

Imaging the Phase Separation Between PEDOT and Polyelectrolytes During Processing of Highly Conductive PEDOT:PSS Films

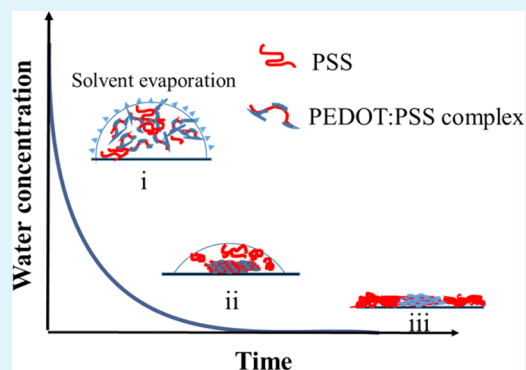
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Supporting Information

ABSTRACT: Treating PEDOT:PSS (Clevios) with certain additives, such as ethylene glycol (EG), dimethyl sulfoxide (DMSO) and sorbitol, has been shown to increase the conductivity of this material from roughly 1 to nearly 1000 S/cm. Using a slow drying method, we show that the additive induced a separation between free PSS and reorganized PEDOT:PSS complexes in the highly conductive PEDOT:PSS films. Additives (DMSO, DEG, and PEG 400) were included in PEDOT:PSS aqueous dispersions at large volume fractions. The mixtures were slowly dried under room conditions. During drying, the evaporation of water resulted in an additive-rich solvent mixture from which the reorganized PEDOT:PSS complexes aggregated into a dense film while free PSS remained in the solution. Upon complete drying, PSS formed a transparent rim film around the conducting PEDOT film. The chemical compositions of the two phases were studied using an infrared microscope. This removal of PSS resulted in more compact packing of PEDOT molecules, as confirmed by X-ray diffraction measurements. X-ray photoelectron spectroscopy and atomic force microscope measurements suggested the enrichment of PEDOT on the film surface after PSS separation. Through a simple drying process in an additive-containing dispersion, the conductivity of PEDOT films increased from 0.1 to 200–400 S/cm. Through this method, we confirmed the existence of two phases in additive-treated and highly conductive PEDOT:PSS films. The proper separation between PSS and PEDOT will be of relevance in designing strategies to process high-performance plastic electrodes.

KEYWORDS: PEDOT:PSS, solvent treatment, additives, conductivity enhancement, organic electronics



INTRODUCTION

The search for organic conducting materials has been driven by rapid development in organic solar cells, flexible energy storage, organic light emitting devices, stretchable electronics, and bioelectronics.^{1–3} It is often desirable in these applications that the electrodes be flexible, stable, highly conductive, and solution processable. Among the candidates, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the extensively studied materials. As a (semi)metallic polymer,⁴ the conductivity of PEDOT can exceed 3000 S/cm. The polymer can be either chemically or electrochemically polymerized from the corresponding monomer EDOT. However, once polymerized, PEDOT is no longer soluble, making it difficult to process through solution. This problem was circumvented by polymerizing EDOT in the presence of a polyelectrolyte, poly(styrene sulfonic acid) (PSS). The water-soluble, negatively charged PSS forms soluble polyelectrolyte complexes with positively charged PEDOT. In this system, PSS functions both as the dopant and stabilizer for PEDOT. The nanostructure of this blend between insulating PSS and the highly conductive PEDOT chains controls the transport properties of the thin film, as has been extensively reported.^{5–8}

The as-prepared film from the PEDOT:PSS dispersion (commercially available as Clevios) typically has a conductivity

of ~0.1–1 S/cm. It was found that the conductivity of the coating could be increased by 2 to 3 orders of magnitude by adding certain additives into the dispersion prior to film deposition or by treating the films with certain solvents or acids post deposition.^{9–12} A main family of the additives consists of polyhydroxyl alcohols, such as sorbitol,^{13,14} poly(ethylene glycol) (PEG),^{15,16} ethylene glycol (EG)^{17,18} or diethylene glycol (DEG).¹⁹ PEG-based nonionic surfactants, such as Triton X-100 and Zonyl FS300, were found to improve the conductivity.^{20,21} Other additives include water-miscible high-boiling-point solvents, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), and dimethyl sulfate (DMS).^{20,22–24} The enhancement could also be induced by ionic liquids.²⁵

The origin of the conductivity enhancement is still under debate. It is commonly proposed in the literature that the increase in conductivity is associated with the phase separation between the insulating PSS and the conducting PEDOT. One major piece of evidence that supports this hypothesis is the decrease of the PSS S 2p signal intensity on film surfaces from

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X-ray photoelectron spectroscopy (XPS) measurements.^{19,26–29} For additive post-treatment methods, where the pristine PEDOT:PSS film was treated with solvents or acids followed by rinsing, the decrease in film thickness and PSS content was also generally observed.^{5,9,30} Some of the highest conductivity (>3000 S/cm) was reported by employing this method,³¹ which suggests the effectiveness of removing insulating materials for enhancing film conductivity. Other changes may also be involved. Additive-treated PEDOT:PSS was found to adopt a morphology that consisted of an interconnected PEDOT network enriched on the surface, as seen in AFM phase contrast.^{19,21,24,25,32,33} Increased connectivity between the PEDOT filaments was reported.³⁴ With the additives, the crystallinity of PEDOT and the size of PEDOT crystal domains in the film was found to be increased.³⁵ It was proposed that some additives, DMSO for example, functioned as secondary dopants for PEDOT, which might increase the doping level of the conducting polymer.¹⁹ A conformational change on the PEDOT chain was also proposed in which PEDOT assumed a more extended conformation,³⁶ facilitating the charge transport.³⁷

