

Novel Route to Pure and Composite Fibers of Polypyrrole

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ABSTRACT: An organic salt (FeAOT) is synthesized by the reaction of sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT) and ferric chloride. It is fabricated into fibers by manual drawing and electrospinning. Long polypyrrole (PPy) fibers are obtained for the first time by a vapor deposition reaction of pyrrole on the FeAOT fibers, and this technique is extended to the synthesis of PPy composite fibers with multiwalled carbon nanotubes (PPy-MWCNT fibers). The

PPy and PPy-MWCNT fibers have a nanoporous morphology, a conductivity of $10\text{--}15\text{ S cm}^{-1}$, and a tensile strength of $12\text{--}43\text{ MPa}$. The electrochemistry and current-voltage characteristics of the PPy fibers are also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1490–1494, 2007

Key words: fibers; conducting polymers; strength; polypyrroles

INTRODUCTION

Fabrication of micro- and nanostructured conducting polymers has attracted continuing interest in the last 12 years.^{1–4} These materials have several unusual and useful properties that make them promising for many potential applications in optics, electronics, biondiagnostics, sensors, and actuators.^{5–10} One of the most powerful and now extensively used methods for synthesizing such structures relied on solid-state templates and an electrochemical or chemical reaction to control the length of such structures.^{11,12} Self-assembly is also an effective route to nanotubes or hollow spheres of conducting polymers.¹³ However, the lengths of the structures are usually short ($<100\text{ }\mu\text{m}$) and depend on the pore lengths of solid templates or the structures of micelles. Electrospinning has been applied to synthesize the fibers of pure and blends of conducting polymers with a length of $>100\text{ }\mu\text{m}$. However, to date, this technique has been limited to processing soluble conducting polymers such as pristine polyaniline and its derivatives.^{14–16} Polypyrrole (PPy) and most other widely used conducting polymers in either the doped or dedoped state are insoluble or intractable or decompose before melting, which prevents the use of conventional polymer-processing techniques in shaping these materials into desired structures.^{17,18} Here, we

report a novel process for fabrication of pure and composite fibers of PPy by vapor deposition polymerization of pyrrole using manually drawn or electrospun fibers of an organic ferric salt as the oxidant and templates instead of processing the polymer directly.

EXPERIMENTAL

Chemicals

Pyrrole (Chinese Army Medical Institute) was distilled under reduced pressure before use and sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT, 99%, Acros) was used directly. Other chemicals were reagent grade and used as received. Multiwalled carbon nanotubes (MWCNTs) were synthesized in this lab by catalytic pyrolysis of C_3H_6 with Fe as the catalyst. The nanotubes were treated in hot $\text{H}_2\text{SO}_4\text{--HNO}_3$ mixed acid (3 : 1) for 15 min according to the procedures reported previously.^{19,20}

Synthesis of AOT and ferric chloride organic salt (FeAOT) and FeAOT-MWCNT composites

FeAOT was synthesized by dissolving 13.3 g (60 mmol) AOT and 5.4 g (20 mmol) FeCl_3 into 800 mL of distilled water. The mixture was stirred at room temperature for 12 h. Then, a red precipitate was collected and dried under a vacuum for 48 h. The rough product was dissolved in 50 mL of chloroform and purified by filtration. Then, the excess solvent was removed under reduced pressure. The clean product was dried under a vacuum at 50°C for 48 h. The molecular formula is $\text{FeC}_{40}\text{H}_{83}\text{O}_{19}\text{S}_2$ or $\text{Fe}[(\text{AOT})_2\text{OH}] \cdot 4\text{H}_2\text{O}$.

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ELEM. ANAL. Calcd for $\text{FeC}_{40}\text{H}_{83}\text{O}_{19}\text{S}_2$: C, 48.58%; H, 8.40%; S, 6.47%. Found: C, 48.35%; H, 8.52%; S, 6.81%.

An X-ray photoelectron spectroscopy (XPS) analysis was conducted and an Fe/S atomic ratio of 1 : 2 was found. According to thermogravimetric analysis (TGA), 8.61% mass remained as Fe_2O_3 after extensive decomposition and the theoretical reserved mass was 8.10%.

FeAOT–MWCNT composites were made by putting a certain amount of MWCNTs (1–5% to FeAOT, w/w) into a methanol solution of FeAOT and mixed by ultrasound vibration. Then, the methanol solvent was removed by rotary evaporation and the remaining solid mixture was dried under a vacuum for 12 h.

