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Influence of a Water Rinse on the Structure and Properties of Poly(3,4-ethylene dioxythiophene):Poly(styrene sulfonate) Films

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Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) films exhibit a complex structure of interconnected conductive PEDOT domains in an insulating PSS matrix that controls their electrical properties. This structure is modified by a water rinse, which removes PSS with negligible PEDOT loss. Upon PSS removal, film thickness is reduced by 35%, conductivity is increased by 50%, and a prominent dielectric relaxation is eliminated. These results suggest that the removed PSS is not associated with PEDOT and that the conductive domain network is not substantially altered by the removal of a significant fraction of insulator. The removal of PSS may benefit organic light emitting diode fabrication by reducing acid attack on indium tin oxide electrodes and lead to more robust performance in switching circuits by extending the working frequency range.

Introduction

The use of conducting polymer dispersions is rapidly increasing because of increases in their conductivity and stability over the past decade. Poly(3,4-ethylene dioxythiophene) (PEDOT),^{1–3} in particular, is used in a wide range of functional applications because cast films are both electronically conductive and optically transparent. These characteristics are required in many applications including antistatic coatings,⁴ flexible electronic interconnects,^{5,6} electrochromic windows,^{7–9} and hole transport layers in organic light emitting diodes (OLEDs).^{10–12}

PEDOT is typically applied in a colloidal form consisting of oxidized PEDOT chains electrostatically associated with a poly(styrene sulfonic acid) (PSS) dopant, with an excess of PSS added to stabilize the dispersion. Solid films cast from this colloidal dispersion exhibit a complex three-dimensional distribution of PEDOT and PSS, a morphology that controls the film electrical properties. Despite the widespread use of PEDOT:PSS, the correlation of PEDOT:PSS film morphology to its electrical properties remains unclear. Factors that influence the morphology

include the dispersion composition and processing such as thermal annealing or solvent treatments.

Previous investigations into the morphology of PEDOT:PSS films using scanning tunneling microscopy revealed an inhomogeneous three-dimensional network of highly conductive PEDOT islands dispersed in an insulating PSS matrix.^{13,14} These studies and others employing deuterated PSS with neutron reflectivity^{15,16} have found a top PSS-rich layer in spin-cast PEDOT:PSS films. Although excess PSS is needed to stabilize the dispersion, these results suggest that the final PEDOT:PSS films contain substantial amounts of PSS that segregates from the PEDOT:PSS complex. Because PSS is an electrical insulator, an excess of PSS could limit the film conductivity. Further, PSS is known to degrade the performance of OLEDs over time by its acid attack on indium tin oxide (ITO) anodes.¹⁵ Studies of the structure and state of unassociated PSS and its role in the development of film morphology could provide new strategies for the optimization of PEDOT:PSS electrical properties.

Here, we investigate the influence of a water rinse on the structural and electrical properties of spin-cast PEDOT:PSS films. We begin with films spin-cast from the most commonly used formulation with a PEDOT to PSS mass ratio of 1:2.5. The films are dried and then washed with water. X-ray reflectivity (XR) and visible–near-infrared (vis–NIR) spectroscopy are used to quantify changes in the film thickness and composition. Direct current and frequency-based electrical measurements are used to probe the electronic conductivity and dielectric relaxations of these films. These measurements provide information about the heterogeneity of the PEDOT:PSS film structure and the association of PSS with PEDOT.

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Experimental Section

[Certain equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.]

Materials. The PEDOT:PSS (Baytron P) dispersion was obtained from H. C. Starck. Dilutions were made with MilliQ (Millipore) filtered deionized water. Dispersions were cast upon borosilicate float glass (Swift Glass) using a Headway spin-processor with a two step process of (1) 500 rpm/s to 1000 rpm for 30 s and (2) 500 rpm/s to 2000 rpm for 90 s.

Structural Characterization. XR was performed on a modified Scintag X-ray diffractometer. Instrumental details are provided elsewhere.¹⁷ The reflectivity profiles were fit using the Parratt formalism¹⁸ following the least-squares algorithm of Ankner and Majkrzak.¹⁹ Composition analysis was performed using vis-NIR spectroscopy. Spectra were collected using a Perkin-Elmer Lambda 9 Spectrophotometer, and data were analyzed using the Beer-Lambert law.