However, until now, only indirect evidence of the phase separation has been reported.⁹ One difficulty is the small length scales of the phase separation. During the film treatment, the formation of PEDOT- and PSS-rich phases on a nanometer scale was suggested by the AFM studies.²⁶ The lack of adequate contrast between the two polymers can also hinder the study of phase separation. In this paper, we studied additive-induced phase separation in PEDOT:PSS films using a very simple imaging method. Three representative solvent additives, DMSO, DEG, and oligomeric PEG (with an average molecular weight of 400 g/mol, denoted as PEG 400), were added to a PEDOT:PSS aqueous dispersion at various volume fractions. The mixture was drop coated onto glass substrates and slowly dried under room conditions. During solvent evaporation, the water fraction first evaporated due to its higher vapor pressure at room temperature (24 mmHg at 25 °C), and the lower vapor pressure liquid additive was left on the substrate, as shown in the schematic illustration of Figure 1. It was found that when

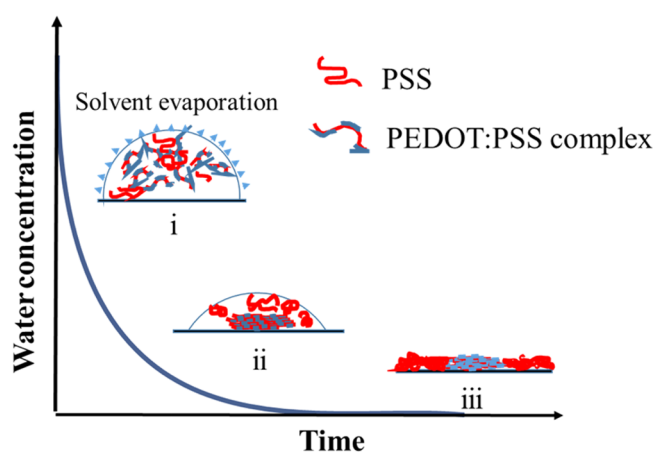


Figure 1. Schematic illustration of the phase separation in a slowly drying PEDOT:PSS droplet. (i) A droplet of PEDOT:PSS aqueous dispersion with DMSO is cast on a solid substrate; (ii) after water evaporation, the PEDOT:PSS complex is enriched while “free” PSS is still dissolved in DMSO; (iii) upon complete drying, the PEDOT:PSS phase and the free PSS phase occupy different regions on the substrate. The water concentration diagram is only illustrative.

water evaporated, the PEDOT:PSS complexes were no longer soluble and aggregated into a film, while a fraction of free PSS, being soluble in the liquid additive, was concentrated into the liquid phase. After complete drying, free PSS was separated from PEDOT:PSS complexes and formed an outer rim around the PEDOT:PSS film. With this method, the coexistence of free PSS and reorganized PEDOT:PSS complexes in additive-treated PEDOT:PSS films, and the liquid–solid phase separation between these two components, was unambiguously confirmed. The chemical composition of the two phases was characterized with IR microscopy. The effects on the film morphology, conductivity, and structure were directly studied using AFM and XRD methods.

EXPERIMENTAL SECTION

Chemical Reagents. Unless specified, all chemicals were purchased from Sigma-Aldrich.

Preparation of PEDOT Films. The substrates (gold-coated silicon wafers or glass) were cleaned with detergent, deionized (DI) water, TL-1 solution (H₂O:30% ammonium hydroxide:30% hydrogen peroxide = 5:1:1 (volume)), and DI water and dried under N₂ flow. The PEDOT:PSS (Clevios PH 1000, Heraeus Precious Metals) aqueous dispersion was blended with DMSO, DEG, or poly(ethylene glycol) (PEG) 400 ($m_n = 400$ g/mol) at various volume ratios. The mixtures were stabilized by stirring under room temperature for ~20 min before being drop cast onto the substrate. It was allowed to slowly dry under room conditions (25 °C and relative humidity (RH) of ~20–30%) for 2 to 3 days. As DEG did not completely dry in air, after 3 days, the samples with DEG were heated at 120 °C for 20 min to remove the solvents. Films obtained from PEG 400 solutions were rinsed with water at least 3 times and air-dried. For samples with different additive volume fractions, the solid content of PEDOT was kept constant. For example, 64 μ L of PEDOT:PSS in 50% DMSO was cast onto the glass substrate, whereas it was 34 μ L for 5% DMSO. In both droplets, the volume of PEDOT:PSS aqueous dispersion was 32 μ L. For thermally annealed pristine PEDOT samples, 0.25% (w/w) Zonyl was added to ensure uniform wetting. The film was drop-cast onto glass substrates and dried at 120 °C.

Characterizations. Photo images were taken on a Nikon D3100 digital camera. Optical micrographs were taken on an Olympus BH-2 optical microscope equipped with a Sanyo VCC29 CCD camera. Sheet resistance measurements were performed on an Alessi 4 point probe (1.25 mm distance) with a Keithley 4200 semiconductor characterization system as the power source. Film thickness was measured on a Veeco Dektak 6 M profilometer.

X-ray diffraction (XRD) was performed on thick film samples (~10 μ m) on a PANalytical X'pert Pro diffractometer using Cu K α radiation (1.5406 Å) at 40 kV and 40 mA. X-ray photoemission spectroscopy (XPS) measurements were carried out on a Scienta ESCA 200 spectrometer with a base pressure of 1×10^{-10} mbar. The measurement chamber was equipped with a monochromatic Al K α X-ray source providing photons with 1486.6 eV. The experimental condition was set so that the full width at half-maximum of the clean Au 4f_{7/2} line was 0.65 eV. All spectra were collected at a photoelectron takeoff angle of 0° (normal emission) at room temperature.

Fourier-transform infrared measurements were carried out with a Bruker HYPERION 3000 microscope using a Tensor 27 spectrometer as the light source equipped with a focal plane array detector (128 \times 128 pixel resolution), giving a lateral resolution of 2 μ m. The system was continuously purged with nitrogen before and during the measurements. Infrared images were captured between 4000 and 800 cm^{-1} and with a 4 cm^{-1} spectral resolution.

