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BRIEF COMMUNICATION

Functionalization of polyamide 6 nanofibers by electroless deposition of copper

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Abstract Polyamide 6 (PA6) nanofibers were prepared via electrospinning. The electrospun PA6 nanofibers were functionalized using electroless deposition technique. Oxygen low temperature plasma treatment was applied to substitute the conventional roughening process using concentrated sulfuric acid-potassium dichromate. The deposition of copper (Cu) on the PA6 nanofibers was characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectroscopy (EDX). The observations revealed the uniform coating of the PA6 nanofibers with thin films of Cu. It was also found that the surface conductivity of the PA6 nanofibers was significantly improved by the Cu deposition. The combination of electrospinning and electroless deposition will provide a new approach to producing the functional nanofibers for various applications.

Keywords Polyamide 6 (PA6), Plasma treatment, Electroless deposition, AFM, Conductivity

Introduction

Polymer nanofibers have been increasingly used in various areas due to their large surface area per unit mass and small pore sizes.[1] Polymer nanofibers are often obtained by electrospinning technique, in which a strong electric field is applied to a polymer solution or polymer melts to overcome the surface tension of a polymer solution.[2]

For a variety of applications it is desirable to make such nanofibers with well-defined surface properties. Nanofibers with specific surface properties are of interest in many technical applications as the surface features affect electrical conductivity, optical property, and biocompatibility. Various techniques have been tried to modify the surface properties of polymer nanofibers, including electroless deposition.[3,4] Electroless deposition has the advantages of uniform coating and there is no current, ultra high vacuum, or high temperatures required in the process.[5]

In this work, polyamide 6 (PA6) nanofibers prepared by electrospinning were used as substrates to form functional nanofibers by electroless deposition of copper. Oxygen nonthermal plasma treatment was applied for the pretreatment of the PA6 nanofibers to replace the etching process using chemical solutions. Plasma treatment has been recognized as an efficient, environmentally friendly method of surface modification. It is produced under vacuum conditions using low power radio-frequent or microwave or direct-current sources. The interactions of the plasma particles on the materials produce modifications of their surfaces in order to add different functional properties with respect to the bulk material.[6]

The deposition of copper on the PA6 nanofibers was characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectroscopy (EDX). The surface conductivity of the PA6 nanofibers was examined using surface resistance measurement.

Experimental

Electrospinning

A polymer solution with 15 wt% of PA6 chips in formic acid was prepared by magnetic stirring for 3 h. A hypodermic needle (type 18G—1.2 mm × 38 mm) containing about 15 mL of the polymer solution was

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used for electrospinning. The electrospinning device consisted of a microinfusion pump (Medical Instrument Co., Zhejiang, China), a high-voltage power supply (Dongwen Co., Tianjing, China), and an aluminum foil as the collector. The flow rate of the solution was set at 1.0 mL/h, and the distance between the tip and the collector was 10.0 cm. A high voltage of 14 kV was applied for electrospinning.

The electrospun PA6 nanofibers were placed in open air for a period of more than 24 h and then in the oven at 55°C for 6 h to remove the residual solvent.

Low temperature plasma treatment

In this process, the electrospun PA6 nanofibers were pretreated by oxygen low temperature plasma instead of being dipped in the conventional concentrated sulfuric acid-potassium dichromate for surface roughening. The plasma treatment was performed in HD-1A low temperature plasma equipment. The treatment parameters are listed in Table 1.

Table 1: Treatment parameters

Gas	Pressure (Pa)	Power (W)	Time (s)
Oxygen	30	45	90

Table 2: Chemical solutions used for pretreatment

Chemical	Formula	Concentration
Sensitization solution		
Stannous chloride	$SnCl_2$	12 g/L
Hydrogen chloride	HCl	40 mL/L
Granulated tin	Sn	2
Activation solution		
Silver nitrate	$AgNO_3$	2 g/L
Ammonia water	$NH_3 \cdot H_2O$	
Reduction		
Formaldehyde:water	$HCHO:H_2O$	1:9

Electroless copper deposition

Tables 2 and 3 give the details of the solutions for pretreatment and electroless deposition of copper.[7] Prior to copper deposition, the nanofibers were pretreated by dipping in the sensitization solution for about 5 min in order to activate the fiber surfaces. A thin metal layer with catalyst was replaced on the surface of the nanofibers, which was the ''catalytic center'' of Cu coating. All pretreatments were performed at room temperature. For deposition of the metal, the pretreated nanofibers were then immersed into the electroless deposition solution maintained at 38°C for approximately 90 min. Care was taken to dip-wash the nanofiber substrates in deionized water prior to each entry into the various solutions mentioned above.

