

# Fabricating polythiophene into highly aligned microwire film by fast evaporation of its whisker solution

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## ABSTRACT

A facile template-free approach to fabricate poly(3-hexylthiophene) (P3HT) into highly aligned microwire film on a large scale via the evaporation of P3HT/Anisole whisker solution has been developed. The microwires in the film typically have the height of 0.8–1.4  $\mu\text{m}$ , width of 2–4  $\mu\text{m}$  and length of 50–1000  $\mu\text{m}$ . X-ray Diffraction and Selected-Area Electron Diffraction results suggest that each microwire is a single crystal with the reduced packing distance of P3HT chains along the  $\pi$ – $\pi$  stacking direction ( $d_{[010]}$  of 6.5 Å) and the interchain direction ( $d_{[100]}$  of 15.7 Å). The closer packing of P3HT chains is likely the key factor promoting the formation of the highly aligned microwires. The aligned P3HT microwire films perform enhanced electrical conductivity, and show no substrate dependence, thus can be fabricated into organic electronic devices in situ.

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## 1. Introduction

One-dimensional (1D) aggregation along the  $\pi$ – $\pi$  stacking direction in conjugated polymers will maximize the intermolecular coupling, leading to the formation of nanowires, nanotubes and microwires [1–4], which is supposed to efficiently improve the carrier mobility of conjugated polymers to promote them to become good candidates for the applications in organic electronic devices [5,6]. Furthermore, unidirectional aligning nanowires or microwires on a large scale by an easy and low-cost method is not only crucial to fundamental researches but also positive to commercial applications [7]. On the other hand, because of the weak intermolecular interactions between polymer chains largely based on Van der Waals interaction [8] and the difficulties to achieve completely smooth surface at nanoscale [9], polymer chains may easily become entangled during the growth, resulting in a trouble to control them packing and orientating into well-defined 1D morphologies from nanoscale to microscale. Therefore it remains a huge challenge to obtain mass production of aligned conjugated polymer nanowires or microwires. In addition, the organic device fabrication process usually consists of two individual steps, which are the preparation of well-defined 1D structure and the fabrication of the 1D structure into devices. Both of these steps

demand a great deal of careful treatments, and how to simplify these steps is another challenge concerning the application of the conjugated polymer nanowires or microwires.

Regioregular poly(3-hexylthiophene) (P3HT), one of the most important conjugated semiconductor polymers because of its high field-effect mobility ( $0.01$ – $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [10], solution processibility and chemical stability [11], has been extensively investigated in organic field-effect transistors, polymer solar cells, and biological sensors. Charge carriers in P3HT film mainly transfer in the coplanar plane consisting of the  $\pi$ – $\pi$  stacking direction and the polythiophene backbone direction [5], with insulating hexyl side chains perpendicular to the plane preventing charge carriers transporting along the side chain direction. Hence, the highly oriented fibrillar structure packing along the  $\pi$ – $\pi$  stacking direction will provide fewer insulating grain boundaries in the charge transport plane [3], leading to higher carrier mobility. Among the varieties of fibrillar structure producing methods, such as thermal annealing [12], directional epitaxial solidification [13,14], solvent vapor annealing [15,16], electro-spinning [17] and Langmuir–Blodgett method [18], the whisker method [19] provides an easy and mass production of high quality crystalline nanowires by the self-assembly of conjugated polymers during precipitation from poor solvents [20,21]. However, the whisker method also has limitations in developing 1D alignment, because the whiskers originated in organic solvents can be hardly arrayed orderly in solution state. Other attempts to fabricate 1D aligned structures by template assisted assembly [16,22] and external electric assisted assembly

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[17,23] require additional apparatuses and processes, and often suffer from transferring the nanowire or microwire films to substrates for device fabrications.

Herein we report a facile, template-free and mass production of 1D oriented alignment of P3HT microwires from P3HT/Anisole whisker solution via the solvent evaporation-induced self-assembly. The combination of the whisker method and the solvent evaporation method enables P3HT directly self-organize into high quality and large scale microwire films on different solid substrates, which align orderly without paying special attention to solvent vapor pressure, and can be fabricated into devices in situ. The current–voltage ( $I$ – $V$ ) measurements reveal that the aligned P3HT microwire films indeed exhibit greatly improved electrical conductivity.

## 2. Experiment

### 2.1. Materials and purification

Regioregular P3HT was synthesized by a modified Grignard metathesis procedure [24,25] and Soxhlet extracted with methanol, hexane and chloroform. The chloroform fraction was dried in vacuum oven at 70 °C for 24 h to get purified regioregular P3HT ( $M_n = 19\,800$ , PDI = 1.2, Regularity > 98.5%).  $^1\text{H NMR}$  (300 MHz)  $\delta$  [ppm] 6.98 (s, 1 H), 2.80 (t, 2 H), 1.70 (m, 2 H), 1.44 (m, 2 H), 0.92 (t, 3 H). Anhydrous anisole (99.7%) was purchased from Sigma–Aldrich and used without further purification. Chloroform was purchased from Shanghai Dahe Chemical Company and used without further purification. Glass covers ( $24 \times 24 \text{ mm}^2$ ) used as solid substrates were pre-cleaned by washing with detergent, de-ionized water, acetone, isopropyl alcohol and de-ionized water in succession, dried in vacuum oven at 70 °C.  $\text{SiO}_2/\text{Si}$  substrates were pre-cleaned with  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  (7:3 in volume) solution, de-ionized water and ethanol, dried in vacuum oven at 70 °C. Platinum foils (99.9%, 0.025 mm thick) used as electrodes in  $I/V$  measurements were purchased from Sigma–Aldrich.

