Poly(3-hexylthiophene)/Poly(methyl methacrylate) Core-Shell Electrospun Fibers for Sensory Applications

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Summary: New electrospun (ES) sensory fibers consisted of poly(methyl methacrylate) (PMMA) core and poly(3-hexylthiophene-2,5-diyl) (P3HT) shell were successfully prepared using a two-fluid coaxial electrospinning process. Field-emission scanning electron microscope (FE-SEM) studies showed that the prepared ES fibers had diameters of 500–700 nm and worm-like surface structure of P3HT on the fiber. Red emission fibers were exhibited from the laser confocal microscope. Upon exposed to air under light for two weeks, significant blue-shifting on both absorption and luminescence spectra was found on the prepared ES fibers. It was probably due to the chain scission occurred in the P3HT and led to the reduced conjugated length. The sensitivity of the ES fibers was much better than that of the spin-coated P3HT film from the comparison on the variation of photophysical properties. Besides, the EPR result indicated the formation of the P3HT · O_2 charge transfer complex (CTC), leading to the fiber conductivity of 10^{-6} S/cm without an external doping. The present study demonstrates that conjugated polymer based ES core-shell fibers may have potential applications for oxygen-sensing devices.

Keywords: core-shell fibers; electrospun; morphology; P3HT; photophysics

Introduction

Poly(3-hexylthiophenes) (P3HT) have been extensively studied for various electronic and optoelectronic device applications due to their superior optoelectronic properties and processibility.[1,2] The reported device applications included field effect transistors, solar cells, electrochromic devices, and chemical sensors.[3–5] However, most of the above studies were based on P3HT thin film or bulk solid state. Until recently, the field effect transistor based on the P3HT electrospun (ES) fibers were explored by Liu[6] and Jenekhe.[7,8] However, sensory applications based on the P3HT core-shell ES fibers have not been fully explored yet.

Electrospinning (ES) has emerged as a new technique to produce various functional nanofibers.[9–21] Conjugated polymer ES fibers showed distinct electronic and optoelectronic properties as compared with films due to the geometrical confinement of ES process.[7,8,12–21] However, the molecular weight or solubility of conjugated polymers might limit the production of uniform ES fibers. Hence, polymer blends with a non-conjugated polymer[17–19] or two-fluid coaxial electrospinning technique[8,20,21] were used to obtain conjugated polymer based ES fibers. The high surface/volume ratio of the ES fibers has attracted extensive studies for sensory applications.[22–24] For example, Kim and his coworkers[22] have developed a new strategy for colorimetric and specific detection of volatile organic compounds (VOCs) based poly(diacetylene)-embedded solvatochromic electrospun fibers. However, the morphology and photophysical properties of conjugated polymer based core-shell ES

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fibers and their sensory applications require further exploration.

In this study, we report the preparation and characterization of electrospun fibers consisted of poly(methyl methacrylate) (PMMA) core and poly(3-hexylthiophene-2,5-diyl) (P3HT) shell, using a two-fluid coaxial electrospinning technique. The fiber morphology was characterized by field-emission scanning electron microscope (FE-SEM) and laser confocal microscope (Confocal). The photophysical properties of the ES fibers were investigated by optical absorption and steady-state photoluminescence (PL). The sensory application of the prepared ES fibers was explored by exposing fiber to air at room temperature under light. Electron paramagnetic resonance (EPR) spectra of ES fibers were measured under air at room temperature. The conductivity of the ES fibers was measured using a 4-point probe technique. P3HT based spin-coated thin film was also prepared and compared with the above ES fibers. Our results suggested the successful preparation of core (PMMA)-shell (P3HT) ES fibers with a worm-like surface structure and such fibers might have potential sensory applications.

Experimental Part

Materials

PMMA (Mw ~ 350,000) and P3HT (Mw ~ 87,000) were both purchased from Aldrich (Milwaukee, USA). High purity chlorobenzene (A.C.S. Reagent grade, J. T. Baker (Phillipsberg, USA)) and tetrabutylammonium perchlorate (TBAP, TCI (Tokyo, Japan)) were used as received.

