Electrospinning of Flexible Conjugated Polymer Nanofibers with Efficient Luminescence and Electrical Conductivity

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Abstract. Herein, we have successfully applied direct electrospinning method to rigid copolymer F8T2. The electrospun F8T2 nanofibers exhibit high anisotropy, strong photosensitivity and remarkably improved luminescence and electrical conductivity compared to spin-coating analogue. Our work provides a promising avenue for flexible and high-quality display applications.

1. Introduction
π-Conjugated polymers that possess unique electrical and optical properties have been extensively investigated as novel functional materials applied to light-emitting diodes (LEDs), photovoltaic cells (PVs), field-effect transistors (FETs), and phototransistor.[1,2] In particular, one-dimensional (1D) nanostructure semiconducting materials including nanofibers, nanowires, nanotubes, have attracted considerable attention in nanoscale electronics assembly.[3] Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] (F8T2) is reported for the intensive use in FETs due to its large charge-carrier mobility up to 0.1 cm² V⁻¹ s⁻¹ upon uniaxial aligning with a rubbed polyimide film.[4] Several researches on the 1D nano-structural F8T2 semiconducting polymer nanowires, nanofibers, nanopillars were reported.[5,6] For instance, Wakayama reported that F8T2 nanowires obtained by nanochannel effect alignment process exhibited carrier mobilities of 3.5 and 2.8 × 10⁻³ cm² V⁻¹ s⁻¹ for 54 and 130 nm wide nanowires, respectively. The carrier mobilities were about three times larger than that of a thin film transistor, which can be attributed to the enhanced polymer chain alignment in the nanochannels.[5] Redmond prepared F8T2 nanowires with mean diameters of approximately 200 nm and average lengths of approximately 15 μm by template method, which were used for ultraminiature photodetectors and exhibited single-nanowire responsivities of approximately 0.4 mAW⁻¹ under monochromatic illumination.[6] However, these methods entail a delicate control of solution chemistry and in particular the creation of nanowires requires the complicated routes. A facile yet controllable method of generating one-dimensional nanostructures is needed.

Electrospinning is a well-established and straightforward method to obtain 1D nanostructures with diameters in a wide range of 40 nm -2 µm and lengths up to kilometers. Moreover, it possesses the advantages of low cost, flexible morphology tuning, and high-throughput continuous production.[7] One of critical factors that contributes to the spinnability of a polymer is its ability to entangle and interact along its polymer chains during the whipping stage, where elongation occurs. However, most of conjugated polymers has a fairly rigid backbone owing to their high aromaticity, resulting in poor entanglements of polymer chains and thus discontinuous and unstable jet, which cannot be directly used
in electrospinning. In addition, the relatively low molecular weight of conjugated polymers compared to those spinnable polymer, lead to poor molecular chain entanglement. Currently, to the best of our knowledge, there are few conjugated polymers such as poly(3-hexylthiophene) (P3HT), and F8T2, that can be directly used in electrospinning and tend to have large diameters up to several to several ten microns, due to the rigid structures of conjugated polymers, which limited their potential applications in micro to nanoscale electronic and optoelectronic devices.[8] For instance, Borges directly electrospun high molecular weight commercial F8T2 copolymer by using xylene solvent at high temperature ~150 °C. However, the obtained FBT2 fiber exhibiting large diameter of 7~15 μm.

Herein, we successfully obtained F8T2 nanofibers with diameters below 300 nm by directly electrospinning custom-synthesized high-molecular-weight F8T2 copolymer using co-solvent of xylene and chloroform solution. To the best of our knowledge, this is the first report of F8T2 nanofiber with diameter below 300 nm by means of electrospinning without any spinning auxiliaries or conductive additives. For comparison, we investigated the optical, thermal and molecular packing properties of electrospun nanofibers and spin-cast film. Finally, these small-diameter conjugated nanofibers exhibit remarkably improved electrical conductivity by 3 orders of magnitude compared to spin-coating analogue, which could be attributed to their highly anisotropic structures caused by electrostatic field.

2. Results and discussion

Conjugated F8T2 copolymers were synthesized by the Stille coupling reaction as depicted in Figure1a. The chemical structure and molecular weight were characterized by 1H NMR and GPC, respectively. The as-synthesized F8T2 polymer exhibits relatively high molecular weight ($M_w = 60000$ g/mol), which is favorable for the formation of continuous jet in the electrospinning process. As shown in Figure 1b, the preparation of pure F8T2 electrospun nanofibers are performed by using DXES-1 spinning equipment with an applied voltage of 12 kV and a feed rate of 0.3 mL/h with a constant tip-to-collector distance of 12 cm. Temperature and relative humidity were set to 25 °C and 40%, respectively. F8T2 exhibits relatively poor solubility in pure xylene solvent at room temperature. Chloroform is a good solvent for π-conjugated polymers, which is already used as an excellent solvent for preparation of pure P3HT nanofibers while its high volatility can easily cause needle blocking. Therefore, the mixed solvent with xylene and chloroform will have advantages as follows: 1) introduction of chloroform solvent is help for high rigid π-conjugated F8T2 polymer freely dispersion into the solution, making polymer chain effective stretching during electrospun process; 2) introduction of xylene solvent will lead to conglutination between fiber bundles and substrate, which could help to decrease contact resistance and improve stability of the resultant optical or electronic devices; 3) the balanced evaporation of mixed solvents and phase separation before fiber formation is favorable for forming thin nanofibers. Note that we have investigated the effects of different volume ratio of xylene and chloroform (2:1, 1:1, 1:2) on the fiber diameters, and as a result mixed solvent with xylene and chloroform ($v/v = 1:1$) is the optimal ratio giving the smallest fiber diameter below 300 nm. As shown in Figure 1c, the representative field-effect scanning electron microscopy (FE-SEM) images of electrospun nanofibers prepared from F8T2 in xylene/chloroform mixed solvents with concentration of 30 mg/mL. This indicates that the co-solvent with optimum volume ratio not only maintain adhesion between the fiber surface and the substrates, but also prevent the coherence of adjacent nanofibers, leading to formation of thin nanofibers.
Figure 1. (a) Synthetic route of F8T2 copolymer. (b) Schematic description of electrospinning of pure F8T2 nanofibers. (c) SEM images of electrospun fibers at a concentration of 30 mg/mL F8T2 in xylene/chloroform (v/v = 1:1) mixed solvent.

