Preparation and characterization of functionalized nanofibers by metallic sputter coatings

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Abstract

In this study, conductive metal films of copper (Cu) and silver (Ag) were deposited onto the polyamide 6 nanofiber nonwoven substrates at room temperature. Atomic force microscopy (AFM) and Scanning Electron Microscopy (ESEM) were employed to study the topography and chemical composition of the nanofibers, respectively. The AFM results indicate a significant change in the morphology of the fibers before and after the sputter coating of the metallic film. A full energy dispersive x-ray analysis (EDX) mounted on the SEM 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. The surface conductivity properties of the fibers were also investigated. The nanofiber nonwovens sputtered with metallic coating showed significant improvement in surface electrical properties.

Keywords: *Nanofibers; Surface; Magnetron sputtering; AFM; ESEM; EDX*

1. Introduction

Polymer Nanofibers are the ultra-fine fibers with very small diameters, ranging from few nanometers to over 100 nanometers. Due to their large surface area per unit mass and small pore size, polymer nanofibers posses many unique properties. Nanofibers have great potential for a wide range of application, such as composites, filtration, biomaterials and many other applications [1].

Among various processing techniques, electrospinning is widely used to produce polymer nanofibers [2]. Electrospinning is a process, by which polymer nanofibers are produced from polymer solution or polymer melt by the application of a strong electric field [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, electrical conductivity, optical property and biocompatibility. 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 fibers. In all of these, sputter coating [4] is one of the most promising techniques to make functional nanofibers. In this study, conductive metal films of copper (Cu) and silver (Ag) were deposited onto the polyamide 6 nanofiber nonwoven substrates at room temperature. Atomic force microscopy (AFM) and Environmental

Scanning Electron Microscopy (ESEM) were employed to study the topography and chemical composition of the nanofibers, respectively. The surface conductivity properties of the fibers were also investigated and compared with ordinary nonwoven materials.

2. Experimental

2.1 Materials

Polyamide 6 was obtained form BASF and used as received. The polymer solution concentration of 15wt.% was prepared by dissolving the polymer in formic acid. The solution was spun from a 50 ml syringe with a needle of 0.5mm diameter. Upon applying a high voltage (15 kV), a fluid jet was ejected from the capillary. As the jet accelerated towards a grounded collector, the solvent evaporated and charged polymer fibers were deposited on an aluminium foil. The nanofiber web was collected for 2 hours and dried in a vacuum oven at room temperature for 24 hours to remove the residual solvent.

2.2 Sputter coating

Sputtering coatings of copper and silver were performed in a magnetron sputter coating system supplied by Shenyang Juzhi Co, LTD. The metallic nanostructures of copper (Cu) and silver (Ag) were deposited, respectively, onto the surface of polyamide 6 nanofiber substrate at room temperature. Coating was performed at a pressure of 0.8 Pa with a power of 60 W. Coating thickness was made for 50nm and 100nm, respectively.

2.3 Scanning Probe Microscope

The scanning probe microscope used in this work was a CSPM4000 atomic force microscopy made by Benyuan Co, LTD. Scanning was carried out in lateral force mode atomic force microscopy and all samples were scanned at room temperature in atmosphere. The scanning size was 1000nm×1000nm, and the scanning frequency was set at 1.0Hz.

2.4 Energy dispersive x-ray analysis

The environmental scanning electron microscopy (ESEM) Philips XL30 integrated with a Phoenix energy-dispersive X-ray (EDX) detector was used to analyze the surface chemical structures [5]. In this study, the nonwoven surface was examined by the energy dispersive x-ray analysis at an accelerating voltage of 20 kV with accounting time of100 s.

