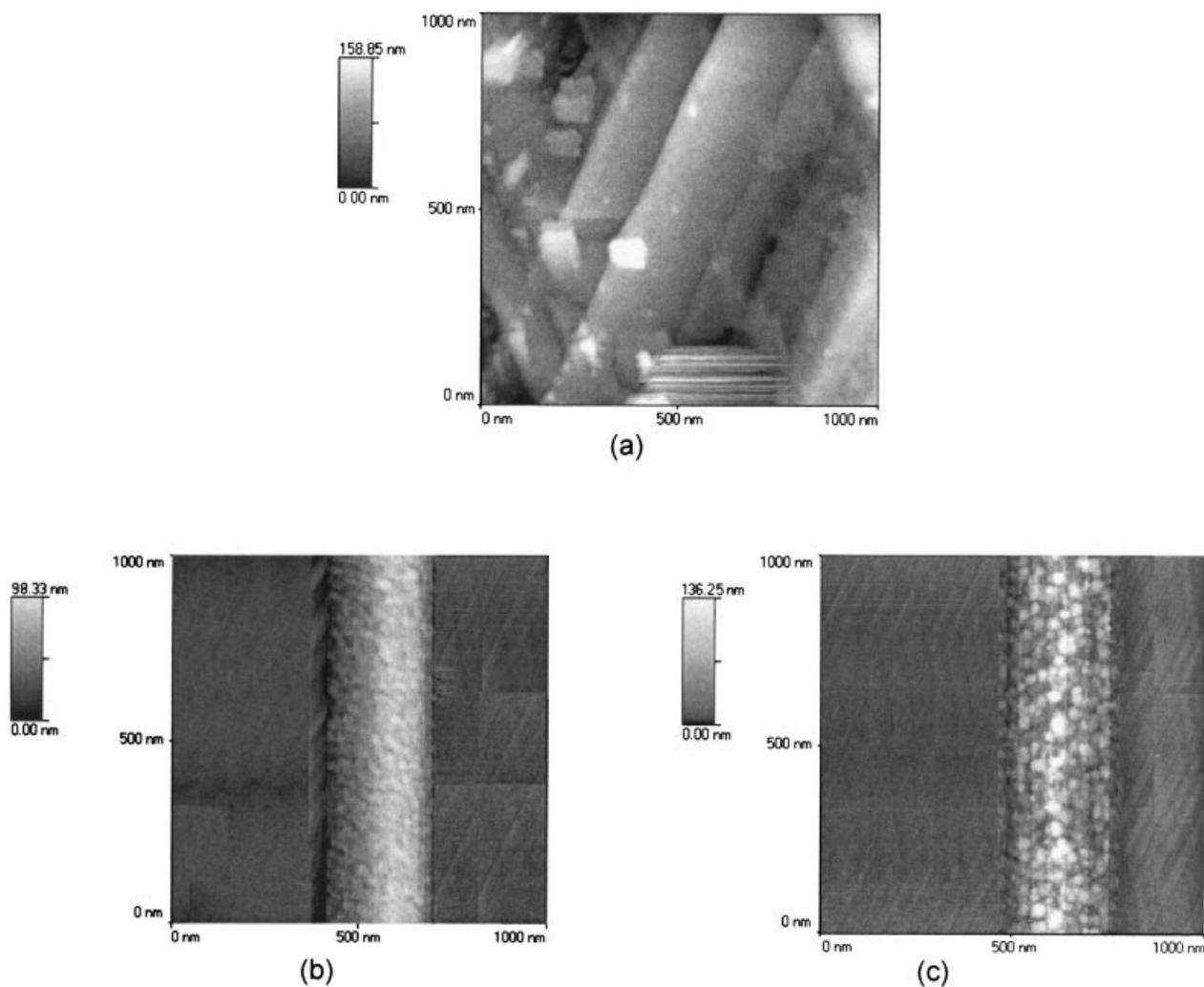
Figure 4 AFM images of PA nanofibers: (a) uncoated, (b) coated for 1min, and (c) coated for 10 min.

ture. The measurements were run in triplicate and the mean value was reported.

RESULTS AND DISCUSSION

ESEM characterization

Figure 2 shows the ESEM images of the uncoated and sputter coated nanofibers. The three-dimensional fibrous web consists of fibers with diameters ranging 200–900 nm and the average diameter is about 500 nm. The ESEM micrographs also show that the nanofibers form a porous web structure, as shown in Figure 2(a). The same structures can also be seen in Figures 2(b) and 2(c). The images in Figure 2 show the varying fiber diameters. No obvious difference between uncoated and coated fiber surfaces can be observed in the ESEM images in spite of the different contrast affected by the sputter coating.

The pore structure of the nanofiber web analyzed by porosimeter is shown in Figure 3. The porosity of the material is about 78.5%, and the mean pore size is about 5.4 μm. Figure 3 reveals the wide distribution of the pore sizes in the nanofiber web.

AFM characterization

AFM images at higher magnification reveal the surface features of uncoated and coated fibers, as shown in Figure 4. It can be seen from Figure 4(a) that the surface of the uncoated nanofiber appears to be relatively smooth, but some foreign particles can also be seen on the fiber surface. It is believed that these particles may be the dusts from the laboratory. Sputter coating significantly alters the surface characteristics of the nanofibers, as illustrated in Figures 4(b) and 4(c). The AFM images of $1.0 \times 1.0 \ \mu m^2$ scan presented in Figures 4(b) and 4(c) represent the fibers coated for 1 and 10 min, respectively. It can be seen that in the initial stage of the deposition, the surface of the nanofibers appears to be rougher than that of uncoated fibers. The nanolayer of Ag cluster is clearly recognized on the fiber surface. The size of the nanocluster varies from few nanometers to over 10 nm. Figure 4(c) displays the growth of the nanocluster on the nanofiber surface, as the deposition is increased to 10 min. The surface roughness is also increased. This behavior can be attributed to the nucleation and island formation on the fiber surface as film is growing. It is also observed that further increase in sputtering time could cause the deformation of the fibers without proper cooling of the substrate.