Electrical Characterization. Electronic measurements were performed using custom test beds. Conductivity test beds were fabricated using negative tone photolithography to define gold features consisting of 1000 Å gold and a 100 Å chromium adhesion layer. Impedance measurements required thermal evaporation of Au atop cast films at a base pressure of 10^{-6} Torr and a deposition rate of 0.5 Å/s. Conductivity measurements were performed using a Keithley 6430 Source-Measurement Unit, and impedance measurements were performed using an HP 4294A impedance analyzer. Conductivity measurements were performed inside a Cascade Microtech Microchamber probe station to minimize electrical noise.

Results and Discussion

The influence of a water rinse on the structure and properties of PEDOT:PSS films was evaluated by measuring the thickness, composition (via vis-NIR absorbance), and electrical properties of unwashed and washed films cast from dilutions of the stock dispersion. The water rinse procedure involved three steps. First, PEDOT:PSS films were spin-cast atop borosilicate float glass substrates. Second, the films were dried at 110 °C under vacuum for 24 h. Third, neutral deionized water was spin-cast upon the dried films at 2000 rpm, resulting in “washed” films. The washed films were re-dried at 110 °C under vacuum. These films on borosilicate float glass were used for both XR measurements and vis-NIR spectroscopy. Gold bottom-contact electrode structures were used to measure conductivity and perform impedance spectroscopy on films with casting and washing conditions identical to those on borosilicate float glass.

Specular XR was employed to measure plane-averaged film thickness and roughness before and after washing. A representative XR dataset is shown in Figure 1a; the logarithm of the reflected intensity is shown as a function of the scattering vector q ($=4\pi/\lambda \sin \theta$, where θ is the incident angle of reflection). The constructive and destructive interference fringes are fit with a model profile composed of a single polymer layer atop borosilicate float glass. The real space profiles in Figure 1b represent the nonlinear least-squares best fits to the reflectivity dataset shown in Figure 1a, where the thickness, roughness, and X-ray scattering length density (Q_c^2) of the polymer layer were allowed to vary.

Water washing reduces the thickness of the film in Figure 1 from 65 to 42 nm. This thickness reduction of

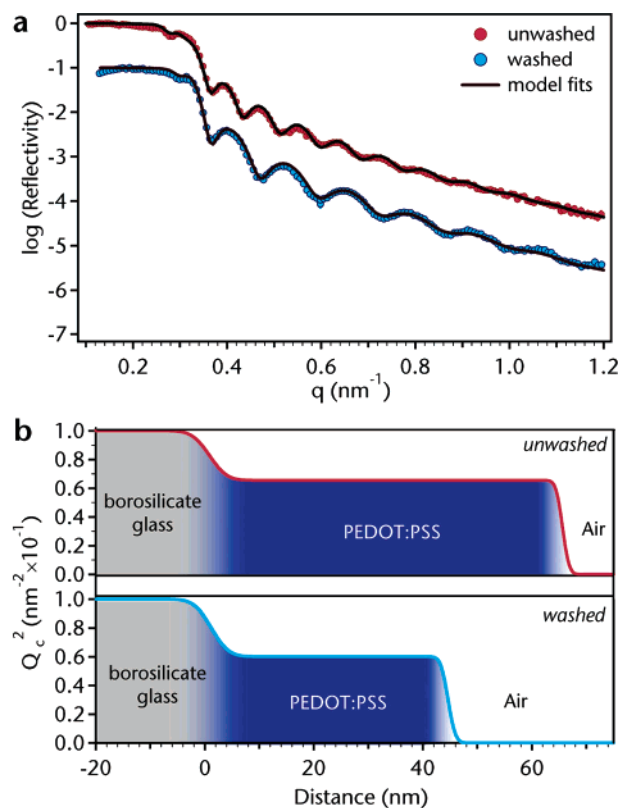


Figure 1. (a) XR for films spin-cast atop borosilicate float glass from a 3:2 dilution of PEDOT:PSS stock to water. The solid lines correspond to the best fit of the data; traces are offset for clarity. (b) Real space X-ray scattering length density profile for unwashed and washed films corresponding to best fits of the traces in a.

Table 1. Film Thickness Loss and PEDOT Loss with Water Washing^a

stock (%)	untreated thickness (nm)	treated thickness (nm)	thickness loss	PEDOT loss
0.33	16.3	11.6	29%	4.5%
0.50	32.9	20.4	38%	4.9%
0.66	65.0	41.8	36%	5.5%
0.83	97.2	56.8	42%	4.2%
1.00	147.0	104.7	29%	1.9%

^a The uncertainty of thickness measurements is <0.5 nm. The uncertainty of PEDOT loss is ± 1.2 %.