### 2.2. Preparation of P3HT microwires

P3HT microwire films were fabricated by a combination of the whisker method and the solvent evaporation method [26]. In general, P3HT (2 mg) was added to anisole (20 ml), and the solution was stirred at 90 °C for 0.5 h until the P3HT completely dissolved to get a transparent orange solution. Then the P3HT solution (0.1 mg/ml) was cooled and stored at 25 °C for at least 2 months to achieve

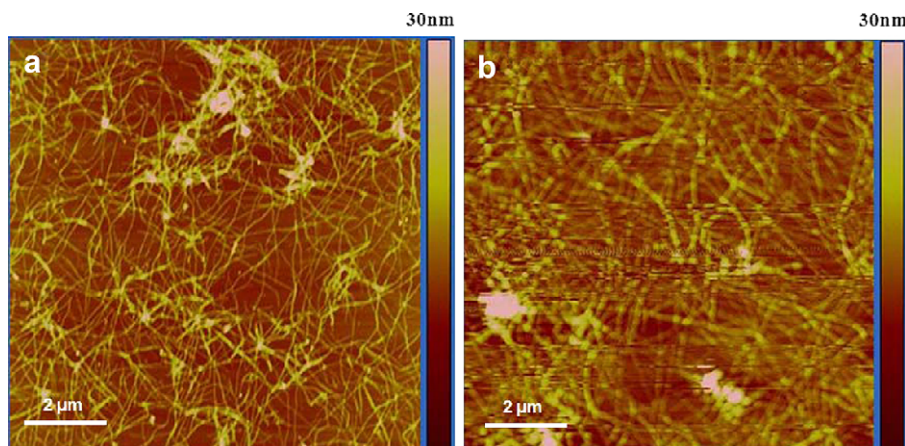
equilibrium state, whose color turned to translucent brown purple. After that, the P3HT solution (0.4 ml) was drop-cast onto a  $24 \times 24 \text{ mm}^2$  glass cover followed by fast evaporation in vacuum oven (Vacuum Degree < 133 Pa) at 25 °C for 2 h, and highly aligned P3HT microwires appeared on the glass substrate. When the evaporating time was reduced to 40 min, a supersaturated P3HT solution first formed, and then slow evaporation of the supersaturated solution at ambient condition for 2 days resulted in randomly oriented P3HT microwires.

### 2.3. Characterization

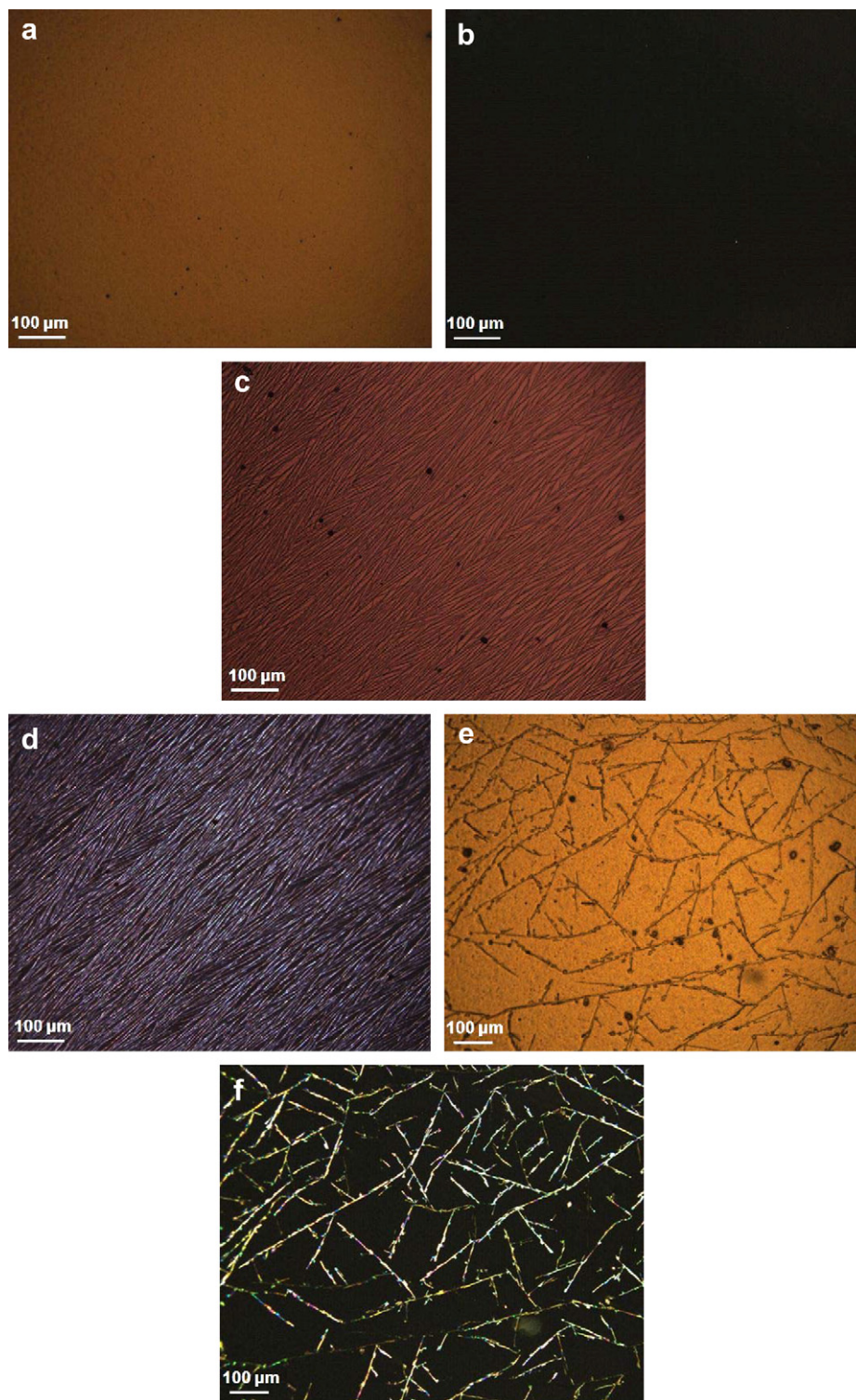
Optical microscopy (OM) and Polarized optical microscopy images (POM) were obtained using an OLYMPUS BX51 microscope equipped with a PixeLINK PL-A662 Megapixel Firewire Camera. Scanning electron microscopy (SEM) was performed on a Tescan TS 5136 MM scanning electron microscope operating at 20 KV. Atomic force microscopy (AFM) was performed on a Veeco Multimode AFM Nanoscope IV in tapping mode. Selected-area electron diffraction (SAED) patterns were obtained using a JEOL JEM-2100F transmission electron microscope operating at 200 kV, and the thin areas on the edges of the microwire were chosen to obtain the diffraction patterns. X-ray diffraction (XRD) data were collected by a PANalytical X'Pert PRO X-ray diffractometer using  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) operating at 40 kV and 40 mA. UV–vis absorption spectra were recorded on Perkin Elmer Lambda 35 and 900 UV–vis spectrophotometers.  $I$ – $V$  measurement was performed by coating the film on two platinum electrodes with an interval of 0.5 mm, and Ohmic contact was established between the film and electrodes. All films for the UV–vis absorption spectra and  $I/V$  characterization measurements were prepared from the same P3HT/Anisole solution.