Electrospinning Setup

A two-fluid coaxial electrospinning technique was used to produce core-shell nanofibers, similar to that reported in the literature.[8,20,21] Figure 1 shows a schematic illustration of our experimental setup. As shown in Figure 1(a), two syringes containing core and shell precursor solutions were used for producing the ES fibers. Note that each syringe was connected to a separate needle, and the needle was placed one inside the other to form two a two-fluid coaxial electrospinning system. 300 mg/ml of PMMA in chlorobenzene (CB) and 5 wt% (with respect to the polymer) of tetrabutylammonium perchlorate (TBAP, a soluble organic salt) and 50 mg/ml of P3HT in chlorobenzene (CB) were used to produce the core and shell of the ES fibers, respectively. The two solutions were fed into the coaxial capillaries by two syringe pumps (KD Scientific Model 100, USA). The feed rates of PMMA and P3HT solution were set at 2 and 0.6 ml/h, respectively. The tip of the shell needle was connected to a high-voltage power supply (chargemaster CH30P SIMCO, USA), and a piece of aluminum foil or silicon wafer was placed 20 cm below the tip of the needle to collect the core-shell nanofibers. The spinning voltage was set at 15 kV. All experiments were carried out at room temperature.

Spin-Coated Film

For the comparison with properties of ES fibers, thin film of P3HT was spin-coated from the chlorobenzene concentration of 50 mg/ml onto glass substrate at a spin rate of 1500 rpm for 60 s.

Characterization

The morphology of the prepared ES fibers was characterized by field-emission scanning electron microscope and laser confocal microscope. The FE-SEM (JEOL JSM-6330F) images were taken using a microscope operated at an accelerating voltage of 15 kV. Before imaging, the samples were sputtered with Pt. Fluorescence optical microscope images were taken using Two Photon Laser Confocal Microscope (Leica LCS SP5). Electron paramagnetic resonance (EPR) spectra of ES fibers were obtained under 1 atm of air at room temperature using EPR spectrometer (Bruker EMX-10). Resistance was obtained on 4-point probe spectrometer (Keithley 2400). The thickness of the fiber mat for conductivity measurement was recorded by using digimatic micrometer (Mitutoyo IP65). UV-visible absorption and photoluminescence (PL) spectra were recorded on UV-visible

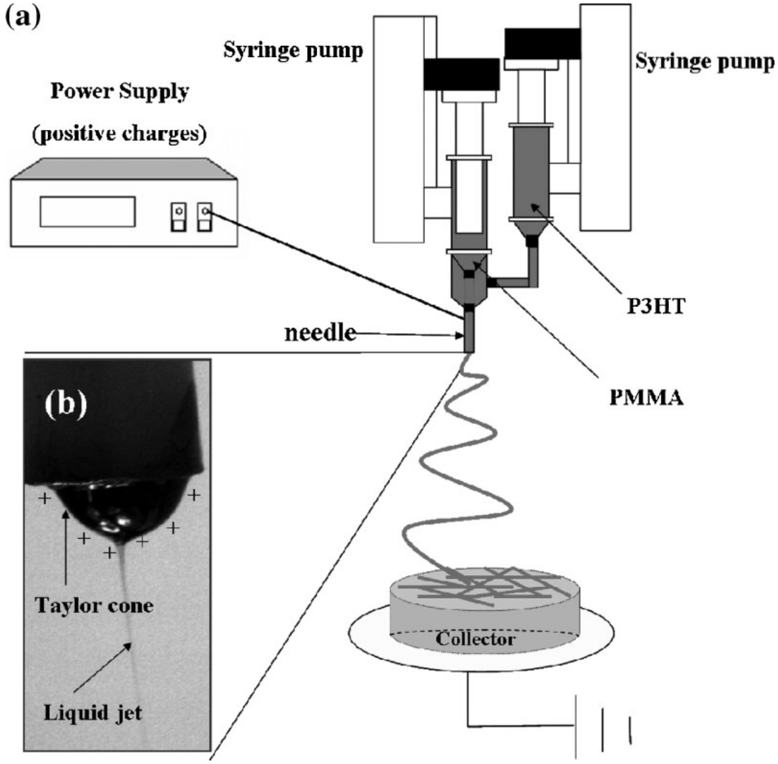

Figure 1.
(a) Schematic illustration of the electrospinning setup used to produce core(PMMA)-shell(P3HT) nanofibers. (b) CCD image of the stable con-jet spinning model.

spectrophotometer (Hitachi U-4100) and Fluorolog-3 spectrofluorometer (Jobin Yvon), respectively.