Figure 2 shows the absorption and photoluminescence emission spectra of F8T2 as spin-coated film and electrospinning membrane. As shown in Figure 2a, the absorption peak of electrospun fibers displays an obviously red-shift by ~20 nm compared to that of spin-coated film. This implies that F8T2 nanofibers may have more extended conformation and better delocalized π-conjugation than spin-coated film format. Moreover, the conjugated length of the polymer chain is possibly increased due to the stretching of the liquid jet during the electrospinning process.[9] In addition, compared with the bulk film, F8T2 nanofibers exhibit a notable photoluminescence decrease in intensity (Figure 2b), which may be caused by the increasing degree of interchain interactions during electrospinning process.[10] Moreover, an pronounced shoulder region of 540–570 nm is found in nanofiber, which is caused by less thermodynamically favorable π-stacking conformation resulting from the collapse or aggregate of the hydrodynamic volume of the polymer chains in the xylene-chloroform phase separation.
Figure 2. Absorption and photoluminescence spectra of F8T2 as spin-coated film and electrospun nanofibrous membrane.

To investigate the effect of electrospinning process on molecular packing, X-ray diffraction (XRD) measurement was employed to characterize the crystalline structure of F8T2 in spin-coated film and electrospun nanofibrous membrane, respectively. As shown in Figure 3, the F8T2 film exhibits two main peaks at 5.675° and 21.875°, which corresponds to lamellar peak (100) with distance of 15.56 Å and π-π stacking peak (010) with distance of 4.06 Å, respectively. On the contrast, the distances of lamellar and π-stacking in nanofibers are decreased to 11.78 Å and 3.54 Å, respectively. This indicates that the F8T2 nanofibers preferentially possess a uniform orientation along the fiber axis due to the strong electric field during the electrospinning process.

Figure 3. XRD patterns of F8T2 spin-coated film and electrospun nanofibrous membrane.
We then used polarized optical microscope (POM) measurement to investigate the presence of anisotropic microstructure in the electrospun fibers (Figure 4). The brightness of the POM image is maximized when such an angle is 90° or 0° (Figure 4a,b) while minimized when the angle between the applied field and the polarizer is 45° (Figure 4c). This clear birefringence phenomenon is related to the alignment of the polymer chains during the electrospinning process: during the fiber formation, polymer chains are stretched in the direction of the fiber.[1] In addition, Figure 4d displays fluorescence micrographs of a single F8T2 nanofiber, which shows strong red emission under green light.

Figure 4. Electrospun F8T2 single fiber observed under cross-polars at (a) 0°, (b) 90° and (c) 45° on the 360° graduated circular stage, respectively; (d) Fluorescence microscopy image of F8T2 nanofiber excited under green light. The scale bar is 5 μm.

To investigate the effect of oriented structure of F8T2 nanofibers on electrical properties, we therefore carried out conductivity measurements of electrospun fibers and as-cast film, respectively. Electrospun nanofibers and spin-coated films were deposited on Pt interdigitated electrodes (IDEs) with an electrode spacing of 5 μm. Current−Voltage (I−V) characteristics were acquired by sweeping between −1 and +1 V with a step size of 0.01 V in the dark.

Figure 5 shows dark I−V curves of these two F8T2 structures. Electrospun nanofibers with diameters ~300 nm displays and significantly improved electrical conductivities by 3 orders of magnitude of $1.67 \times 10^{-8}$ S/cm compared to that of spin-coated film of $4.66 \times 10^{-5}$ S/cm. This high electrical conductivity is attributed to the enhanced molecular orientation arising from extensional deformation in the electrospinning process and afterward during solid state drawing.

Figure 5. I−V curves of F8T2 spin-coated film (black) and electrospun fiber (red), showing distinct electrical conductivities.
3. Conclusions
In conclusion, we have successfully used the co-solvent to prepare pure F8T2 nanofibers by electrospinning method without any spinning auxiliaries. The obtained F8T2 nanofibers show ultrafine diameter below 300 nm, exhibiting favorable thermal, optical and electron conductivity properties. XRD results showed that F8T2 nanofibers are stretched axially during the strong electric field of the electrospinning process and therefore preferentially possess a uniform orientation along the nanofiber axis. PL spectra indicated that F8T2 fibers exhibit strong photosensitivity and photoluminescence. More importantly, the conductivity of electrospun F8T2 fibers with small diameter is higher than that of the as-cast film, owing to the more extended conformation and better delocalized π-conjugation of molecular chain distribution within the nanofibers than in the bulk film. Our work provides a promising avenue for flexible and high-quality display applications.

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