EDX analysis

The nanoclusters sputtered on the PA nanofiber surfaces are also confirmed by EDX analyze. Figure 5
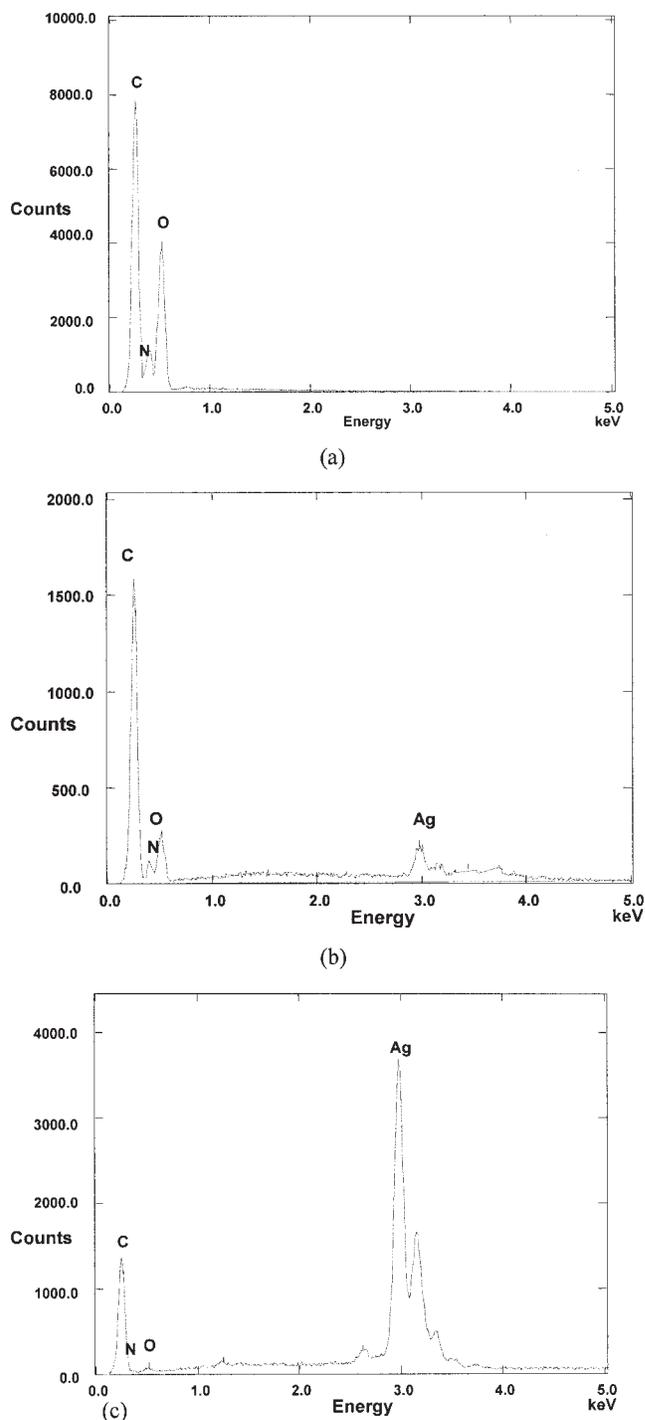
Figure 5 EDX spectra of PA nanofibers: (a) uncoated, (b) coated for 1 min, and (c) coated for 10 min.

shows the EDX spectra of the fibers before and after the sputter coating. It can be seen that the fiber dominantly consists of C, O, and N before the sputter coating, as illustrated in Figure 5(a). A significant amount of Ag on the fiber surface after coating compared with the original fiber can be seen in Figure 5(b). It can also be seen that the amount of C, O, and N becomes lower compared with that in Figure 5(a). This

TABLE I
Resistance Values

Materials	Resistance (Ω/cm)
Untreat fiber web	Out of range (over 10^4)
Treated for 1 min	2.5×10^2
Treated for 10 min	1.4×10^{-1}

is attributed to covering of the nanoclusters on the fiber surface. The higher amount of Ag on the fiber surface is detected as the coating time is increased to 10 min, as indicated in Figure 5(c).

Surface conductivity

Table I shows the results of the surface resistance measurements. The results indicate that the surface conductivity of the nanofibers is considerably altered by the silver sputter coating. The surface conductivity is very poor before the coating. The resistance is out of the range of the meter. A significant increase in conductivity is found on the fiber surface coated for 1 min. Further increase in conductivity can be achieved as the coating time is extended to 10 min. The increase in surface conductivity is attributed to the formation of the nanolayer of silver clusters, as shown in Figures 4(b) and 4(c).

CONCLUSIONS

Nanofibers have been increasingly used in a wide range of applications ranging from filtration to biomaterials. The functionalization of polymer nanofibers by depositing well-controlled structures on nanofibers would expand the applications of nanofibers, based on changes to both the physical and chemical properties of the nanofibers. This paper has reported the coating of functional silver structures on polymer nanofiber surface. It has been shown that the sputter coating can be used to modify the surfaces of polymer nanofibers. Sputter coating provides new approaches to the functionalization of polymer nanofibers at low temperature. The modification of polymer nanofiber surface has great potential for nanofibers in such applications as biomaterials, electronics, and medical devices.

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