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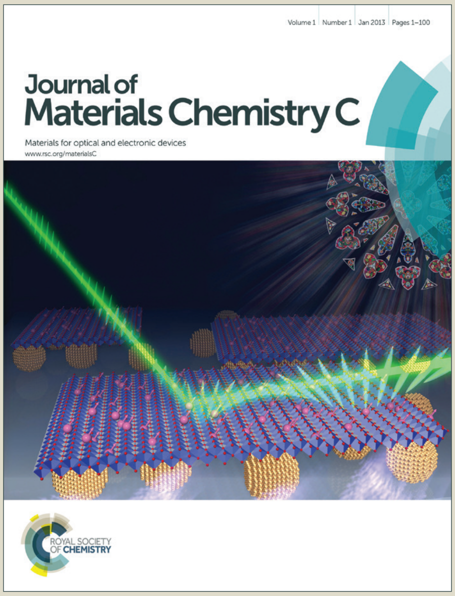

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ARTICLE

Nanowires with Unusual Packing of Poly (3-hexylthiophene)s Induced by Electric Fields

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We promote the nanowire formation in thin film of poly(3-hexylthiophene) (P3HT) by applying a strong electric field. The molecular packing in the resulted nanowires is surprisingly different from that usually obtained by thermal annealing or from dilute solutions: in the electric-field annealing case the P3HT backbones are parallel to the nanowire axis; while in the former cases its backbones are perpendicular to the wire axis. Furthermore, this unusual one-dimensional nanowires exhibit improved crystallinity and electric conductivity compared to its corresponding thermal annealed sample. The growth of the unusual nanowires is attributed to the introducing of the dipolar interactions at the polymer ends by the electric field. This kind of nanowires creates effective charge transport pathways along the intrachain route and contributes to the enhanced conductivity of the P3HT films.

Introduction

Conjugated polymer is widely regarded as a promising semiconducting polymer for use in field-effect transistors (FETs), biosensors, and solar cells.[1-4] Among various conjugated polymers, Poly(3-hexylthiophene) (P3HT) has attracted more attention for its excellent chemical stability, high performance, and simple preparing technology.[4, 5] Organized nanostructures of P3HT are mainly obtained by self-assembling from its dilute solutions or thermal annealing around its crystallization temperature, giving rise to the formation of one-dimensional (1D) nanowires,[6] which provide good vertical pathways for charge transport in fabricating vertical-type electronics such as photovoltaic devices.[7-9] In addition, long nanowires exhibit a low percolation threshold and an excellent mechanical property.[10] Typically, P3HT nanowires can be formed with an average width of ~15 nm and the thickness of 1.6~5 nm, corresponding to one or several P3HT monolayers.[11, 12] The equilibrium anisotropy of its 1D nanostructure is determined by several kinds of interactions such as π−π stacking interactions, the hydrophobic interactions between side chains, and interfacial interactions between the solution and polymers. The dominant force of π−π stacking interaction results in P3HT chains preferably packing as 1D nanowires with (010) direction (the π−π stacking direction) parallel to the nanowire axis.[9, 13, 14]

Directing nanowire growth with other packing modes (*i.e.*, chain backbones parallel to nanowire axis) has attracted great attentions, because the packing of conjugated polymers within the nanowires determines the charge transport route and transport mechanism.[15] Therefore, it is of importance to explore a strategy to guide the assembling process of polymer chains. The self-organized structures of P3ATs are greatly influenced by the length of the alkyl side chains, molecular weight, the quality of the solvent, and annealing temperature, resulting in different kinds of assembled structures such as nanorings and nanobelts.[12, 16, 17] Although many useful nanostructures have been obtained, 1D P3HT nanowires preferably packed with polymer chains parallel to the nanowire axis are scare.[18] Control of polymer backbone packing direction within nanowires, especially simultaneous control of polymer chain alignment and high crystallinity, remains a challenge.

Electric fields are widely used to induce colloidal particles assembling into chains by employing an extra force due to the dipolar interactions among the particles.[19-22] In the last decade, particles that can be manipulated under electric fields have been extended to different shapes such as polyhedral particles, rod-like particles and chiral colloidal clusters.[19, 23-25] Similarly, rod-like conjugated polymers also have an induced dipolar for charges being able to migrate along the backbones within a conjugation length which was suggested to be 20-30 monomers (7.8-11.7 nm) in P3HT.[26,27, 28] Chen *et al.* have used an electric field of 0.6 V/μm normal to the film surface during the solvent-drying process, and found the crystallinity of the P3HT/PCBM film enhanced slightly. In addition, the width of the crystalline fibrils increased and amorphous boundaries decreased during the electric field treatment.[29] Recently, Lee *et al.* have applied an electric field of 0.2V/μm on P3HT thin film with the field along the in-plane direction. They found the crystalline domains size increased by 13.4% after being applied the electric field.[30] These reports prove evident effects of the electric field on conjugated polymer organization. However, the assembling of polymer chains induced by the dipolar interactions was not reported in these literatures. A possible reason is that the dipolar moment of conjugated polymers is too weak as compared to that of the particles. To maximize the electrostatic force between the chain ends, an electric field as high as 30 V/μm on P3HT film was built in the present work, by employing an insulated layer such as thermal-growth SiO_2 layer, which has a dielectric breakdown strength of 10^3 V/μm.[31] Here, we focus on the packing behavior of the rigid P3HT chains under strong electric fields and have found that the polymer chains are able to assembly into nanowires with their backbones parallel to the wire axis, this is in contrast to the supposed molecular packing formed in nanowires in the absent of the electric field (with polymer backbones perpendicular to the wire axis). And these long nanowires are able to form a 3D connecting network after electric-field annealing. We also observe individual P3HT chains packing in single nanowires with perfect order. These unusual nanowires have exhibited excellent crystallinity and improved electrical properties.