Fabrication of PPy and PPy–MWCNT fibers

FeAOT and FeAOT–MWCNT fibers were fabricated by heating the salt or its composites to 60°C and then manually drawing with a glass stick or electrospun at 6 kV into fibers (distance between anode and cathode contacted to earth = 15 cm).

In a typical synthesis of PPy or PPy–MWCNT fibers, FeAOT or FeAOT–MWCNT fibers were placed in a reaction vessel (100 mL) equipped with a sealing apparatus and a monomer loading reservoir. After removing the air in the vessel with dry nitrogen gas, pyrrole was injected into the reaction chamber. The monomer was evaporated gradually and contacted to the salt fibers. After deposition polymerization of pyrrole for 24 h, the fibers were washed repeatedly with methanol.

Characterizations

Electrochemical examinations were performed on a model 283 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. A free-standing PPy fiber was used as the working electrode and a platinum wire (diameter = 1 mm) was used as the counterelectrode. All potentials were referred to a saturated calomel electrode. The current–voltage (i – V) curves were measured by polarization in a potential range of –2 to +3 V with two platinum electrodes (separated by 6 mm) contacted to the polymer film or the fibers. XPS was conducted using a PHI5300 ESCA/610SAM X-ray photoelectron spectrometer (Physical Electronics) under a pressure lower than 10^{-8} Torr. The morphology of the fibers was studied using a KYKY2800 (Beijing Scientific Instrument Company) or a JSE-6700F (JEOL) scanning electron microscope after sputter coating with platinum. Raman spectra were recorded on an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC) employing a 633-nm laser beam and a charge coupled device detector with 4 cm^{-1} resolution.

The spectra were recorded using a 20 power objective and accumulated for 30 s. The elemental analysis was carried out with a Flash RA1112 elemental analyzer (ThermoQuest). TGA was performed on a TGA 2050 (TA Company). The tensile strengths of the fibers were measured using a WD-1 electronic stretching machine (Changchun, China). The dc conductivity was measured by a conventional four-probe technique with microsized platinum electrodes (diameter = 5 μm).

RESULTS AND DISCUSSION

PPy and PPy–MWCNT fibers from manually drawn salt fibers

AOT is usually used as a surfactant in the formation of emulsions and inverse emulsions.²⁰ When 3 mol AOT reacted with 1 mol ferric chloride in water, an organic ferric salt (FeAOT) as a red precipitate was produced. According to the results of the elemental analysis, XPS examinations, and TGA, the chemical formula of FeAOT can be simply represented by $\text{Fe}[(\text{AOT})_2(\text{OH})] \cdot 4\text{H}_2\text{O}$. FeAOT is a soft solid at room temperature and can be changed into a viscous fluid by slight heating. Thus, pure FeAOT and its composites can be fabricated into fibers by manual drawing and electrospinning at an evaluated temperature (e.g., 60°C) and then solidifying at room temperature.

The pyrrole vapor deposited on FeAOT or its composite fibers and polymerized into PPy or PPy composite fibers. The diameters of the polymer fibers fabricated from manually drawn salt fibers are in the range of several to 100s of microns, and their lengths can reach several decimeters [Fig. 1(A,B)]. These fibers have porous structures with a pore size on the nanometer scale [Fig. 1(C,D)]. The nanosized pores resulted from removing the remaining oxidant and oligomers in the as-formed fibers by washing with methanol. The PPy fibers are constructed of nanoparticles of the polymer and possess many cracks with widths of less than 100 nm [Fig. 1(C)]. The composite fibers contain a certain amount of MWCNTs (PPy–MWCNT fibers) and have a fibril morphology [Fig. 1(D)]. The fibrils are carbon nanotubes with uniform PPy coatings. Mechanical drawing of the salt composite resulted in a partial orientation of the nanotubes in the composite fibers, as shown in Figure 1(D).

The tensile strengths of a pure PPy fiber with a diameter of about 160 μm were 12 ± 0.8 MPa. This value is smaller than that of the normal flat PPy films prepared by electrochemical deposition (23 ± 0.5 MPa), mainly because of the porous structures of the fibers. The conductivity of this PPy fiber, which was measured by the four-probe technique, was about 14 S cm^{-1} , which is close to that of elec-