## 3. Results and discussion

Anisole plays an important role in the growth of P3HT microwires since it provides proper surroundings for the self-seeding process by which P3HT chains self-organize into 1D whiskers via  $\pi$ – $\pi$  interaction. Further organization of P3HT into aligned 1D microwires can be induced via the subsequent solvent evaporation of the whisker solution. In a typical experiment, P3HT self-seeded when the solution cooled from 90 °C to room temperature, followed by solution crystallization at 25 °C over 2 months. In order to disclose the solution crystallization process, the P3HT/Anisole whisker solution was spin-cast onto the  $\text{SiO}_2/\text{Si}$  substrate, leading



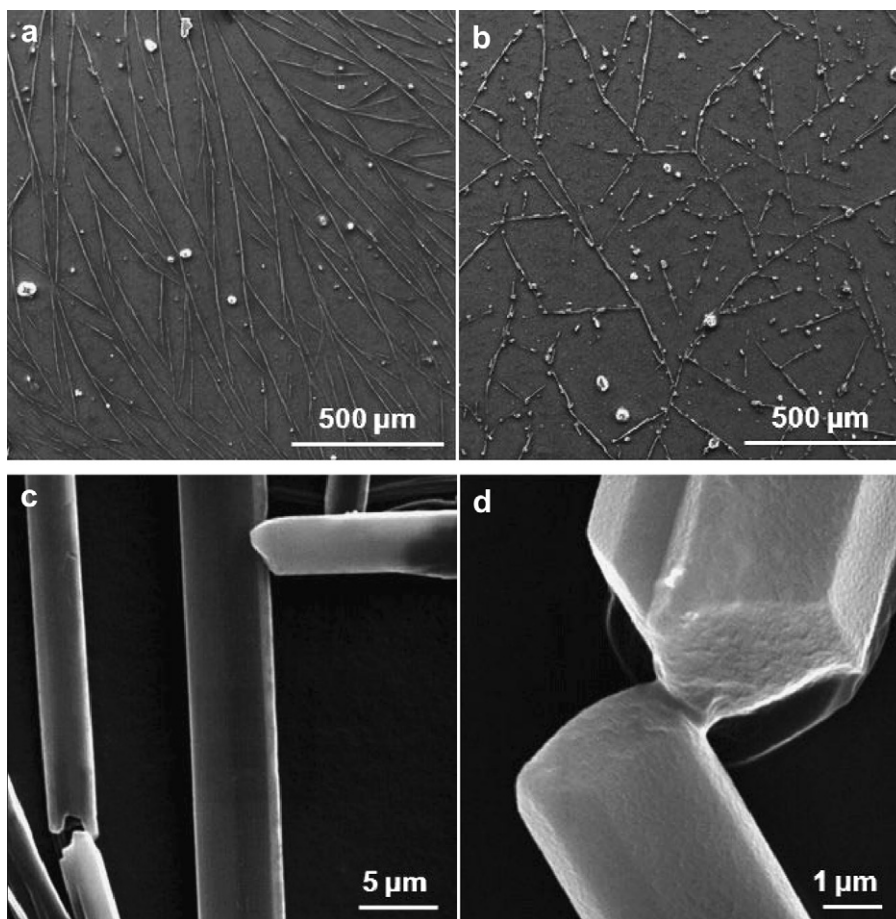
**Fig. 1.** AFM images of P3HT whiskers. The whiskers were prepared in 0.05 mg/ml P3HT/Anisole solution, and then spin-cast at 3000 rpm onto the  $\text{SiO}_2/\text{Si}$  substrate. (a) The height image of P3HT whiskers obtained from fresh prepared P3HT/Anisole solution. (b) The height image of P3HT whiskers obtained from the P3HT/Anisole solution stored at 25 °C for 2 months.