Results and discussion

The P3HT film in the thickness varying from 30 nm to 50 nm was prepared by spin coating its chloroform solution onto an n-type Si substrate covered with an electrically insulating layer of 300 nm- thick SiO_2. It is believed the SiO_2 layer can improve the maximum electric field strength that could be applied for its high breakthrough voltage. In this way, the hybrid layer, made of P3HT thin film and thin SiO_2 layer, could bear a high field vertical to the surface before breaking through despite of the P3HT thin film is a conductive layer. After the remaining solvent being removed in vacuum, the film was covered with an FTO glass as a top electrode, leaving an air gap of 200 nm from the bottom electrode. A hot stage was placed to assist the chain movement by heating. The setup (Figure 1) was heated to a temperature of 170 °C and a voltage of 52 V was applied to the two plates immediately, resulting in an electric field of 30 V/μm on the polymer layer, which is several orders of magnitude higher than most reports on studying particles assembly. The leak current was monitored by a multisource measurement with a value ranging from 10^{-2}~10^{-1} μA. After an electric field was applied for several minutes to several hours, the setup was cooled to room temperature in argon before the electric field was removed.

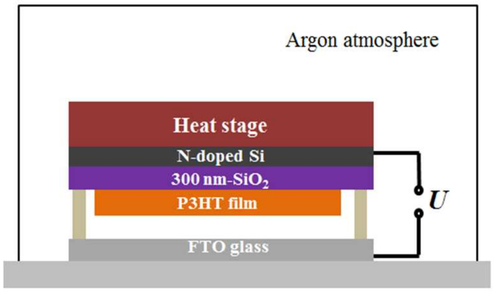

Figure 1. Schematic representation of the experimental setup and procedure for processing poly(3-hexylthiophene) into nanowires.

Morphologies. Figure 2 shows surface topography image of the P3HT films measured by AFM measurement with tapping mode. AFM tapping images of thermal annealed film (Figure 2a) showed featureless morphology at 170 ℃ or formed grain-like crystallites with 100-200 nm in length and 15~25 nm in width at higher temperature (*i.e.* 200 ℃ as shown in Figure 2b). In the absence of any external constraints, π-π interaction between aromatic backbones is the dominant driving force for polymer chain assembling. Through one-dimensional (1D) heterogeneous nucleation, P3HT polymers linearly grow to 1D nanowires with the growth direction coinciding with the π-π stacking direction. Thus the thermal annealed nanowires have the same width as the chain contour length when the polymer molecular weight is not very high.[32, 33, 13] Figures 2c and 2d illustrate the morphologies of the P3HT films under an electric field for 30 min and 8 h, respectively. Both the AFM tapping image and phase image clearly show the nanowires distributing in the film on the substrate. With an electric field annealing for 30 min, the film becomes rough with a height difference of 10~20 nm. The high density nanowires are clearly identified in the phase image, since it visualizes the hard-soft contrast of the crystalline-amorphous areas in the semicrystalline P3HT. The cross-sectional line profiles taken across the height image of Figure 2e the growth of wire width of ~40 nm and a height of ~8 nm in average. After increased field-annealing time to 8 h (Figures 2d and 2f), the density of the nanowires decreased and the nanowires grew wider to ~60 nm in average.

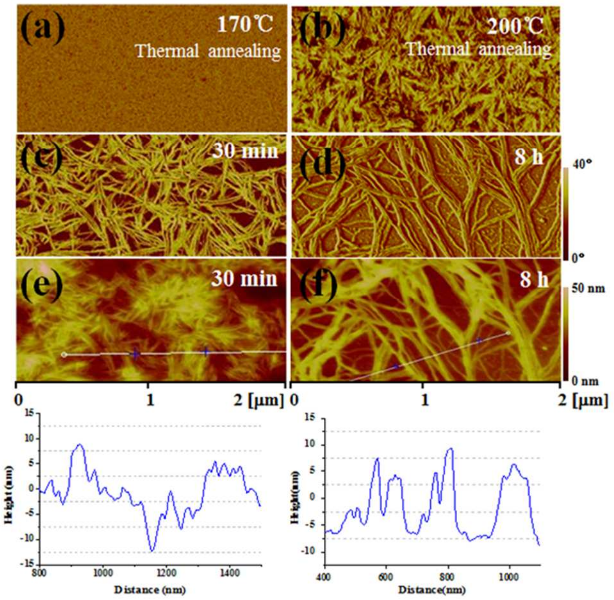

Figure 2. Representative P3HT nanowires formed under electric fields via AFM phase and height images. Phase images of thermal annealed film at (a) 170 °C and at (b) 200 °C. The electric field strength is 30V/μm and the annealed time is (c) 30 min, (d) 8 h. The bottom of the AFM height images are the cross-sectional line profile of the nanowires. For all images, the scanning size is 2 × 2 $μm^2$.

AFM height images prove the assembly in P3HT film displays an interconnecting network consisting of randomly connected nanowires, as shown in Figure 3. The vertical positions of the wire surfaces disperse from -25 nm to 30 nm on the substrate, indicating the nanowires formed a 3D network. The length of an individual nanowire is over 10 micrometers. 3D connecting structure could reduce grain boundaries between neighboring wires and reduce charge carriers scatter at the inter-wire sites.[10] Thus this kind of structure is believed to be useful for vertical-type electronics, in which charges migrate mainly normal to film surface direction.[34]

The fluctuation of film surface seem to increase when being applied an electric field from these AFM height images. By comparing the roughness of the films with and without an electric field, it was found that the surface roughness of the film increased from ~2 nm (RMS) for the thermal annealed sample to a significantly larger roughness of 16 nm for the electric field annealed sample. The increased roughness is attribute to the electrohydrodynamic instabilities at polymer liquid/air interfaces induced by an electric field.[35] However，it is not easy to generate deep instabilities (*i.e.* pillars span the two parallel electrodes) in this experimental condition due to the high viscosity of stiff backbone of conjugated polymers.[36, 37]

