Control of Self Organization in Conjugated Polymer Fibers

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ABSTRACT We propose new strategy to facilitate the fabrication of conjugated polymer fiber with higher oriented structures, which focused on electrospinning of a blend solution of regioregular poly(3-hexylthiophene) (*rr*-P3HT) and poly(vinyl pyrrolidone) (PVP). SEM observation revealed that the blend system forms homogeneous composite nanofibers. This system exhibits the specific feature of strong interchain contribution of P3HT from UV−vis absorption, fluorescence spectroscopic, XRD, and photoelectron spectrometric (for HOMO levels) investigations. We also demonstrate the removal of the PVP component from the P3HT/PVP composite fibers through the selective extraction and such strong interchain stacking of pristine P3HT fiber mat can be remarkably maintained.

KEYWORDS: self organization • conjugated polymer • poly(3-hexylthiophene) • nanofibers • interchain packing

Poly(3-hexylthiophene) (P3HT), one of the widely utilized conductive polymers, has been intensively studied in various optoelectronic devices, especially organic photovoltaic cells (1, 2) and field-effect transistors (3, 4). Self organization in properties, which depends critically on processing conditions, is one of the key factors in capability of P3HT devices. It is believed that self-organizing properties of P3HT, including both electronic and optical ones, are sensitive to molecular packing (5−7). Influence of the molecular packing controlled by polymer regioregularity (1) or temperature (5) on the optoelectronic properties of P3HT have been reported in the literature.

One-dimensional (1D) nanomaterials, including nanofibers, nanowires, nanotubes, nanobelts, etc., have been attracting considerable attention during the past decade (8, 9) because when the diameters of materials are shrunk to sub-micrometers or nanometers, there appear to be several specific characteristics such as improved mechanical performance, very large surface area to volume ratio, and flexibility in surface functionalities (10). In addition, optoelectronic properties of 1D nanofibers of P3HT are promising for efficient charge transporting materials of organic molecular devices. Here we focused on the new strategy to facilitate the fabrication of 1D nanofibers of P3HT with highly oriented structure. We adopted and applied electrospinning, which is attributable to regulating the interchain packing of P3HT chains and domains in nanofibers.

We have reported the fabrication of conductive polymer nanofibers by electrospinning of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) blended with poly(vinyl pyrrolidone) (PVP), followed by getting rid of the nonconductive polymer part by Soxhlet extraction (11−13). Because of low solubility of P3HT, P3HT phase was separated from P3HT/PVP solution and formed gel-liked viscose at room temperature. Therefore, electrospinning was performed at 60°C by using a heated, jacketed syringe to increase the solubility of P3HT and decrease the viscosity of the P3HT/PVP solution. Homogeneous P3HT/PVP composite nanofibers with an average diameter about 300 nm were fabricated from blended P3HT/PVP solution in a mixed solvent of chlorobenzene and methanol as shown in images c and e in Figure 1. After the removal of PVP from as-spun fibers by Soxhlet extraction, pure P3HT fibers were obtained as a spindlelike structure with wrinkled surface aligned in fiber direction (Figure 1f). These results suggest that there was a phase separation of P3HT and PVP in the sub-micrometer scale occurred during instability. The confinement and electric field during electrospinning could enhance the orientation of these phases and polymer chains in fiber direction resulted in high orientation of P3HT phase after the removal of PVP. This phenomenon was also observed in the case of MEH-PPV/PVP fibers (12, 13). In addition, the removal of PVP resulted in decreasing diameter of fibers and thickness of fiber mats, and the enhancement of contact parts of fiber mats.

Figure 2 shows normalized adsorption and emission spectra of electrospun fibers compared with solutions and films. In solution, the presence of PVP did not affect the profiles of the spectra, except the shoulder at 2.0 eV of P3HT/PVP and optical colors of the solutions are almost the same because of the diluted solution used (see the color of P3HT solution in Figure 1a).

