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Unraveling the Order and Disorder in Poly(3,4-ethylenedioxythiophene)/Poly(styrenesulfonate) Nanofilms

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ABSTRACT: Conductive polymer poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) exhibits a tunable conductivity ranging from 0.1 to 4380 S cm⁻¹ under different doping and/or dedoping strategies. However, the dependence of macroscopic electrical properties on the evolution of the microstructure is not clearly understood. This is the first study that systematically investigated the spatial arrangement of the ordered and disordered phases in PEDOT/PSS nanofilms by bright-field (BF), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS) and element-thickness mapping. Our observations clarify how amorphous PSS hinders electrical transport at various length scales in the PEDOT/PSS films. Moreover, the mechanism for an enhancement in 3 orders of magnitude in electrical conductivity was proved by TEM investigation, which is mainly due to a more uniform dispersion by dedoping that opens PEDOT nanoparticle clusters in PEDOT/PSS films. Our microstructural and electrical studies show that the change in spatial arrangement and interaction of small PEDOT domains plays a considerable role in the final electron transport.

INTRODUCTION

Conductive polymers attract significant interest because of their facile tunability in electrical properties and processability, which make them popular for the next generation of flexible electronics.¹⁻¹² In conductive polymers, highly anisotropic molecules have high conductivity along their backbone chains, moderate conductivity between chains and low conductivity between widely spaced lamellar planes.¹³⁻¹⁵ Carrier trapping normally results from structural disorder or amorphous grain boundaries between crystallites. A simple macroscopic electrical measurement cannot sufficiently clarify the complex transport mechanism between crystalline grains. However, analytical electron microscopy (AEM) can directly image the spatial arrangement of ordered and disordered phases in conductive polymers.

Previous studies report direct observation of the microstructure of conductive polymer nanofilms under transmission electron microscopy (TEM).¹⁶⁻¹⁷ Takacs et al. found a high degree of molecular order in poly[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5-·(2,2'-bithiophene) by using a combination of high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). It is possible to spatially resolve a highly ordered "face-on" lamella nanostructure over the entire film.¹⁶ Wirix et al. revealed a three-dimensional lamellar structure formed by the stacking of conjugated backbones of poly(3-hexylthiophene) by cryo-TEM.¹⁷ The results obtained by TEM provide insight into grain size, connectivity and crystalline order. Moreover, it is possible to extract information about molecular packing and orientation, local order and disorder and phase segregation.¹⁸⁻²⁰

Another important conductive polymer, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS), has gained tremendous interest due to its facile tunable conductivity that can be varied from 0.1 to 4380 S cm⁻¹ using different doping and/or dedoping strategies.¹¹⁻¹³ PEDOT/PSS has served as an excellent candidate to replace indium tin oxide (ITO), has reached the requirements for use in current-driven devices such as displays and touch panels and is also approaching the requirements for solar cells.²¹⁻²² In addition to tunable conductivity, this polymer has the advantages of flexibility, low-cost production processes such as printing, safe handling and large scale availability. Despite the intensive research that has been conducted on PEDOT/PSS, the relationship between microstructure and conductivity remains poorly understood. To date, only the core–shell structure of PEDOT/PSS grains in nanofilms has been observed under TEM.²³ In an earlier study, we confirmed that the core–shell microstructure is characterized by a PEDOT nanocrystal-rich core surrounded by an insulating PSS-rich shell.²⁴ Furthermore, 73
we correlated the microstructural change with its macroscopic electrical and mechanical properties at different temperatures. Our previous results highlight the importance of considering microstructural changes as a design element and also show the potential to extract information about phase segregation. To date, the most enlightening studies on conductive polymer films come from insights into their microstructure over a wide range of length scales.\(^{1,2,10}\) This is based on the fact that electronic transport is sensitive to connectivity between conductive domains and defects within and at the domain boundaries.\(^{25}\) Therefore, this investigation will help to further clarify the correlation between microstructure and electrical properties.

Here, we use bright-field transmission electron microscopy (BF-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to provide evidence of the changes in PEDOT/PSS nanofilm microstructure when induced during annealing process and solvent dedoping. We have gained new insights into the correlation between microstructure and electrical conductivity by unraveling the overall morphology, grain boundary and interconnectivity of conductive domains in PEDOT/PSS thin films. These results may encourage the development of strategies to further improve the performance of next-generation organic semi-conductors.

