

Electroless deposition of nickel on electrospun fibers of 2-acrylamido-2-methyl-1-propanesulfonic acid doped polyaniline

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Abstract

Micron size diameter fibers of 2-acrylamido-2-methyl-1-propanesulfonic acid doped polyaniline were prepared via electrospinning. The conductivity of individual fibers was found to be lower than that of a cast film of the same polymer. Using the electroless deposition technique, the fibers were coated with thin films of nickel. The metal coated the fibers uniformly, as was evident from SEM spectroscopy without any lateral overlap, leading to a decrease in its resistance by three orders of magnitude while retaining the large surface area that is inherent to small diameter fibers. In this work, we combine the electrospinning and electroless deposition techniques to prepare, in a matter of minutes, metal-coated fibrous polymer substrates with large surface area.

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1. Introduction

Electrospinning is a simple method used in the preparation of polymer fibers. While the variation in the fiber diameter is large, nevertheless, the fibers prepared via this method typically have diameters much smaller than is possible to attain using standard mechanical fiber-spinning technologies. Although discovered in the 1930s [1], electrospinning is increasingly becoming very popular in the preparation of polymer fibers either in the form of individual fibers or non-woven fiber mats. Using this technique, it is now possible to spin polymer fibers (both conducting and non-conducting) under ambient conditions with diameters ranging from several micrometers to a few nanometers [2–9]. While the conductivity of electrospun non-conducting and conducting polymer fibers is less than that of conventional metals, one can overcome this drawback by depositing metals on individual fibers using the electroless deposition technique [10–13]. The advantage of this technique is that it is non-destructive and one can have the fibers uniformly coated with metals to yield highly conducting substrates. Unlike conventional metal evaporation, electroless deposition cov-

ers the entire fiber with the metal, not just that portion of the fiber in the direct line of sight path from an evaporation source. In addition, no current, ultra high vacuum, or high temperatures are needed in the electroless deposition procedure, which is much simpler and faster. The main purpose of this endeavor was to prepare highly conducting high surface area substrates that could be used, for example, in catalytic reactions.

The insulating emeraldine base form of polyaniline was doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) and dissolved in dichloroacetic acid (DCA) in order to prepare the spin dope necessary for fiber preparation. Although the conductivity of the as-prepared fibers did not show similar behavior when compared with cast films of the same polymer, the fibers surprisingly could be coated rather easily with nickel without any lateral overlap, thereby yielding high surface area metallic substrates. The ability to tune the conductivity of polyaniline from the insulating to the metallic regime [14] leads to the possibility of having rectifying Schottky contacts at the metal–polymer interface. Additionally, it is also possible to dissolve the host polyaniline fiber to give a simple method of preparing metallic nanotubes. This paper presents the combination of electrospinning and electroless deposition as an easy method of preparing high surface area conducting substrates.

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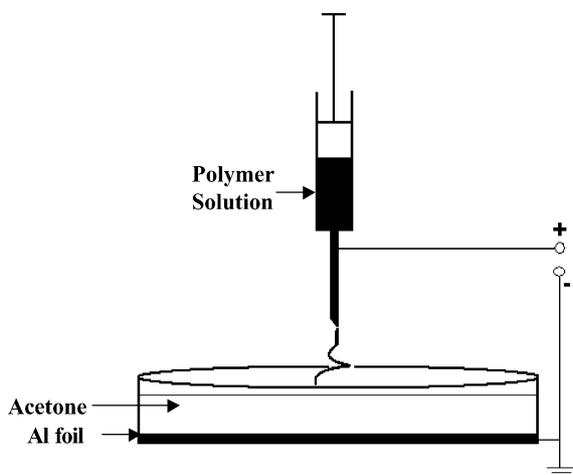


Fig. 1. Electrospinning apparatus used for spinning fibers of AMPSA-doped polyaniline from dichloroacetic acid. The applied potential was 28 kV and the distance between the tip of the hypodermic needle and the acetone bath was 3 cm. A slight pressure was applied to the piston to maintain a slow flow of the polymer solution through the needle.

2. Experimental

2.1. Chemicals

High molecular weight emeraldine base polyaniline (EB) was purchased from Santa Fe Science and Technologies. AMPSA and DCA were purchased from Aldrich. All chemicals were used as received.