The absorption and emission peaks of both P3HT and P3HT/PVP films appeared at the same wavelengths as shown in Figure 2b, and the peaks were greatly red-shifted as compared to those of the solutions. The reason for the peak shift to lower energy is the self-organization of regioregular (*rr*) P3HT chains, which tend to stack into planar structures known as “lamellae”, which are perpendicular to the film

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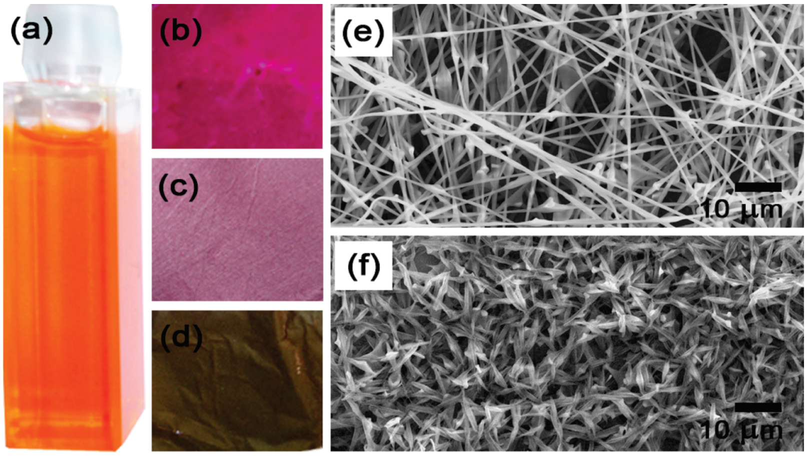

FIGURE 1. (a−d) Optical images and (e, f) SEM images of (a) P3HT solution [0.1% w/v], (b) P3HT film, (c, e) P3HT/PVP composite fibers, and (d, f) P3HT fibers (resulted from Soxhlet extraction of P3HT/PVP composite fibers). Film was prepared by casting from a 2% w/v P3HT solution while P3HT/PVP composite fibers were electrospun from a 6% w/v P3HT/PVP solution (P3HT:PVP = 2:4).

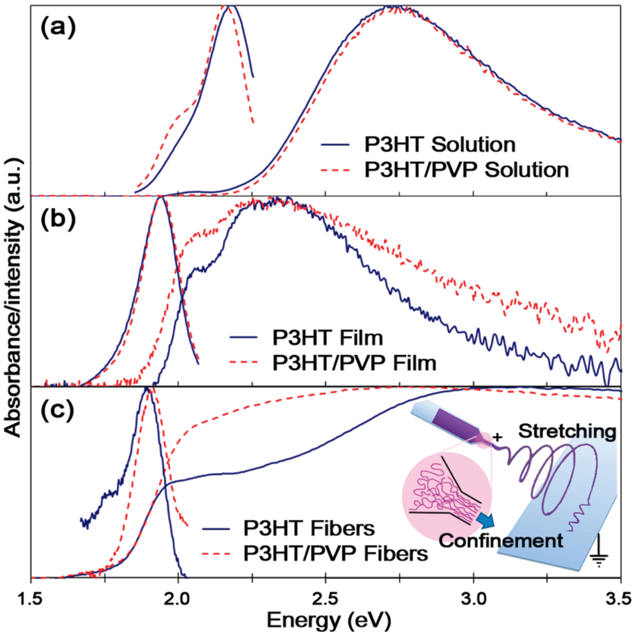

FIGURE 2. Absorption (right) and emission (left) spectra at room temperature of (a) solutions, (b) films, and (c) fiber mats, of pristine P3HT and P3HT/PVP. Excitation wavelength for emission was 520 nm. Concentration for P3HT and P3HT/PVP solutions (in a) were 0.1 and 0.15 (P3HT:PVP = 0.5:1)% w/v, respectively. P3HT film (in b) was prepared by casting from a 2% w/v P3HT solution, whereas P3HT/PVP composite film and fibers (in b and c) were cast or electrospun from a 6% w/v P3HT/PVP solution (P3HT:PVP = 2:4). P3HT fibers (in c) were obtained from Soxhlet extraction of P3HT/PVP composite fibers. Inset is schematic illustration for confinement and stretching in electrospinning.

substrate. Closely packing of the lamellas enables such that of optical and charged excitations adopt interchain character or interplane stacking due to the short interchain interlayer (14). These interchain contributions are believed to be responsible for the distinct shoulder observed on the low-energy side of the absorption maximum (5, 14) in P3HT films. From the results, the distinct shoulders of absorbance spectra are observed at 2.1 eV (Figure 2b).