**EXPERIMENTAL SECTION**

**Materials.** PEDOT/PSS aqueous dispersion, Clevios P and PH1000 were purchased from HC Starck, Inc. Ethylene glycol (EG) was purchased from Sigma-Aldrich.

**Preparation of PEDOT/PSS Films.** PEDOT/PSS nanofilms for TEM imaging were prepared in a clean room to avoid contamination; and the procedures are reported in a previous study\(^{26}\) and illustrated simply in Figure S1. (1) a silicon wafer was spin-coated with a 10 μm AZ9210 photore sist film at a speed of 2400 rpm and baked at 110 °C for 180 s; (2) this photore sist was treated in an O₂ plasma cleaner to improve its hydrophilicity; (3) a dispersion of PEDOT/PSS was spin-coated on the AZ9210-coated wafer at 5000 rpm and air-dried; (4) samples were cut into small squares (3 × 3 mm\(^2\)) and immersed in an acetone bath, next 200-mesh holey-carbon copper grids (Pacific Grid Tech) were used to catch the PEDOT/PSS nanofilms that float off the wafers; and (5) samples were then separated into three groups: the first group was dried in ambient air (21 °C, RH at 65%), the second group was annealed at 120 °C for 15 min and the third group was immersed in EG for 2 h followed by annealing at 150 °C in air for 15 min to remove EG before observation.

We used quartz wafers to prepare uniform spin-coated PEDOT/PSS nanofilms for AFM imaging. Wafers (2.5 × 2.5 cm\(^2\)) were placed for 1 min in an oxygen plasma cleaner for oxidation at 200 mTorr oxygen gas and 40 W. This process helped to remove any dust, improved the wettability of the quartz wafers, and finally enhanced the uniformity of the nanofilm. Spin-coating of PEDOT/PSS nanofilms was performed on treated quartz wafer at a speed of 5000 rpm/min for 60 s. These films were subsequently annealed on a hot plate at 120 °C for 20 min in ambient atmosphere. EG-treated samples were obtained by using the same protocol for preparing TEM samples.

PEDOT/PSS microfilms for XRD and XPS tests were prepared by casting 23 g of Clevios P and PH1000 aqueous solution on polycarbonate sheets (7 × 7 cm\(^2\)). The polycarbonate sheets were made by hot pressing, as described in previous studies.\(^{26,27}\) The PEDOT/PSS films were dried in ambient air (26 °C, RH at 65%) for 96 h. Films with a thickness of about 50 μm were peeled off from the polycarbonate sheets and annealed in air at 150 °C for 2 h. Solvent treatment of the films were performed by immersing them into an EG bath for 2 h and then annealed again in the air at 150 °C for another 2 h. CMT-SR2000N four-probe system with a probe space of 1 mm (Materials Development Corporation). The electrical conductivity (σ) of the thin film was defined as

\[
\sigma = \frac{1}{R \cdot f} = \frac{I}{V \cdot t \cdot KU}
\]

(1) Considering that all films had a thickness (t) below 50 nm (well below half the probe spacing), we used the classical thin film correction constant (K), which is defined as

\[
K = \frac{\pi}{\ln(2)} = 4.532
\]

(2) U (V) is the measured voltage and I (A) is the prescribed current.\(^{26}\) On each sample, we measured the sheet resistance at 10 different locations, then the measured values were averaged. The thickness of each film was measured by a Dektak 8 surface profilometer (Veeco Instruments Inc.).