Surface morphology and component analysis

The surface morphology of the nanofibers was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM used in this work was Hitachi S4800 (Japan) and the AFM was CSPM4000 (Benyuan, China). The AFM scanning was carried out in contacting-mode and all specimens were scanned at ambient conditions.

The composition analysis was performed on the Hitachi S4800 energy dispersive X-ray spectroscopy (EDX).

Effect of plasma treatment on the water adsorption

The effect of the plasma treatment was characterized by water adsorption. Each sample of the nanofiber was cut into the size of 1 cm × 4 cm. The specimens were placed on a CDCA-100F adsorption apparatus (Camtel, UK). When the specimen was immersed into water at room temperature, the water adsorption was detected and recorded. The water adsorption was plotted as a function of time.

Table 3: Chemicals used for electroless deposition

	Chemical formula		Concentration
Solution A	Potassium sodium tartrate	$C_4H_4KNaO_3 \cdot 4H_2O$	15 g/L
	Sodium hydrate	NaOH	10 g/L
	Sodium carbonate	Na_2CO_3	4 g/L
	Potassium ferrocyanide	$K_4Fe[CN]_6 \cdot 3H_2O$	0.1 g/L
	2,2′-Bipyridyl	$C_{10}H_8N_2$	20 mg/L
	Disodium ethylene diamine tetraacetate	$Na_2H_2EDTA \cdot 2H_2O$	15 g/L
Solution B	Copper sulfate	$CuSO_4$	25 g/L
	Nickel chloride	$NiCl_2$	4 g/L
	Formaldehyde	HCHO	30 mL/L

Surface resistance

The surface resistance of the nanofiber was measured by a four-point probe SX1934 (Baishen Technology, China). The four probes with ∅0.5 mm are all made of tungsten carbide, and the distance between two probes is 1 mm. Samples were all tested 10 times in the same direction, and then the average values were obtained.

Results and discussion

Surface morphology

The SEM images in Fig. 1 show structures and surface morphology of the electrospun PA6 nanofibers without and with Cu coating. The images clearly reveal the three-dimensional fibrous structures of the PA6 nanofibers. The nanofibers are randomly oriented. The nanofibers have diameters ranging from less than 100 nm to over 300 nm, as presented in Fig. 1a. The nanofibers maintain their porous structures, but the diameters of the nanofibers are obviously increased after the Cu deposition, as shown in Fig. 1b. The nanofibers coated with Cu have diameters ranging from 300 nm to 600 nm. The coating looks quite uniform on the nanofibers and the Cu particles are clearly recognized, as revealed in Fig. 1b.

The AFM observations further verify the surface morphology of Cu-coated nanofibers, as shown in Fig. 2. The images clearly show the nanostructures of the deposited clusters of copper formed on the nanofiber surfaces. The sizes of the clusters vary from about

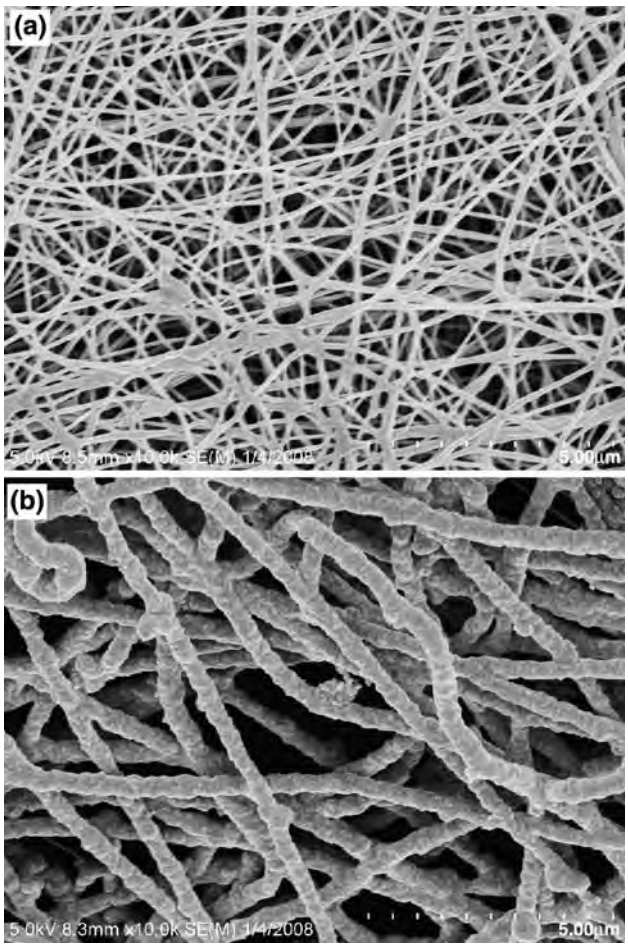

Fig. 1: SEM images of the electrospun PA6 fibers before and after Cu deposition: (a) as-spun and (b) after Cu deposition

