Structural origin of anisotropic transport in electrically conducting dichloroacetic acid-treated polymers

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Abstract

The post-deposition treatment of water-processable, polymer acid-templated conducting polymers with dichloroacetic acid has recently been shown to enhance in-plane conductivity by orders of magnitude. Here, we evaluate both the in-plane and out-of-plane conductivities of dichloroacetic acid-treated conducting polymer films, and track the accompanying evolution of film structure and composition. Films of poly(ethylene dioxythiophene)-poly(styrene sulfonic acid), PEDOT–PSS, exhibit improvements in both in-plane and out-of-plane conductivities following dichloroacetic acid treatment, associated with the removal of excess PSS from the surface. Conversely, polyaniline–poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PANI–PAAMPSA, films are characterized by high anisotropies in conductivity, with the in-plane conductivity being orders of magnitude higher following DCA treatment and the out-of-plane conductivity substantially lower after the same treatment. Our experiments indicate that this unusual electrical anisotropy results from a vertically inhomogeneous composition profile.

1. Introduction

Conducting polymers exhibit several advantages over conventional conducting materials, such as light weight, mechanical flexibility, and low-cost. To harness these advantages, however, the limited processability of conducting polymers must be overcome. Water-soluble polymer acids have been successfully used as charge-balancing templates during synthesis to render conducting polymers, such as poly(ethylene dioxythiophene), PEDOT, and polyaniline, PANI, water dispersible. The improved processability, however, comes at the expense of conductivity, with losses due to the incorporation of the electrically insulating hydrocarbon-based polymer acids [1].

Several solvent additives have been proposed for improving the conductivity of poly(ethylene dioxythiophene)-poly(styrene sulfonic acid), PEDOT–PSS; these treatments have resulted in conductivity improvements by several orders of magnitude [2–8]. Various conductivity enhancement mechanisms have been put forward, including charge screening from residual solvent [2], removal of excess PSS leading to improved connectivity between conductive grains [3,5], conformational changes in PEDOT chains leading to increased interchain interactions [4,8], and preferential solvation of the conducting polymer complex in the presence of a co-solvent [6]. It remains unclear, however, whether these mechanisms by which the dissimilar additives act upon PEDOT–PSS can be generalized to other solvents or polymer-acid templated conducting polymers. In spite of the challenges in understanding the structural origins of conductivity enhancement in PEDOT:PSS by solvent addition, preparations which incorporate solvent additives for conductivity enhancement are commercially available, and organic electronic devices comprising such conducting polymers as electrode materials or charge selective layers are widely reported [5–7].

Recently, we have introduced post-deposition treatment of conducting polymers with dichloroacetic acid...
(DCA) as an alternative to the incorporation of solvent additives, providing a means of increasing the conductivity of polymer-acid templated PEDOT and PANI by up to 3 orders of magnitude [9]. Significant conductivity enhancements have also been achieved in PEDOT–PSS treated with dimethyl sulfoxide [10], sulfuric acid [11], geminal diols [12], or amphiphilic fluoro compounds [12] following film deposition. With these post-deposition treatments, water-dispersible conducting polymers exhibiting nominally low conductivities can be patterned and their conductivities subsequently recovered. The incorporation of patterned DCA-treated polymers as electrodes in organic field-effect transistors (OFETs), organic solar cells (OSCs), and organic light emitting diodes (OLEDs) have yielded devices that are no longer limited by series resistances that plague the performance of devices with otherwise untreated conducting polymer electrodes [9–11].

For proton-doped conducting polymers, such as PANI–PAAMPSA or PANI–PSS, the conductivity enhancement arising from DCA treatment is attributed to disruptions of the electrostatic interactions between the conductive polymer and its polymer acid template, accompanied by structural relaxation. Structural relaxation via such post-deposition treatment was shown to rely on both the acidity of DCA and the solubility of the polymer acid in DCA [13]. PEDOT–PSS, albeit an oxidatively doped polymer, also undergoes a similar conductivity enhancement upon exposure to DCA. In this case, however, the acidity of DCA does not play an essential role. Instead, it is the solubility of the polymer acid, PSS, in DCA that is proposed to lead to partial removal of the insulating PSS overlayer at the PEDOT–PSS film surface, a mechanism similar to that reported when PEDOT–PSS is cast from dispersions containing diethylene glycol or mixtures of sorbitol, N-methylpyrrolidone and isopropanol [3,5]. Thus, while post-deposition DCA treatment leads to similar conductivity enhancement in both polymer acid templated PANI and PEDOT, the detailed mechanism by which this improvement occurs appears to depend on the nature of association between the conducting polymer and its polymer acid template.