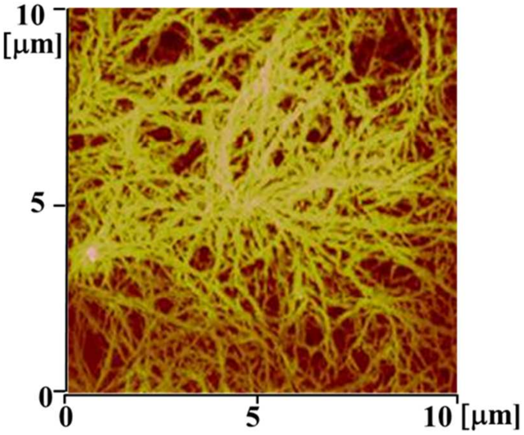

Figure 3. AFM height image of electric-field treated film for 11 h. The electric field strength is 30V/μm and the annealing temperature is 170 °C. P3HT nanowires form 3D connecting network. An individual nanowire in the image has an average length over 10 μm and an average width over 100 nm. The height scale of the height image is 100 nm.

Structure characterization of the nanowires. HRTEM is a useful tool to directly give the detailed packing of polymer chains at molecular scale. We performed the TEM and HRTEM to further understand the nanowires with an electric field treatment at early stage. The film was transferred to a copper grid in diluent HF solution for TEM characterizations. A wire-like P3HT film with distinct dark and bright lines is shown in Figure 4a, which was treated under an electric field for 5 min. Its corresponding HRTEM pattern (Figure 4c) reveals the wire-like P3HT film actually consists of randomly distributed crystalline nanowire with width of 1~3 nm. The nanowires form in a circle composed of connected P3HT chains bridged with head to end and the nanocrystalline lamella are clear in the HRTEM image. The extended length of the nanocrystalline is about 13 nm (Figure 4c), corresponding to a single chain length for the P3HT (M_n of P3HT measured by GPC is actually over estimated by 70%). Grain boundaries between two adjacent nanocrystalline lamellae show an angle in the range of 20°~60°. The reasonably smooth connection indicates there may be an end-to-end interaction to organize the assembled P3HT chains. For longer time treatment (*i.e.*30 min), the nanowire grew to 5~30 nm in width and over one micrometer in length, as shown in Figures 4b and 4d. The P3HT chains in the film aggregated into a network in the form of densely connecting nanowires, in consistent with the corresponding AFM images. With increasing electric field-annealing time, the nanowire became more stiff and the grain boundary angle decreased to about 0° and the cross point became undistinguished. Both HRTEM images identify "edge-on" orientation of crystalline with periodic lamellar pattern corresponding to a π-π stacking distance of 0.37 nm. The clear HRTEM image also shows excellent crystallinity of the P3HT nanowires, as HRTEM image is in essence a 2D projection from the diffraction of the 3D crystalline structure.

Based on the above HRTEM and AFM images, we propose the electric field induced P3HT nanowire packing structure as shown in Figure 4e. Within a single P3HT nanowire, the P3HT backbones are parallel to nanowire axis, which is much different from the self-assembled nanowires of P3HT by thermal annealing or solvent vapor annealing.[12, 14] This kind of unusual anisotropic packing has also been found in BBL nanobelts and it is believed there is likely an extraordinary strength of intermolecular interactions originating from the rigid and planar backbone of BBL chain.[38] Obviously, the nanowires of P3HT in our experiment have a more ordered chain packing than the BBL nanobelts judging from the SAED results. The TEM micrograph for the samples in the absence of applied field proves that the thermal annealed film consists of both wire structure and amorphous region. Complementary HRTEM examinations reveal no periodic fringed pattern within these wires. HRTEM image of polymer chain packing is in essence the reciprocal space of diffraction pattern in P3HT single crystalline structures and therefore the crystallization of nanowire has a great affection on the resolution of its HRTEM images. It means the P3HT nanowires by thermal annealing have a lower degree of crystallization than that obtained by electric-field annealing. Actually, to the best of our knowledge, HRTEM image of P3HT nanowires by thermal annealing or in solution have not been reported in literature because of its semi-crystalline structure.

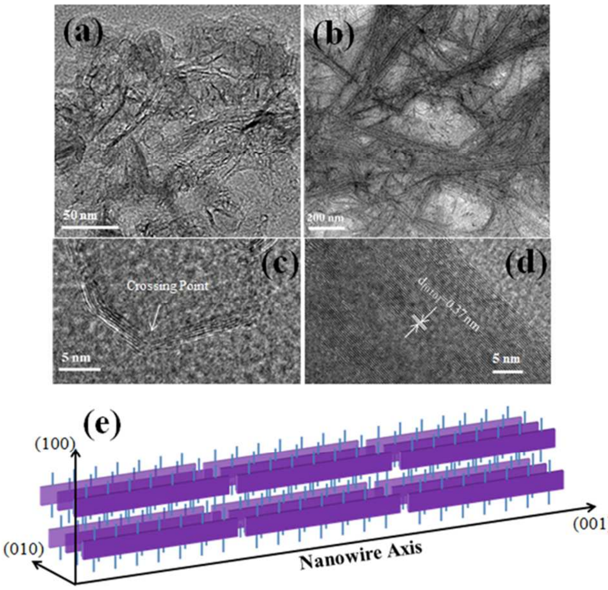

Figure 4. Representative TEM images of P3HT wires at 170 °C under an electric field for (a) 5 min and (b) 30 min. (c) and (d) are the corresponding HRTEM images, respectively. The clear stripes indicate excellent crystalline structures of the nanowires. (e) Schematic represents the P3HT chain packing within an individual nanowire.

