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BRIEF COMMUNICATION

Surface functionalization of polymer nanofibers by ITO sputter coating

Qufu Wei, Huifeng Wang, Yang Xu, Bingyao Deng

Abstract In this study, transparent conductive films of tin-doped indium oxide (ITO) were deposited onto the polyamide 6 (PA6) nanofiber substrates at room temperature. Atomic force microscopy (AFM) was employed to study the morphology of the nanofibers, respectively. The AFM results indicated a significant change in the morphology of the nanofibers before and after the ITO sputter coatings. The light transmittance and surface conductivity of the ITO-deposited nanofibers were also investigated. It was found that the surface resistivity of the PA6 nanofiber with the ITO deposition had a significant drop and the ITO deposition obviously affected the light transmittance of the PA6 nanofibers.

Keywords Nanofibers, Tin-doped indium oxide, Surface, Sputtering

Introduction

Polymer nanofibers are the fibers with very small fiber diameters less than 1000 nm. Polymer nanofibers posses many unique properties since these fibers have very large surface area per unit mass and small pore size. Nanofibers with special structures and properties have great potential for a wide range of application in many industries.[1]

Nanofibers have been produced by various techniques.[2–4] Among all these techniques, electrospinning has been widely used to produce polymer nanofibers. Electrospinning is the technique which uses a strong electric field to produce polymer nanofibers from polymer solution or polymer melt. If electrostatic forces overcome the surface tension of a polymer solution, a charged jet is ejected and moves toward a grounded electrode. The electrospun nanofibers can be collected on a substrate located on the counter electrode.[5]

Polymer nanofibers with specific surface properties are of interest in many technical applications as the surface features affect adhesion, adsorption, electrical conductivity, optical property, and biocompatibility. Modification of polymer nanofibers improves the surface properties of these materials in order to meet some special applications.[6] In this study, transparent conductive films of tin-doped indium oxide (ITO) were deposited onto the polyamide nanofiber substrates by sputter coating at room temperature. Sputter coating has been considered an environmentally friendly technology since it is performed in dry state without any chemical solution. ITO nanomaterials have great potential in solar cell, light emitting diodes, electromagnetic shielding, and anti-ultraviolet applications.[7]

The morphology of the nanofibers was examined by atomic force microscopy (AFM). The optical and electrical properties of the ITO-deposited nanofiber materials were also studied.

Experimental

Preparation of nanofibers

The polyamide 6 (PA6) nanofibers were prepared by electrospinning. PA6 (characteristic viscosity 2.8) and 88% formic acid were all used as-received. The PA6 solution with a concentration of 18 wt% was prepared by dissolving PA6 in formic acid. The laboratory electrospinning apparatus consisted of a syringe, a needle, and a high-voltage power supply in which a positive voltage was applied to the polymer solution through the needle attached to the syringe, as

Q. Wei (✉), H. Wang, Y. Xu, B. Deng
Key Laboratory of Eco-Textiles, Ministry of Education, Jiangnan University, Wuxi 214122, P.R. China
e-mail: qfwei@jiangnan.edu.cn

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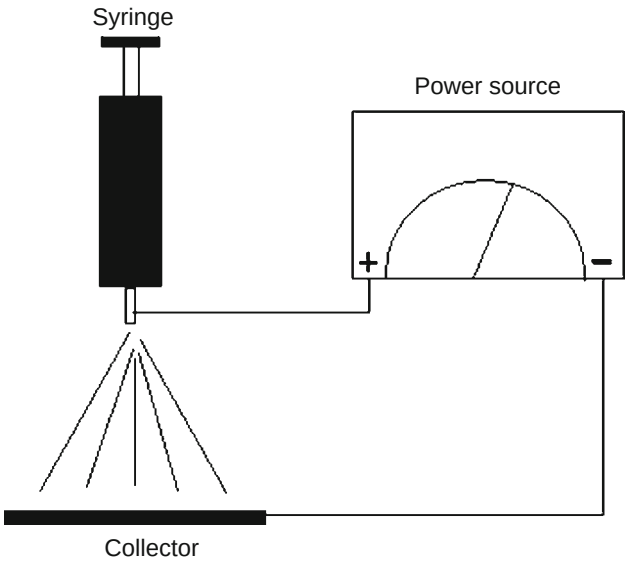

Fig. 1: Schematic view of electrospinning apparatus

presented in Fig. 1. The solution jet was formed by electrical force, when the electrical potential increased to 16 kV. The nanofibers in a non-woven form were collected on an aluminum foil. The ejection rate of the solution was 0.2 mL/h, and the distance between the tip and the collector was 12 cm. The fiber web was formed by collection of fibers for 6 h.