2.2. Preparation of the spin dope

EB (0.38 g) was mixed with AMPSA (0.52 g) and ground together using a mortar and pestle in air for about 20 min. In a 10 ml glass vial, 0.56 g of this grey, powdered mixture was added to about 3.0 ml of DCA and stirred manually with a glass rod for approximately 15 min to form a viscous, deep green color spin dope used in the preparation of fibers. The acid chosen dopes the insulating emeraldine base to the conducting salt form of polyaniline and also has the solvating group necessary to dissolve it in DCA for post-processing of the polymer in the conducting form [15–17].

2.3. Fiber preparation

Fig. 1 shows the experimental setup for the preparation of AMPSA-doped polyaniline fibers. The apparatus consists of a high voltage low current transformer, a B-D 27G1/2 hypodermic needle, and an aluminum (Al) foil that served as a cathode. The fibers were collected in a glass Petri dish containing acetone. In the experimental setup the hypodermic needle filled with the spin dope was placed vertically downward with the tip of the needle about 3 cm above the acetone surface. The Al foil was placed under the Petri dish containing the acetone and was connected to electrical ground. The positive end of the transformer was attached to the needle and the voltage raised to about 28 kV. Care must be taken to avoid sparking as the acetone could ignite. Upon application of slight pressure to the piston of the hypodermic needle, fibers of the polymer were seen to coagulate in the acetone. The fibers were then collected by inserting a small piece of an Al foil or a piece of oxidized silicon wafer into the acetone and lifting them up. They were then dried in an oven at 100 °C for 24 h to remove trace amounts of DCA before performing any experiments on them.

2.4. Electrical characterization

The uncoated single fiber used in the electrical characterization was captured directly on pre-patterned oxide-coated Si wafers with 10 μm lead separation. For the metal-coated fiber, a single fiber was carefully broken off the metal-coated fiber mat and two leads were connected at either end of the fiber with silver paint and connected to a Keithley Model 6517A electrometer for conductivity measurements. The diameter of the uncoated and metal-coated fibers were of the same order of magnitude. Free-standing films were also prepared by casting a few drops of the polymer solution on an oxidized Si wafer that was later placed in an oven at 100 °C overnight. Temperature dependence of the conductivity of both the film and the fiber was achieved using a Cryo Industries closed-cycle helium refrigerator.

Table 1

Chemicals used for the Ni bath and for the pretreatment of fibers

Chemical	Formula	Concentration
Ni bath solution		
Nickel sulfate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	29 g/l
Sodium hydrophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	17 g/l
Sodium succinate	$\text{NaO}_2\text{CCH}_2\text{CH}_2\text{COONa} \cdot 6\text{H}_2\text{O}$	15 g/l
Succinic acid	$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$	0.36 g/l
Pretreatment solutions		
Stannous chloride–HCl	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O} - \text{HCl}$	0.1 g/l – 0.1cc/l
Palladium chloride–HCl	$\text{PdCl}_2 - \text{HCl}$	0.1 g/l – 0.1cc/l

Deionized water was used to dissolve the chemicals listed above.

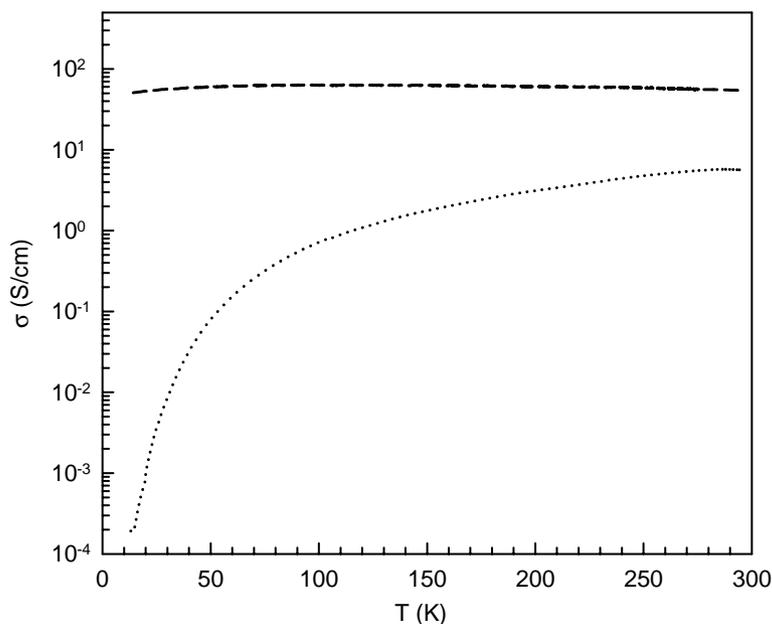


Fig. 2. Two-probe conductivity versus temperature measurements of AMPSA-doped polyaniline cast film (---) and electrospun single fiber (···).