AFM measurements were performed in tapping mode in an EnviroScope microscope equipped with a NanoScope IV controller (Veeco) by using commercial silicon cantilevers with a nominal spring constant of 40 N/m.

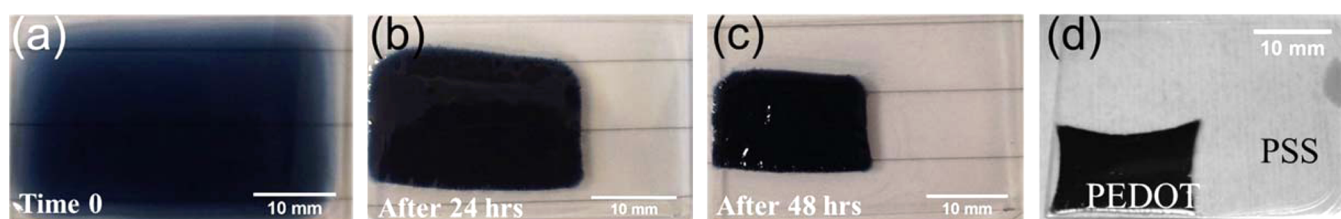


Figure 2. Photographs of PEDOT:PSS in 50% DMSO:H₂O drying in air. (a) to (c), the drying process of PEDOT:PSS in 50% DMSO over 48 h at room temperature; (d) completely dried film shows a concentrated PEDOT area surrounded by a transparent PSS area. Scale bar represents 10 mm.

Table 1. Film Thickness and Conductivity of PEDOT:PSS Films Dried from Water:DMSO Mixed Solvents

DMSO concentration (%)	droplet volume (μL)	wetting ratio (%) ^a	PEDOT area ratio (%) ^b	PEDOT thickness (μm)	R_s ($\Omega \text{ sq}^{-1}$)
0	70	91–94	100	4.56 ± 0.45	21088 ± 580
5	34	45–56	88–90	5.01 ± 1.35	11 ± 6
10	36	38–48	68–86	5.30 ± 1.46	5 ± 2
20	40	31–39	37–48	11.62 ± 3.00	4 ± 2
50	64	88–94	21–22	10.06 ± 1.06	4 ± 3

^aArea ratio of droplet wetted area on the 1.25×1.25 glass slide. ^bPercentage ratio of PEDOT area to the whole polymer film area.

RESULTS

Drying of PEDOT:PSS in Mixed Solvents. The drying of the PEDOT:PSS dispersion in 50% DMSO (volume fraction to PEDOT:PSS aqueous dispersion) is shown in Figure 2. When cast onto a glass substrate, the mixture was a transparent deep blue sessile droplet with minimum dewetting. It was allowed to dry at 25 °C under ~20% RH for 48 h. After the initial 24 h, a large fraction of the solvents evaporated. The solid content aggregated into a black film that suspended in the remaining clear solution. As the DMSO has a relatively low vapor pressure at 25 °C (0.42 mmHg) and is not known to form azeotropes with water, it was reasonable to estimate that the remaining liquid has a very high fraction of DMSO.³⁸ After 48 h, all of the solvents evaporated. Compared to its wet state, the black film visibly shrank, reducing to 1/4 of the size of the original droplet. A transparent film was left on the region that was originally covered by the clear solution.

It was found that the black area was electrically conducting, indicating that it contained PEDOT. The transparent film, on the other hand, was insulating. Clearly, two components existed in the PEDOT:PSS dispersion treated with DMSO, where one component collapsed into an insoluble black film upon water evaporation, and the other remained soluble in the DMSO-rich liquid and formed a transparent film layer after complete drying.

When PEDOT:PSS was slowly dried from 50% DEG or 50% PEG 400 solutions, a similar effect was also observed. These two additives have also been used to improve the conductivity of the PEDOT:PSS films.^{16,39} With even lower vapor pressure, DEG dries slowly at room temperature. After 72 h, there was still a layer of liquid on the substrate (Supplementary Figure S1). However, PEDOT:PSS collapsed into a black film in this remaining liquid. The remaining solvents were then removed by heating at 120 °C. A transparent film was found on the solvent wetted area. As there was a receding liquid/solid contact line, the transparent film adopted a concentric-ring structure. The thickness of the transparent film as measured by a profilometer varied from 1 to 5 μm (Supplementary Figure S2). In the case of PEDOT:PSS in 50% PEG 400, the oligomeric PEG could not be thermally dried. After several days of drying under room conditions, a large amount of liquid PEG remained. Like in the case of DMSO and DEG, PEDOT:PSS

concentrated into a black film that could be easily picked up from the clear PEG liquid.

PEDOT:PSS was also dried with different DMSO volume fractions to study the effects of initial additive concentration on phase separation and film conductivities. Typically, a sessile droplet of the mixture was cast onto a $1.25 \times 1.25 \text{ cm}^2$ glass slide and dried under room conditions for 48 h. As shown in Table 1, four different compositions were employed: 5, 10, 20, and 50% DMSO. The volumes of the droplets were chosen such that, in all the groups, the total PEDOT:PSS solid content were the same. The differences in initial volumes and wetting abilities of these compositions resulted in the different coverage of the films on the substrates after drying. As shown in Figure 3,