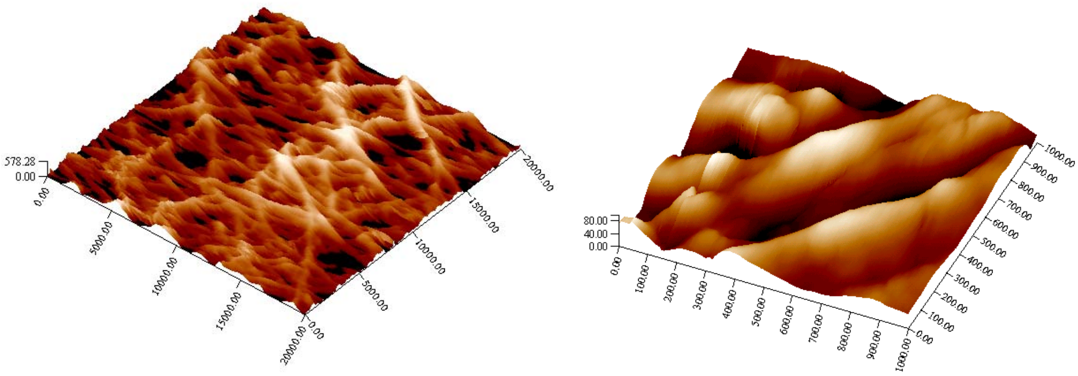
2.5 Electrical conductivity

The electrical resistivity was measured using a collinear four-probe array. The apparatus used was SX1934 made by Baishen Technologies. In order to minimize the deviations brought by the unevenness of textile surface, the resistivity of each sample was measured 3 times, and the average values were used.

3 Results and Discussion

3.1 SPM observation

The PA6 nanofibers show three-dimensional fibrous structure, consisting of fibers with diameters ranging from less than 200nm to over 600 nm as displayed in Fig.1a. The higher magnification of the AFM image reveals the details of the fiber surface, as shown in Fig.1b. It can be seen that the fiber surface is relatively smooth.

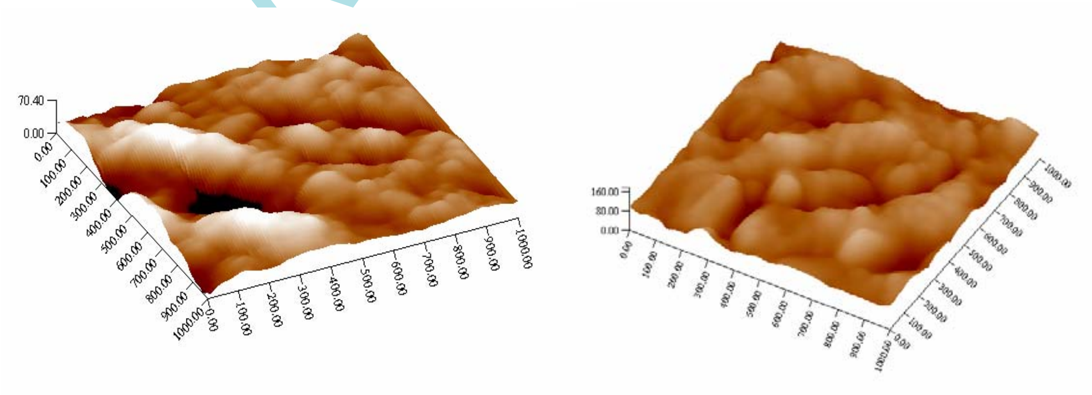


(a) (b)

Fig. 1 AFM images of PA6 nanofibers: (a) scan size 20000nmx20000nm; (b) scan size 1000nmx1000nm

