Convenient fabrication of conjugated polymer semiconductor nanotubes and their application in organic electronics

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Organic heterojunction is indispensable in organic electronic devices, such as organic solar cells, organic light-emitting diodes and so on. Fabrication of core–shell nanostructure provides a feasible and novel way to prepare organic heterojunction, which is beneficial for miniaturization and integration of organic electronic devices. Fabrication of nanotubes which constitute the core–shell structure in large quantity is the key for the realization of application. In this work, a simple and convenient method to prepare nanotubes using conjugated copolymer of perylene diimide and dithienothiophene (P(PDI-DTT)) was demonstrated. The relationship between preparation conditions (solvent atmosphere, solution concentration and pore diameter of templates) and morphology of nanostructure was studied systematically. P(PDI-DTT) nanotubes could be fabricated in regular shape and large quantity by preparing the solution with appropriate concentration and placing anodic aluminium oxide template with nanopore diameter of 200 nm in the solvent atmosphere. The tubular structure was confirmed by scanning electron microscopy. P(PDI-DTT) nanotubes exhibited electron mobility of 0.02 cm² V⁻¹ s⁻¹ in field-effect transistors under ambient condition. Light-emitting nanostructures were successfully fabricated by incorporating tetraphenylethylene into polymer nanotubes.
1. Introduction

Study on organic semiconductors is in the ascendant, in virtue of diversity and easy tailoring of organic molecules [1–3]. Progressively, organic electronic devices based on organic semiconductors exhibited characteristics of light weight, low cost and flexibility [4], such as organic solar cells (OSCs) [5–7], organic light-emitting diodes (OLEDs) [8–10], organic light-emitting transistors (OLETs) [11–13] and so on. Indispensable component of the above devices is active layer which usually adopts organic semiconductor heterojunction that consists of at least two kinds of semiconductor. Organic semiconductor heterojunction played corresponding roles in different devices. In OSCs, different organic semiconductors that constitute heterojunction take part in the process of light absorption and exciton diffusion, and charge separation takes place at the interface of the two materials. In OLEDs and OLETs, certain materials transport charge carrier, while others give out light and the interfaces in the heterojunction have a great effect on the charge injection. Consequently, organic heterojunction is attracting more and more research interest [14–16].

Preparation of organic semiconductor heterojunction is the foundation of application and functionality for organic electronics. Bulk heterojunction is the most common which could be obtained by processing mixture of semiconductors in solution or co-evaporating semiconductors in vacuum, and therefore, the heterojunction exists in the whole structure. Layer-by-layer heterojunction could be obtained by depositing semiconductors one layer after another and the heterojunction takes up a small fraction of the whole architecture and the function of charge transport is performed by the respective layer [9,11]. Bulk heterojunction is generally adopted by OSCs [17], while layer-by-layer heterojunction is ordinarily used in OLEDs and OLETs [11,18]. Similarly, core–shell structure at nanometre scale provides a novel idea for construction of organic heterojunction, in which each component is continuous to ensure high charge carrier transport mobility. Moreover, nanostructure is propitious for integration and miniaturization of organic electronic devices.

Nanotubes could be used as either the core or the shell in the core–shell structure and some semiconductor nanotubes have been prepared [19–22]. Amphiphilic organic small molecules were the most used, and they can self-assemble to form nanotubes through supramolecular interaction [21–25]. An achiral π-conjugated fluorinated fused pyrazine derivative spread at the air/water interface can form nanotubes with lateral compression of 70 mN m⁻¹ [20,26]. Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] nanorods could be transformed from nanorods to nanotubes upon thermal annealing beyond melting point [27]. However, there were not many kinds of materials developed to prepare nanotubes, and the preparation methods were relatively homogeneous. Charge transport property was not investigated which is one of the crucially important characteristics of organic semiconductors.

A conjugated copolymer of perylene diimide and dithienothiophene (P(PDI-DTT)) (structural formula of which is shown in figure 1a) is suitable for solution processing, and exhibits fine charge transport characteristic and excellent light absorption property [28]. It has been used as semiconductor layer in organic field-effect transistors (OFETs), the highest mobility of which reached 0.06 cm² V⁻¹ s⁻¹ [29]. P(PDI-DTT) was also used as electron acceptor to prepare bulk p–n heterojunction in OSCs and the highest power conversion efficiency reached 3% [28,30]. P(PDI-DTT) showed a wide range of application in organic optoelectronics [31].

Fabrication of P(PDI-DTT) nanotubes to study their charge transport property and preparation of corresponding heterojunction are of great interest in terms of fundamental and application research. Wetting of anodic aluminium oxide (AAO) templates is a commonly used method to prepare one-dimensional nanomaterials [32]. Employment of polymer solution rather than polymer melt is more economic.