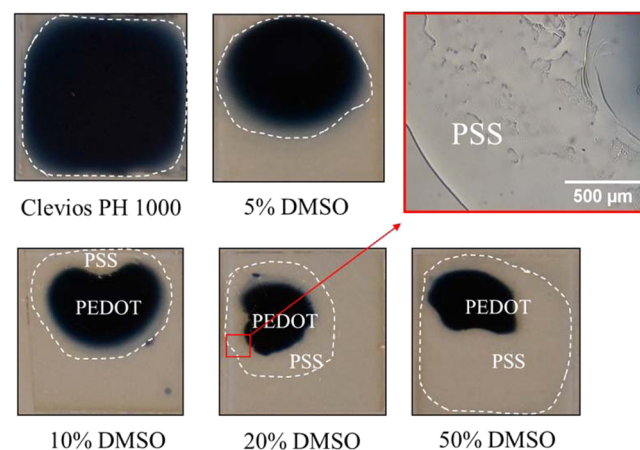


Figure 3. Drying of PEDOT:PSS at different DMSO concentrations.

all the samples that had DMSO showed lateral phase separation of a black PEDOT film and a transparent ring. The size of the ring film largely depended on the total volume of DMSO. In 50% DMSO, the mixture contained a substantially larger volume of DMSO than for 5% DMSO (32 μL versus 2 μL). After the formation of the PEDOT film during solvent evaporation, the DMSO-rich solution remaining in the droplet covered a significantly larger area than that of 5% DMSO. Therefore, the transparent film deposited from this solution was able to cover a larger area on the substrate, forming a wider

“ring” around the PEDOT film after its complete drying. It was also observed that the PEDOT film typically floated on the droplet surface. Although the macroscopic accumulation of a PEDOT-rich phase on the liquid–air interface should be the result of phase equilibrium in the slow drying process, it suggests that a vertical phase separation may accompany the lateral phase separation during the drying. In higher DMSO concentrations, where the droplet of the remaining DMSO-rich solution was larger in volume, the PEDOT film was smaller in area but thicker (Table 1). For the PEDOT:PSS aqueous dispersion without additives, phase separation was not observed (Figure 3).

Conductivity of Phase-Separated PEDOT Films. The slow drying of PEDOT:PSS with DMSO additives did not require thermal annealing. As shown in Table 1, there was a large variation in the film thickness, typically thicker in the center and thinner on the edge. The pristine PEDOT:PSS dried at room conditions had a sheet resistance of ~ 20 k Ω /sq, corresponding to the conductivity range of 0.1 S/cm. The addition of DMSO at all concentrations decreased the resistance of PEDOT films by several orders of magnitude. For example, the ~ 5 μ m thick film dried from 10% DMSO had a sheet resistance of ~ 5 Ω /sq, corresponding to a conductivity of roughly 400 S/cm, which is 1000 \times higher than that of the pristine PEDOT:PSS film. The conductivity of PEDOT films from other DMSO concentrations was estimated to be in the same range. This conductivity was at the same magnitude of the reported conductivity of DMSO-treated PEDOT films, which was usually reported to be ~ 100 to 1000 S/cm.^{26,37} These slowly drying films were also later subjected to thermal annealing at 140 $^{\circ}$ C in air for 20 min, and no significant change in conductivity was observed.

The sheet resistance of the PEDOT film dried from 50% DEG and 50% PEG 400 was also measured (Table 2). For 50%

Table 2. Film Thickness and Conductivity of PEDOT:PSS Films Dried from Water:DEG or Water:PEG 400 Mixed Solvents

	droplet coverage (%)	PEDOT coverage (%)	PEDOT thickness (μ m)	R_s (Ω sq $^{-1}$)
50% DEG	100	20–23	11,06 \pm 0.77	6 \pm 2
50% PEG 400	100	33–35	3.65 \pm 1.45	14 \pm 3

DEG, the film was thermally dried without any rinsing. A sheet resistance of 6 \pm 2 Ω /sq was found. The conductivity was roughly estimated to be on the order of ~ 150 S/cm. For PEG 400, the film was rinsed with water and dried at 120 $^{\circ}$ C. The sheet resistance was 14 \pm 3 Ω /sq for ~ 3.6 μ m thick film, and the conductivity was ~ 200 S/cm. Previously, PEG was reported to increase the conductivity of PEDOT:PSS from 0.1 S/cm to up to 17.7 S/cm.¹⁶ Here, the PEG400 samples at 200 S/cm approached the same magnitude of conductivity as for PEDOT obtained from DEG- and DMSO-treated samples.

Chemistry of Phase-Separated Films. The chemical compositions of the two phases were studied with an IR microscope. Figure 4a shows an optical micrograph of the border of the PEDOT film and the transparent ring dried from 50% DMSO on a gold substrate. The IR spectra of position I on the black PEDOT film and position II on the transparent film (Figure 4a) are shown in Figure 4b. It is clear that the black film contains both PEDOT and PSS. Characteristic PSS absorption peaks from $-\text{SO}_3^-$ asymmetric and symmetric

stretching near 1236 and 1037 cm^{-1} , respectively,⁴⁰ are observed in both spectrum I and II. In spectrum I, the region between 1652 and 1540 cm^{-1} is dominated by the C=C asymmetric stretching in the PEDOT thiophene ring,^{41,42} whereas in the transparent film, this peak disappeared. Instead, the characteristic PSS SO_3^- symmetric (1037 cm^{-1}) and asymmetric stretchings (1236 cm^{-1}) were found in the spectrum of position II^{40,43} (a comparison of IR spectra taken from PSS sodium salt standard, the transparent region, and the dark film can be found in Figure S5; for assignment of other significant absorptions, see Table S1). To confirm that the transparent film was PSS separated from PEDOT:PSS complexes, the film was soaked in deuterium water. It was found that the transparent film was readily dissolved in D_2O whereas the black PEDOT film was still intact. The ^1H NMR spectrum (Figure S3) of the collected solution showed chemical shifts at 7.5 and 6.5 ppm that were characteristic for sulfonated aromatic protons on the benzene ring, as well as broad peak between 2 to 1 ppm for $-\text{CH}_2-\text{CH}-$ protons.⁴⁴ Because of the low concentration of solute, the integration on these peak intensities was not accurate. Nevertheless, the IR and ^1H NMR spectra both suggested that the transparent film was PSS that separated from PEDOT:PSS.