Other field-annealing temperatures were also explored in the present study. At the temperatures lower than 160 °C or higher than 210 °C, nanowires were not found in their TEM images. However, when the electric field-annealing temperature was at 200 °C, a lot of looped nanowires (nanorings) were observed with a diameter ranging from 10 nm to 30 nm and a width ranging from 2 nm to 5 nm, as shown in Figure 5a. The corresponding HRTEM image (Figure 5c) shows the P3HT chains packing with the polymer backbones parallel to the long axis of the nanorings. Interestingly, part of the nanowire is actually half-looping, leaving a head-to-end distance of about 2 nm as shown in Figure 5d. Compared to rod-like polymer chains in Figure 4c with a lower annealing temperature of 170 °C, the polymer chains seem flexible and a part of chains can bend over 90°. This indicates that the annealing temperature exerts a profound influence on the stiffness of polymer chains. At higher temperatures, polymer chain are easy to bend, while at lower temperatures, polymer chain are stiff and rod-like. Bright diffraction rings are observed from the SAED pattern of the field-treated film (Figure 5b), identifying the existence of the crystalline (020) plane with a π-π stacking distance of 0.37 nm. Nanorings have been also found in our previous reports referred to self-assembly of poly (3-alkylthiophene) diblock copolymer in solution.[16] Obviously, the polymer chain packing behavior here in the nanowires is different from that in diblock copolymer formed nanowires, indicating a different process of nanoring formation under the electric field.

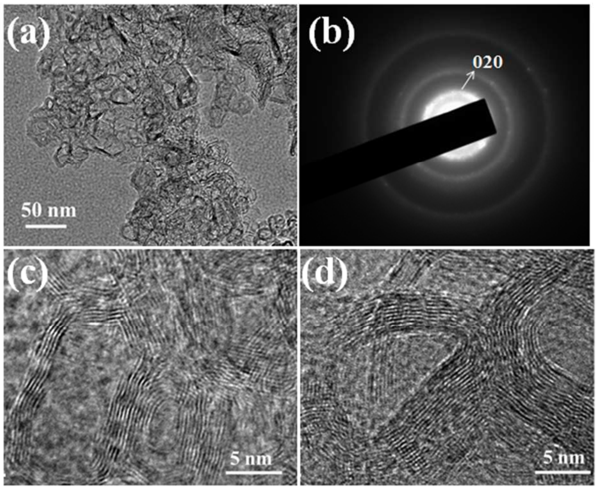

Figure 5. (a) Representative TEM image of P3HT film under an electric field for 5 min. Nanorings were observed with the diameter of 15~50 nm and the width of 1~10 nm. (b) Corresponding SAED pattern of the TEM image. (c) and (d) HRTEM images show the detail of chain packing in the nanorings. Closed rings (c) and half-closed rings (d) are found with polymer backbones parallel to the circumferences of the nanorings.

The impact of electric fields on the structural changes was investigated by UV-vis absorption spectra, which are correlated with the structural properties of the thin films of the crystalline nanowires.[39, 40] For the thermal annealed film, the 0-0 contribution at 610 nm and the dominating 0-1 contribution at 560 nm were visible from the black curve in Figure 6. The ratio of 0−0/0−1 absorbance peaks is about 0.8, indicating a significant interchain coupling (H-aggregate).[41] For the films treated by electric-field annealing for 30 min, the 0−0/0−1 intensity ratio shows an increase, implying the larger conjugation length within the polymer chain.[28] Furthermore, both 0−0/0−1 absorbance peaks exhibit red shifts by ~10 nm when the P3HT films went from thermal annealing to the electric-field annealing. The increased 0-1 intensity is due to the ordered stacking of the polymer backbones in the films, and the increase of 0-0 intensity is correlated with the degree of interchain order, which indicates the crystallinity of the field-treated film is enhanced.[5, 42]

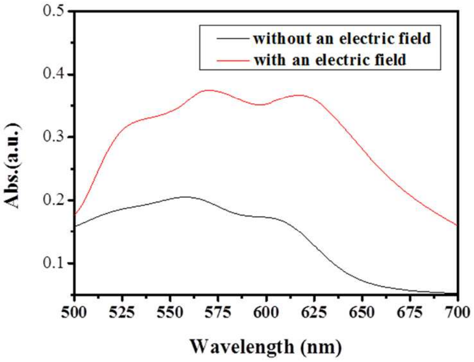

Figure 6. Absorption spectra of the P3HT thin film treated by thermal annealing (black line) and by an electric field of 30 V/μm (red line). All the films were annealed at 170 °C for 30 min.

Mechanism of anisotropic nanowires with high crystallinity. Apparently, the electric field is able to assist the packing of P3HT chains. In fact, electric fields are widely used to enable the manipulation of the dipolar interaction between the spherical colloids, leading to long colloid chains along the electric field direction, while short-range attractions such as van der Waals forces keep the assembled colloids from dispersing. We believe similar mechanism exists in the electric field induced P3HT nanowires. In the process of thermal annealing, both π-π stacking and van der Waals interaction govern the self-assembly of P3HT, and π-π stacking force dominate the self-assembled behavior, resulting in polymer chain perpendicular to the nanowire axis.[18, 38] Charge could delocalize within a conjugation length along the backbone but are laterally confined in the polymer chain, generating an intrinsic dipole moment under electric fields.[15, 28, 43, 44] For a ribbon like ladder-type polymer, the chain ends determine the effective conjugation length of the polymer.[45] In other conjugated polymers such as P3HT, however, the effective conjugation is often reduced by structural defects or torsional disorder. Thus for low molecular weight P3HT, the conjugation length corresponds to the length of the polymer chain. For the 11~19 kg/mol P3HT, it was proven the conjugation length was about the half of polymer chain length through the MALDI-TOF MS measurements.[46] The conjugation length of P3HT was also suggested to be 20-30 monomers (7.8~11.7 nm) according to the calculations reported by Kim.[27] The conjugation length in our experiment should be even larger due to the increased 0−0/0−1 ratio. Based on these facts, it is reasonable to deduce that the whole P3HT chain may consist of only one or two conjugation lengths. Therefore, we believe there is a large probability for the dipole charges distributing in the chain ends.