36% does not increase roughness; the interfacial width between the PEDOT:PSS layer and air remains 3–4 nm. Notably, Q_c^2 , which is directly proportional to the electron density of the film, does not increase upon washing but remains constant within error. These films do not densify upon washing, so we conclude that the water rinse physically removes polymer. Thickness reductions upon washing PEDOT:PSS films with initial thicknesses from 16 to 147 nm were measured with XR and are shown in Table 1. Regardless of the initial thickness, 30–40% of each film was removed by water washing, while the film roughness remained unchanged.

Because PEDOT and PSS have similar elemental compositions and presumably similar mass densities, their scattering length densities should be similar. XR alone is insufficient to determine what components are removed. To determine the identity of the lost component, we use vis-NIR spectroscopy as a quantitative analysis tool. vis-NIR spectroscopy was performed at wavelengths from 500 to 2500 nm. The spectrum of an unwashed film in Figure 2 exhibits a metallic absorbance at high wavelengths

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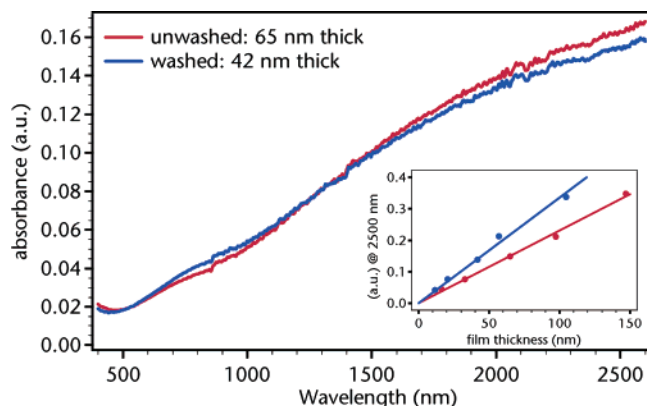


Figure 2. UV-vis absorbance of PEDOT films atop borosilicate float glass. Spectra are referenced to the bare glass. Inset demonstrates the Beer-Lambert law. Experimental standard uncertainty of absorption measurement is $\pm 1.2\%$ by comparing multiple spectra of the same film.

(peaking beyond the low-energy limit of our source) that is characteristic of highly doped PEDOT.²⁰ PSS-only films exhibit no absorbance across the same spectral range. Because absorbance in this range is due only to PEDOT, the film composition can be quantified using the Beer-Lambert law

$$A(\lambda) = \epsilon(\lambda)bc \quad (1)$$

where A is the absorbance, ϵ is the molar absorptivity, b is the path length (film thickness), and c is the analyte concentration.

Because PEDOT:PSS films contain only PEDOT and PSS, and $\epsilon(\lambda = 2500 \text{ nm}) = 0$ for PSS, composition calculations require only $\epsilon(\lambda = 2500 \text{ nm})$ for PEDOT. The as-cast films obey the Beer-Lambert law by exhibiting a linear variation in absorbance vs film thickness with slope $A/b = 23 \text{ } 100 \text{ cm}^{-1}$ (see Figure 2 inset). The mass ratio of PEDOT to PSS in solution is 1 to 2.5; we assume that the ratio is retained in unwashed films. The mass densities of the films can be estimated from the reflectivity critical edge,²¹ which is a measure of the film electron density. The electron density of the films does not change; it is $1.27 \times 10^{-5} \text{ } \text{\AA}^{-2}$ before washing and $1.28 \times 10^{-5} \text{ } \text{\AA}^{-2}$ after washing. This similarity suggests that the mass densities of PSS and PEDOT are nearly identical, which can be confirmed by neglecting the film composition and calculating the mass density from the electron density. Assuming the film is pure PSS results in a calculated mass density of 1.44 g/cm^3 , whereas assuming pure PEDOT results in a mass density of 1.46 g/cm^3 . This difference is within measurement uncertainty. From the mass ratio and a mass density of 1.45 g/cm^3 , we find that the molar concentration of PEDOT c is 2.9 M . We then find that $\epsilon(\lambda = 2500 \text{ nm})$ is $7920 \text{ M}^{-1} \text{ cm}^{-1}$ for PEDOT.

This molar absorptivity can be used to determine the composition of washed films if it does not change during washing. We must first assume that the PEDOT retains its doping level. Changes in doping level would change the ratio of absorbance at 600 nm to absorbance at 2500 nm ; this ratio does not change substantially, so this assumption is reasonable. Next we must assume that washing does not cause the films to roughen and scatter light. Scatter would increase the apparent absorbance at higher energies more than at lower energies (Rayleigh

scatter $\propto \lambda^{-4}$); this effect is not apparent, so this assumption is also reasonable. Additional support for this assumption is provided by the similar roughness of unwashed and washed films, as measured by XR.