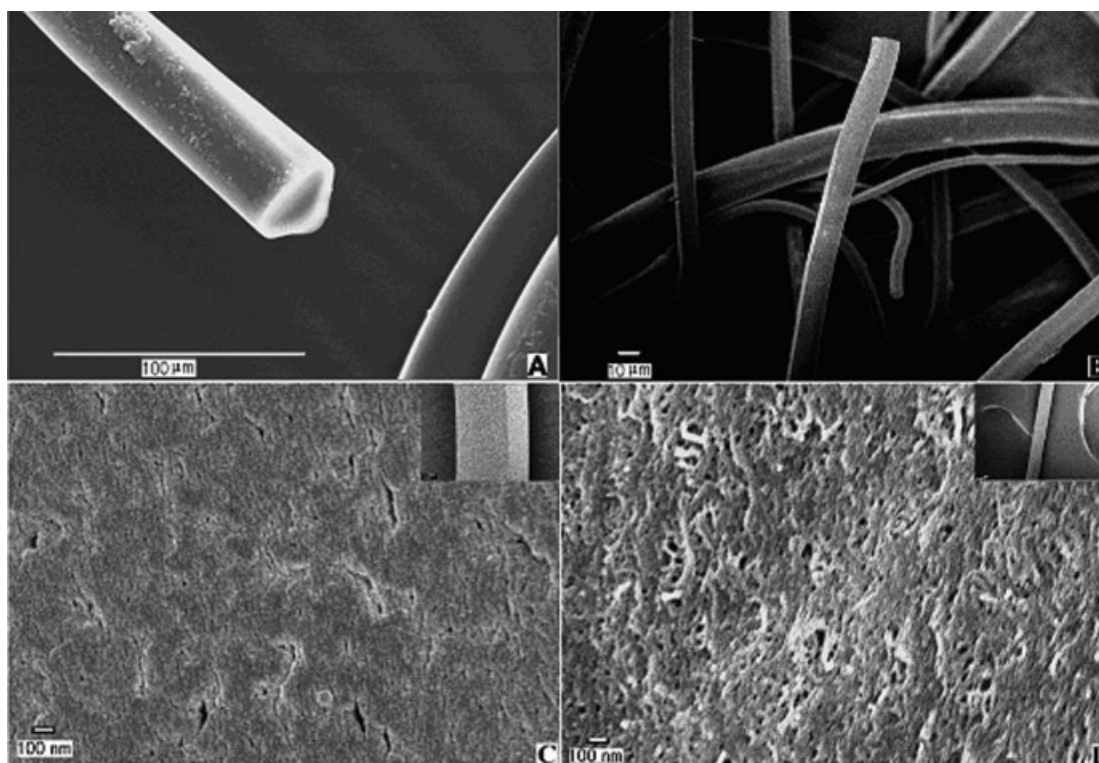


Figure 1 SEM photographs of (A, C) PPy fibers and (B, D) PPy-MWCNT fibers fabricated by chemical deposition polymerization of pyrrole on manually drawn FeAOT or FeAOT-MWCNT fibers.

tro-synthesized PPy films (15 S cm^{-1}). The addition of MWCNTs increased the strength while slightly decreasing the conductivity of the PPy fibers. The optimum weight content of MWCNTs in the FeAOT-MWCNT composite for high-strength fibers was tested to be about 1.3%. The PPy-MWCNT fibers synthesized from this salt composite showed a maximum tensile strength of $43 \pm 1 \text{ MPa}$, and their conductivity was about 10 S cm^{-1} . The weight content of MWCNTs in these fibers was estimated to be about 15% by weighing the feeding MWCNTs and the resulting PPy-MWCNT fibers.

PPy and PPy-MWCNT fibers from electrospun salt fibers

Electrospinning is an electrostatically induced self-assembly process wherein fibers are produced.²¹ Figure 2 provides optical photographs and SEM images of PPy and PPy-MWCNT fibers fabricated by the reactions of the electrospun FeAOT or FeAOT-MWCNT fibers with pyrrole vapor. As can be seen from this figure, the diameters of the PPy fibers are relatively uniform and have values of $5 \pm 2 \mu\text{m}$ [Fig. 2(B)]. However, the diameters of PPy-MWCNT fibers had a large-scale range of 5–50 μm [Fig. 2(C,D)]. The pure and composite PPy fibers fabricated by electrospinning can form nonwoven cloths, as shown in Figure 2(A,C).