In this study, we measured the evolution of film structure, surface composition, and both in-plane and out-of-plane conductivities of PEDOT–PSS and PANI–PAAMPSA, as a function of DCA treatment time. Out-of-plane charge transport plays a dominant role in devices with stacked geometries, such as diodes and solar cells; however, this transport configuration has yet to be evaluated in highly conductive DCA-treated polymers. Our studies indicate that while PEDOT–PSS and PANI–PAAMPSA both exhibit improved in-plane conductivities following DCA treatment, the two polymers show divergent out-of-plane conductivities and structural evolution, corroborating the notion of two distinct processes by which DCA impacts conductivity in such polymer acid-templated systems.

2. Experimental methods

Glass and indium tin oxide (ITO)-coated glass substrates, for in-plane and out-of-plane conductivity measurements, respectively, were cleaned by sonication in acetone, 2-propanol, and water, followed by UV-ozone treatment. Thin polymer films were prepared by spin-coating aqueous dispersions of PEDOT–PSS (Heraeus Clevios P, used as-received) and PANI–PAAMPSA (synthesized according to previous published procedures [14], and dispersed in deionized water at 5 wt%) onto glass or ITO-coated glass. The films were baked at 150 °C for 20 min to remove residual water. DCA treatment was performed by immersing the samples into DCA (Acros Organics, 99+%) preheated to 100 °C for specified times ranging from 15 s to 30 min. Residual DCA was removed by baking the samples at 170 °C and then exposing the films to <10⁻⁶ Torr vacuum for at least 1 h.

In-plane conductivity was measured using a four-point probe configuration, implemented with an Agilent 4155C Semiconductor Parameter Analyzer. Top-contact gold electrodes were deposited by thermal evaporation. Atomic force microscope (AFM) and conductive atomic force microscopy (C-AFM) characterization were carried out under ambient conditions using a Veeco Dimension 3100 AFM, Nanoscope V Controller, and an Extended TUNA Module. We used standard dynamic mode silicon cantilevers for tapping mode imaging (nominal spring constant k = 50 N/m, resonance frequency f₀ = 350 kHz), and PtIr-coated cantilevers for C-AFM mapping and current-voltage measurements (nominal k = 0.2 N/m, f₀ = 13 kHz). Film RMS roughness was measured from 2 μm × 2 μm tapping mode images. Refined spring constants were determined for each C-AFM tip using the Sader method [15]. The C-AFM tip radius was estimated from images taken on an FEI XL30 field-emission scanning electron microscope. Unless otherwise noted, current mapping was performed with an applied force of 10–15 nN and an applied sample voltage of 0.1 V. At this sample bias, we retained Ohmic behavior and precluded possible surface modifications which can occur at much higher voltages [16]. Current-voltage measurements at pre-specified positions on an evenly spaced 21 × 21 point grid covering an area of 1 μm × 1 μm were automated by using the Nanoscope software’s “point and shoot” feature.

Angle-resolved high-resolution X-ray photoelectron spectroscopy (HR-XPS) was performed using a Scienta ESCA 300 spectrometer. The instrument has an 8 kW rotating anode source and a 7-crystal monochromator for providing highly monochromated Al Kα X-rays (1486.7 eV), and a 300-mm radius hemispherical analyzer and position-sensitive detector for high-energy resolution and enhanced signal-to-noise. Spectra obtained by collecting photoelectrons emitted normal to the surface of the conducting polymer films correspond to using a takeoff angle of 90° with respect to the surface. Electron collection at takeoff angles of 90° and 15° were employed, corresponding to sampling depths of about 10 and 3 nm, respectively. The analyzer pass energy was set to 150 eV, providing an analyzer resolution of 0.15 eV. Each S 2p and N 1s spectrum was calibrated against the C 1s peak, set at 284.50 eV binding energy (BE). Curve fitting for both S 2p and N 1s regions was accomplished by employing CASA XPS MFC Application software version 2.3.15. A Shirley background was selected to account for inelastic scattering [17]. The peaks associated with the S 2p doublet
and N 1s singlet were fitted using a Gaussian/Lorentzian ratio of 70/30. For PEDOT–PSS, the full-width-at-half-maximum (FWHM) of each of the S 2p peaks was set to 1.1 eV for PSS and 0.9 eV for PEDOT. For PANI–PAAMPSA, the FWHM of each of the S 2p peaks was set to 1.1 eV while those of the N 1s peak was set to 1.3 eV.