TEM images of PEDOT/PSS were taken by using a Titan G² 80-300 CT (FEI Company) at an accelerating voltage of 300 kV, equipped with a field-emission electron source. Combined with low-dose and high-voltage imaging,\(^{26,28}\) we were able to minimize the beam damage on the samples. The PEDOT/PSS samples were analyzed with bright-field TEM (BF-TEM) and high-angle annular dark-field scanning electron microscopy (HAADF-STEM) observation modes. BF-TEM micrographs were digitally recorded using a US4000 charged-couple device (CCD) camera (Gatan, Inc.); HAADF-STEM micrographs were recorded with an analogue detector (E. A. Fischione, Inc.). In addition, electron energy loss spectroscopy (EELS) investigations were made by setting the instrument in TEM-170 diffraction mode, using a GIF Tridiem postcolumn energy filter (Gatan, Inc.). The specimens were loaded in the TEM chamber by a 621 cryo-transfer holder (Gatan, Inc.). Samples were first investigated at room temperature (RT) and then cooled down to −177 °C (LT) by filling the holder’s dewar flask with liquid nitrogen. BF-TEM images were acquired with a total electron dose of 50 e− Å\(^{-2}\); while HAADF-STEM images were acquired with an total electron dose of around 187 e− Å\(^{-2}\). At these low dose values, only the limited or no structural degradation of the samples was observed during the data acquisition. To further reduce the beam damage, the imaging conditions were optimized on a sacrificial-area. In this way the useful data was acquired from an undamaged area with a minimum electron dose. The entire image acquisition and data processing were performed using the GMS v1.8.3 microscopy suite software (Gatan, Inc.). The average diameter of grains, gap between grains and nanoparticles were measured from 50 different locations determined from a line measurement by ImageJ. Diameter of particles is defined as the diameter of the smallest circle in which the particle can be embedded. For the EELS 190 element mapping, the energy-filtered TEM was applied to determine the spatial distribution of C and S elements, using a GIF Tridiem postcolumn energy filter (Gatan, Inc.). Therefore, this investigation will help to further improve the performance of next-generation organic semi-conductors.
elements maps, respectively. Moreover, a three-window method of element mapping was adapted to generate these maps. Atomic force microscopy images of spin-coated films on quartz wafers were taken using an Agilent S500 (Aglent Technologies) microscope in the tapping mode over a window of 1 μm × 1 μm. A rotated tip etched silicon probe (Bruker Corporation) with a force constant of 2.8 N m⁻¹ was used.

Grazing incident wide-angle X-ray scattering (GIWAXS) measurements were performed at D-line, Cornell High Energy Synchrotron Source (CHESS) at Cornell University. A wide band-pass (1.47%) X-ray with a wavelength of 1.167 Å was shone on the thin films with a grazing incidence angle of 0.15°. A 50 × 50 mm CCD detector (Medoptics) with a pixel size of 46.9 μm was placed at a distance of 95 mm from the 209 samples. A 1.5 mm wide tantalum rod was used to block the intense scattering in the small-angle area. The exposure time was 1 s.

Normal wide-angle X-ray diffraction (WAXD) tests were performed from 2 to 35° in a continuous mode using a Bruker D8 Advance powder X-ray diffractometer, with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. To generate a relatively high intensity of the peak, a slow increment at 0.02° and slow scan speed at 12 s/step was applied. Percent crystallinity was determined by Diffract. EVA software (Bruker).

X-ray photoelectron spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multichannel plate and delay line detector under a vacuum of 1 × 10⁻⁷ mbar. All spectra were recorded using an aperture slot of 300 × 700 μm. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gauss/Lorentz peak shape. XPS quantification was performed by applying the appropriate relative sensitivity factors to the integrated peak areas.

RESULTS AND DISCUSSION

Annealing-Induced Microstructural Rearrangement

First, we confirmed the high purity of PEDOT/PSS nanofilms (PH1000) by using energy-dispersive X-ray spectroscopy (EDX) (Figure S2) and found results consistent with previous P film studies. The traceable sodium (Na) was most likely from the catalyst during the fabrication process of PEDOT/PSS. In the absence of annealing, both P and PH1000 nanofilms showed fuzzy rings in their selected area electron diffraction (SAED) patterns. In fact, air-dried PH1000 exhibited no clear segregation between amorphous and crystalline phases (as shown in the Figure S3), indicating that PEDOT chains are randomly oriented in the spin-coated PEDOT/PSS films with no clear polycrystalline structure. Figure 1 and Figure S4 show electron micrographs of PH1000 and P nanofilms, respectively, after annealing in air at 120 °C for 15 min. The annealing process caused grains of PH1000 and P films to redistribute uniformly (Figure 1 and Figure S4). However, because the grains were densely packed in annealed P films, we were not able to resolve the core–shell structure of the grains. Alternatively, grains in the annealed PH1000 film were evenly distributed with an average grain diameter of 40 ± 7 nm, as shown in the BF-TEM images (Figure 1, parts a and b). The
inset in Figure 1a shows the SAED patterns of the annealed PEDOT/PSS nanofilm, reveals an amorphous, randomly oriented polycrystalline material. Next, using HAADF-STEM analysis we obtained high-resolution images of the samples by enhancing the Z-contrast of the film. The average diameter of separated grains with arbitrary shapes measured from Figure 1, parts c and d, was 48 ± 10 nm, slightly larger than that measured from the BF-TEM image (Figure 1, parts a and b). In a previous study, the reason behind this diameter difference is discussed in detail.24 The intensity distribution of the marked area in Figure 1d confirmed that the grains are in a core–shell structure (Figure 1e). A relatively lower intensity at the border compared to that at the center allowed us to determine an average shell thickness of 7 ± 2 nm.