We determine the composition of washed films by considering their Beer-Lambert law behavior with slope $A/b = 33 \text{ } 500 \text{ cm}^{-1}$ (see Figure 2 inset). Dividing this slope by $7920 \text{ M}^{-1} \text{ cm}^{-1}$, the solid PEDOT concentration c is 4.2 M . Using the density described above, the mass ratio of PEDOT to PSS is 1 to 1.4. Using the PEDOT concentrations before and after washing, we calculate the absolute stoichiometric loss of PEDOT upon washing. PEDOT losses range from 2 to 5% and are quantified in Table 1.

We conclude that water washing of PEDOT:PSS films removes PSS but does not substantially remove PEDOT. For each film, $\sim 36\%$ thickness is lost and at most 5% PEDOT is lost. PEDOT loss can account for at most 2% of the total 36% thickness loss; PSS must account for the remaining 34%. Water washing therefore removes 40–50% of PSS within cast films. The remaining material may be composed of PEDOT:PSS with multiple electrostatic associations between polymer chains. These electrostatic associations are irreversible in water for ionic complexes between strong polycations and polyanions.^{22,23} The well-known layer-by-layer assembly technique exploits this irreversibility for film fabrication.²⁴

The large amount of PSS washed away from these films cannot arise solely from the enriched surface layer of PSS identified in neutron reflectivity studies. These studies showed that PSS-rich surface layers make up only 10% of the total film thickness even when the PEDOT to PSS ratio was 1 to 6. This surface layer proportion is far less than the 35% lost upon washing.^{15,16} Water washing must also remove PSS from within the film bulk causing changes in structure and composition.

Morphological changes resulting from the removal of unassociated PSS can be probed with conductivity measurements. The conductivity test bed consists of paired gold stripes 1 mm long with spacing x varying from 25 to $100 \text{ } \mu\text{m}$, as illustrated in the Figure 3a inset. PEDOT films were cast atop the test bed. The electrode potential difference was scanned linearly between $+100$ and -100 mV . A linear current response to potential (not shown) was attained for both unwashed and washed films. The slope of the response is due to electrode-to-electrode resistances. These resistances are shown in Figure 3a as a function of the electrode spacing x . These data can be used to separate the test bed contact resistance from the overall film resistance. We observe that the film resistance drops in the washed film. By combining this resistance drop with a cell constant that incorporates the XR thickness measurement, we determine that film conductivity is modestly increased by 50% upon washing from 0.4 to 0.6 S/cm .

The conductivity change upon removing 40–50% of the insulating PSS is consistent with a model of a PEDOT:PSS film as a percolating conductor-insulator composite. In this model, the volume fraction of conductive filler (PEDOT) in unwashed films is above the percolation threshold required for an orders-of-magnitude increase in conductivity. The removal of insulating PSS results in a small, linear conductivity gain. These results imply that water washing, PSS removal, and network collapse do not substantially change the connectivity between PEDOT domains in the thin film network.

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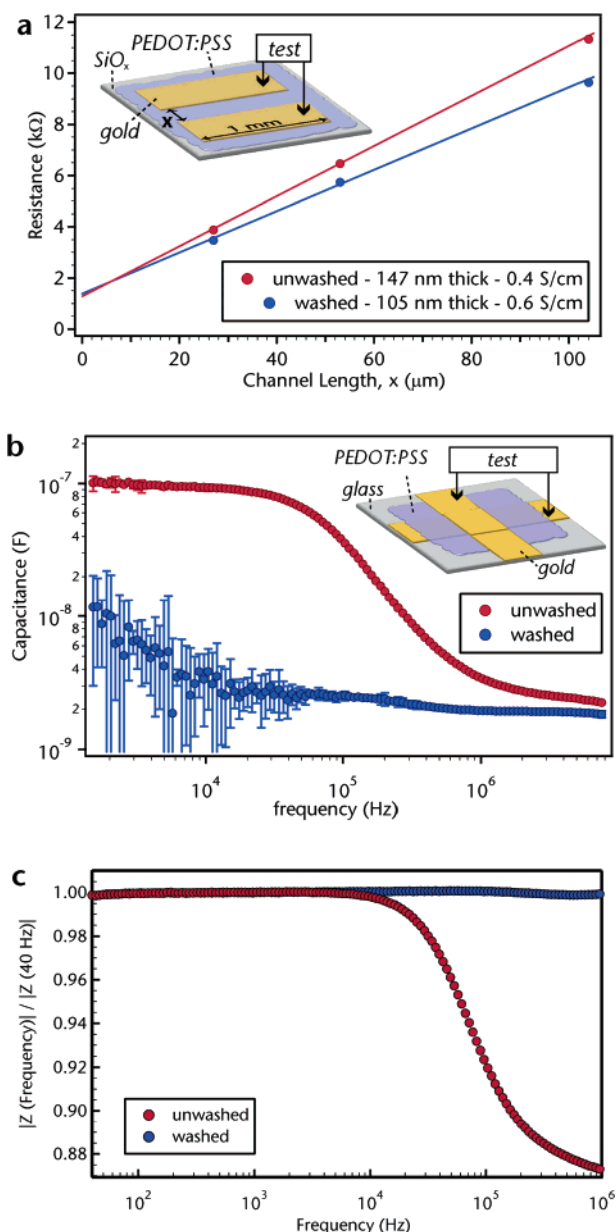