In this work, solution with moderate concentration, pore with appropriate diameter and structure and solvent atmosphere were selected as the preparation conditions. The solution flowed into nanopores favourably, and evaporated slowly. P(PDI-DTT) nanotubes of regular shape came into being and exhibited electron transport property in FET measurement. Blend solution of P(PDI-DTT) and tetraphenylethylene (TPE) (figure 1b) wetted AAO, giving nanostructures with P(PDI-DTT) as the shell and TPE as core.

2. Experimental methods

2.1. Materials

P(PDI-DTT) polymer was synthesized according to previously reported procedure [28]. TPE (98%) was purchased from Innochem and used directly without further purification. AAO templates were purchased from Whatman.
2.2. Preparation of polymer nanotubes

Concentration of P(PDI-DTT) in chloroform was 5 mg ml$^{-1}$. AAO templates were 60 µm in thickness, 2.5 cm in diameter and the aperture of the nanopore was 200 nm. AAO was made ready by ultrasonic cleaning in ethanol and acetone, respectively, then drying in an oven. One hundred microlitre solution of P(PDI-DTT) was dipped on the AAO template (figure 2b), which was placed in a Petri dish with chloroform atmosphere (figure 2a).

After 2 days, the template was taken out from the Petri dish. The polymer deposited on the AAO template was ground off by a sandpaper of 2000 mesh (figure 2c). The AAO template was got rid of by soaking into 3 M potassium hydroxide (KOH) aqueous solution for 15 min (figure 2d), then the polymer nanotubes were gathered in a beaker and rinsed with secondary water twice, and finally P(PDI-DTT) nanotubes were dispersed in ethanol (figure 2e).

2.3. Characterization of nanotubes

Optical microscopy (Olympus BX51) and scanning electron microscopy (SEM, Hitachi S-4800) were used to characterize the morphology of the nanotubes. The acceleration voltage of SEM was 15 kV. Transmission electron microscopy (TEM, JEM-1011) and corresponding selected area electron diffraction (SAED) were used to characterize the structure and crystallinity of the nanotubes on carbon-coated copper grids. The acceleration voltage of TEM was 100 kV. Inverted fluorescence microscope (Olympus IX83) was used to record fluorescence image of nanostructures. The fabrication of nanotube FET is described below [33].

The suspension was deposited on OTS-modified SiO$_2$ [34], which was then thermally annealed at 100°C in vacuum to remove solvent; subsequently, the drain and source electrodes were made by gold-layer sticking technique [35]. Measurement of charge carrier transport property was performed by Keithley 4200-SCS semiconductor characterization system. The mobility in the saturated regime was extracted from the following equation: $I_{DS} = C_i \mu (W/2L)(V_{GS} - V_T)^2$, where $I_{DS}$ was the drain current, $C_i$ the
capacitance per unit area of the gate dielectric layer, and $V_{GS}$ and $V_T$ were the gate voltage and threshold voltage, respectively. Electrical characterization was performed in ambient atmosphere.

3. Results and discussion

3.1. Fabrication and morphology characterization of perylene diimide and dithienothiophene polymer nanotubes

Formation of nanostructure was greatly impacted by the preparation conditions, such as environmental atmosphere, pore diameter and structure and concentration of solution. Solvent atmosphere slowed solution evaporation, ensuring fluidity of the solution. In this work, the preparation process proceeded in a Petri dish (figure 2), which consisted of a disc bottom and a cover made of glass. The container of chloroform in the Petri dish created solvent atmosphere, in virtue of the volatility of chloroform and impermeability of the Petri dish to some extent, which slowed down the evaporation of the P(PDI-DTT) solution. Consequently, P(PDI-DTT) in chloroform was more likely to flow into the pores, which was beneficial for nanostructure formation.

Conversely, when the container of chloroform was not placed in the Petri dish in advance, the solution dropped on the AAO template evaporated rapidly to achieve vapour–liquid equilibrium, which led to discontinuity of nanostructure and loose packing in the nanotube (figure 3). The selection of appropriate side of AAO templates was crucial for the fabrication of nanotubes. The AAO template was commercially available, and the pore diameter value of 200 nm was marked on the external packing. Nevertheless, the fact was that the AAO template had two different sides: the nanopore diameter of the front side was about 240 nm and that of the reverse side was about 120 nm (figure 1). The employment of the front side was beneficial for acquirement of nanotubes; however, the reverse side gave thinner rods (figure 3), which implied that larger diameter of nanopores was helpful for the formation of nanotubes.