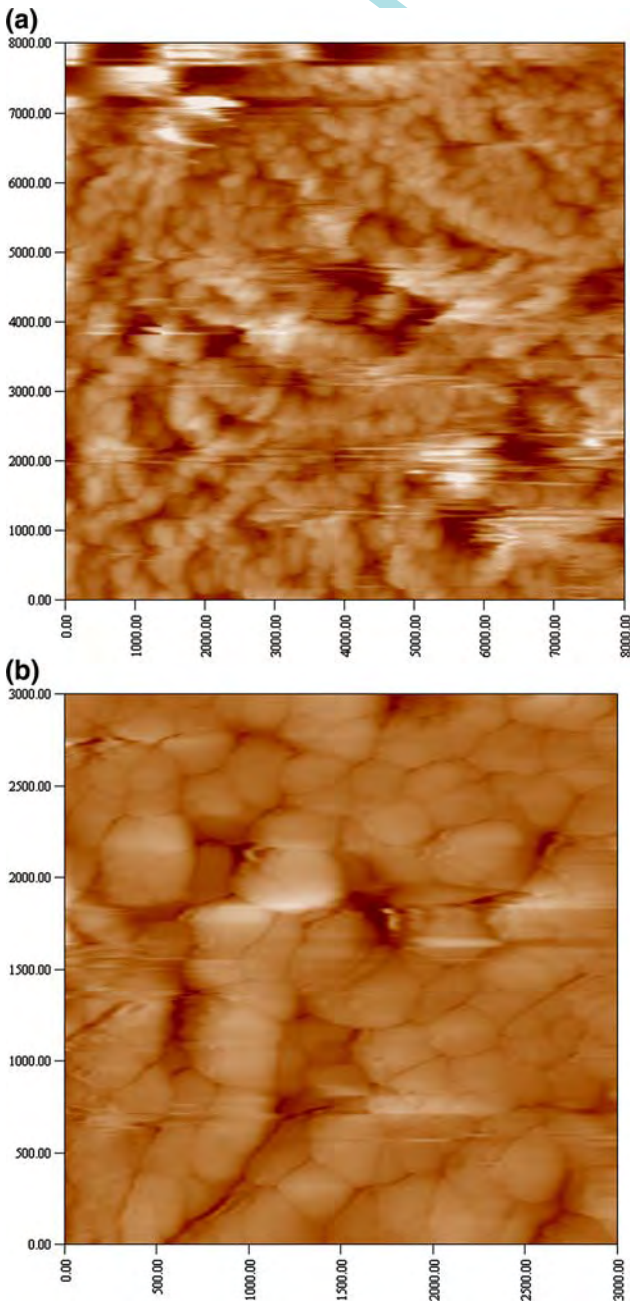

Fig. 2: AFM images of Cu deposition on the nanofibers: (a) 8 μm × 8 μm scan and (b) 3 μm × 3 μm scan

100 nm to over 300 nm as revealed by the AFM analysis. At a low magnification, it can be seen that the Cu clusters are coated tightly over the fiber surfaces in the image of 8 μm × 8 μm scan, as illustrated in Fig. 2a. These coated clusters will further increase the surface area of the nanofibers. The image of 3 μm × 3 μm scan in Fig. 2b shows that the nanoclusters on the nanofiber surface have dense structures.

EDX analysis

The results of EDX analysis are presented in Fig. 3. The EDX spectrum in Fig. 3a clearly shows the main compositions of carbon and oxygen on the nanofiber. It is obvious that the element of copper appears in the EDX spectrum after Cu coating, as shown in Fig. 3b. It is also observed that the content of copper reaches up to 76.96% and the content of carbon and oxygen drops significantly after the Cu deposition. This is attributed to the coverage of the nanofibers by the copper layer on the fiber surface.

Water adsorption

The results of water adsorption before and after pretreatment by oxygen low temperature plasma are presented in Fig. 4. It clearly shows that the plasma treatment significantly improves the water adsorption of the nanofibers. This can be attributed to the fact that the treatment has an effect of surface etching, which