**Fig. 2.** Morphological features of P3HT microwire films. All films were prepared from 0.1 mg/ml P3HT/Anisole solution. (a) OM image and (b) POM image of P3HT film on the glass cover with no microwires. The film was prepared by drop-casting 0.4 ml fresh prepared solution followed by the fast evaporation. (c) OM image and (d) POM image of highly aligned P3HT microwire film on the glass cover showing the microwires all oriented along the same direction. The film was prepared by drop-casting 0.4 ml P3HT/Anisole solution stored for 2 months followed by the fast evaporation. (e) OM image and (f) POM image of randomly oriented P3HT microwires on the glass cover. The film was prepared by drop-casting 0.4 ml P3HT/Anisole solution stored for 2 months followed by the slow evaporation.

to the formation of dense network of P3HT whiskers as shown in Fig. 1, which implied that the P3HT in the film inherited its morphology in the solution [26], and mass P3HT whiskers had already been stably dispersed in the solution phase. For the fresh prepared whisker solution (Fig. 1a), the height image clearly shows

that the whiskers are uniformly distributed on the substrate, and each whisker grows to several microns long with homogenous widths in the range of 90–130 nm. However, for the whisker solution stored for 2 months (Fig. 1b), the widths of the whiskers extend to the range of 180–210 nm and more whiskers are present



**Fig. 3.** SEM images of P3HT microwires. (a) SEM image of the aligned P3HT microwires on the glass cover produced by fast evaporation in vacuum oven for 2 h. (b) SEM image of the randomly oriented P3HT microwires on the glass cover produced by slow evaporation at ambient pressure for 2 days. (c) SEM image showing that the aligned P3HT microwires have uniform widths and high quality crystal morphology. (d) SEM image showing the cross-sections of aligned P3HT microwires with well-defined facets.

compared with that from the fresh prepared solution. It is believed that the longtime crystallizing process in solution leads to further growth or mergence of the whiskers in anisole [27]. Note that further growth of whiskers made the AFM image a little blurred, which also appeared in repeated experiments.

The longtime solution crystallizing process in anisole is necessary and crucial to the subsequent formation of P3HT microwires via evaporation, judging from the absence of microwires by evaporating fresh prepared P3HT/anisole whisker solution. Hence, anisole not only acts as an appropriate solvent for the effective precipitation of P3HT into whiskers but also allows the solution crystallization of P3HT, which leads to better packed structures. As will be shown later, XRD results indeed reveal that the P3HT chains self-assemble into well-organized  $\pi$ - $\pi$  stacking structures in the microwires. The stable dispersion of P3HT whiskers in anisole without macroscopic precipitation even 2 months later facilitates the solution crystallizing process. The growth of microwires from other poor solvents, such as cyclohexane, hexane and toluene via the whisker method [26], was not observed. Usually, in such poor solvents, P3HT whiskers precipitated within a few days or even several hours at room temperature.

Evaporation rate of the solvent is another key factor to the growth of aligned P3HT microwires. In fact, evaporation-induced self-assembly has recently been found to be a facile way to fabricate aligned organic fibers using conjugated small molecules [7,9], and here we firstly demonstrate that it is also a potential approach to fabricate highly aligned conjugated polymer microwires. Different

from the growth of small molecule fibers, a long enough solution crystallizing process before evaporation is necessary for the growth of P3HT microwires, as we mentioned above. Fig. 2a and b show that no microwires formed on the surface of glass cover after the solvent evaporation of the fresh prepared whisker solution. However, large areas of aligned microwires emerge on the substrate (Fig. 2c) after the solvent evaporation of the whisker solution stored at 25 °C for two months. The microwires prepared in Fig. 2c are dense and highly aligned without twisting. The alignment area in which all microwires align in one direction can extend to millimeters in length and width. In the experiment, it is often to see only one alignment area can cover the whole glass cover ( $24 \times 24 \text{ mm}^2$ ) in the same orientation. Polarized optical microscopy in Fig. 2d shows that the P3HT chains nucleate and pack along the same direction, giving rise to highly ordered microwires with good optical transparency under polarized light.

There are two stages in the solvent evaporation process, one is that the solution reaches supersaturated state with the evaporation of anisole, followed by the P3HT chains crystallizing into 1D microwires under the control of  $\pi$ - $\pi$  interaction after further evaporation of the supersaturated P3HT/Anisole solution. At the latter stage, fast evaporation in vacuum oven for 1 h leads to the formation of aligned microwires, and slow evaporation at ambient pressure for 2 days leads to the formation of randomly oriented microwires as shown in Fig. 2e and f. The randomly oriented microwires do not contact with each other as closely as the aligned microwires, and thus cover less area of the substrate with large free space between each other.