The sensory characteristic of the prepared materials was tested as described below. The ES fibers or spin-coated thin films were exposed to air at room temperature and under light in a hood after one day, one week and two weeks, respectively. The variation of the photophysical properties or conductivity was recorded to check the sensory characteristic on oxygen.

Results and Discussion

Fabrication and Morphology of Core(PMMA)-Shell(P3HT) Electrospun Fibers

Figure 1(a) illustrates the schematic setup used for the fabrication of core-shell ES nanofibers. The core (PMMA)-shell (P3HT) fiber was produced using a two-fluid coaxial electrospinning technique. The two-fluid electrospinning provides the following advantages for obtaining P3HT ES fibers. First, the PMMA core serves as a supporting aid for P3HT shell. Note that the molecular weight and solubility of P3HT could not be used to produce ES fibers using a single-capillary spinneret.[17–21] Second, the two fluid flow rates were used to tune the core/shell ratio as well as the surface structure of the prepared ES fibers. Figure 1(b) shows the CCD image of the stable cone-jet spinning model during two-fluid coaxial electrospinning process. As shown in Figure 1(b), a stable Taylor cone was completely covered with shell material (P3HT, red color), indicating that the PMMA core was successfully encapsulated by the P3HT shell.

Figure 2(a) and 2(b) show the FE-SEM image and the laser confocal microscopy

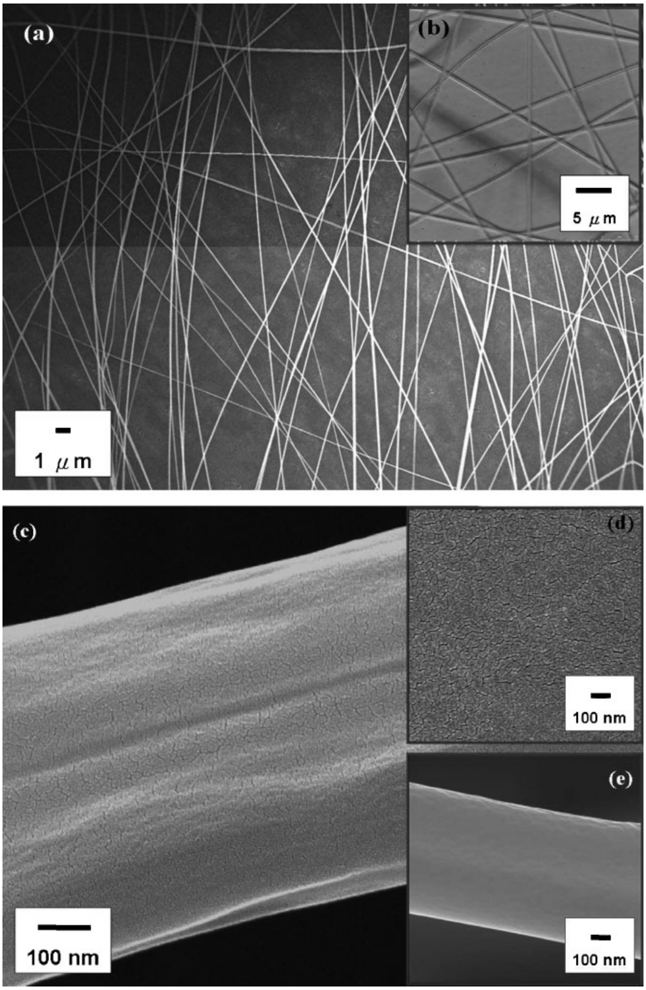

Figure 2.
(a) FE-SEM image of core(PMMA)-shell(P3HT) ES fibers. (b) The laser confocal microscopy image of the above ES fibers. (c) The enlarged FE-SEM images of Figure 2(a). (d) FE-SEM image of P3HT spin-coated films. (e) FE-SEM image of PMMA ES fibers.