Note that the black regions (10–100 nm) between the separated grains occupy nearly 40% of the area (estimated from Figure 1d). To get a deeper understanding of the chemical structure on the PEDOT/PSS nanofilm, EELS analysis was performed on the dark (A), the shell (B), and the core (C) regions to represent different locations of the PEDOT/PSS nanofilms, as marked in Figure 1d. Figure 1f shows that the π* excitation of the unsaturated C=C bond was located at 286.0 eV for both the dark (A) and shell (B) region, but shifted to 287.6 eV for the core region (C). Despite that the π* peak is associated with sp2 carbon in all cases, the C=C bond environment is different in PSS (C=C−C) and PEDOT (C=C−O). This shift reveals that sp2 in the core region originates more from PEDOT than PSS and clearly identifies the dark region as mainly PSS segments. Results were verified by performing graphite bonding (sp2) quantification at different locations. The quantification was based on the fact that the low-loss and K-edge spectra of sp3 carbon and sp2 carbon differ substantially, enabling us to use EELS to quantify the relative sp3 (diamond-like) and sp2 (graphitic) bonding.3 The fraction of graphite bonding (R) is determined by

\[
R = \frac{I_2(\pi*)}{I_1(\pi*)} \frac{I_1(\Delta)}{I_0}
\]

where \(I_2(\pi*)\) is the K-shell intensity in the π*-peak and \(I_1(\Delta)\) represents K-loss intensity integrated over an energy range \(\Delta\) (50 eV) starting at the threshold. The ratio of low-loss and zero-loss intensities \(I_1(\Delta)/I_0\) corrects for plural scattering present in \(I_1(\Delta)\). Thus, the fraction of graphite bonding (sp2) is evaluated as

\[
f = \frac{R}{R_s}
\]

where \(R_s\) is the value of R measured from the spectrum recorded from graphitized carbon under the same TEM conditions and found out to be 0.40. From these equations, the fractions of graphite bonding (R) are determined to be 22%, 27%, and 42% for the dark region, the shell and the core, respectively. This confirms that the core is a PEDOT-rich area compared with the surroundings, which are mainly rich in PSS. An experiment was also performed in a cryo state under the HAADF-STEM mode to reduce background intensity,24 which can reduce observation noise and improve resolution for observing the core–shell structure (Figure 2a). Moreover, the high contrast quality of cryo-TEM images enables sizing of nanoparticles as small as 1.5 to 5 nm; the average size was 3.0 ± 1.0 nm (Figure 2b). The bright nanoparticles observed within the grains are suspected of being PEDOT nanocrystals, separated from each other by PSS segments.

Elemental analysis shows the core region is rich in carbon (C), while sulfur (S) is distributed throughout the grains (Figure 3): the intensity distribution of the marked area in Figure 3, parts a and b, confirms that C is about 8 times more intense than S. This agrees with the carbon to sulfur atomic ratio in both PEDOT and PSS.24 Moreover, the composite-color map in Figure 3c shows that free PSS region has less S than does the grain region. The thickness of the PEDOT/PSS film in the grain region (bright) is higher than that of free PSS region (dark), as shown by the film-thickness map (Figure 3d). The absolute thicknesses of all films were estimated from an effective mean free path,30 and details will be further discussed in the following sections.

From the analysis of TEM micrographs and elemental maps (Figures 1, 2 and 3), we summarize that there are three types of nonconductive boundaries that hinder the electrical transport in the annealed PEDOT/PSS films, as illustrated in Figure 4: (1) free PSS (10–100 nm) in PEDOT/PSS films, (2) a PSS-rich shell (7 ± 2 nm) surrounding the PEDOT-rich core, and (3) bonded PSS (<5 nm) between PEDOT islands inside the PEDOT-rich core.