Therefore, it can be concluded that the slow evaporation produces not only disordered arrangement but also less amounts of microwires. The growth of the microwires, especially the alignment of microwires, is more likely a kinetically controlled process considering that it only operates efficiently by the fast solvent evaporation.

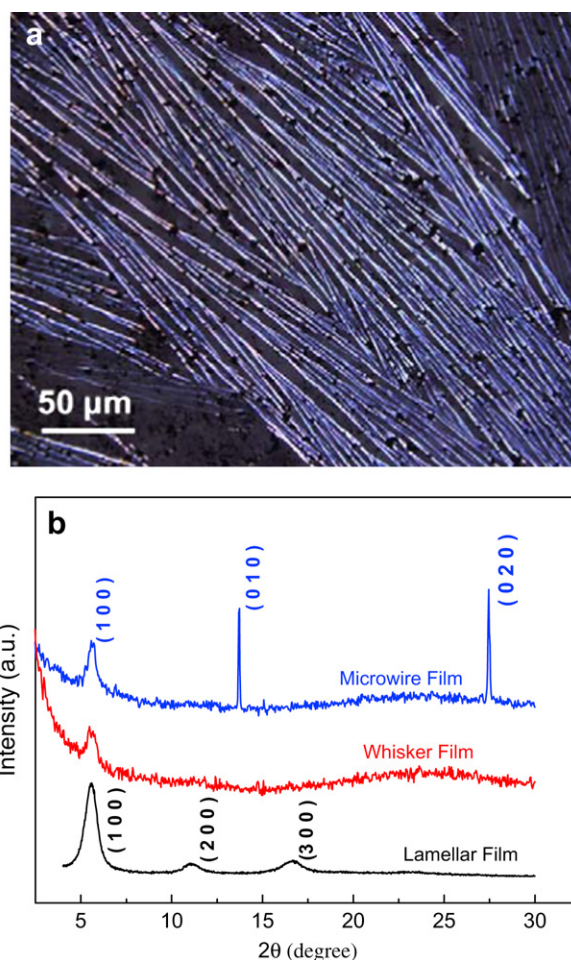
The detailed morphology of the microwires is further characterized by SEM, which is shown in Fig. 3a that the aligned microwires branch off in the growing direction, while the branches still prefer to array along the same direction with the trunk microwires. The trunk microwires are defined as the microwires extending along the same direction more than 500  $\mu\text{m}$  without branching. In this work, the lengths of most trunk microwires are in the range of 500–1000  $\mu\text{m}$ , and the branch microwires typically have shorter lengths in the range of 50–200  $\mu\text{m}$ . It is worth to note that the aligned microwires with branches potentially are of great benefit to achieving high carrier mobility in the whole film, since the association of the carrier transport in ordered domain and the grain-to-grain dominated charge hopping can form high-mobility percolation path, and at the same time the volume of amorphous structure in the film is also decreased [28]. In contrast, the lengths of the randomly oriented microwires in Fig. 3b are in the range of 50–500  $\mu\text{m}$ , much shorter than that of the aligned microwires. The aligned microwires have the widths in the range of 2–4  $\mu\text{m}$  as shown in Fig. 3c, while the randomly oriented microwires do not have regular shape in the growth direction as if there is a lack of development into well-grown morphology. According to the cross-section image shown in Fig. 3d, the microwires have well-defined facets with regular shapes. Nonetheless, for simplicity, we will still use height and width as the parameters to roughly estimate the dimensions of the microwires. The typical dimension parameters of the aligned microwires are 0.8–1.4  $\mu\text{m}$  in height, 2–4  $\mu\text{m}$  in width, and 50–1000  $\mu\text{m}$  in length. The P3HT microwires prepared from anisole are able to align into 1D structure on glass,  $\text{SiO}_2/\text{Si}$  and KBr substrates, implying that the aligned microwire films can be produced on a large scale independent of the substrates, which is more suitable to be fabricated into organic electronic device in situ.

The XRD pattern of the aligned P3HT microwire film in Fig. 4 shows the appearance of the [0 1 0] and [0 2 0] peaks, which are attributed to the mass formation of aligned microwires as they are absent in both the P3HT whisker film prepared from anisole and the P3HT lamellar film without fibrillar structures from chloroform. The  $\pi$ – $\pi$  stacking distance of aligned P3HT microwires obtained from the XRD pattern, with [0 1 0] reflecting a d-spacing of 6.50  $\text{\AA}$  and [0 2 0] reflecting a d-spacing of 3.25  $\text{\AA}$ , is in agreement with the SAED result shown later. Compared to the normal P3HT edge-on orientation, the  $\pi$ – $\pi$  stacking distance in the aligned microwires decreases slightly from 3.8  $\text{\AA}$  to 3.25  $\text{\AA}$ , accompanied with the [0 2 0] diffraction peak shift from 23° to 27°, indicating a much closer packing of the P3HT chains in the growth direction. Similar results were reported in PBTDT [29], in which the  $\pi$ – $\pi$  stacking distance of the polythiophene backbones shrank from 3.8  $\text{\AA}$  to 3.3  $\text{\AA}$  after thermal annealing. Considering the  $\pi$ – $\pi$  stacking distances of polythiophene backbones being independent of the length of the side chains [26], the closer packing found in this work is the same as that in PBTDT. The interchain distance  $d_{[100]}$  of the P3HT packing also decreases from 16.6  $\text{\AA}$  in the lamellar film to 15.7  $\text{\AA}$  in the aligned microwire film (calculated using the Bragg's equation). Such decrease of  $d_{[100]}$  was also reported in the P3HT film from 16.5  $\text{\AA}$  to 15.6  $\text{\AA}$  with the addition of 1,8-octanedithiol [30], as well as in the PBTDT film from 20.5  $\text{\AA}$  to 15.6  $\text{\AA}$  after thermal annealing [29], which indicates that the P3HT chains are also better packed along the interchain direction in the aligned microwires.