ITO deposition

ITO deposition was performed on a magnetron sputter coating system JZCK-420B (Juzhi Co., Ltd., China). The nanofiber samples were placed on the sample hold in the sputtering chamber and one side of the sample faced the sputtering target. The chamber was pumped to a base pressure of 3×10^{-3} Pa before the introduction of the sputtering gas. The ITO target used was a ceramic target of 2 in. with a composition of 97 wt% In_2O_3 and 3 wt% SnO_2. Pure Ar (99.999%) was used as sputtering gas. All samples were processed under a pressure of 0.5 Pa, at room temperature, with an argon flow rate of 20 sccm and the sputtering power of 100 W.

The thickness of the deposition layer was measured using the coating thickness detector of FTM-V (Tairao Co., Shanghai, China) fixed in the sputtering chamber. The sample holder with a rotation speed of 100 rpm was introduced in order to improve the uniformity of ITO film deposited on the nanofibers. The ITO films were deposited at 50, 100, and 150 nm, respectively.

Surface characterization

The fibrous structure of the PA6 nanofibers was observed by SEM. The SEM used was HITACHI S-4800. The surface morphology of the PA6 nanofibers was examined by AFM. The AFM used in this study was a CSPM4000 (Benyuan, China). Scanning was carried out in contact mode AFM and all samples were scanned at room temperature in atmosphere.

Optical and electrical properties

The optical properties of the PA6 nanofiber samples deposited with ITO thin films were analyzed by ultraviolet and visible light spectrophotometer (UV–Vis). The UV–Vis spectroscopy used was a Perkin-Elmer Lambda 900. Its scanning accuracy is 0.2 nm and the UV–Vis spectra were obtained by scanning the transmittance of the PA6 nanofiber samples in the wavelength ranging from 300 to 600 nm.

The resistivity was measured by the four-point probe method (Baishen Technology, China). It is suited to measure resistance, electrical resistivity, and square resistance. These four probes with Φ0.5 mm were all made by Tungsten Carbide and the distance between each two probes was 1 mm. All samples were tested for 20 times on the same direction and then the average values were obtained.

Results and discussion

Surface structures

The PA6 nanofibers show three-dimensional fibrous structure, consisting of fibers with diameters ranging from <100 to >400 nm as displayed in Fig. 2a. The surface morphology is not clear in the SEM image, but the higher magnification of the AFM image reveals the details of the electrospun PA6 nanofiber surface, as shown in Fig. 2b. It can be seen that the surface of the electrospun PA6 nanofiber looks relatively smooth before the ITO deposition.

The deposition of ITO films significantly alters the surface characteristics of the PA6 nanofibers as illustrated in Fig. 3. The AFM image of 1000 nm × 1000 nm scan clearly shows surface feature of the PA6 nanofibers sputtered with ITO films. The ITO clusters grow on the PA6 nanofiber surface as the ITO deposition is 50 nm. Figure 3a shows that the ITO clusters deposited on the PA6 nanofibers have variable sizes ranging from about 20 to 50 nm. The larger clusters are formed by the aggregation of the smaller particles.[8] As the deposition thickness is increased to 100 nm, the ITO clusters not only cover the PA6 nanofiber surface, but also fill the pores of fibrous web, as shown in Fig. 3b. It is also observed that the ITO clusters deposited on the PA6 nanofibers become evener. The growth of the ITO clusters is also obvious, as indicated in Fig. 3b. This is attributed to the collision of the sputtered ITO particle during the deposition process. The increase in deposition thickness