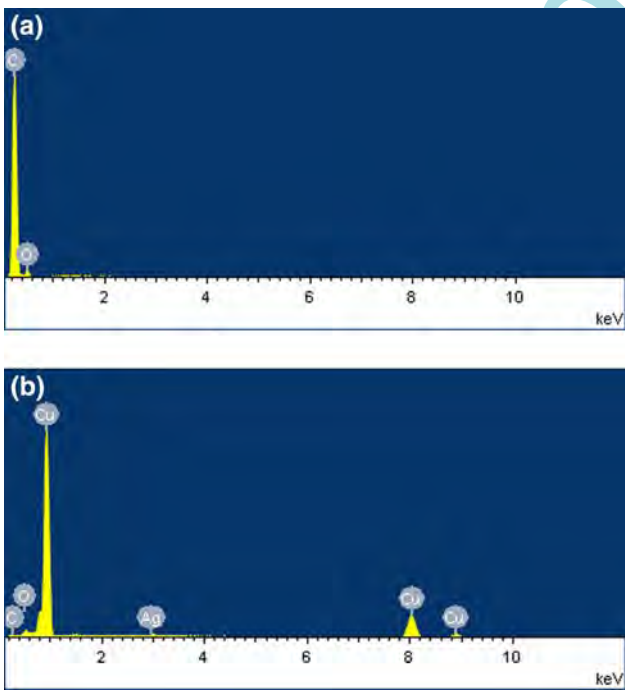

Fig. 3: EDX spectra of the electrospun PA6 fibers: (a) as-spun (b) after Cu deposition

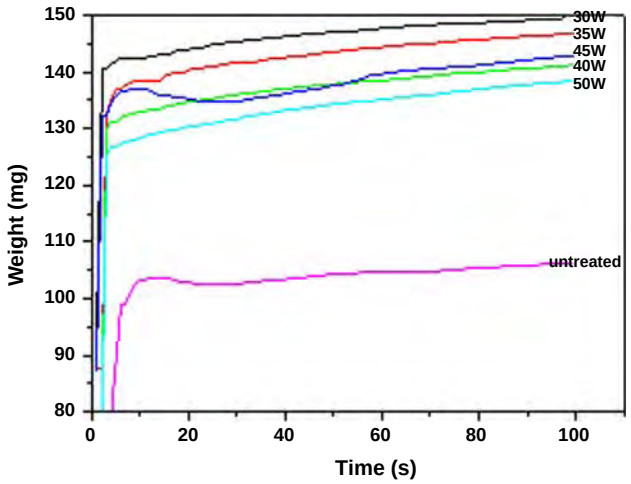

Fig. 4: Water adsorption

brings a microscopic roughness to the fiber surfaces.[8] At the same time, the molecules on the surface of the nanofibers are also excited or fractured to shorter bonds, and some functional groups such as carboxyl groups, carbonyl groups, and hydroxyl radicals may be introduced onto the nanofiber surface after the plasma treatment. Consequently, the surface of the nanofibers becomes more hydrophilic.[9]

The experimental results indicate that the plasma treatment presents more similar physical and chemical characteristics to the roughening effect using the conventional concentrated sulfuric acid-potassium dichromate solution.

Surface resistance

The ion source of Cu in electroless deposition is copper salt. If the concentration of Cu^{2+} is too high, the plating bath is not stable. The deposition rate becomes

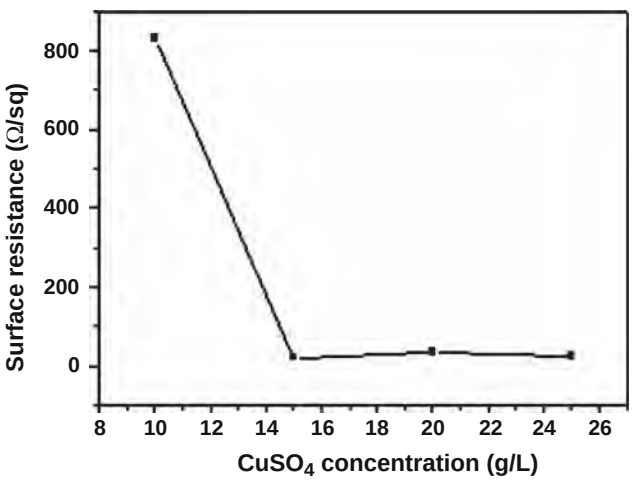

Fig. 5: $CuSO_4$ concentration on the surface resistance

slow if the concentration of Cu^{2+} is too low. The effect of $CuSO_4$ concentration on the surface resistance of Cu-coated nanofibers is shown in Fig. 5. The surface resistance decreases from 831.35 ohm/sq to 24.41 ohm/sq as the concentration of $CuSO_4$ changes from 10 g/L to 25 g/L. This is attributed to the increase in thickness with the increase of the $CuSO_4$ concentration in the deposition process.

Conclusion

It has been shown that electroless deposition of Cu on electrospun PA6 fibers covered individual fibers uniformly with the metal Cu. The metal deposition significantly changed the surface morphology and surface conductivity. It has been revealed that the high surface area of the fibrous structure was retained since the coating was formed on individual fibers.

The electrospun PA6 fibers coated with metals have potential uses as antistatic filters, electromagnetic radiation shielding, and other applications.

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