The Raman spectra of MWCNTs, PPy fibers, and PPy-MWCNT fibers are demonstrated in Figure 3. In the spectrum of pure MWCNTs (spectrum a, Fig. 3), the 1592 cm^{-1} band is attributed to the E_{2g} mode of the graphite wall²² and the 1617 cm^{-1} band is assigned to the E_{2g} mode of a single-cylinder nanotube.²³ The band at 1334 cm^{-1} is related to slightly disordered graphite.²⁴ In the spectrum of PPy fiber (spectrum b, Fig. 3), the 1575 cm^{-1} band represents the C=C backbone stretching of PPy. The double peaks at about 1053 and 1081 cm^{-1} are associated with the C-H in-plane deformation,²⁵ and the other double peaks at 1330 and 1370 cm^{-1} are attributed to the ring-stretching mode of PPy.^{25,26} The bands located at about 963 and 933 cm^{-1} are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively.^{27,28} The Raman spectra of the composite fibers showed the bands related to PPy and MWCNTs (spectra c,d, Fig. 3) simultaneously. In comparison (spectra b–d, Fig. 3), the intensity of the 1334 cm^{-1} band increases with the increase of MWCNT content. The Raman spectral results described above confirmed the formation of pure and composite fibers of PPy and the polymer chains were in the oxidized (doped) state. Elemental analysis results demonstrated that the pure PPy fibers had a chemical formula of $\text{C}_{9.42}\text{N}_{1.00}\text{H}_{12.83}\text{O}_{5.14}\text{S}_{0.27}$, indicating the doping level of the polymer was about 0.27.

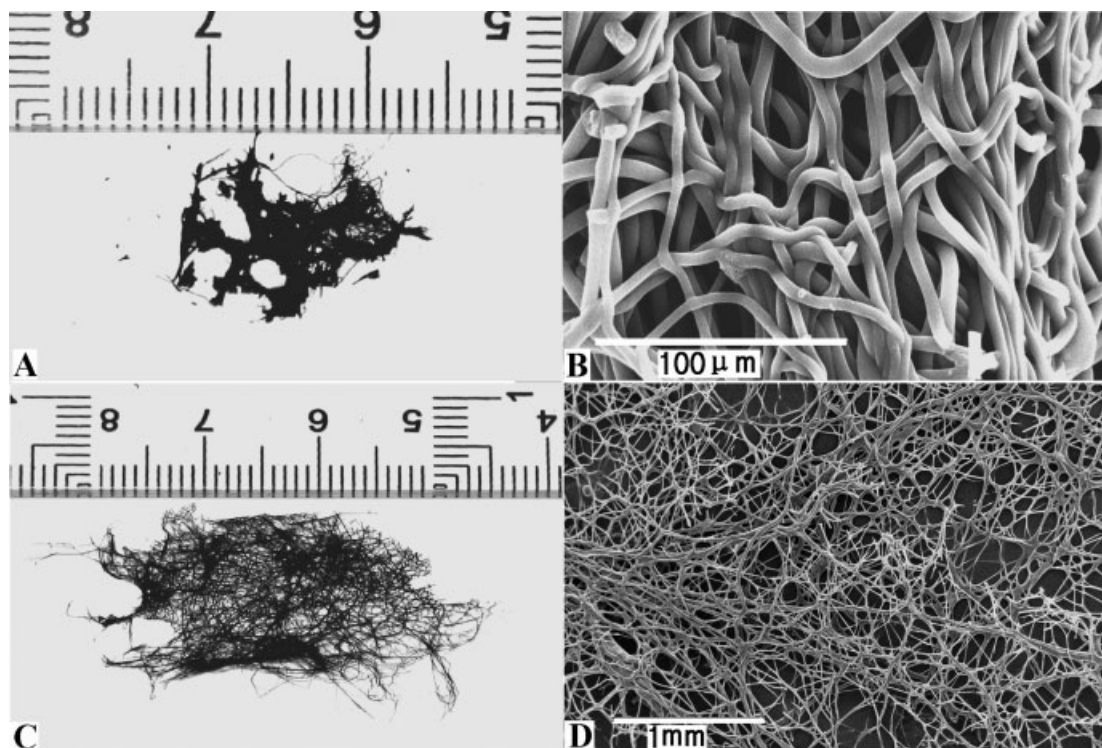


Figure 2 (A, C) Optical pictures and (B, D) SEM images of (A, B) PPy fibers and (C, D) PPy-MWCNT fibers (MWCNT weight content = 15%) fabricated by chemical deposition polymerization of pyrrole on electrospun FeAOT or FeAOT-MWCNT fibers.

Electrochemistry and i - V characteristics of PPy fibers

A PPy fiber with a 15-mm length and 145- μm diameter was fixed by a stainless steel clamp and an approximate 3.0-mm fiber was immersed in 1.0 mol L⁻¹ LiClO₄ aqueous solution, which acted as the working elec-

trode. The fiber had good electrochemical stability and the steady-state cyclic voltammograms represented strong and broad anodic and cathodic peaks [Fig. 4(A)]. The current densities were proportional to the scan rate, indicating a redox couple fixing on the fiber [Fig. 4(B)].