Changes in Microstructure by Solvent Dedoping.35 Charge carriers cannot easily pass through amorphous PSS regions, which hinders the electrical transport in the PEDOT/PSS films; therefore, they should be excluded from the conduction process. EG dedoping of PEDOT/PSS films can partially remove the amorphous, nonconductive PSS regions, leading to enhanced electrical conductivity of up to 3 or 4 orders of magnitude and the charge carrier density increased by a factor of 1.5.32,26,31,32 We have confirmed this result in our EG dedoped PEDOT/PSS films: spin-coated films were immersed in an EG bath for 2 h and followed by annealing in air at 150 °C for 15 min. The conductivity of the PEDOT/PSS film increased by 3 orders of magnitude: from 0.1 ± 0.03 to 329.0 ± 18.9 S·cm−1 and from 1.0 ± 0.2 to 1344.3 ± 147.1 S·cm−1, for P and PH1000 films, respectively (Figure 5a). We also noticed that the transparency at 550 nm are 96.5 and 351 ± 0.2 to 1344.3 ± 147.1 S·cm−1, for P and PH1000 films, respectively (Figure 5b).26 These results indicate that EG dedoping does not have a significant effect on the transparency of the films. The conductivity enhancement will be explained by using a combined investigation from TEM, AFM, GIWAXS, and XPS as follows. First, we used TEM to determine absolute thickness...
The procedure for estimating specimen thickness within a region defined by the incident beam (or an area-selecting aperture) is to record a low-loss spectrum and compare the area under the zero-loss peak with the total area under the whole spectrum. Absolute thickness of the PEDOT/PSS nano film for TEM imaging is estimated from an effective mean free path $\lambda$ given by

$$\lambda = \frac{\ln(I_0/I)}{\lambda \beta}$$

(5)

where $\lambda$ is expressed by

$$\lambda \approx \frac{106F(E_0/E_m)}{\ln(2\beta E_0/E_m)}$$

(6)

In this equation, $\lambda$ is in nm, $\beta = 10$ mrad, and $E_0$ is the accelerating voltage of 300 kV; $F$ is a relativistic factor (0.512 for $E_0 = 300$ keV) defined by

$$F = \frac{1 + E_0/1022 \text{ keV}}{(1 + E_0/511 \text{ keV})^2}$$

(7)

$E_m$ is defined by

$$E_m \approx 7.6(Z_E)^{0.36}$$

(8)

$$Z_E \approx \frac{\sum f_i(Z_i)^{1.3}}{\sum f_i}$$

(9)

where $Z_E$ is the effective atomic number. $f_i$ is the atomic fraction of each element of atomic number $Z_i$. By use of a 376 formulation of PEDOT/PSS, $(C_6H_6O_2S)_{0.443}(C_8H_8O_3S)_{n-3}(H_2O)_{3.6}$, $Z_E$ is solved as 5.86 and $E_m$ is solved as 14.36 keV. From eqs 8 and 9, we know that the mean free path (MFP) calculation depends on the atomic fraction of each element and atomic number. It is possible to introduce errors between points with high-PEDOT content and points with high PSS content. As a result, we carefully calculated the MFP, $\lambda$ of pure PEDOT, pure PSS and PEDOT/PSS complex and found out to be 180.6, 181.6, and 189.0 nm, respectively. Therefore, we can assume that $\lambda$ is constant everywhere in the PEDOT/PSS film. The relative and absolute thicknesses of PEDOT/PSS films are listed in Table 1.

After EG dedoping, we noticed a considerable reduction in the absolute thickness of self-standing PEDOT/PSS nanofilms: from 56.7 to 34.0 nm and from 52.9 to 32.1 nm for P film and...
PH1000 film, respectively. Figure 6 shows the BF-TEM images of EG-treated PEDOT/PSS films. Although grain structures are not easily determined at low magnifications for either EG-P or EG-PH1000 films, at a high magnification, the diameter of PEDOT/PSS grains in P film was markedly reduced from 60.3 ± 5.7 nm to 10.2 ± 2.4 nm after EG dedoping (Figure 6, parts a and b). However, the grain structures of the EG-PH1000 film could not be resolved under a high BF-TEM magnification.