3. Results and discussion

The in-plane conductivity of PEDOT–PSS and PANI–PAAMPSA films, shown in Fig. 1, was measured as a function of DCA treatment time using a four-point probe setup. Five samples were examined under each condition. For both PEDOT–PSS and PANI–PAAMPSA, a rapid rise in conductivity is observed seconds after DCA exposure and the conductivity saturates after 3 min. The conductivity of PEDOT–PSS increases from 0.14 ± 0.01 S/cm to 190 ± 20 S/cm, while the conductivity of PANI–PAAMPSA increases from 0.31 ± 0.01 S/cm to 9.5 ± 0.5 S/cm.

The obtained conductivities for PEDOT–PSS are comparable to prior published values for DCA-treated films. The maximum conductivity of PANI–PAAMPSA, however, is roughly four times lower than the previously documented value [9]. We speculate that this discrepancy stems from differences in the processing conditions. To ensure consistent experimental conditions for measuring the time evolution of the film properties, we opted to allow the samples to soak in DCA, as opposed to the rigorous agitation in DCA that was previously employed to treat PANI–PAAMPSA films [9].

The out-of-plane conductivity of PEDOT–PSS and PANI–PAAMPSA is significantly more difficult to assess, as four-point probe measurements cannot be easily carried out on the cross-sections of these films. Instead, we used conductive atomic force microscopy (C-AFM) [18] to estimate the out-of-plane conductivity and spatially map the local out-of-plane current-carrying capacity of PEDOT–PSS and PANI–PAAMPSA films, before and after DCA treatment, with the underlying ITO as an electrode and the metal-coated AFM tip as the second electrode. We also performed current mapping by imaging in contact mode and recording the current as a function of position while a bias voltage (100 mV, unless otherwise noted) was applied between the tip and sample. As shown in Fig. 2, even after short DCA exposure times of 15 s, drastic changes in the C-AFM conductance histograms and current maps take place.

Prior to DCA treatment, PEDOT–PSS films exhibit a narrow conductance distribution with less than 10% of the conductance above 5 nS, as featured in the histogram in Fig. 2a. The C-AFM current map is characterized by isolated 10–20 nm diameter conductive “hot spots”. This observation is consistent with previous C-AFM measurements on pristine PEDOT–PSS [16,19,20] and structural models that propose the presence of tens-of-nanometer sized conductive PEDOT grains surrounded by insulating PSS [21,22]. Following DCA treatment, the conductance distribution broadens and features a tail towards high conductance, as seen in the histogram in Fig. 2b. In contrast with untreated films, 45% of the vertical conductance exceeds 5 nS, and 7% exceeds 50 nS. The conductivity map (inset of Fig. 2b) features isolated hot spots similar to those observed in the untreated film (inset of Fig. 2a), although the current levels at these hot spots are 10 times higher than those in the untreated PEDOT:PSS film.

PANI–PAAMPSA, on the other hand, exhibits very different out-of-plane electrical characteristics compared to PEDOT–PSS. As seen in the C-AFM map in the inset of Fig. 2c, the untreated film is predominantly covered with conductive patches spanning tens to hundreds of nanometers. This observation is consistent with a conductive, protonated PANI-rich surface, as previously proposed [13]. The conductance histogram exhibits a broad distribution with 47% of the vertical conductance exceeding 5 nS and 14% exceeding 50 nS. Unexpectedly, Fig. 2d indicates a dramatic drop in the out-of-plane conductance of PANI–PAAMPSA following DCA treatment (note the change of scale in Fig. 2d) while the spatial distribution of the current-carrying capacity becomes more homogeneous with 91% of the vertical conductance below 2 × 10⁻⁴ nS. The periodic oscillations, i.e., wavy features, observed throughout the micrograph in the inset of Fig. 2d are due to instrumental noise, as the current levels were near the detection limit.