2.5. Electroless deposition

Table 1 gives the details of the solutions used for the electroless deposition of nickel [10]. Prior to metal deposition, the fibers were pretreated by dipping them each for about 2 min in stannous chloride–HCl and palladium chloride–HCl solutions in order to activate the fiber surfaces. For deposition of the metal, the pretreated fibers were then immersed into the Ni bath maintained at 50 °C for approximately 20 min. After this step the fibers had a bright metallic shine on their surface. Care was taken to dip-wash the fiber substrates in clean deionized water prior to each entry into the various solutions mentioned above. A JEOL Model JSM 6360 scanning electron microscope (SEM) was used to image the fibers.

3. Results and discussion

Fig. 2 shows the temperature dependence of the conductivity of a thin cast film and an individual fiber of AMPSA-doped polyaniline. The conductivity of the cast film shows metallic behavior down to about 90 K, below which the conductivity begins to drop. In contrast however, it is noted that the conductivity of the fiber is very different. After showing a slight initial increase in the conductivity down to 290 K the conductivity fell by over four orders of magnitude as the temperature was lowered over the same temperature range as that used for the cast film. This could be attributed to the rapid evaporation of the solvent during the electrospinning process, resulting in an amorphous rather than a crystalline structure in the fiber as could have been the case in the cast film, where the solvent

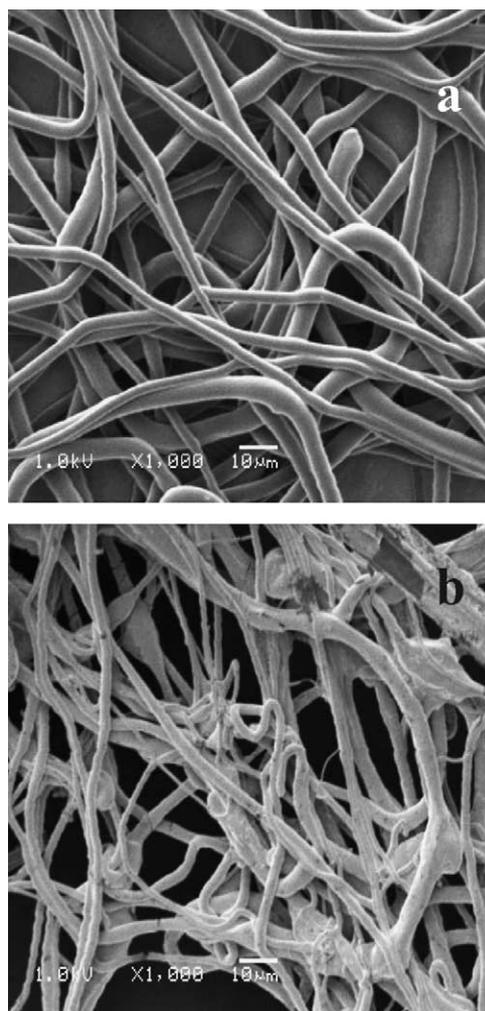


Fig. 3. Low magnification SEM images of AMPSA-doped polyaniline fibers: (a) as-spun; (b) after Ni coating.