Figure 7 illustrates HAADF-TEM images at different magnifications, which provide more detail about structural changes after EG dedoping. The grains observed in the high-magnification EG-P film BF-TEM images are spherical and small islands. In the EG-P film, the nanoparticle diameter ranges from 0.9 to 2.3 nm with an average diameter of 1.4 ± 0.3 nm. In the EG-PH1000 film, the nanoparticle diameter ranges from 1.0 to 2.6 nm with an average diameter of 1.6 ± 0.4 nm. These structures on the nanofibrillar have been reported for other conductive polymers (e.g., polyacetylene, in which the fibrillar morphology is due to an oriented arrangement of particles of about 10 nm). Here, we found that removal of PSS results in a reduction of particle size to about half that of pristine PEDOT/PSS films (3.0 ± 1.0 nm); these particles become more conductive in EG-PEDOT/PSS films. Second, these conductive particles are densely packed and connected compared with those in pristine PEDOT/PSS films. The main effect of EG dedoping is to produce a more uniform dispersion of conductive nanofibrils, which are assembled into clusters (grains) before dedoping but become homogeneously dispersed after dedoping.

To confirm the microstructure of the films with EG dedoping, AFM images were taken to probe the changes on the surface microstructure of the films. As shown in Figure S5, EG-P films have clearer grain structures than pristine films, whereas EG-PH1000 films display elongated nanofibril structures. The height images show that all films are reasonably smooth on quartz wafers with a small root-mean-square (rms) roughness measured from the height images. Prior to dedoping, the rms roughness of pristine P film and pristine PH1000 films were 0.96 and 1.27 nm, respectively, but after EG dedoping, the roughness increased to 1.69 and 2.03 nm, respectively (Figure 6). This increase in roughness agrees with observations of EG-PEDOT/PSS films and suggests partial removal of PSS segments in PEDOT/PSS films. More importantly, EG dedoping partially removes amorphous PSS, resulting in a clear grain structure in EG-P film but an elongated fibril structure in the EG-PH1000 film.

To understand electrical transport in PEDOT/PSS films, the film microstructure was investigated by grazing incident wide-angle X-ray scattering (GIWAXS) in Figure S6. For pristine Clevios P and PH1000 films, three peaks are observed in both directions at approximately qz = 5.1, 12.8, and 18.0 nm−1, corresponding to the d-spacing of 1.23, 0.49, and 0.35 nm, respectively. The peak at qz = 5.1 nm−1 indicates lamellar stacking of PEDOT nanocrystal, the (010) peak at qz = 18.0 nm−1 indicates π−π stacking of PEDOT chains, and the broad peak at qz = 12.8 nm−1 is attributed to the amorphous halo of randomly distributed PSS. To conclude, the strong scattering isopy of PEDOT in pristine PEDOT/PSS films...
reveals that the PEDOT chains orient randomly in PEDOT/PSS films. Figure S6 also presents the WAXS pattern of EG-P and EG-PH1000 films showing a higher intensity from π−π stacking. It is worth noting that after EG dedoping, the π−π stacking peak of pristine P and PH1000 films shifts from $q_z = 17.8$ and 17.9 nm$^{-1}$ to $q_z = 18.0$ and 18.4 nm$^{-1}$, respectively.

The above peak shifts correspond to a reduction in the π−π stacking distances from 3.52 and 3.51 Å to 3.49 and 3.41 Å, respectively. The shorter distance indicates stronger π−π interactions between adjacent PEDOT nanocrystals, facilitating electron transport in these directions. After EG dedoping, intensity of the scattering peak at $q_z = 5.1$ nm$^{-1}$ increased and the peak became more obvious. Specifically, the peak at $q_z = 5.1$ nm$^{-1}$ for P and PH1000 films shifted to $q_z = 6.0$ and 6.2 nm$^{-1}$ after EG dedoping. These results suggest that EG treatment increases the order of PEDOT nanocrystals and that these crystals should form a layered structure. Because of the ultrathin thickness (40–60 nm) and isotropic morphology of the PEDOT/PSS nanofilms, the out-of-plane π−π stacking intensity was smeared, as shown in inset of Figure S6. This makes the direct identification of the lamellar stacking difficult and from that we cannot observe a clear out-of-plane π−π stacking even though it is possible to see them after integration. However, the (100) out-of-plane diffraction of lamellar packing strongly indicates the edge-on orientation of molecules on the substrate.