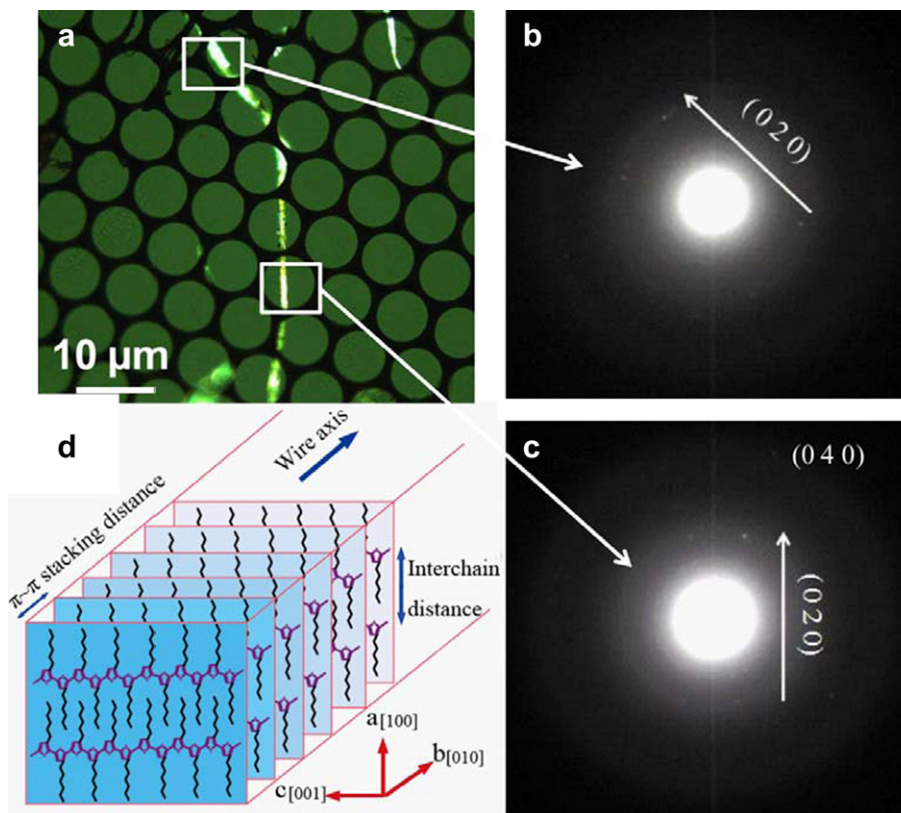
The aligned P3HT microwire film was lifted apart the glass cover by dipping in water, transferred onto a copper grid (Fig. 5a), and characterized by the selected-area electron diffraction (SAED). It is

hard to obtain clear diffraction spots as the microwires are about 1  $\mu\text{m}$  thick, and we select the thin areas on the edges to get the diffraction patterns, in which we can see [0 2 0] and [0 4 0] diffraction spots in Fig. 5b and c. The SAED patterns obtained from different parts of the same microwire show that the microwire is a single crystal, and the diffraction spots are equivalent to a repeating period of 3.25  $\text{\AA}$  along the [0 2 0] direction, which is the  $\pi$ – $\pi$  stacking direction [29,31]. The SAED patterns indicate that the P3HT microwires are high quality crystals adopting the edge-on orientation, in which the  $\pi$ – $\pi$  stacking direction is parallel to the substrate, as depicted in Fig. 5d.

Combining the XRD and SAED results, it can be concluded that the aligned P3HT microwire owns a more coplanar plane structure, in which P3HT chains are both better packed along the  $\pi$ – $\pi$  stacking direction and the interchain direction [32]. We expect the closer packing coplanar structure will greatly enhance the charge carrier transport efficiency. Although further crystallographic studies on well-grown P3HT crystals are needed before the exact crystalline parameters can be obtained, reasonable lattice parameters for the aligned P3HT microwires can now be given as:  $a \sim 15.70 \text{\AA}$ ,  $b \sim 6.50 \text{\AA}$  and  $c \sim 8.36 \text{\AA}$  based on the orthorhombic crystal unit [33] as shown in Fig. 5d.