The out-of-plane conductivity, σ⊥, of the polymer films can be estimated given the conductance, G, the length of the conduction path, ℓ, and the cross-sectional area, A:

\[ \sigma_\perp = \frac{G\ell}{A} \] (1)
We took the average conductance, determined from the average slopes of individual current–voltage curves, as \( G \). By using the average conductance, we assign equal weight to each sample position. The conduction path corresponds to the film thickness, measured by AFM. Finally, assuming no spread of current, the cross-sectional area, \( A \), corresponds to the tip-sample contact area. We estimated \( A \) with the Hertz equation for a spherical tip in contact with a uniform elastic medium [23]:

\[
A = \pi \left( \frac{r^2}{K} \right)^{2/3}
\]

where \( r \) is the tip radius, \( F \) is the force between tip and substrate, and \( K \) is the elastic modulus of the sample. The radii of the AFM tips used in these experiments were measured from scanning electron microscope images of each tip. The total force, \( F \), given by the sum of the adhesion and applied forces, was averaged based on three force-distance curves for each cantilever. From literature, the elastic modulus for PEDOT–PSS [24] and PANI–PAAMPSA [25], were taken as 2 GPa and 1 GPa, respectively.

We note that our estimation of the out-of-plane conductivities does not account for contact resistance introduced by the experimental setup. For this reason, we are unable to compare the out-of-plane conductivities to the in-plane conductivities obtained from four-point probe measurements. We should, however, be able to compare the out-of-plane conductivities extracted in this manner across individual C-AFM measurements, assuming that the contact resistance does not vary considerably from measurement to measurement. In principle, the contact resistance can be estimated based on transmission line analysis of films of different thickness; however, inhomogeneities in the vertical direction of the films, discussed further below, hinder such an approach.

The out-of-plane conductivity of the PEDOT–PSS films before and after DCA treatment was determined to be 0.012 ± 0.007 S/cm and 0.12 ± 0.04 S/cm, respectively. For PANI–PAAMPSA, the corresponding values are 0.50 ± 0.05 S/cm and \((3.1 ± 0.5) \times 10^{-6}\) S/cm, respectively. While the out-of-plane conductivity of PEDOT–PSS increases by an order of magnitude after DCA treatment, the out-of-plane conductivity of PANI–PAAMPSA appears to have decreased dramatically, by five orders of magnitude upon treatment.

To elucidate the structural origins of the dramatically different conductivity responses of PEDOT–PSS and PANI–PAAMPSA films to DCA-treatment, we tracked the topography of the films as a function of DCA-treatment time. As shown in Fig. 3a–c, there is a modest increase in the RMS roughness of PEDOT–PSS films as a result of DCA treatment, rising from 0.93 nm to above 1.5 nm over the course of 10 min. At the same time, the thickness of the PEDOT:PSS films decreases by about 10%, from 110 nm to

![Image](image-url)
98 nm. These structural changes are consistent with the removal of excess insulating PSS from the PEDOT:PSS film surface, leading to better conduction between PEDOT:PSS grains [9].

In contrast to PEDOT–PSS, PANI–PAAMPSA starts off as a rough film characterized by an RMS roughness of 39 nm, as seen in Fig. 3d. Previous experiments indicate that this roughness stems from the presence of sub-micron-sized particles with an enhancement of conductive, protonated PANI at the exterior [13]. Upon DCA treatment, we find that the surface topography becomes significantly smoother and flatter (Fig. 3e–f), reaching a final RMS roughness of 1.7 nm after 30 min of DCA exposure. Concurrently, the film thickness decreases by almost 30%, from 840 nm to 600 nm. The large initial thickness, relative to that of PEDOT–PSS films, is limited by the size of the sub-micron particles that comprise PANI–PAAMPSA films [13].