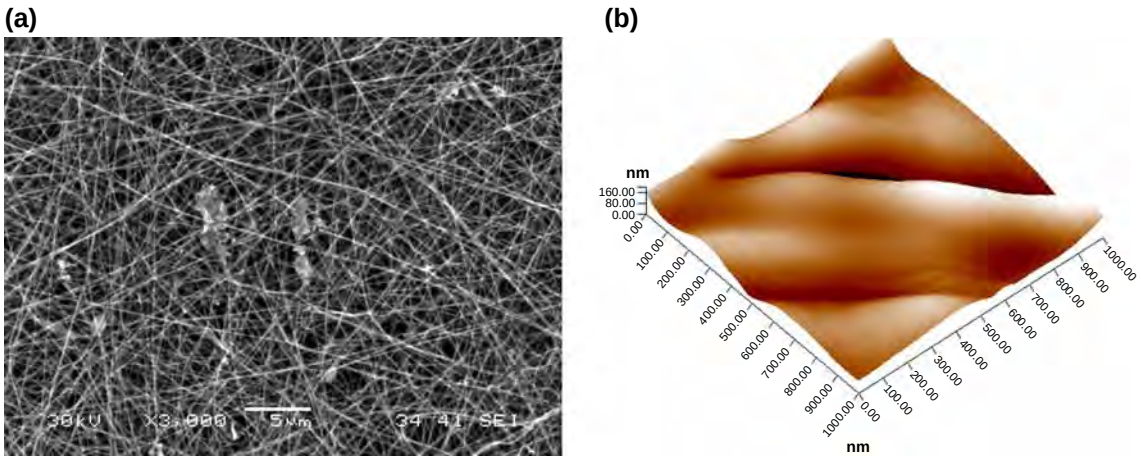

Fig. 2: Images of PA6 nanofibers by (a) SEM; (b) AFM

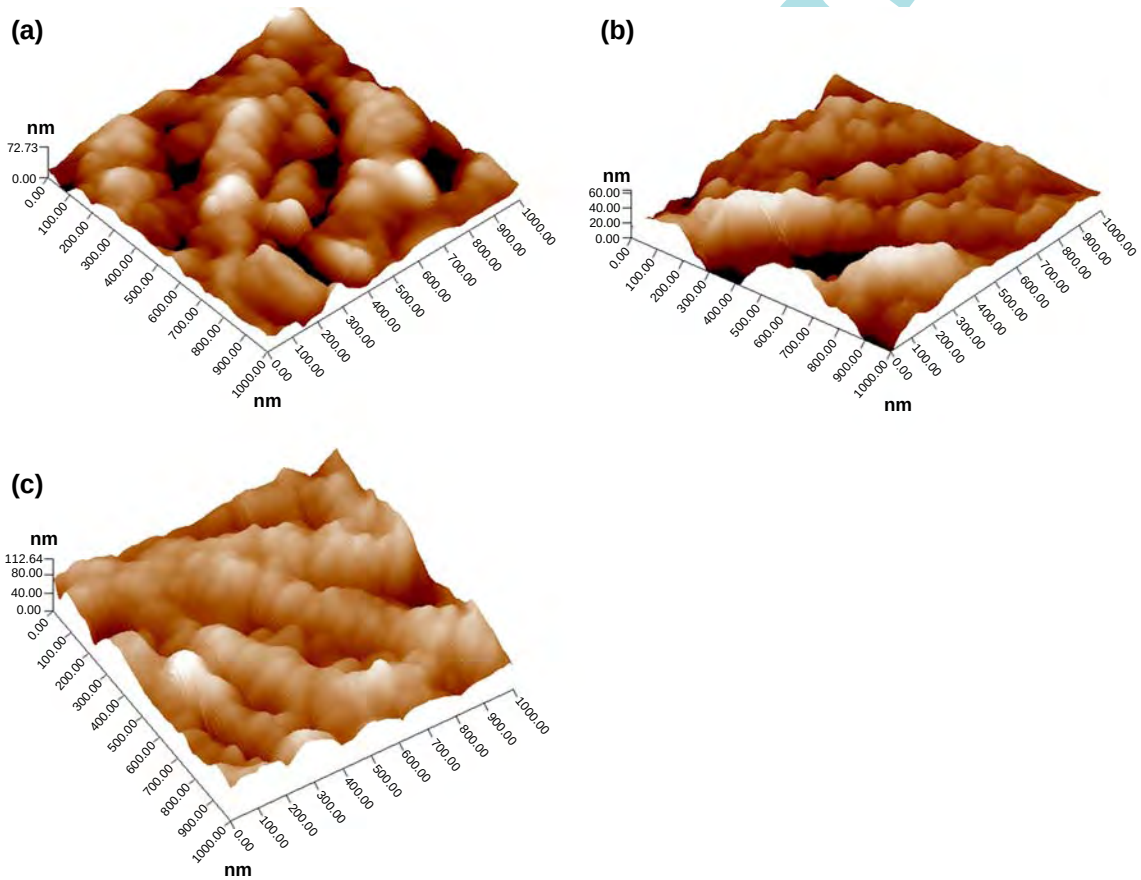

Fig. 3: Surface morphology of the PA6 nanofiber deposited with ITO: (a) 50 nm; (b) 100 nm; (c) 150 nm

