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Sub-micrometer Conducting Polyaniline Tubes Prepared from Polymer Fiber Templates

Hong Dong, Sudhindra Prasad,
Verrad Nyame, and Wayne E. Jones, Jr.*

*Department of Chemistry, State University of New
York at Binghamton, Vestal Parkway East,
Binghamton, New York 13902*

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Conducting polymers are an attractive class of materials for a variety of advanced technologies as they possess electronic, magnetic, and optical properties similar to metals while retaining the flexibility and processibility of conventional polymers.[1,2] Among conducting polymers, polyaniline (PANi) is one of the most extensively studied for electronic and optical applications[2,3] due to its relative environmental stability and interesting redox properties. In recent years, PANi nanostuctural materials including nanofibers and nanotubes have been prepared by different strategies for potential application in nanoelectronic devices.[1] Various approaches for the preparation of micro- or nanotubes of conducting polymers have been reported with or without the aid of templates. Current template-based preparations involve synthesizing a tubular structure of PANi within the pores of membranes such as alumina[4] and track-etched polycarbonate.[5] Besides template methods, self-assembled microtubes and nanotubes of PANi have been obtained by “in situ doping polymerization” in the presence of β-naphthalene sulfonic acid as a dopant.[6]

The approach of using electrospun polymer fibers as templates[7] provides great versatility for the design of tubular materials with controlled dimensions. Examples such as poly(*p*-xylylene) and TiO_2 have been prepared using this approach by the Greiner group.[7−9] In this paper, we describe the application of a fiber templating approach to conducting polymer tubes and the preparation of tubes of PANi in both doped and undoped forms. This approach provides a relatively simple method to fabricate long PANi tubes.

The construction of PANi tubes in our work begins with the preparation of core polymer fibers with diameter in the sub-micrometer range using an electrostatic, nonmechanical electrospinning process. Electrospinning, first patented in the 1930s,[10] has received intense interest in the past decade due to its application in the preparation of polymer fibers with length $>100\ \mu$m and diameters in the range of 30−2000 nm.[11] The morphology and diameter of the fibers can be influenced by process variables[12] and solution properties,[13] such as the applied voltage, solution concentration, polymer molecular weight, solution surface tension, dielectric constant of the solvent, and solution conductivity. Electrically conducting nanofibers have been prepared using electrospinning as pure conducting polymer and blends of conducting polymer with insulating polymer.[14]

The selection of the core polymer to be used as the fiber template is critical to the process. Several polymers can be fabricated into ultrafine fibers by electrospinning. For example, in this study, polystyrene (PS) fibers and poly(methyl metharylate) (PMMA) fibers with diameters ~200 nm have been prepared from 80 mg/mL PS and 70 mg/mL PMMA in *N*,*N*-dimethylformamide (DMF) solution containing an organic tetrabutylammonium chloride salt, respectively. An additional key requirement is that the decomposition temperature of the core fibers should not exceed the threshold to cause structural damage to the outer shell material, in this case PANi. Poly(L-lactide) (PLA) was selected as a suitable fiber template[7,15] since it can be processed into fibers with diameters in the sub-micrometer range by electrospinning and has a relatively low decomposition temperature of 235−255 °C.[16] This low decomposition temperature reduces the possibility of cross-linking and other structural damage in the PANi that would lead to poor conductivity during thermolysis of the core.

The electrospun PLA fibers were prepared by dissolving PLA (180 mg/mL) in CH_2Cl_2/DMF (65/35) solution. Methylene chloride (CH_2Cl_2) is an ideal base solvent since PLA has very good solubility in CH_2Cl_2; DMF was used as a cosolvent due to its high dielectric constant, which facilitates the formation of uniform and ultrafine nanofibers. The morphology and fiber diameter of the PLA electrospun fibers produced at room temperature and a spinning voltage of 20 kV were examined using scanning electron microscopy (SEM). The SEM image, shown in Figure 1a, reveals an average PLA fiber diameter of ~750 nm. The long electrospun PLA fibers ($>100\ \mu$m) appear to be randomly distributed in a fibrous mat.

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* To whom correspondence should be addressed. E-mail: wjones@binghamton.edu. Fax: (607) 777-4478.