The i - V curve for a PPy fiber (diameter = 20 μm) is demonstrated in Figure 5, which gives a linear

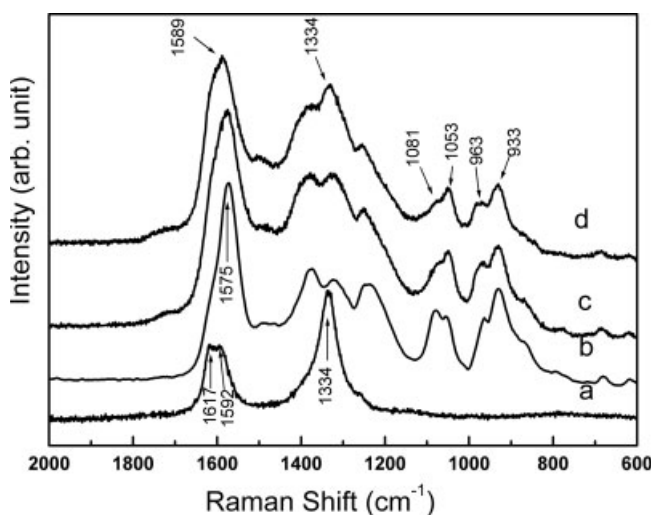


Figure 3 Raman spectra of pure MWCNTs (spectrum a), PPy fibers (spectrum b), and PPy-MWCNT fibers with MWCNT content of 15 (spectrum c) and 30% (spectrum d).

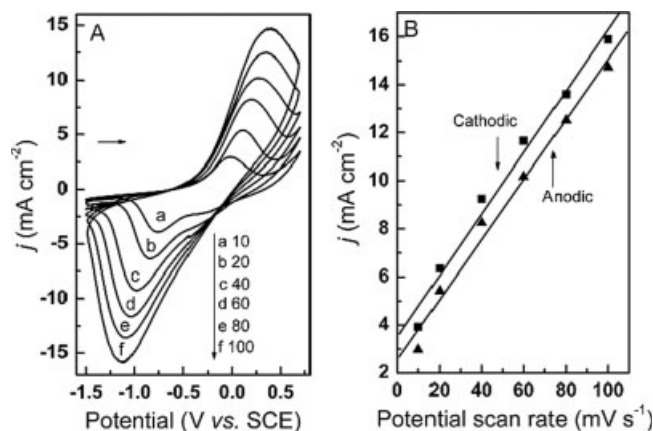


Figure 4 (A) Cyclic voltammograms of PPy fibers at different potential scan rates and (B) the relationship between the current density of the redox waves and the potential scan rate.

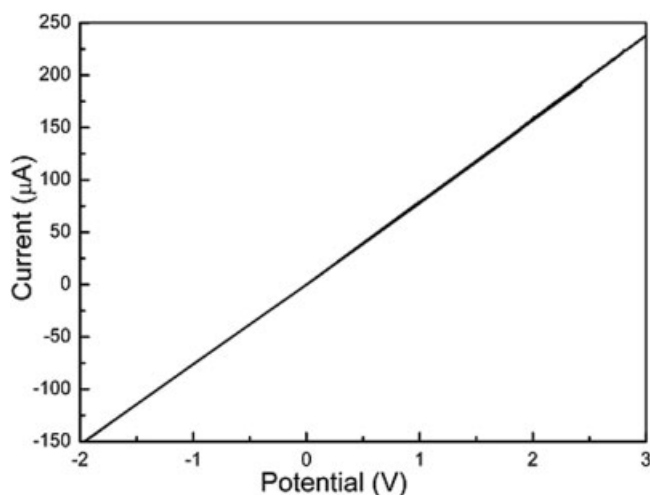


Figure 5 The current–voltage curve of a PPy fiber in the potential range of -2 to $+3$ V with a potential scan rate of 20 mV s^{-1} .

relationship. The i – V curves of PPy–MWCNT fibers have similar features. The pure resistance characters of PPy and PPy–MWCNT fibers indicate that these materials are promising for the fabrication of chemical sensors.

CONCLUSION

An FeAOT organic salt was synthesized by the chemical reaction of FeCl_3 and AOT. The pure FeAOT and its mixtures with carbon nanotubes were processed into long fibers by manual drawing or electrospinning. Vapor deposition polymerization of pyrrole using the FeAOT fibers or their composites as the oxidant and templates produced pure or composites of PPy fibers. The PPy and PPy–MWCNT fibers had nanoporous structures and high specific surface area, good electrical and mechanical properties, and linear i – V characteristics, which provide potential applications in the fabrication of chemical sensors and other electronic or electrochemical devices.

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