By integrating the IR signal intensity from 1652 to 1540 cm^{-1} , a range that was dominated by PEDOT ring stretching,⁴⁵ the distribution of PEDOT could be mapped. As shown in Figure 4c, there was a high intensity in the PEDOT IR signal from the black film. The signal intensity decreased from the center of the black film to the edge, as the thickness decreased in this manner. In the transparent film region, the integrated intensity became minimal. Conversely, integration of the PSS SO_3^- IR signal intensity from 1060 to 1015 cm^{-1} showed that PSS was distributed on both the black film and the transparent film (Figure 4d). The profiles of the signal intensities for IR absorptions characteristic for PEDOT and PSS are plotted in Figure 4e. It was clear that from the black film region to the transparent film region, there was a sharp decrease of PEDOT intensity, where it almost vanished in the transparent region, whereas for PSS, the signal intensity was relatively stable across the border. This confirmed that the black film contained PEDOT and PSS, presumably in the form of a polyelectrolyte complex, whereas the transparent film should predominantly consist of PSS.

Surface Properties of Phase-Separated PEDOT:PSS Films. PEDOT:PSS films are known to be very hydrophilic. Air-dried pristine PEDOT:PSS can again be readily dispersed in water. The PEDOT:PSS film dried from 5 to 50% DMSO, conversely, showed resistance to water. Although they swelled in water, the films could not be redispersed.

The surface chemistry of the PEDOT:PSS films without water rinsing was studied by XPS. As shown in Figure 5, two types of S 2p signals were found on the samples. The higher binding energy peak around 168 eV was contributed by the sulfur atoms in PSS, whereas the two peaks at lower binding energy (165 to 163 eV) could be assigned to the sulfur atom in PEDOT.^{19,46–48} From the integrated S 2p peak area ratio between PEDOT and PSS (denoted as $R_{\text{T/S}}$, where T refers to thiophene and S refers to sulfonate), it was found that the macroscopic phase separation led to a significant decrease of PSS content on the film surface. $R_{\text{T/S}}$ was 0.21 for pristine PEDOT:PSS dried in air. For PEDOT:PSS dried from 5% DMSO, $R_{\text{T/S}}$ increased to 0.26. The largest macroscopic phase separation (vertical and lateral) was observed on the

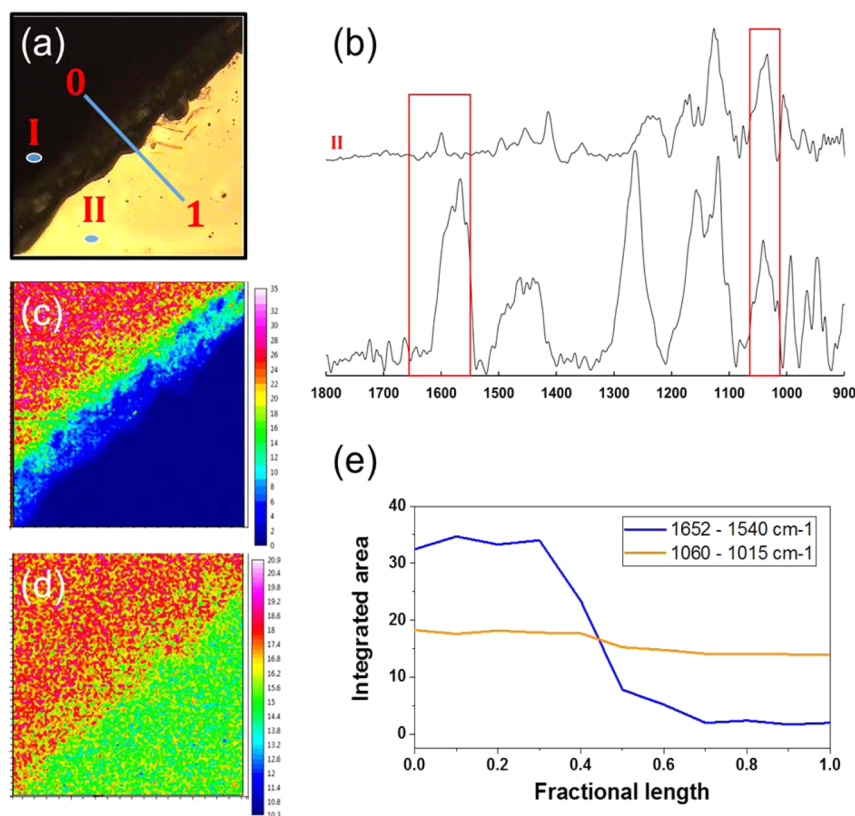


Figure 4. IR microscopy reveals the distributions of PSS and PEDOT:PSS on a film dried from PEDOT:PSS in 50% DMSO. (a) Reflection image showing the black film (PEDOT:PSS) and the transparent PSS film on a gold substrate. The size of the image is $300 \times 300 \mu\text{m}^2$. (b) IR spectra obtained at positions I and II in (a) with absorptions characteristic for PSS and PEDOT indicated; the left box indicates the region from 1652 to 1540 cm^{-1} from C=C asymmetric thiophene ring stretching in PEDOT, and the area in the right box is dominated by SO_3^- stretchings in PSS. For assignment of other peaks, see Table S1. (c) Intensity distribution map of the integrated peak area between 1652 and 1540 cm^{-1} , characteristic of PEDOT. (d) Intensity distribution map of the integrated peak area between 1060 and 1014 cm^{-1} from PSS. (e) The integrated area intensity profiles for the two spectral regions along the line indicated in (a).