The concentration of solution affected dispersity and integrality of nanotubes. Solution with high concentration (greater than 10 mg ml$^{-1}$) led to much residue on the template, which was hard to grind off by sandpaper. After removing the template, the nanotubes conglutinated with each other by the residue, making it hard to disperse. Low concentration (less than 3 mg ml$^{-1}$) fragmented nanotubes. The reason was that the solution could not soak the inwall continuously and completely or only formed thin layer on the wall of the pore, which was fragile. In such cases, the nanotubes were easy to be broken in the dispersion process. TEM (figure 4) showed that, for the nanotube, external diameter was 230 nm and the tube wall was thin. SAED revealed that the nanostructures were all amorphous. Consequently, appropriate concentration was necessary for nanotube fabrication. The formation of nanotubes was a dynamic equilibrium process to a great extent, and strict control of preparation condition was indispensable.

3.2. Field-effect transistor characterization of perylene diimide and dithienothiophene polymer nanotubes

Ultimately, the charge carrier transport property was characterized by FET configuration under ambient atmosphere (figure 5). The P(PDI-DTT) nanotubes exhibited electron transport characteristics with
mobility of 0.02 cm² V⁻¹ s⁻¹, $I_{on}/I_{off}$ of $10^5$ and $V_T$ of 10 V. The mobility was higher than that of film measured under inert atmosphere with the same bottom-gate top-contact configuration [28], but was lower than that of film measured with top-gate bottom-contact configuration [29] reported in previous work. The nanotubes exhibited environmental stability to a certain extent; however, it was still not excellent enough to obtain stable output curves. For the polymer of P(PDI-DTT), encapsulation was probably a feasible way to improve air stability.

**Figure 3.** TEM images of P(PDI-DTT) nanotubes dispersed on carbon-coated copper grids. Preparation condition: (a) without container of chloroform in Petri dish; (b) with reverse side as the template.

**Figure 4.** (a) SEM image of P(PDI-DTT) nanotubes in a bunch. (b) TEM image of P(PDI-DTT) nanotubes dispersed on carbon-coated copper grids. (c) TEM image of single P(PDI-DTT) nanotube.

**Figure 5.** Transfer curve of polymer nanotube.
3.3. Fabrication of core–shell structure

As mentioned above, major application of nanotubes is the fabrication of heterojunction. TPE shows aggregate-induced emission. Polymer nanotubes incorporating TPE particles were obtained by wetting the AAO templates with mixed solution of P(PDI-DTT) and TPE in 1 : 3 weight ratio. Figure 6 shows inverted fluorescence microscope images of the nanostructure with exciting light of different intensity. It was clearly seen that TPE particles were capable of being encapsulated in the nanotubes and the particles that could not be encapsulated scattered on the cover glass. The light-emitting nanotubes were short, because TPE particles were irregular, cutting off the nanostructures when they were dispersed in ethanol. In this way, organic/polymer nanostructures with both moderate electron transport and light-emitting property were easily fabricated, which provided a new approach for preparing OLETs. The core–shell nanostructure made invisible nanostructure visible, and have potential application in cell imaging.

4. Conclusion

Nanotubes of P(PDI-DTT) in large quantity were successfully prepared. This work highlights the importance of preparation conditions. Solvent atmosphere, appropriate dimension of the pore and moderate solution concentration were beneficial for obtaining regular nanotubes. The nanotubes of P(PDI-DTT) exhibited preferable FET performance than film with the same device configuration. Electron mobility of P(PDI-DTT) nanotubes was 0.02 cm² V⁻¹ s⁻¹, I_on/I_off was 10⁵ and V_T was 10 V. It was also demonstrated that P(PDI-DTT) was able to encapsulate TPE particles, forming light-emitting nanostructures. In a word, P(PDI-DTT) nanotubes have potential application for future organic electronics owing to the hollow structure and electron transport property.

Data accessibility. Preparation of P(PDI-DTT) and the fabrication of field-effect transistor based on nanotube was the key to reproduce the work. The detailed procedure to prepare P(PDI-DTT) was clearly elaborated in the supporting information of Zhan et al. [28] (‘A high-mobility electron-transport polymer with broad absorption and its use in field-effect transistors and all-polymer solar cells’ (doi:10.1021/ja071760d)). Gold-layer sticking technique to fabricate field-effect transistor was clearly elaborated on page 1512 in [35] (‘High-performance air-stable bipolar field-effect transistors of organic single-crystalline ribbons with an air-gap dielectric’ (doi:10.1002/adma.200702145)). Data are available at Dryad (http://dx.doi.org/10.5061/dryad.2mg67hq) [36].

Authors’ contributions. L.M. and X.Z. designed the research. S.D. synthesized P(PDI-DTT). L.M., X.L. and Y.L. performed the experiments with support from X.Z. L.M. drafted the manuscript. X.Z., S.D., Y.L. and X.L. revised the manuscript. All authors contributed to the general discussion.

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