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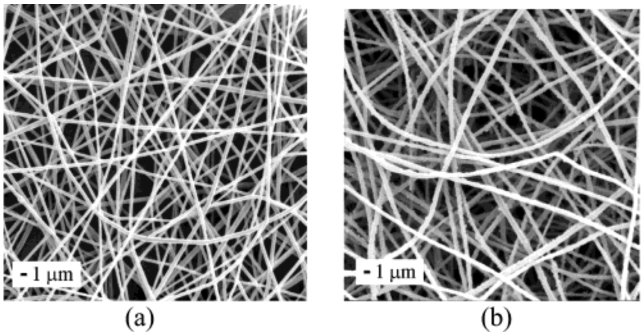

Figure 1. SEM images of (a) a fibrous mat of the electrospun PLA fibers and (b) PANI-EB/PLA coaxial fibers prepared by in situ deposition.

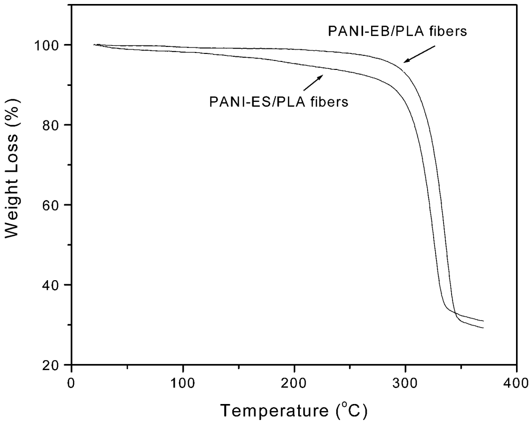

Figure 2. TGA thermograms of PANi-ES/PLA fibers and PANi-EB/PLA fibers.

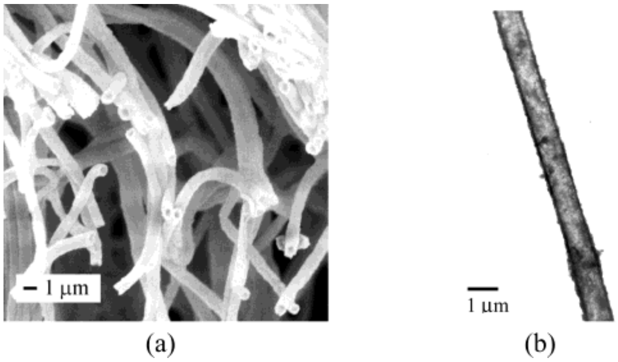

Figure 3. PANi tubes after thermal removal of core fibers: (a) SEM image of a cross section of PANi-EB tubes; (b) TEM image of one PANi-EB tubule.

PANi was deposited on the PLA fibers by in situ polymerization. The PLA fibers were suspended in aniline solution (2 mL of aniline in 100 mL of 1 M HCl solution). The deposition of PANi was initiated by the addition of an equal volume of ammonium persulfate solution as oxidant (1.45 g of $(NH_4)_2S_2O_8$ in 100 mL of 1 M HCl solution).[17] The wall thickness of the PANi was a function of deposition time (4−20 min), consistent with a similar observation of polyaniline deposited on glass slides reported previously.[18] Deposition times longer than 6 min in some cases led to PANi clusters and particles on the surface of individual fibers.

PANi produced by this "in situ deposition" was in conductive emeraldine salt (ES) form, which can be converted into the nonconductive emeraldine base (EB) form by soaking the PANi-ES/PLA fibers in dilute ammonia (0.1 M). The morphology of the PANi-EB/PLA fibers (average diameter 880 nm) obtained by 5 min of coating is shown in Figure 1b. From the SEM image, it is clear that a relatively smooth coating of PANi was achieved on the surface of the PLA fibers.

The thermal behavior of PANi-ES/PLA fibers and PANi-EB/PLA fibers was investigated by thermogravimetric analysis (TGA) to monitor the core polymer removal and tube formation (Figure 2). At temperatures below the decomposition of the PLA fibers (~280 °C), the weight loss of PANi-ES/PLA fibers was ~5%. This was attributed to the loss of the dopant HCl and residual solvent. The thermal instability of PANi-ES coated on the surface of the PLA fibers was consistent with the instability of HCl-doped PANi salt described previously.[19−21] In contrast, no weight loss was observed during heat treatment of PANi-EB/PLA fibers up to the decomposition temperature of the core PLA fibers. This was consistent with the fact that the structural decomposition of PANi-EB does not occur until 500 °C.[21] On the basis of these experiments, the emeraldine base form of PANi was selected as the wall material to be used during thermal removal of the fiber core.