Normal WAXS (Figure S7 and Table S1) were also performed with 50 μm thick PEDOT/PSS films. The results are comparable to those of the GIWAXS. We verified that after EG dedoping, the π−π stacking distance of PEDOT chains reduced from 3.48 to 3.41 Å and from 3.46 to 3.38 Å for P and PH1000 films, respectively.

Surface analysis of PEDOT/PSS films before and after EG dedoping were further investigated by XPS. High-resolution XPS of the S 2p core-level spectra are shown in Figure S8. The S 2p core-level spectra have two distinct peaks from 162.0 to 166.0 eV and from 166.0 to 171.0 eV. The S 2p$^{3/2}$ components at 163.5 and 167.8 eV correspond to sulfur atoms of the PEDOT and the sulfonate fragment of PSS, respectively. The experimental PEDOT-to-PSS ratio ($R_s$) was determined by quantitative analysis of the S 2p core-level spectra. In P and PH1000 films, an $R_s$ of 0.42 and 0.41 were measured, respectively; EG dedoping caused the $R_s$ increase to 0.47 and 0.56, respectively. This change clearly suggests that PSS is partially removed from PEDOT/PSS films by EG dedoping.

Though the TEM images of PEDOT/PSS have been shown before in the film or fiber structure, we extend this work by BF-TEM images of PEDOT/PSS nanofilms after EG dedoping. (a and b) EG-P nanofilms at different magnifications. (c and d) EG-PH1000 nanofilms at different magnifications.
by providing a clear visualization of its disordered and ordered structure. Furthermore, using AEM, XRD and XPS analyses of PEDOT/PSS films, we can offer more detailed information on their structure. Figure 7 illustrates the microstructural change of PEDOT/PSS films by EG dedoping. The EG dedoping of PEDOT/PSS film leads to the following four effects: (1) free PSS segments are mostly removed, which directly induced the formation of the nanofibrils in the film; (2) a PSS-rich shell surrounding the PEDOT-rich core are partially ruptured, allowing the conductive PEDOT nanoparticles to exit and connect with each other, resulting in improved interconductivity; (3) part of PSS in the PEDOT-rich core region is removed due to EG weakens the electrostatic interaction between PEDOT and PSS; and (4) the π–π stacking distance is reduced, leading to improved conduction in the two-dimensional lamellar. From the observations and characterizations of the structural change of PEDOT/PSS films made here, we can state that the deposition of the PEDOT/PSS from a dispersion results in a less-ordered layer system with a large amount of PSS between them: the originally several nanometre particles assemble into 50 nm grains with help from the electrostatic bonding of PEDOT and PSS. These large-sized grains can be reopened and their size reduced to their original several nanometre particles by EG dedoping by the removal of amorphous PSS. As a result, microstructural changes toward nanofibrils consist of densely packed PEDOT nanoparticles with less amorphous PSS boundaries, which leads to the high conductivity of PEDOT/PSS films. Partial removal of PSS might have a stronger influence than molecular orientation within PEDOT crystallites in determining electrical conductivity.

**CONCLUSION**

In summary, we systematically investigated the microstructure of the PEDOT/PSS nanofilm using a combination of BF-TEM and HAADF-TEM techniques. We found that PEDOT/PSS grains are evenly distributed after thermal annealing. TEM images together with EELS analysis on the annealed films clearly revealed the location of different phases in PEDOT/PSS nanofilms. Meanwhile, EG dedoping improved the conductivity through morphological changes and molecular reorientation within crystalline domains: correlated to grain ruptures toward smaller and more densely packed PEDOT nanoparticles together with an enhanced crystallinity, the removal of PSS domains and a reorientation of the conjugated PEDOT molecules. Information presented here will be integral to understanding structural formation during all processing steps involved in realizing an organic semiconductor device with optimized performance.

**ASSOCIATED CONTENT**

* Supporting Information
  Sample preparation and characterization, additional TEM images, AFM images, GIWAXS data, normal WAXS data and XPS curves. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b00851.

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**Notes**
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