Absorption peak of P3HT/PVP and P3HT fibers were broader than film, which may due to reduction of anisotropy in the lamellae. However, the distinct shoulders at 2.1 eV are still able to be observed, which indicates that there is high interchain packing in the fibers. Onset of the absorption spectrum is frequently used to estimate the adiabatic transition energy (E_{00}), which is an experimental determination of the S_0−S_1 transition energy in materials with nonmirror symmetric absorption−emission spectra (15). Onset of the absorption spectrum in fibers is lower than that in film (Figure 2b,c), which indicates lower E_{00}. That means longer conjugate length and less steric effects of the alkyl chain in the fibers than that in films which are the results from more tightly packing in molecular chains. Stokes shift, a difference between the positions of the band maxima of the absorption and emission spectra, has been well-discussed in various reports (16). It was found that larger Stokes shift is attributed to less steric effects of the alkyl chains (16) in fibers compared to that in film. These results correspond to the remarkable shift of the emission peaks of the fibers from those of the films. Emission peaks at 1.95 eV as shown in Figure 2b shifted to peaks at 1.90 eV (Figure 2c), indicating closer packing of the lamellas in fibers. The closer packing of P3HT chain lamellas attributed from the orientation of molecular chain along the fiber axis during instability of electrospinning due to nanostructure confinement, electric field, and very large stretching (see inset of Figure 2).

The molecular packing of P3HT fiber driven by electrospinning resulted in the improvement of crystallinity, which was observed by X-ray-diffraction (XRD) measurements. As shown in Fig. 3, the diffraction patterns (diffraction angle $2\theta = 5.3°$ for the (100) peak) indicate that blend and pristine P3HT fibers show a well-organized packing structure with the degree of order, inferred from the peak intensity, higher than films. The diffraction pattern at diffraction angle 2θ of 5.3° from a well-organized structure of *rr*-P3HT was also reported by Kim et al. (1). It should be noted that the secondary peaks in X-ray diffraction pattern of P3HT/PVP or P3HT fibers at diffraction angle 2θ of 11° refer to relatively high crystallinity of PVP in composite fibers and refer to interpolymer face-to-face stacking of the thiophene rings in P3HT fibers (17).

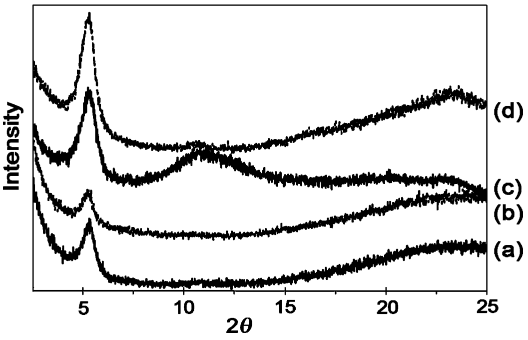

FIGURE 3. X-ray diffraction patterns of (a) pristine P3HT/PVP film, (b) P3HT film, (c) P3HT/PVP fiber mat, and (d) P3HT fiber mat. P3HT film was prepared by casting from a 2% w/v P3HT solution while P3HT/PVP film and fibers were casted or electrospun from a 6% w/v P3HT/PVP solution (P3HT:PVP = 2:4). P3HT fibers were obtained from Soxhlet extraction of P3HT/PVP composite fibers.

Not only UV—vis adsorption, fluorescence, and crystallinity, but difference in molecular packing in fibers as compared to film also affect to HOMO level of the materials. Ionization energy, an estimated HOMO level, of P3HT nanofibers was −5.15 eV, which was lower than that of P3HT film (−5.06 eV) (see the Supporting Information).

In summaries, new strategy to facilitate the fabrication of conjugated polymer fibers with highly oriented structure based on high interchain stacking is reported. For this purpose, electrospinning of a blend polymer system composed of regioregular poly(3-hexylthiophene) (*rr*-P3HT) and poly(vinyl pyrrolidone) (PVP) was carried out. SEM observation revealed that the blend system forms homogeneous nanofibers. This system exhibits the specific feature of strong interchain contribution of P3HT from UV—vis absorption, fluorescence, XRD, and photoelectron spectrometric measurements. We also demonstrate that removal of the PVP component from the mixed fiber of P3HT-PVP through the selective extraction and such strong interchain stacking of pristine P3HT fiber mat can be remarkably maintained. The obtained P3HT nanofibers may be widely applicable for various specific applications, such as photovoltaic cells, thin film transistors, light-emitting diodes, and so on.

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

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