Exposure to DCA is thought to disrupt the electrostatic interactions that hold PANI and PAAMPSA; since DCA is also a good solvent for PAAMPSA, this process also enables plasticization of the PANI–PAAMPSA particles that make up the film. This plasticization allows for large-scale structural relaxation and compaction of the film. In light of the extreme conductivity anisotropy of the DCA-exposed films, however, we anticipate some compositional anisotropy consisting of highly conductive layers that facilitate in-plane transport interspersed with poorly conductive layers that hinder out-of-plane transport.

The composition of the PEDOT–PSS and PANI–PAAMPSA films was measured by angle-resolved high-resolution X-ray photoelectron spectroscopy (HR-XPS). XPS spectra recorded in the sulfur region on untreated and 15-s DCA-treated PEDOT–PSS films are shown in Fig. 4. The distinct chemical environments, and hence unique binding energies, of the sulfur atoms in PEDOT and PSS make it possible to quantify the relative contents of PEDOT and PSS near the surface of PEDOT–PSS films [21]. The XPS spectra collected in the sulfur region were deconvoluted into two sets of S 2p$_{3/2,1/2}$ spin-orbit split doublets: one at 163.6 and 164.7 eV BE arising from the thiophene moiety in PEDOT, and the other at 167.9 and 169.1 eV BE stemming from the sulfonic acid groups in PSS [21,26]. The sulfur doublet associated with PEDOT were fitted with an asymmetric tail at higher binding energies to account for p-doped thiophene, i.e., PEDOT$^+$, having delocalized charge and hence a continuum of associated binding energies [26].

Using a collection angle of 90° (sampling depth ca. 10 nm), XPS reveals that the molar content of sulfonic acid, relative to the total surface concentration of sulfur, decreased modestly from 75.8% to 74.1% after DCA treatment. At a collection angle of 15° (sampling depth ca. 3 nm), XPS reveals a decrease in molar content of sulfonic acid from 81.3% to 70.7% following DCA exposure. Nominally, the PEDOT–PSS, as-received, consists of 65.5 mole% PSS. In agreement with previous studies, the pristine PEDOT–PSS film surface is enriched in PSS [21,26,27]. This enrichment, however, is reduced by DCA treatment, particularly in the topmost few nanometers of the film.

These observations, along with the topography and conductivity data, suggest that excess PSS that is unassociated with PEDOT is stripped from the surface during DCA treatment, since DCA is a good solvent for PSS. As PSS is removed from the surface, conductive PEDOT grains are exposed and the resistive barriers between PEDOT grains are reduced, thus improving both in-plane and out-of-plane transport. By the same token, this removal of the
PSS insulating layer leads to a concomitant increase in film roughness and a slight reduction in film thickness. Prior UV–Vis absorption measurements on DCA-treated PEDOT:PSS indicate that the conductivity enhancement is not accompanied by significant changes in the bulk structure of the film [9]. Although DCA treatment predominantly affects structure near the PEDOT:PSS film surface, the observed increases in conductivity are intrinsic to the films, and are not merely a result of a reduction in contact resistance. The increase in intrinsic in-plane conductivity upon DCA treatment is evident from four-point probe measurements, which eliminate instrumental contact resistance. Out-of-plane conductivity was also observed to increase upon DCA treatment, albeit measured in a two-point configuration. The in-plane and out-of-plane conductivity increases can be understood on the basis that less insulating PSS intervenes in the path of charge flow after the PEDOT:PSS films are exposed to DCA. A similar conductivity enhancement mechanism has been proposed for films cast from PEDOT–PSS dispersions containing diethylene glycol or mixtures of sorbitol, N-methylpyrrolidone and isopropanol; these solvent additives also lead to reduced PSS content at the film surface compared with pristine, as-cast films [3,5]. As is the case with DCA, these solvent additives have been cited as good solvents for PSS. The 180% increase in PEDOT to PSS ratio at the surface upon DCA treatment is comparable to the 230% increase cited for the sorbitol, N-methylpyrrolidone, and isopropanol solvent additive mixture [3].