leads to the growth of the ITO clusters formed on the PA6 nanofibers and more compact deposition, as revealed in Fig. 3c. Figure 3c indicates that the ITO clusters are deposited on the PA6 nanofibers and the pores among the nanofibers. The growth of the deposited ITO cluster is also observed, as illustrated in Fig. 3c.

Optical properties

The optical properties of the PA6 nanofibers before and after the ITO deposition were examined by the transmittance of the UV–Vis light through the material. Figure 4 shows the transmittance of the PA6 nanofibers with and without ITO deposition. The PA6

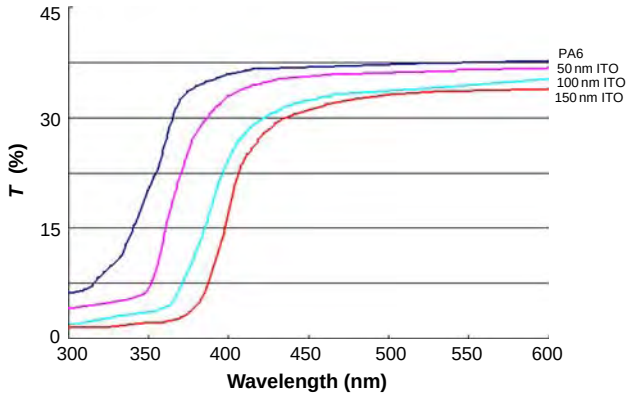

Fig. 4: Transmittance of the PA6 nanofibers

nanofiber web without ITO deposition shows the transmittance of about 35% in the wavelength range between 400 and 600 nm, indicating a good transmittance of visible light. The transmittance drops gradually from 35% to less than 10% in the wavelength range between 400 and 300 nm, indicating the UV shielding effect of the PA6 nanofiber web, as revealed in Fig. 4. It can also be observed from the UV–Vis spectra in Fig. 4 that the ITO deposition obviously affects the light transmittance of the PA6 nanofibers. The ITO-deposited PA6 nanofibers have the transmittance slightly lower than that of uncoated PA6 nanofiber over the wavelength range between 450 and 600 nm, revealing the transparent property of the ITO depositions in visible light range. The transmittance of ultra-violet (UV) from 300 to 400 nm by the ITO depositions is obviously observed in Fig. 4. It is also found that the thickness of the ITO deposition has certain effect on the transmittance of UV light through the samples. The UV shielding effect of the ITO deposition is attributed to its chemical structure of ITO.[9]

Electrical property

The PA 6 nanofibers have a very high surface resistivity, which is over 10^6 Ω cm, indicating the electrical insulation property. The ITO deposition, however, significantly improves the electrical properties of the PA6 nanofibers. The surface resistivity of the PA6 nanofiber with 50 nm ITO deposition shows a significant drop from over 10^6 Ω cm to about 1.25×10^3 Ω cm. The surface resistivity of the PA6 nanofibers is further reduced to about 0.58×10^3 Ω cm, as the ITO deposition thickness is increased to 100 nm, indicating better surface conductivity. The increase in the ITO thickness leads to the formation of compact and improved coverage of the ITO clusters on the nanofibers, resulting in better conductivity. The further increase in ITO thickness up to 150 nm leads to the decrease in resistivity down to about 0.12×10^3 Ω cm.

Conclusions

The PA6 nanofibers prepared by electrospinning were functionalized by the surface deposition of ITO film using sputter coating technology. The ITO deposition significantly altered the surface structures and the properties of the PA6 nanofibers. ITO deposition formed a nanofilm on the PA6 nanofibers, leading to the improvement in surface conductivity of the UV shielding. The functional nanofibers have great potential in many industrial applications.

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