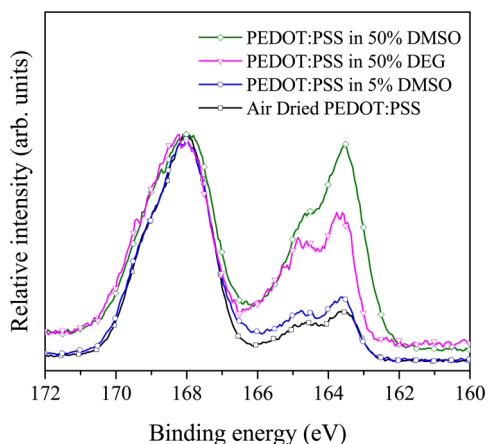


Figure 5. XPS of PEDOT:PSS films.

PEDOT:PSS dried from 50% DMSO. Consistent with this observation, $R_{T/S}$ increased to 0.80. When the PEDOT film was thermally dried from 50% DEG, a thin layer of PSS was left on the film as the film swelled in the PSS:DEG solution. Nevertheless, the $R_{T/S}$ increased to 0.58.

Structural and Morphological Changes Induced by Additives. PEDOT:PSS is commonly known as a largely amorphous material.⁴⁹ The X-ray diffraction (XRD) pattern obtained from a fast thermal annealed pristine PEDOT:PSS

film with 0.25% Zonyl (Figure 6) showed a broad diffraction peak that corresponded to the d -spacing of 3.4 \AA at 2θ of $\sim 26^\circ$. This diffraction arises from PEDOT thiophene ring π - π stacking (d_{010}).⁵⁰ Another peak was found at 2θ of $\sim 18.4^\circ$, corresponding to a d -spacing of 4.8 \AA . This distance can be attributed to the PSS benzene ring π - π stacking.^{4,51} When pristine PEDOT:PSS was slowly dried under room conditions, the film showed diffraction peaks at $2\theta = 25.7^\circ, 18.1^\circ, 13.7^\circ$ and 6.9° , corresponding to $d = 3.5, 4.8, 6.4,$ and 12.8 \AA , where the 13.7° peak could be attributed to the d_{200} reflection of PEDOT side-by-side packing d_{100} reflection at 6.9° . When the films were dried from DMSO, there was a shift of d_{010} reflection from 25.7° to 26.2° , suggesting a decrease of π - π stacking distance from 3.5 to 3.4 \AA . The reflection at 18.1° , however, was retained.

It was found that washing with water did remove the transparent PSS ring from the PEDOT:PSS film with separated PSS. The PEDOT:PSS films from 20% DMSO, 50% DMSO, 50% PEG 400, and 50% DEG were carefully rinsed with water and air-dried. It was found that, after drying, a new peak appeared around $2\theta = 3.9^\circ$, corresponding to $\sim 23 \text{ \AA}$ distance. This peak was attributed to the lamella stacking of PEDOT and PSS chains [(d_{100})] by Nara Kim et al.⁵¹ In their work, immersing the PEDOT:PSS film in ethylene glycol also removed PSS and increased the intensity of the lamella stacking peak.⁵¹ In some of the samples, there was also a decrease in the PEDOT d_{010} peak intensity after rinsing, which

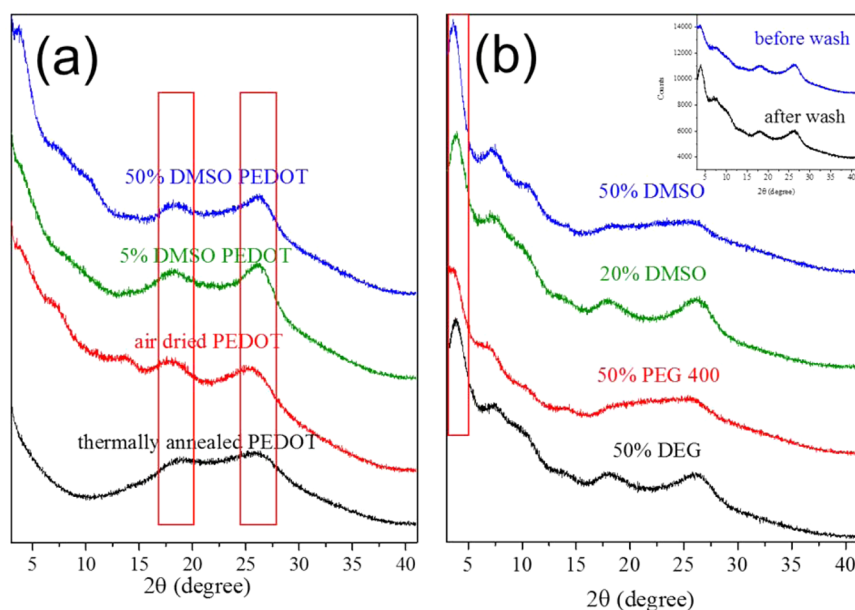


Figure 6. XRD of PEDOT:PSS films. (a) XRD spectra of thermally annealed pristine PEDOT, air-dried pristine PEDOT, and PEDOT:PSS film dried from 5% DMSO and 50% DMSO. (b) XRD spectra of PEDOT:PSS films dried with 50% DEG, PEG 400, 20% DMSO, and 50% DMSO; all of the samples have been rinsed to remove excess PSS on the film surface, and the inset shows the spectra before and after rinsing for the 20% DMSO sample.

might be a result of the rearrangement of crystalline domain orientations. Overall, this result suggested that the removal of free PSS allowed PEDOT:PSS to pack into a denser and more organized structure, which would help explain the conductivity enhancement of additive treatment generally reported in the literature.