image of the prepared core shell ES fibers, respectively. Uniform ES fibers with the diameters ranging from 500–700 nm are observed in Figure 2(a). Also, red emission fibers are shown in Figure 2(b). It indicates the formation of the P3HT shell since the PMMA is a non-fluorescent polymer. The core/shell ratio estimated from their precursor solutions is around 29:1 using the densities of 1.30 and 1.20 g/cm^3 for P3HT and PMMA, respectively. The detailed microstructure could be further explored by the enlarged FE-SEM images and its comparison with the homopolymer. Figure 2(c) shows the enlarged FE-SEM image of the prepared core-shell ES fibers from Figure 2(a). A worm-like surface structure is observed in the figure. Such surface structure is also shown on the surface of the P3HT spin-coated film (Figure 2(d)), similar to that reported in the literature.[25] On the contrast, the FE-SEM image of PMMA ES fiber shows a relatively smooth surface, as shown in Figure 2(e). Thus, the worm-like structure exhibited ion the surface of the prepared core-shell ES fiber is attributed to the P3HT shell.

Photophysical Properties and Sensory Application

Figure 3 shows the UV-vis absorption spectra of the prepared core-shell ES fibers exposed to air under light at room temperature for one day, one week and two weeks, respectively. Note that the optical absorption spectrum of the as-spun fibers and that of one-day exposure is almost the same. The inset figure shows the optical absorption spectra of the P3HT spin-coated film for one-day and one-week exposure, respectively. As shown in the figure, the longest wavelength absorption maximum ($\lambda_{\rm max}^{\rm abs}$) are observed at 534, 422, and 350 nm after exposed to air for one day, one week, and two weeks, respectively. Such significant blue shift on $\lambda_{\rm max}^{\rm abs}$ suggests the decrease of the effective conjugated length of the ES fiber upon air-exposure. As reported in the literature,[26] P3HT reacted with oxygen under irradiating light led to the chain scission and decreased conjugation length. On the contrast, the $\lambda_{\rm max}^{\rm abs}$ of the P3HT spin-coated films is observed at 532 and 528 nm after exposed to air for one day and one week, respectively, as shown in the inset of Figure 3. The much larger blue shift on $\lambda_{\rm max}^{\rm abs}$ on the ES fibers than that of the spin-coated film is due to the high surface-area-volume ratio of the former, leading to an efficient interaction between P3HT and oxygen.

Figure 4 shows the photoluminescence (PL) spectra of the prepared core-shell ES fibers after exposed to air for one day, one week and two weeks, which were excited at 534, 422, 350 nm, respectively. Similar to the absorption spectra, the photoluminescence spectrum of the as-spun fibers and that exposed to air for one day is almost the same. The emission maxima ($\lambda_{\rm max}^{\rm PL}$) of the prepared core-shell ES fibers decreases from 667 nmof one-day exposure, to 576 nm of one-week exposure and 507 nm of two-week exposure, with the emission color of red, orange, and green, respectively. The trend on the emission maxima is consistent with those of absorption. The blue-shifting on the photophysical properties of the ES fibers suggested that P3HT probably degraded by oxygen under irradiating light.[26] Similar to the case of the absorption, an insignificant variation on the luminescence maxima was found on the P3HT spin-coated film with different exposure-to-air time, as shown in the inset

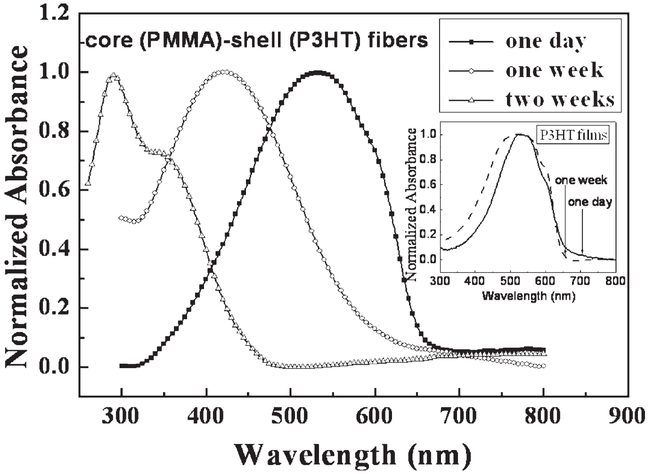

Figure 3.
UV-vis absorption spectra of the prepared core(PMMA)-shell(P3HT) ES fibers exposed to air for one day, one week and two weeks, respectively. The inset shows the P3HT spin-coated films exposed in the air for one day and one week, respectively.