Figure 7 depicts the proposed process of the nanowire formation under an electric field. In the electric field normal to the film surface, each P3HT chain bears an induced dipole moment along the backbone direction. After being heated above their glass transition temperature, the P3HT chains start to move and self-assembly into end-connecting nanowire. The main driving force in this process is the dipolar interactions between the chain ends. For the sake of polymer bending at a high temperature (*i.e.* 200 °C), the narrow nanowires could make themselves into a hoop and nanorings form. This step of assembling, in our observation of the HRTEM experiments, takes less than 5 min, which may be attributed to the long-range electrostatic interaction of the dipoles. The next step of the polymer assembling is the widening of the nanowires, which is mainly driven by π-π interaction between aromatic backbones. In this step, the nanowires could grow up to 100 nm in width and over 10 μm in length after electric-field annealing for 11 h.

We believe that heating at high temperature (170°C) provides the thermal energy to bend the otherwise straight chain backbones under the electric field. Initially, it is possible that three or more slightly bending chains are connected by the dipole interactions, forming the inner core of the hoops or nanorings. Later more and more chains join this process and finally develop into the hoops and nanorings. Indeed, a careful inspection shows that each chain backbone in the fibrils is only slightly bent, although the fibrils form hoops and nanorings. The large bending of the fibrils is due to an accumulative effect.

The crystallinity of the P3HT films was characterized by X-ray grazing incidence diffraction (GIXRD) measurements using synchrotron X-ray radiation. Two films spin-coated from chloroform solution were prepared with 40 nm thickness, determined by AFM measurement. The two films were annealed at 170 °C with and without electric field (30V/μm) for 30 min, respectively. The nanocrystalline alignment was investigated using 2D GIXRD measurement, which probes all the crystalline plane orientations in the thin film. Both the 170 °C annealed films with and without the electric field show arc pattern (*h*00) along the Q_z direction (Figures 8c and 8d), which indicates the chains in the nanocrystallines are packing in "edge on" configuration through the process of electric field annealing. the electric field illustrate that the two films exhibit a crystalline structure with "edge on" configuration. Thus the strong diffraction and the appeared second-order diffraction (Figure 8d) suggest the enhancement in crystallinity of the film under the electric field. The high crystallinity of the film is also in agreement with the HRTEM results from the nanowires.

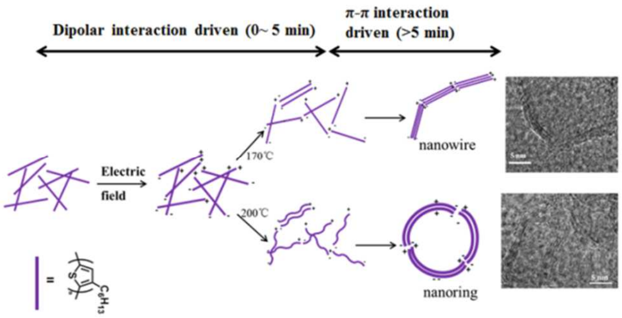

Figure 7. Schematic diagram of possible mechanisms for P3HT to assemble into nanowires or nanorings under an electric field.

1D GIXRD pattern along the Q_z direction recorded the enhanced crystallinity of the film quantitatively. For the thermal annealed film, the out-of-plane diffraction shows a weak reflection at an interlayer *d*-spacing of 16.36 Å (2theta=4.35°). The interlayer spacing is consistent with the reported structure model, where the side chains of P3HT are interdigitated with each other.[47] After an applied electric field, the intensity of the peak increases about 4.8 folds at (100) reflection (Figure 8b). The same (100) position of 2theta indicates the interlayer spacing does not change with and without the electric field. The crystalline size along the direction normal to the surface can be calculated by Scherrer equation, in which the average crystalline size in (100) direction is inversely proportional to full width at half maximum (FWHM) of the (100) peak.[29, 30] As shown in Figure 8b, the FWHM of (100) reflection decreases from 0.28° to 0.18° after electric-field annealing. This indicates the crystalline domains are 55.6% larger than those treated with thermal annealing in the absence of the electric field. Therefore, it is reasonable to deduce the crystallinity of electric field annealed film is triple higher than its thermal annealing counterparts by comparing (100) peak area in 1D-GIXRD results.

The GIXRD measurements proved the "edge on" configuration of the crystalline packing on the substrate. And reorientation of P3HT nanocrystallites under the electric field was not found in our experiment. This seems different from the aligning of inorganic nanorods or conjugated polymers in a solution, which are able to stand perpendicular to the underlying substrate.[48, 49, 26] Nanorods tend to align the induced dipole moment along the electric field. The absence of this kind of P3HT reorientation may be attributed to the weak dipole moment of conjugated polymer and unfavorable interfacial interactions between polymer chains and the SiO_2/Si substrate when the long chains stand normal to the film surface.[28]