Surface Topography of PEDOT:PSS Films after Phase Separation. Atomic force microscopy (AFM) was employed to study the surface morphology of PEDOT:PSS films (Figure 7). The pristine PEDOT:PSS film dried from air has a fibrous morphology. These nanofibers were formed by grains that had diameters of ~ 10 nm. With additives and after the following phase separation, the size of these grains changed significantly. All the samples showed a bumpy surface morphology with varying contribution of grains and nanocrystals (Supporting Information). The phase contrast images of 5% DMSO, 50% DMSO, and 50% DEG films (Figure S4) similarly highlight the increase of grain size and roughness of the treated samples with respect to the pristine PEDOT:PSS film.

DISCUSSION

The PEDOT:PSS dispersion is prepared by chemically polymerizing EDOT in the presence of PSS.⁸ PSS provides the negative charge to stabilize a partially positively charged PEDOT chain.⁵² Through electrostatic attractions, the short PEDOT chain is attached to the PSS chain, forming a polyelectrolyte complex that can be dispersed in aqueous medium.⁵³ Although the doping concentration of PEDOT through different methods was usually reported to be around a 30% molar ratio^{54–56} in the PEDOT:PSS complex, excessive PSS sulfonic groups are required to keep the complex dispersible.⁵² The weight ratio between PEDOT and PSS in commercially available PEDOT:PSS dispersion (Clevios, previously known as Baytron P) varies from 1:2.5 to 1:20,^{35,52} which corresponds to a EDOT unit to sulfonic acid molar ratio of 1:2 to 1:15. In the dispersion, the PEDOT:PSS complex is usually described as a microgel system, where a

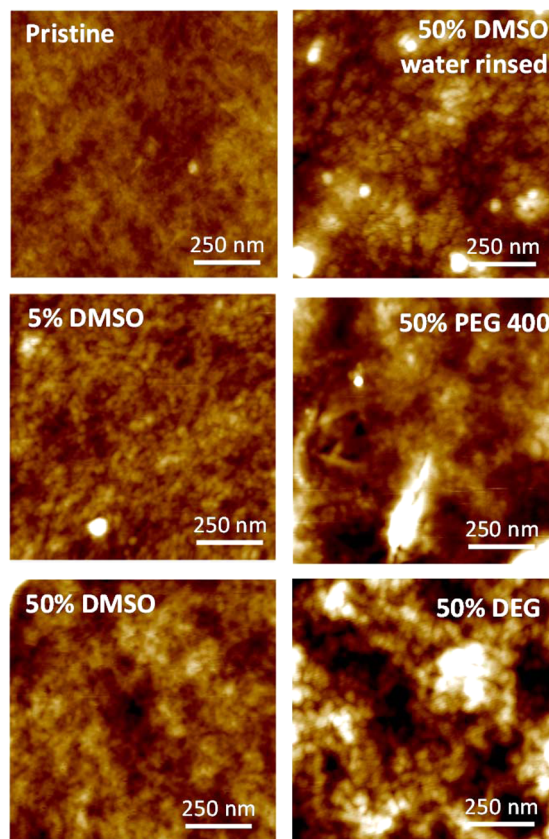


Figure 7. Topography AFM images of different PEDOT:PSS films. The z-scale is 20 nm.

PEDOT-rich center is surrounded by excessive PSS. The size of the gel particles is in the range of 20–500 nm.⁸

The affinity between PEDOT and PSS in the complex has been considered to be very strong. Previously, no separation

between PEDOT and PSS in the PEDOT:PSS complex (PEDOT:PSS molar ratio = 0.8:1) was found via capillary electrophoresis.⁵⁷ In recent years, using 20 mM borate buffer (pH 9.4), Diah et al. showed that “free” PSS could be separated from the Clevios P PEDOT:PSS complex.^{58,59} In their experiment, the optimized PEDOT:PSS with a conductivity of 5.2 S/cm was obtained at a monomer feed ratio of 1:1.25 (EDOT:PSS weight ratio) and reaction time of 12 h. For that composition, ~ 73% of PSS is still associated with PEDOT during capillary electrophoresis. However, there was a substantial amount of free PSS that was separated from the polyelectrolyte complex.⁵⁸

It is widely described that the removal of PSS from the PEDOT:PSS complex enables the conductivity enhancement observed in highly conductive PEDOT films. The actual depletion of PSS from the complex was well supported by the observations from prepared and processed highly conductive PEDOT films. In this method, pristine PEDOT:PSS films were immersed in reagents such as acids¹⁰ or EG followed by rinsing.³¹ After treatment, it was found that the film thickness decreased. UV and XPS spectra suggested the PSS content also decreased in these films.^{9,10,60} It was concluded that concentrated sulfuric acid treatment removed more than 70% of PSS from the pristine PEDOT:PSS film.⁶¹ The removal of insulating PSS apparently led to the better connectivity of the exposed PEDOT grains, which explains the increased conductivity.³⁴ However, for PEDOT:PSS films deposited directly from aqueous dispersion that contains additives, the separation of PSS from PEDOT was less clear.

Here, we demonstrate for the first time that free PSS is separated from PEDOT:PSS complexes and extracted into the high boiling point additive phase after water evaporation. The separation led to a dramatic increase in film conductivity. We used a slow drying method, which allowed for equilibrium of the two polymer phases during drying. It was observed that the PEDOT:PSS complex slowly aggregated into a dense and compact film during solvent evaporation. Although swelled in the remaining additive-rich solvents, the film could no longer be dispersed either in water or additives. IR microscopy and XPS confirmed that this film contained both PEDOT and PSS. Conversely, free PSS without PEDOT was found to concentrate in the remaining additive phase. As the additives were added at large volume fractions, free PSS dissolved in them was able to spread outside the PEDOT:PSS film. After complete drying, a transparent PSS ring around the PEDOT:PSS film was deposited from this solution.