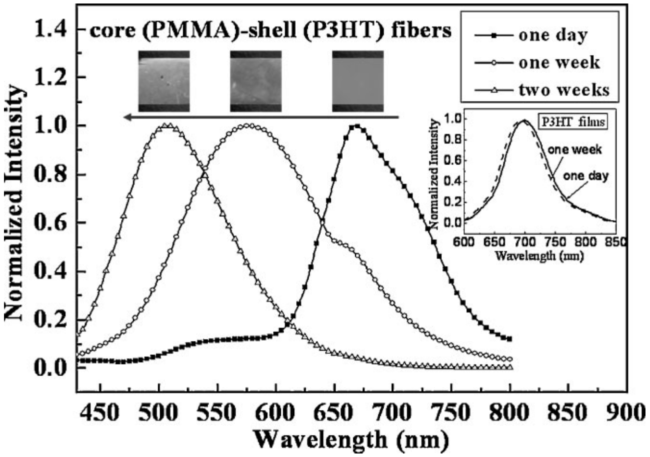

Figure 4.
Photoluminescence spectra of the core(PMMA)-shell(P3HT) ES fibers exposed to air for one day, one week and two weeks, respectively.

of Figure 4. The strong luminescence color-changing (from red to green) in the prepared core-shell ES fibers indicated their potential sensory applications.

EPR and Electronic Properties

Figure 5 shows the EPR spectra of the prepared core-shell ES fibers after exposed in air for one day and two weeks, respectively. As shown in the figure, an enhanced EPR signal intensity of the ES fibers from the one-day exposure of air to the two-week exposure. Also, the EPR signal of the ES fibers after one-day exposure exhibits a Gaussian line shape with a peak-to-peak with 5.50 G and a g-value of 2.0034. But the peak-to-peak width increased to 6.00 G. and the g-value decreased to 2.0026 for the case of two-week exposure. The broader Gaussian line shape and higher signal intensity suggested the possible formation of the P3HT $\cdot$ O_2 charge transfer complex (CTC), i.e., P3HT and O_2 contain unpaired electrons.[27] The conductivity of the ES fibers after the two-week exposure was 1×10^{-6} S/cm, using a 4-point probe technique. Note that the conductivity of such charge transfer complex was reported to be around $10^{-6} \sim 10^{-9}$ S/cm. However, the conductivity of the ES fibers for the one-week exposure was insignificant. The above results on the photophysical properties and conductivity suggested that the photodegradation of the ES fibers occurred first and followed by forming the charge transfer complex. On the contrast, the P3HT spin-coated film did not show any measurable conductivity under a similar exposure condition. The present study suggests that the core (PMMA)-shell (P3HT) ES fibers could be potentially used as new gas sensory materials.

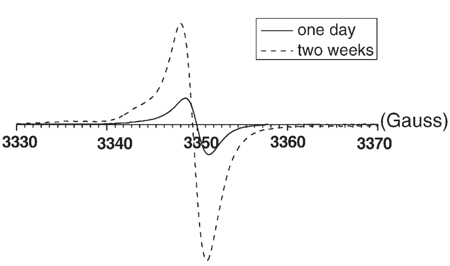

Figure 5.
EPR spectra of core(PMMA)-shell(P3HT) ES fibers exposed in the air as a function of time such as one day and two weeks.

Conclusions

In this study, core (PMMA)-shell (P3HT) electrospun nanofibers with a warm-like structure of P3HT were successfully prepared using a two-fluid coaxial electrospinning technique. Significant blue-shifting on the absorption or luminescence peak of the prepared ES fibers was shown after exposed to air under light. The degradation of the P3HT shell might lead to the above blue shift. However, insignificant spectra shifting on the P3HT spin-coated film was observed under similar exposure condition in comparison with that of the ES fibers since the latter had a high surface-area-volume ratio. The EPR and conductivity results indicated the formation of charge transfer complex (CTC) on the ES fibers after exposed to air for two weeks. The experimental results suggested that the photodegradation of the ES fibers occurred first and followed by forming the charge transfer complex. The prepared conjugated polymer core-shell electropsun fibers may have potential application for sensory application.

Acknowledgements: The financial supports from National Science Council of Taiwan (NSC 97-2221-E002-024-MY3), National Taiwan University (Excellent Research Projects), and Ministry of Economic Affairs of Taiwan (96-EC-17-A-08-S1-015) are highly appreciated.

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