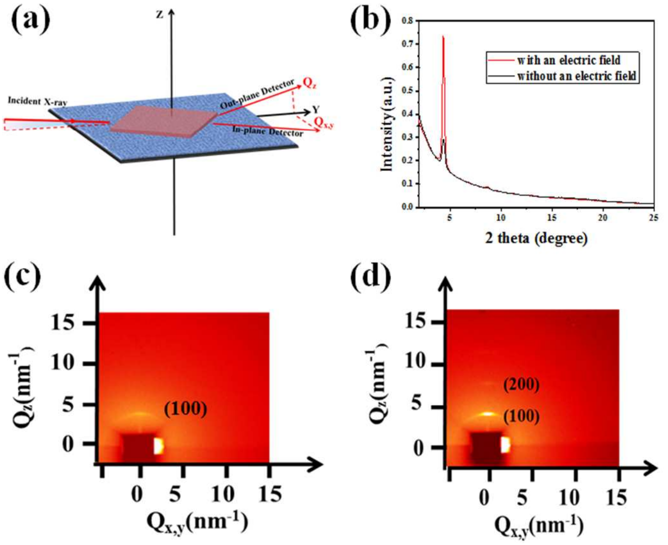

Figure 8. X-ray grazing incidence diffraction (GIXRD) experiment of the P3HT films. (a) Schematic illustration of the synchrotron GIXRD measurement for P3HT films on a Si/SiO_2 substrate where the incidence angle of the synchrotron X-ray beam is 0.15°. (b) Out-of-plane X-ray diffraction pattern of the P3HT films with thermal annealing at 170 °C for 30 min (black line), with electric-field annealing at 170 °C for 30 min (red line), respectively. (c) and (d) 2D GIXRD images of the P3HT thin films without and with electric-field annealing. Both (100) and (200) diffractions can be found for the electric-field annealed film in out-of-plane (Q_z) direction.

To achieve chain packing with high crystallinity, polymers have to overcome many energy barriers, which are caused by the rearrangement of chain conformations. Thus ordered arrangement of polymer chains have lower energy barriers and promote the crystallinity of polymers in the process of polymer crystallization.[18,50,51] We used this hypothesis to explain the enhancement of the crystallinity in P3HT films treated by electric fields. The main driving force of P3HT crystallization is thought to be π-π stacking interactions in the case thermal annealing or in a solution, resulting in a crystallinity of 10%~20%.[13,33] Most of polymer chains in the P3HT film are in random distribution around crystalline phase. A key step to help the process of crystallization is to assemble the polymers in an ordered state by further short-range chain interactions.[52] Under a strong electric field, an extra force from the dipolar interactions connects the P3HT chains end by end, thus assists the arrangement of the disordered chains in the amorphous region. As a result, an electric field may facilitate P3HT crystallization by promoting chain arrangement, giving rise to an enhanced crystallinity of the P3HT films.

Electrical properties. It is interesting to compare the electrical property of the electric-field annealed P3HT films with that of the thermal annealed films. The measured current for the spin-coated film has tripled during thermal annealing for 30 min at 170 ℃ without electric field (Figure 9). With an electric field annealing of 30 V/μm for 30min, the conductivity of P3HT increases substantially, being more than one order-of-magnitude (from 0.05 μA to 1.2 μA) higher. The improvement in conductivity is due to a combination of increased crystallinity and preferred orientation of P3HT chains in the nanowires. It has been suggested that π-π stacking of the conjugated polymer chains allows hole delocalization between the chains and provides a transport route along the interchain direction, rather than only the transport process along the intrachain (backbone) direction in amorphous regions.[15] Thus increased proportion of crystalline area facilitates charge transport in the P3HT films. Of the two transport processes, charge transport along the backbone is much easier than that along π-π stacking direction, indicating the P3HT nanowires with backbones parallel to the wire axis are more suitable for charge transport than the P3HT nanowires with π-π stacking parallel to the wire axis.[53]

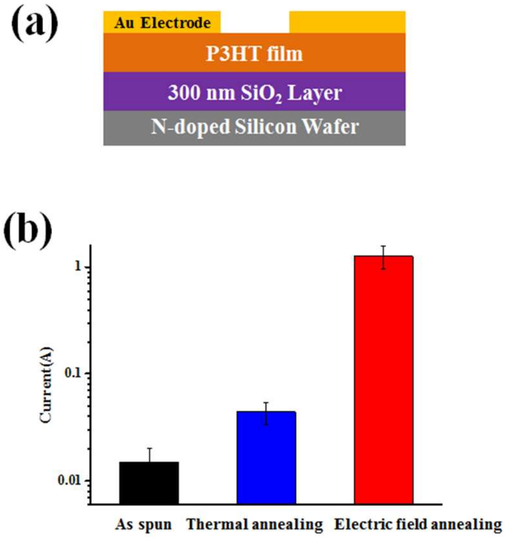

Figure 9. Electrical conductivity of spin-coated P3HT films without annealing (black), with thermal annealing at 170 °C for 30 min (blue) and with electric-field annealing at 170 °C for 30 min (red), respectively. (a) Scheme of the electrical conductivity measurement; Two probe Au electrodes were deposited on the film directly. (b) Current measurements for P3HT thin film with different treatments at an applied voltage of 10 V.

Conclusions

In summary, we have devised a simple and effective route to control the hierarchically structured assembly of P3HT nanowires with polymer backbones parallel to the nanowire axis. It offers a complementary use of electric fields to obtain anisotropic nanostructures, by utilizing dipolar attractions between the polymer ends. The resultant preferential end-to-end attachment within nanowires formed a connecting network, with increased crystallinity as well as enhanced conductivity. Different from most inorganic nanorods or conjugated polymers in a solution, we have not observed P3HT chain reorientation normal to the film surface and the chains keep in an "edge on" orientation throughout the process of the electric-field annealing. On extrapolation to the use of electric field adjusting P3HT chain self-assembly, the special molecular packing of wires on nanoscale may provide a viable extending to highly efficient photovoltaic devices and field-effect transistors.

Experimental section

Materials. Highly doped n-type Si substrates coated by a layer of thermally-grown SiO_2 (*i.e.*, ~300 nm thick) was purchased from Materials Technology Company. Silicon oxide colloids with a diameter of 200 nm were purchased from Sigma-Aldrich. Poly(3-hexylthiophene) (P3HT) was synthesized by a modified Grignard method in our lab as our reported previously with a molecular weights of 11 kg/mol, which is determined by gel permeation chromatography (GPC) using a Agilent 1100 system (calibration: polystyrene standards). Differential scanning calorimetry (DSC) was performed using Q2000 at a heating and cooling rate of 10 °C/min under N_2 flow. The crystallization temperature and melt temperature are 185 °C and 219 °C, respectively. Chloroform and hydrofluoric acid (HF) were purchased from Sigma-Aldrich without further purifications. The fluorine-doped tin oxide (FTO)-coated glass slide with a resistance of about 20 Ω was used as the transparent electrode on top.