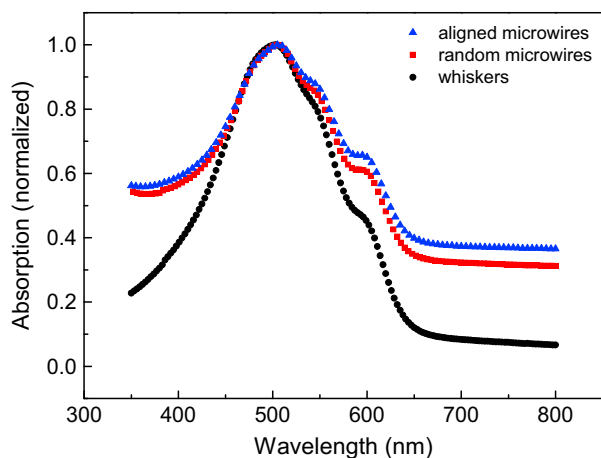
**Fig. 4.** Crystalline structure characterizations of the P3HT films with different morphologies. (a) POM image of the aligned P3HT microwires showing uniform optical transparency under polarized light. (b) XRD patterns of P3HT films prepared from P3HT/ $\text{CHCl}_3$  solution and P3HT/Anisole solution with different morphologies. The appearance of [0 1 0] and [0 2 0] peaks is due to the mass formation of aligned 1D P3HT microwires.



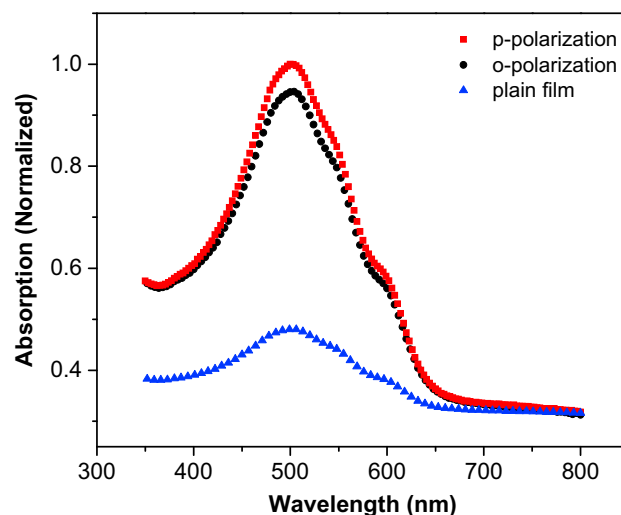
**Fig. 5.** SAED patterns of the aligned P3HT microwire. (a) POM image of the aligned P3HT microwire transferred onto a copper grid. (b) and (c) SAED patterns of the P3HT microwire in the panes of (a) showing that the microwire is a single crystal with preferential growth along the  $[0\ 2\ 0]$  direction with a repeating period of 3.25 Å. (d) Schematic representation of the self-assembly of P3HT chains into microwires.

Two factors may result in the closer packing of P3HT chains in the microwires. One is attributed to the difference between the solubility parameter  $\delta$  of P3HT and that of anisole [26,34]. For a polymer, it can be readily dissolved in a solvent if their  $\delta$  difference is small. The  $\delta$  of P3HT can be divided into two parts: one is the  $\delta$  of the thiophene rings, with a value of  $9.8\text{ cal}^{1/2}\text{ cm}^{-3/2}$  at room temperature; the other is the  $\delta$  of hexyl side chains, with a value of  $7.3\text{ cal}^{1/2}\text{ cm}^{-3/2}$  at room temperature. The P3HT can hardly dissolve in nitromethane due to the  $\delta$  of nitromethane ( $11.1\text{ cal}^{1/2}\text{ cm}^{-3/2}$ ) is far from both that of thiophene rings and hexyl chains, while P3HT

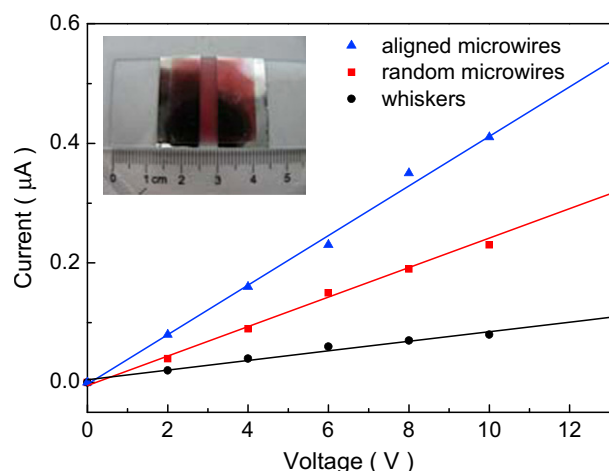
can easily dissolve in chloroform as both the  $\delta$  of thiophene rings and hexyl chains are close to that of chloroform ( $9.3\text{ cal}^{1/2}\text{ cm}^{-3/2}$ ). In contrast, the  $\delta$  of anisole is  $9.5\text{ cal}^{1/2}\text{ cm}^{-3/2}$ , which is closer to that of thiophene rings but farther from that of hexyl chains compared with chloroform. Therefore, it is reasonable that the P3HT chains tend to well-defined 1D aggregation under



**Fig. 6.** Normalized UV–vis absorption spectra of P3HT films with different morphologies. All films were prepared from the same P3HT/Anisole solution with a concentration of 0.1 mg/ml, and the thicknesses of the films were controlled by drop-casting same volume (0.4 ml) solution on the glass covers.