XPS spectra of the nitrogen and sulfur regions are shown in Fig. 5a and b, respectively, for untreated, 15-second DCA-treated and 30-min DCA-treated PANI–PAAMPSA films. The nitrogen spectra consist of N 1s peaks from three chemical components: a peak at 399.8 eV BE corresponding to neutral amide groups, one at 400.8 eV BE that has been linked to polarons in PANI–PAAMPSA (denoted N\textsuperscript{1}), and one at 402.0 eV BE attributed to protonated PANI nitrogen that is ionically associated with sulfonic acid groups in PAAMPSA (denoted N\textsuperscript{2}). In the sulfur region, there are two S 2p\textsubscript{3/2,1/2} doublets associated with the sulfonic acid in PAAMPSA: ionized sulfonic acid (SO\textsubscript{3}\textsuperscript{−}) at 167.5 and 168.7 eV BE, and neutral sulfonic acid (SO\textsubscript{3}\textsuperscript{H}) at 168.6 and 169.8 eV BE [13,28].

Upon DCA treatment, the amount of ionically associated PANI and PAAMPSA, represented by the concentration of N\textsuperscript{1} and SO\textsubscript{3}\textsuperscript{−}, decreases substantially near the film surface. In the top 10 nm of the film (90° collection angle), after 30 min of DCA treatment, the concentration of N\textsuperscript{1}, relative to total nitrogen concentration, decreases from 37.2% to 19.7%, while the concentration of SO\textsubscript{3}\textsuperscript{−}, relative to the total concentration of sulfur, decreases from 94.9% to 76.7%. These changes are more pronounced at the topmost 3 nm of the film, with decreases in relative N\textsuperscript{1} and SO\textsubscript{3}\textsuperscript{−} concentrations from 34.6% to 13.5%, and 91.1% to 70.6%, respectively. As nitrogen protonation serves to dope PANI, such a reduction in ionic association is expected to result in a corresponding decrease in conductivity.

A reduced conductivity at the surface, however, does not explain the significantly diminished out-of-plane conductivity of DCA-treated PANI–PAAMPSA. High in-plane conductivities were measured via electrical contact at the film surface. Furthermore, C-AFM measurements on 15-s DCA-treated PANI–PAAMPSA films performed in a lateral geometry, whereby current through the conducting polymer film is measured between the AFM tip and a patterned, top-contact electrode, reveal conductive hot spots, which provide conductive pathways that laterally connect the two electrodes (Fig. 6). That the lateral C-AFM measurements exhibit conductive hot spots at the surface indicates that the greatly reduced out-of-plane conductivity of PANI–PAAMPSA is not purely a consequence of surface modification that resulted in a uniformly insulating layer atop. Given that the conductive spots are not observed in measurements conducted in the vertical geometry (Fig. 2d), however, we do not believe these pathways to percolate through the entire depth of the film, suggesting internal inhomogeneity within the PANI–PAAMPSA films that inhibit out-of-plane charge transport more than it does in-plane charge transport. Further evidence that the reduced out-of-plane electrical transport in DCA-treated PANI–PAAMPSA is a consequence of changes in internal film structure is provided by UV–Vis spectroscopy. Previous measurements show substantial changes in the UV–Vis absorption spectrum of PANI–PAAMPSA upon
While the in-plane conductivity of both PEDOT–PSS and PANI–PAAMPSA are greatly enhanced by DCA exposure, the influence of DCA on out-of-plane transport is vastly different in the two systems, i.e., out-of-plane transport is improved in PEDOT–PSS and severely hindered in PANI–PAAMPSA upon DCA exposure. These functional dissimilarities arise from fundamentally different structural evolutions upon DCA exposure: PEDOT–PSS films become marginally thinner and rougher, while PANI–PAAMPSA films become substantially thinner and smoother. These structural modifications are believed to result from PSS removal in the case of PEDOT–PSS, and plasticization resulting in structural reorganization and densification of PANI–PAAMPSA films. The high conductivity anisotropy in PANI–PAAMPSA films following DCA treatment, characterized by efficient in-plane transport and poor out-of-plane transport, results from vertical inhomogeneities in composition. DCA-treated PEDOT–PSS exhibits enhanced in-plane and out-of-plane conductivities, making it generally suitable as a highly conductive, solution processable polymer. PANI–PAAMPSA exhibits an unusually pronounced conductivity anisotropy following DCA treatment, making it a candidate for novel applications requiring high in-plane and low out-of-plane conductivities.

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