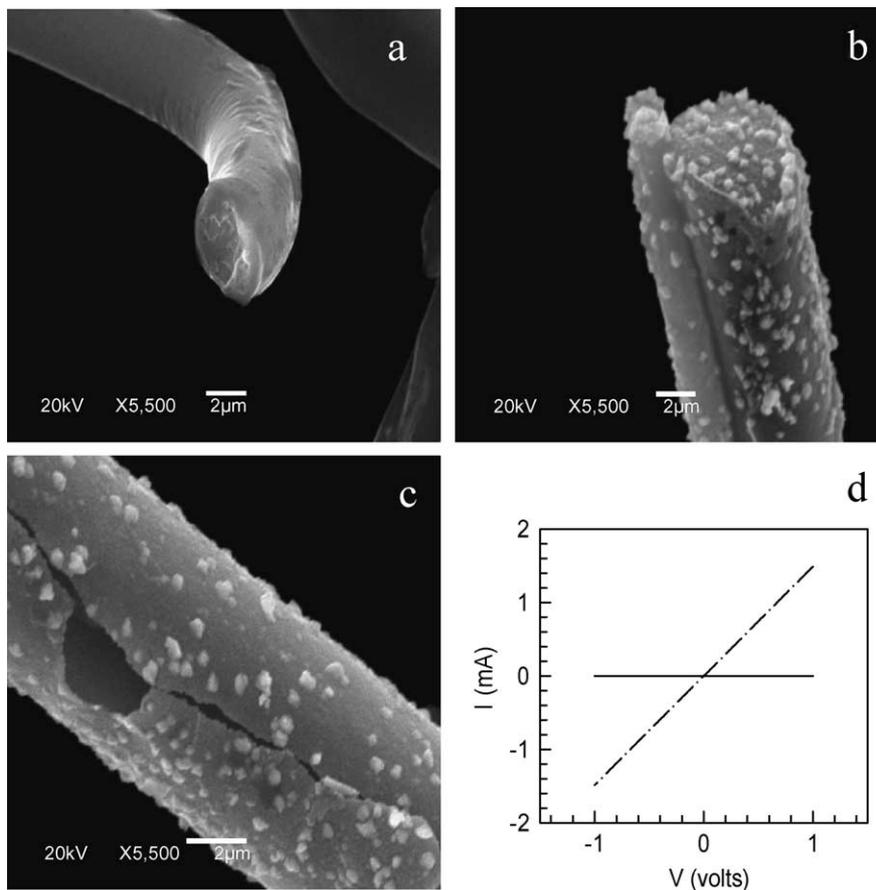


Fig. 4. High magnification SEM images of individual fibers of AMPSA doped polyaniline: (a) As-spun. (b and c) After Ni coating. The Ni-coated fibers appear to have crystallites of the metal covering the surface as remnants of the deposition process. (d) Current–voltage curves taken at 298 K for as-spun single AMPSA-doped polyaniline fiber (—) and for a similar fiber with Ni coating (---).

evaporated relatively slowly leading to larger crystalline regions [17]. It could also be a result of physical confinement of the polymer chains within the fiber together with dense chain packing due to the electric field used in the electrospinning process that reduces ring flipping that is responsible for charge delocalization [16]. Similar temperature dependences of the conductivity as seen for the fiber were observed for a spin-cast film of the polymer where the thickness of the film was about 1 μm .

In order to increase the conductivity of the fibers while retaining the high surface area the fibers were coated with nickel. The electroless deposition technique employed is nondestructive and coats the fibers uniformly in minutes, without the need of high vacuum or high temperatures. Fig. 3(a) and (b) shows low magnification SEM images of the electrospun fibers placed on an Al foil without and with the metal coating, respectively. Most of the fibers had diameters ranging from about 2 to 10 μm and were several centimeters long. The surface features of the as-spun fibers were relatively smooth, except for some fibers that showed the formation of a thin detached “skin” as the fibers coagulated into the acetone bath. As seen in Fig. 3(b) the metal coating is uniform except at the upper right-hand corner

where part of the Ni has flaked off. Fig. 4(a)–(c) shows magnified SEM images of the fibers. Once again as seen in Fig. 4(a) the uncoated fibers have a smooth morphology with apparently no voids at this magnification. Fig. 4(b) and (c) shows the fibers after the Ni deposition. The coating is relatively uniform with the presence of a number of nucleating Ni centers, which were formed during the deposition process. The thickness of the Ni layer was estimated to be about 100 nm. Once coated with the metal the fibers were found to be brittle, as would be expected. The crack in the Ni coating on the fiber as seen in Fig. 4(c) could be attributed to handling the fiber while mounting it on the SEM stage.

Fig. 4(d) shows the current–voltage characteristics of single fibers of AMPSA-doped polyaniline with and without nickel at 298 K. There is about three orders of magnitude decrease in the resistance of the fibers when coated with nickel. The “ohmic” response of the fibers at 298 K to an applied voltage is consistent with the metallic nature of the uncoated fiber and in the uniform coating of the metal in the Ni-treated fiber. The increase in the conductivity of the metal-coated fiber while still maintaining the high surface area is a useful feature and could be

exploited in the preparation of electrodes for catalytic reactions.

4. Conclusions

Using the electrospinning-process fibers of polyaniline doped with AMPSA were prepared from DCA. The fiber diameters ranged from 2 to 10 μm and had lower conductivities as compared to cast films prepared from the same polymer solution. In order to retain the high surface area inherent to fibers and raise the fiber conductivity, the fibers were coated with Ni using the electroless deposition technique. The metal coated the fibers uniformly, leading to a decrease in the fiber resistance by about three orders of magnitude. Thus, using the combination of electrospinning and electroless deposition one can prepare large surface area conducting substrates where in principle one could use either conducting or nonconducting fibers as the substrates.

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