Figure 3. (a) Conductivity of unwashed and washed PEDOT:PSS films. The experimental standard uncertainty was less than 2%; error bars are not visible. (b) Frequency dependent capacitance of washed and unwashed films. Error bars indicate experimental standard deviation at each point. (c) Impedance normalized to its value at 40 Hz to eliminate electrode resistance, which is in series with PEDOT:PSS and does not vary with frequency.

Frequency-dependent capacitance measurements also suggest that the PSS removed by water washing is not associated with PEDOT. The capacitance test bed consisted of crossed gold stripes 2 mm wide sandwiching PEDOT:PSS films, as illustrated in the Figure 3b inset. The capacitance spectra of unwashed and washed PEDOT:PSS films are different as shown in Figure 3b. Unwashed films exhibit a strong relaxation at 2×10^5 Hz that almost disappears in washed films. There are two possible origins of this relaxation; it may arise from the ionic conductivity

of dissociated ions within PSS domains or it may arise from Maxwell–Wagner effects^{25,26} caused by discrete PSS domain polarization. Both of these mechanisms are possible only if there exist domains of unassociated PSS within the unwashed PEDOT:PSS films. Washing away this PSS results in a more rigid matrix that is consistent with a tightly bound and electrically conductive polyelectrolyte complex. The variation in overall impedance with frequency is shown in Figure 3c. Because the washing step removes the prominent dielectric relaxation, the working frequency is increased from 10 kHz to 1 MHz. We do observe a small decrease in the washed sample impedance magnitude beginning at 4×10^5 Hz that may be the onset of a relaxation extending into the MHz range. The loss of the relaxation feature due to the loss of unassociated PSS upon washing should lead to more robust performance in switching circuits because of the extension of the working frequency range.

The relatively modest increase in the conductivity of washed PEDOT:PSS films suggests that the conductive network is not substantially changed by the removal of unassociated PSS. To achieve larger conductivity gains, processing variations must increase the intrinsic performance of PEDOT or alter the network structure between PEDOT domains. For example, recent reports of 100-fold increases in conductivity when PEDOT:PSS is treated with polar organic solvents are consistent with increased interchain interactions and changes in the PEDOT chain conformation.²⁷ Here, the removal of insulating PSS, which should statistically increase the number of PEDOT interchain encounters, is insufficient to boost electrical conductivity so dramatically. Polar organic solvent addition must specifically facilitate electronic interactions between PEDOT chains when interchain encounters occur.

Summary

The complex structure of interconnected conductive PEDOT domains in an insulating PSS matrix can be changed by a simple water rinse or wash. From XR measurements of thickness and vis–NIR spectroscopy measurements of composition, the water wash removes a large quantity of PSS with negligible PEDOT loss. These results suggest that the removed PSS is unassociated with the PEDOT and confirm that the interconnected conductive domains are not substantially altered by the removal of a significant fraction of the insulator. Other strategies to further increase the conductivity of PEDOT:PSS films should instead focus on changing the intrinsic conductivity of PEDOT or by substantially changing the morphology of the PEDOT domains. The removal of PSS by a simple water wash has potential advantages in reducing the acid attack of PSS on indium tin oxide electrodes for OLEDs or increasing the PEDOT:PSS working frequency range in switching circuits from the loss of a capacitive characteristic.

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