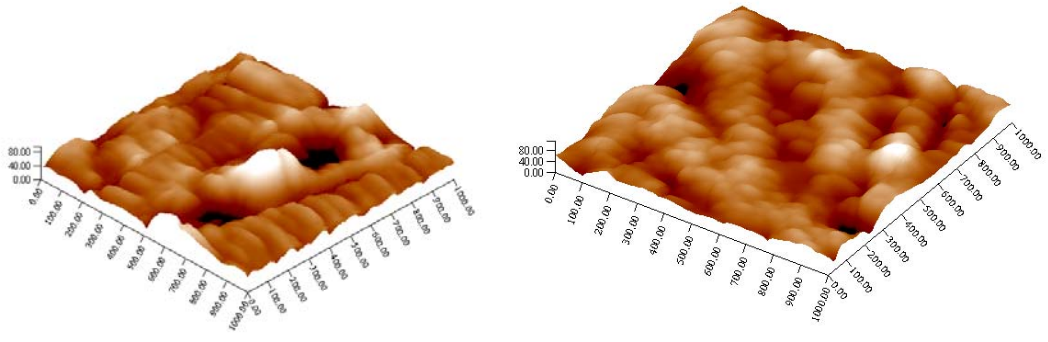
The metallic sputter coating significantly alters the surface characteristics of the PA6 nanofibers as illustrated in Fig.2 and Fig.3. The AFM image of 1000nm×1000nm scan clear shows surface feature of the nanofibers sputted with Cu and Ag. The Cu clusters scatter on the PA6 nanofiber surface after the 50nm coating, but the clusters have variable sizes, as illustrated in Fig.2a. The average size of the sputtered Cu cluster is about 20.5nm. As the coating thickness is increased to 100nm, the Cu clusters not only cover the nanofiber surface, but also fill the pores of fibrous web, as shown in Fig.2b. The growth of the Cu clusters is also observed and the size of the sputtered Cu cluster is further increased. This is attributed to the collision of the sputtered Cu grains. The increase in sputter coating time leads to the growth of the Cu clusters and more compact deposition.

The similar phenomenon is also observed on the nanofibers coated with silver, as displayed in Fig.3. The Ag clusters grow and cover the pores of the web as the coating thickness is increase to 100nm. The increase in sputter coating time also leads to the growth of the Ag clusters and more compact deposition on the nanofiber surface.



(a) (b)

Fig. 2 Surface morphology of the Cu sputter coated nanofiber: (a) 50nm coating; (b) 100nm coating.



(a) (b)

Fig. 3 Surface morphology of theAg sputter coated nanofiber: (a) 50nm coating; (b) 100nm coating.

3.2 EDX analysis

The metallic funtionalization of the nanofibers is also confirmed by EDX analyses, as shown in Fig.4.