Experimental procedure. SiO_2/Si substrates were sequentially cleaned by ultrasonication in acetone, isopropyl alcohol, followed by Piranha solution (H_2SO_4: H_2O_2= 3: 1) and deionized water. P3HT was dissolved in chloroform at 90 °C and purified with a 0.22 μm PTFE filter to yield a ~5 mg/ml P3HT/chloroform solution. The P3AT solution was then spin coated on the SiO_2/Si substrates at 3000 rpm for 60 s, resulting in a film with a thickness of 30~50 nm. The FTO-coated glass slides were cleaned by washing in an ultrasonic bath with acetone and isopropanol, and exposing to oxygen plasma for 15 min. A small air gap of typically 200 nm between the two parallel plates was created by spreading silicon oxide colloids onto the film before mounting the top electrode. The plate capacitor was connected to a power supply (Keithley 2400 DC) and a vertical electric field was then applied on the P3HT film. The leak current was monitored by a multisource measurement. Both the two electrodes were contacted using conductive carbon paint. The setup was placed to a hot stage with the accuracy of 1 °C and heated to the temperature of 170~200 °C. To prevent the P3HT film from being oxidation, an argon flow was conduct to keep the film in inert atmosphere conditions.

Characterization. All 2D X-ray grazing incidence diffraction (GIXRD) pattern and 1D GIXRD pattern of P3HT were obtained using a wavelength of λ=0.124 nm at BL14B1 of Shanghai Synchrotron Radiation Facility. The exposure time was 50 seconds for 2D pictures. For 1D GIXRD measurement, the exposure time was 1 seconds and the scan step was 0.05°. The incidence angle was 0.15° in our measurements. The morphologies of the films were characterized on a Bruker Multimode AFM Nanoscope IV with tapping mode. For the characterizations of high-resolution transmission electron microscope (HRTEM), a dilute HF aqueous solution was used to float off the film from SiO_2/Si substrate and then we transfer the film to a copper grid. The film was characterized using a JEOL JEM-2100F field-emission transmission electron microscope with the working voltage at 200 kV. In order to minimize the burn effect of electron beam and obtain clear HRTEM images, we reduced the operating voltage to 100~150 kV and employed the exposure time for the thin film as short as possible. Absorption spectra of the P3HT films were measured with a Lambda 750 UV-Vis spectrophotometer in ambient.

Conductivity measurement. Current measurements were performed at a constant applied voltage on the nanowires formed on the Si/SiO_2 substrate. Two 4 mm-length Au electrodes separated by a 100 μm gap were thermally deposited on the films. The electrodes were prepared by depositing 60 nm Au on the P3HT thin films through a mask by thermal evaporation at a vacuum of 2×10^{-6} mbar. The electrical characterization was measured using a Keithley 6913 power supply in glove box.