The slow drying process does not require thermal annealing of the films. Thus, it minimized the conductivity and structural changes that could be induced by the annealing.^{62,63} The conductivity of PEDOT:PSS films obtained in this method reached 200 to 400 S/cm, which is close to that of spin-cast and thermally annealed PEDOT films. Structural changes also accompanied the phase separation. A decrease in PEDOT π - π stacking distance from 3.5 to 3.4 Å was observed. When the PSS ring film was further removed by water rinsing, a more compact and extended conformation of the PEDOT:PSS polyelectrolyte complex pair was revealed by XRD. However, the further removal of PSS after phase separation seemed to have limited effects on film conductivity. For the 5- μ m thick PEDOT:PSS film dried from 20% DMSO, the sheet resistance before washing was ~8 Ω /sq. There was no significant change in sheet resistance after washing.

Consistent with the observation of macroscopic separation of free PSS from PEDOT:PSS, we found decreased PSS concentration on the film surface. An increase of polymer grain size was also found by AFM. The morphological changes suggested that the removal of insulating free PSS from PEDOT:PSS colloids promoted the aggregation of conducting PEDOT, which would explain the improved connectivity for these polymers.

It is clear from these experiments that two components, free PSS and PEDOT:PSS complexes, coexist in the PEDOT:PSS dispersion that is treated with additives. The separation of the two components during drying was driven by the solubility differences of the two polymer systems in the additives. The high-boiling point additives serve as solvents for free PSS. The fast water evaporation resulted a solid-liquid phase separation where the PEDOT:PSS complexes precipitated out while free PSS was concentrated into the remaining additive-rich solution. In spin-coated PEDOT:PSS films, fast solvent removal and a relatively smaller additive volume fraction (typically 5% for DMSO) is likely to keep the phase separation at much smaller length scales (typically nanometer scale as observed by AFM). In both conditions, the evaporation rate difference between water and the additive could promote the separation of free PSS from the PEDOT:PSS complex.

Besides the role of the additives as solvents for free PSS, other mechanisms may have been involved in enhancing the film conductivity. In a recent paper by Palumbiny et al.,⁶⁴ the structural evolution of PEDOT:PSS in EG-treated dispersions during drying was investigated in situ by grazing incidence wide-angle X-ray scattering (GIWAXS). It was shown that the water evaporated within 100 s, and the complete evaporation of EG took ~450 s during annealing. After the evaporation of water, a change in PEDOT packing started to take place in the evaporating EG. It was characterized by increasing q of PEDOT π - π stacking from 1.73 to 1.82 \AA^{-1} , corresponding to a decrease in real-space distance from 3.63 to 3.45 Å. The authors proposed a model in which EG promoted the interchain coupling of PEDOT segments, thus enhancing the conductivity. Similar to their work, we found that PEDOT π - π stacking distance was decreased from 3.5 to 3.4 Å. We also found that the reorganized PEDOT:PSS films swelled in the additive rich solvents, which suggests an interaction between insoluble PEDOT:PSS complexes and additives.

Coulomb charge screening effects of the additives, especially that of polyalcohols, have been proposed as a mechanism of conductivity enhancement.^{23,65} It was proposed that the polar additives would weaken the electrostatic interactions between PEDOT and PSS,⁶⁵ thus promoting separation of the two polymers. During the course, the screening may also cause the redistribution of PEDOT on PSS chains, facilitating the “release” of free PSS. Besides charge screening effects, it is also necessary to take into account other interactions such as hydrogen bonding and chemical reactions between PSS sulfonate groups and additives. It was found that poly(styrenesulfonate) and DMF can form hydrogen bonds at >60 °C.⁶⁶ It is also known that DMF reacts with sulfonic acid to form sulfonamides.⁴⁴ Alcohols and PEGs can form sulfonic esters with PSS.⁴⁴ It has been demonstrated that polyalcohols, such as glycerol and ethylene glycol, were able to cross-link sulfonated polymer films through this reaction.⁶⁷ Not only do these interactions provide the free energy that favors the dissolving of PSS in the additive phase,⁶⁸ the reactions between additives and sulfonic groups can also block the electrostatic

interactions between PEDOT and PSS, thus promoting reorganization and separation.

CONCLUSIONS

We found that a fraction of PSS could be separated from the PEDOT:PSS complex with additives such as DMSO, DEG, and PEG 400. During drying, the free PSS was extracted into the additive phase. This process was visualized using a simple slow drying method. Typically, PEDOT:PSS aggregated into a compact film after the evaporation of water, and free PSS was found in the remaining additive. Upon complete drying, the reorganized PEDOT:PSS film was found to be surrounded by a transparent PSS film. XPS confirmed that there was a significant increase of PEDOT to PSS ratio on the surface after the separation of PSS. The observed macroscopic phase separation can explain the conductivity enhancement from the solvent additives generally reported, as all the films that dried with additives reached the conductivity range of 200–400 S/cm without thermal annealing. The removal of PSS from the PEDOT:PSS complex resulted in a more compact packing of the complex. The XRD pattern suggested that there was a decrease of PEDOT π - π stacking distance from 3.5 Å for air-dried pristine PEDOT:PSS to 3.4 Å. A peak at a lower angle with a d -spacing of ~ 23 Å was also found after the removal of free PSS. Compared to pristine PEDOT:PSS, the phase-separated PEDOT:PSS had a more bumpy surface morphology. In sum, by slowing the solvent drying process during fast thermal annealing for spin-coated PEDOT:PSS films under room temperature and high additive concentration conditions, we confirmed an enrichment of PSS in the additive phase after water evaporation. This phase separation of PSS and the PEDOT:PSS complex due to solubility differences led to a conductivity increase by 2000–4000 fold. It was also accompanied by structural and morphological changes that can explain the increased conductivity of PEDOT:PSS films treated with these additives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05439.

Additional optical images, AFM images, film roughness, NMR spectrum, additional IR spectrum of PSS sodium salt standard, and the assignment of IR peaks (PDF)

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Notes

The authors declare no competing financial interest.

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