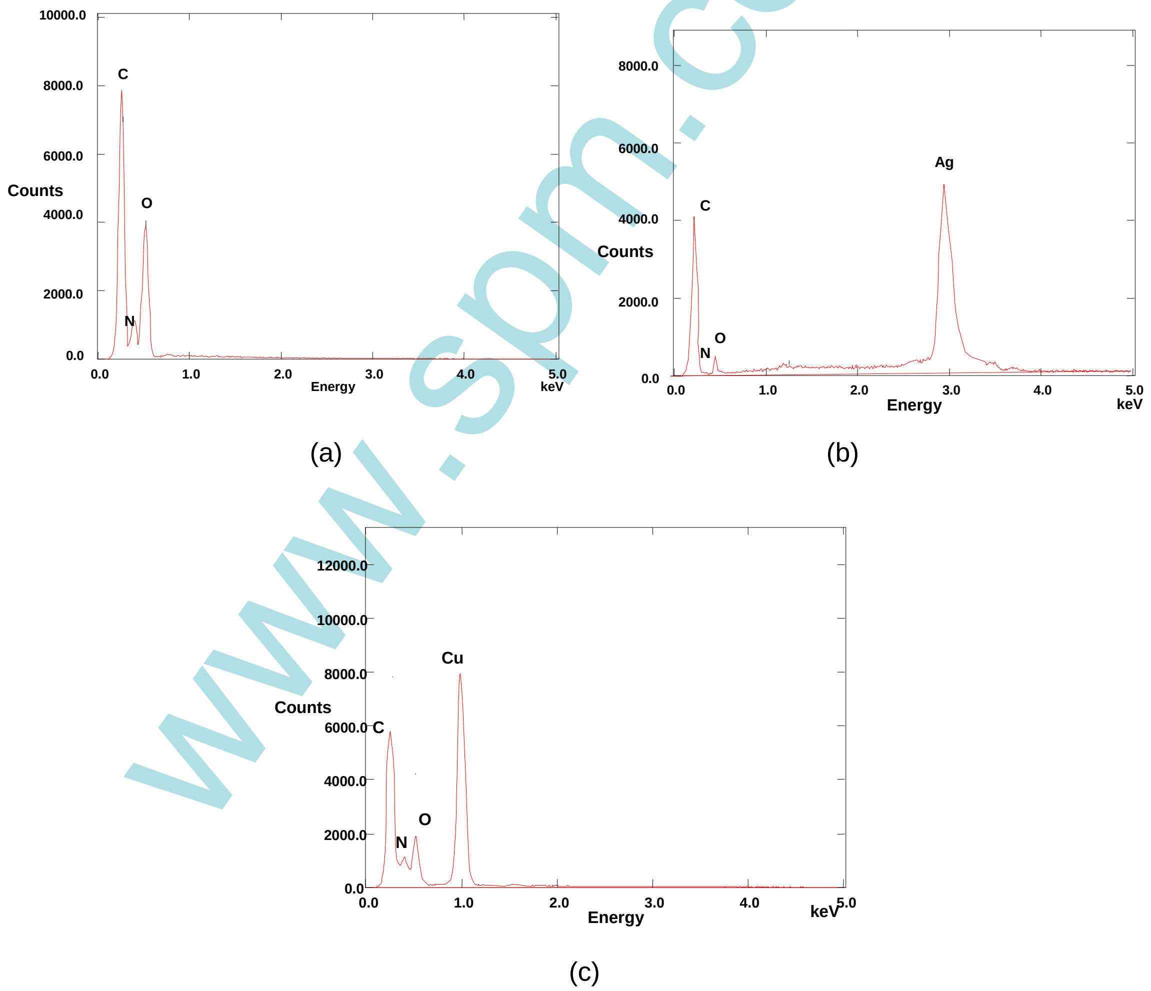


Fig. 4 EDX spectra of the nanofibers before and after sputter coating: (a) PA6 nanofibers; (b) Cu coated; (c) Ag coated

It can be seen from Fig. 4a that the surface of the nanofibers dominantly consists of C, O and N before the sputter coating. The composition of hydrogen (H) in the material is too light to be detected in the EDX analysis. The EDX spectra reveal that Cu and Ag peaks are clearly detected, as shown in Fig. 4b and Fig. 4c. A significant amount of Cu and Ag on the nanofiber surface after copper sputter coating appears in the spectra, but the amount of C, O and N is reduced in the EDX spectra at the same time, indicating the coverage of the surface by metallic coating.

3.3 Electrical property

The nanofibers have a very high surface resistance, which is over 104 Ωcm, indicating the electrical insulation property. The metallic sputter coating, however, significantly improve the electrical properties of the nanofibers. The surface resistivity drops to about 0.45Ωcm for Cu coating and 0.14Ωcm for Ag coating, as the coating has a thickness of 50nm. The surface resistivity of the nanofibers is further reduced to about 0.08 Ωcm for Cu coating and 0.03Ωcm for Ag coating , as the coating thickness is increased to 100nm, indicating better surface conductivity. The increase of the coating thickness leads to the formation of compact and improved coverage of the metallic clusters on the nanofibers, resulting in better conductivity. The results also clearly reveal the better surface conductivity of the nanofibers coated with silver than those coated with Cu in the same coating thickness.

4 . Conclusions

This study has revealed that metallic sputter coating could significantly improve the surface electrical properties of polymer nanofibers. The conductive nanofibers offer great potential for such applications as electromagnetic shielding, anti-static cloth, anti-explosion filters and sensors.

Acknowledgement

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References

[1] J. Doshi, D.H. Reneker. J. Electrostat. 35, 151(1995).
[2] D.H. Reneker, I. Chu. Nanotechnology, 7, 216(1996).
[3] W.J.Li, C.T. Laurencin, E.J. Caterson, R.S. Tuan, F.K. Ko. .J. Biomed. Mater. Res. 60, 613(2002).
[4] K. Wasa, S. Hayakawa. Handbook of Sputter Deposition Technology, Noyes Publications, Park Ridge, NJ, 1992.
[5] Q.F. Wei, X.Q. Wang, R.R. Mather, A.F. Fotheringham. Appl. Surf. Sci. 220, 217(2003).