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Notes and references

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1. H. Sirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741-1744.
2. J. Janata and M. Josowicz, *Nat. Mater.*, 2003, **2**, 19-24.
3. M. He, W. Han, J. Ge, W. J. Yu, Y. L. Yang, F. Qiu and Z. Q. Lin, *Nanoscale*, 2011, **3**, 3159-3163.
4. M. He, W. Han, J. Ge, Y. L. Yang, F. Qiu and Z. Q. Lin, *Energ. Environ. Sci.*, 2011, **4**, 2894-2902.
5. J. Ge, M. He, F. Qiu and Y. L. Yang, *Macromolecules*, 2010, **43**, 6422-6428.
6. M. Brinkmann and P. Rannou, *Macromolecules*, 2009, **42**, 1125-1130.
7. H. Xin, F. S. Kim and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2008, **130**, 5424.
8. J. S. Kim, J. H. Lee, J. H. Park, C. Shim, M. Sim and K. Cho, *Adv. Funct. Mater.*, 2011, **21**, 480-486.
9. A. L. Briseno, S. C. B. Mannsfeld, S. A. Jenekhe, Z. Bao and Y. N. Xia, *Mater. Today*, 2008, **11**, 38-47.
10. S. B. Jo, W. H. Lee, L. Z. Qiu and K. Cho, *J. Mater. Chem.*, 2012, **22**, 4244-4260.
11. A. Zen, M. Saphiannikova, D. Neher, J. Grenzer, S. Grigorian, U. Pietsch, U. Asawapirom, S. Janietz, U. Scherf, I. Lieberwirth and G. Wegner, *Macromolecules*, 2006, **39**, 2162-2171.
12. J. H. Liu, M. Arif, J. H. Zou, S. I. Khondaker and L. Zhai, *Macromolecules*, 2009, **42**, 9390-9393.
13. C. Melis, L. Colombo and A. Mattoni, *J. Phys. Chem. C*, 2011, **115**, 576-581.
14. S. Hugger, R. Thomann, T. Heinzel and T. Thurn-Albrecht, *Colloid. Polym. Sci.*, 2004, **282**, 932-938.
15. R. A. Street, J. E. Northrup and A. Salleo, *Phys. Rev. B*, 2005, **71**, 165202.
16. M. He, L. Zhao, J. Wang, W. Han, Y. L. Yang, F. Qiu and Z. Q. Lin, *ACS Nano*, 2010, **4**, 3241-3247.
17. F. S. Kim, G. Q. Ren and S. A. Jenekhe, *Chem. Mater.*, 2011, **23**, 682-732.
18. J. A. Lim, F. Liu, S. Ferdous, M. Muthukumar and A. L. Briseno, *Mater. Today*, 2010, **13**, 14-24.
19. N. Yanai, M. Sindoro, J. Yan and S. Granick, *J. Am. Chem. Soc.*, 2013, **135**, 34-37.
20. M. E. Leunissen, H. R. Vutukuri and A. van Blaaderen, *Adv. Mater.*, 2009, **21**, 3116.
21. H. R. Vutukuri, A. F. Demirors, B. Peng, P. D. J. van Oostrum, A. Imhof and A. van Blaaderen, *Angew. Chem. Int. Edit*, 2012, **51**, 11249-11253.
22. A. Yethiraj and A. van Blaaderen, *Nature*, 2003, **421**, 513-517.
23. D. Zerrouki, J. Baudry, D. Pine, P. Chaikin and J. Bibette, *Nature*, 2008, **455**, 380-382.
24. G. J. Vroege and H. N. W. Lekkerkerker, *Rep. Prog. Phys.*, 1992, **55**, 1241-1309.
25. Y. J. Min, M. Akbulut, K. Kristiansen, Y. Golan and J. Israelachvili, *Nat. Mater.*, 2008, **7**, 527-538.
26. W. S. Chang, S. Link, A. Yethiraj and P. F. Barbara, *J. Phys. Chem. B*, 2008, **112**, 448-453.
27. J. Clark, C. Silva, R. H. Friend and F. C. Spano, *Phys. Rev. Lett.*, 2007, **98**, 206406.
28. H. L. Cheng, J. W. Lin, M. F. Jang, F. C. Wu, W. Y. Chou, M. H. Chang and C. H. Chao, *Macromolecules*, 2009, **42**, 8251-8259.
29. C. C. Lin, Y. Y. Lin, S. S. Li, C. C. Yu, C. L. Huang, S. H. Lee, C. H. Du, J. J. Lee, H. L. Chen and C. W. Chen, *Energ. Environ. Sci.*, 2011, **4**, 2134-2139.
30. S. W. Lee, C. H. Kim, S. G. Lee, J. H. Jeong, J. H. Choi and E. S. Lee, *Electron. Mater. Lett.*, 2013, **9**, 471-476.
31. K. V. Shcheglov, C. M. Yang, K. J. Vahala and H. A. Atwater, *Appl. Phys. Lett.*, 1995, **66**, 745-747.
32. R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. S. Liu, J. M. J. Frechet and M. F. Toney, *Macromolecules*, 2005, **38**, 3312-3319.
33. S. Malik and A. K. Nandi, *J. Polym. Sci. Pol. Phys.*, 2002, **40**, 2073-2085.
34. G. M. Newbloom, K. M. Weigandt and D. C. Pozzo, *Macromolecules*, 2012, **45**, 3452-3462.
35. E. Schaffer, T. Thurn-Albrecht, T. P. Russell and U. Steiner, *Nature*, 2000, **403**, 874-877.
36. F. A. de Castro, F. Nuesch, C. Walder and R. Hany, *Journal of Nanomaterials*, 2012, **2012**, 478296.
37. D. R. Barbero and U. Steiner, *Phys. Rev. Lett.*, 2009, **102**, 248303.
38. A. L. Briseno, S. C. B. Mannsfeld, P. J. Shamberger, F. S. Ohuchi, Z. N. Bao, S. A. Jenekhe and Y. N. Xia, *Chem.Mater.*, 2008, **20**, 4712-4719.

39. L. Hartmann, K. Tremel, S. Uttiya, E. Crossland, S. Ludwigs, N. Kayunkid, C. Vergnat and M. Brinkmann, *Adv. Funct. Mater.*, 2011, **21**, 4047-4057.
40. J. Liu, Y. Sun, X. Gao, R. Xing, L. Zheng, S. Wu, Y. Geng and Y. Han, *Langmuir*, 2011, **27**, 4212-4219.
41. E. T. Niles, J. D. Roehling, H. Yamagata, A. J. Wise, F. C. Spano, A. J. Moule and J. K. Grey, *J.Phys.Chem. Lett.*, 2012, **3**, 259-263.
42. R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 222-228.
43. F. Schindler, J. M. Lupton, J. Muller, J. Feldmann and U. Scherf, *Nat. Mater.*, 2006, **5**, 141-146.
44. A. Salleo, T. W. Chen, A. R. Volkel, Y. Wu, P. Liu, B. S. Ong and R. A. Street, *Phys. Rev. B*, 2004, **70**, 115311.
45. P. Prins, F. C. Grozema, J. M. Schins, S. Patil, U. Scherf and L. D. A. Siebbeles, *Phys. Rev. Lett.*, 2006, **96**, 146601.
46. C. Scharsich, R. H. Lohwasser, M. Sommer, U. Asawapirom, U. Scherf, M. Thelakkat, D. Neher and A. Kohler, *J. Polym. Sci. Pol. Phys.*, 2012, **50**, 442-453.
47. K. Tashiro, M. Kobayashi, T. Kawai and K. Yoshino, *Polymer*, 1997, **38**, 2867-2879.
48. S. Gupta, Q. L. Zhang, T. Emrick and T. P. Russell, *Nano Lett.*, 2006, **6**, 2066-2069.
49. M. Zorn, M. N. Tahir, B. Bergmann, W. Tremel, C. Grigoriadis, G. Floudas and R. Zentel, *Macromol. Rapid Comm.*, 2010, **31**, 1101-1107.
50. M. Muthukumar, *Eur. Phys. J. E*, 2000, **3**, 199-202.
51. K. Zhao, L. J. Xue, J. G. Liu, X. Gao, S. P. Wu, Y. C. Han and Y. H. Geng, *Langmuir*, 2010, **26**, 471-477.
52. F. Binsberg, *Nature*, 1966, **211**, 516-517.
53. Y. K. Lan and C. I. Huang, *J. Phys. Chem. B*, 2009, **113**, 14555-14564.

SYNOPSIS TOC

Nanowires with Unusual Packing of Poly (3-hexylthiophene)s Induced by Electric Fields

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Unusual nanowires in thin films of poly (3-hexylthiophene) have been prepared by applying an electric field.