**Fig. 7.** Polarized UV–vis absorption spectra (black and red) of the aligned P3HT microwire film and plain P3HT film (blue) without surface morphology, in which the o-polarization (black) indicates the polarization of light is orthogonal to the microwire growth direction while the p-polarization (red) indicates the parallel direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** I/V measurements of the P3HT films with different morphologies. The measurements were performed in situ on the platinum electrodes, with the same intervals of 0.5 mm as shown in the inset. All films were prepared from the same P3HT/Anisole solution with a concentration of 0.1 mg/ml, and the thicknesses of the films were controlled by drop-casting same volume (0.4 ml) solution on the glass covers.

solvophobic interactions, which maximizes the  $\pi$ - $\pi$  stacking interaction between the thiophene rings [2]. Another factor is the longtime crystallizing process in solution. The closer  $\pi$ - $\pi$  stacking in the microwires implies that the intermolecular interaction between the  $\pi$ -conjugated P3HT in anisole is enhanced. In fact, the whisker solution stored for 2 months has already exhibited decrease in the interchain distance, which is consistent with the report that the annealing process can lead to reduced packing distance of interchains in P3HT [29,35]. The enough long solution crystallizing process allows P3HT chains pack densely as much as possible, and then the enhanced  $\pi$ - $\pi$  interaction of PHT chains effectively drives the mass growth of aligned microwires during the solvent evaporation.

Normalized UV-vis absorption spectra of the whisker film and microwire film at room temperature are shown in Fig. 6, in which three typical absorption peaks in solid P3HT are observed. All three types of P3HT films with different morphologies have the same type of UV-vis absorption curve, and each curve has three peaks at 510 nm, 550 nm and 610 nm. The peak at  $\lambda = 510$  nm is due to the intrachain  $\pi$ - $\pi^*$  transition of P3HT, a related absorption maximum was  $\lambda = 450$  nm in good solvent [3]. The peak at  $\lambda = 550$  nm is from the absorption of extended conjugated length because of the ordered packing of P3HT backbone in the solid state. The peak at  $\lambda = 610$  nm is attributed to the absorption of the interchain transition of P3HT, which is related to the degree of interchain order [36,37]. The increases of the absorptions at  $\lambda = 550$  and 610 nm with the growth of aligned P3HT microwires confirm that the aligned P3HT microwires have longer conjugation length and higher degree of interchain order than that of the randomly oriented microwires and nanowires.

Fig. 7 is the polarized UV-vis absorption spectra of the aligned P3HT microwire film and plain P3HT film without surface morphology. For the plain film prepared by drop-casting fresh prepared solution followed by the fast evaporation, the absorption intensities of the p-polarization and o-polarization are nearly the same, thus we only show the absorption intensity of the p-polarized light. For the microwire film, the absorption intensity of p-polarization is only slightly higher than that of o-polarization, indicating that our microwires do not show a high out-plane or in-plane anisotropy in the microwires. This is significantly different from the polarized UV-vis absorption spectra of the friction-transferred

P3HT and P3DDT films [32], in which a large anisotropy in absorption regarding the drawing direction of friction-transfer was observed, indicating the polymer backbones were arranged parallel to the drawing direction. However, in our case it seems that the P3HT backbones are not parallel to the microwire growth direction, the detailed molecular packing within a single microwire is complicated and remains to be investigated. What we can conclude from the polarized UV-vis absorption spectrum is that, in the microwire film, there is much more in-plane and out-plane anisotropy than the film without microwires, as the absorption intensity of p-polarization in the microwire film is much higher than that in the plain film.

To investigate the possibility of the aligned P3HT microwire film applied in organic electronic devices, the current-voltage (I-V) measurement of the microwire and whisker films was performed in situ on glass covers with platinum electrodes to evaluate their electrical conductivity characteristics. As shown in Fig. 8, the contacts between the P3HT films and platinum electrodes are Ohmic contacts, and the electrical conductivities in P3HT microwire films are greatly increased, especially in the aligned P3HT microwire film. The increased electrical conductivities demonstrate that the highly ordered crystallites and preferential chain orientation in the  $\pi$ - $\pi$  stacking direction indeed promote the efficient long-range migration of the carriers inside the microwires, because the effective intermolecular  $\pi$ -electron delocalization due to the extended chain order and conjugation length in the aligned microwires are in favor of high carrier mobility [38]. A maximum current of 0.41  $\mu$ A at 10 V is obtained in the aligned microwire film, suggesting that it can be readily used in organic electronic devices [3,39,40], and we expect that better electrical properties may be achieved in more optimized electronic devices such as organic field-effect transistors.

#### 4. Conclusion

To summarize, we developed a facile method to realize the self-assembly of conjugated polymers into highly aligned microwires by the combination of the whisker method and the solvent evaporation method without using templates. The investigations on morphology and crystalline feature of the microwires suggest that three external conditions are crucial to the growth of aligned microwires, which are, suitable solvent with appropriate solubility parameter, long enough solution crystallizing process and fast solvent evaporation procedure. Furthermore, the better packed structures along the  $\pi$ - $\pi$  stacking direction and the interchain direction are two key factors that promote the growth of the aligned microwires. The aligned P3HT microwire film performs good electrical conductivity property due to the high interchain order and long conjugation length. Such aligned P3HT microwire film can be prepared on different solid substrates, which makes our approach to be a potentially facile method for the preparation and fabrication of aligned conjugated polymers into organic electronic devices in situ.

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