Thermal removal of the PLA core was performed by heating PANi-EB/PLA fibers under inert helium in a tube furnace ramped from room temperature up to 310 °C at 5 °C/min atmosphere, followed by holding at 310 °C for 1 h. Figure 3a is a SEM image showing a cross section of the tubes created by this process. These samples were obtained by freeze fracture from liquid nitrogen. The average diameter of the PANi-EB tubes was approximately 890 nm with 70-nm-thick walls produced from a 5-min coating time. The transmission electron microscopy (TEM) image of a single PANi tube shown in Figure 3b clearly indicates that a hollow tubular structure has been formed. The pore size of the tubes can be tuned by control of the diameter of PLA fiber template by simply adjusting the physical properties of polymer solution. Variations in the solution stoichiometry for deposition and deposition time can be used to control the thickness of PANi wall.

The PANi-EB tubes and commercial PANi-EB powder (from Aldrich) were compared by Fourier transform infrared spectroscopy (FTIR) (Figure 4). The spectrum of the tubes is similar to that of the powder, except for the absorption at 1752 cm^{-1}, which can be assigned to the residual PLA. The characteristic absorptions of PANi,[22] such as stretching vibrations of the quinonoid ring at 1588 cm^{-1} and benzenoid ring at 1503 cm^{-1}, were observed in the spectra of the tubular PANi. Thus, we conclude that the structural integrity of PANi was maintained after the thermal pyrolysis of the PLA fiber core.

The nonconductive PANi-EB tubes can be redoped and converted into the conductive PANi-ES form by HCl

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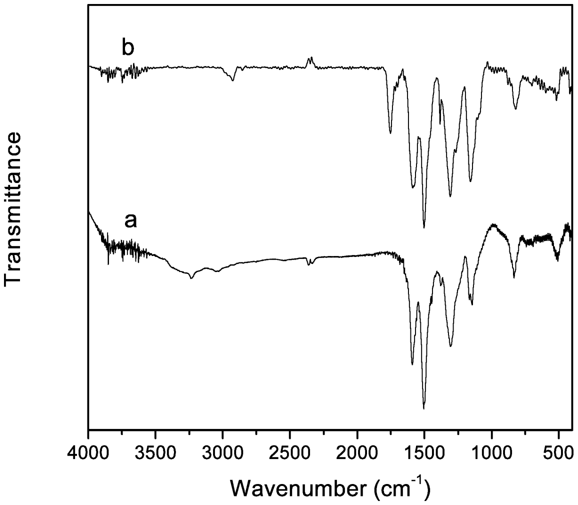

Figure 4. FTIR spectra of (a) PANi-EB powder and (b) PANi-EB tubes. The spectra are offset for clarity.

or other acid dopants. The sheet conductivities of thin films of PANi-ES/PLA fiber materials and PANi-ES tubular were measured by the four-probe method.[23] Initial results showed that the conductivity of PANi-ES/PLA fibers was 0.38 S/cm, and the conductivity of PANi-ES tubes was 0.28 S/cm. Thus, there was no significant decrease in conductivity for the PANi tubes relative to the PANi-ES/PLA fibers as a result of the thermal processing and subsequent re-doping. It is interesting to note that the conductivity of the PANi-ES/PLA fibers and PANi-ES tubes prepared by this template method is the same order of magnitude as that of thin films of PANi (~0.4 S/cm) deposited on glass by the same in situ deposition procedure.[24] Given the porous nature of the nanofiber and tube mat shown in Figure 1, a significant decrease in sheet conductivities was expected. This result implies that the individual fibers in the mat may have a higher conductivity than the bulk. An upper limit of the fiber conductivity can be estimated by using the fiber diameter as the film thickness when calculating the sheet resistance by the four-probe method. The 890-nm fiber diameter applied in this manner gives a net sheet conductivity of 18 S/cm. Further characterization of individual fiber and tube electronic properties are currently underway using a method described previously.[14]

In summary, PANi tubes with sub-micrometer diameter have been prepared in both conducting and insulating forms through a fiber templating approach. SEM and TEM images demonstrate the formation of the tubular morphology that can be systematically controlled by process conditions.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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