Electrochemistry of Conductive Polymers. 45. Nanoscale Conductivity of PEDOT and PEDOT:PSS Composite Films Studied by Current-Sensing AFM

Hyo Joong Lee,† Joowook Lee,‡,§ and Su-Moon Park*,†,§

Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang, 790-784, Korea (ROK), and School of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, 689-805, Korea (ROK)

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[Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] (PEDOT:PSS, Baytron P) composite films were prepared under various conditions and their conductivities were studied by the current-sensing atomic force microscopy (CS-AFM) technique. Topographic and current images of pristine and additive-treated PEDOT:PSS as well as electrochemically synthesized PEDOT films were obtained in nanoscale using the CS-AFM. The as-prepared pristine PEDOT:PSS films showed a low population of conductive spots isolated by large insulating regions; both their population and the conductivities increased upon addition of a few additives to the PEDOT:PSS solution before spin-coating. From the current−voltage (I−V) traces recorded at a few representative spots of different electronic states, much improved pathways for charge percolation appeared to have been established in the additive-treated films. Electrochemically prepared PEDOT films showed much better electrical properties compared with spin-casted films of chemically prepared polymers. The conductivity of all these films was shown to be significantly enhanced by the electrochemical doping process.

Introduction

Recently, “organic electronics” based on π-conjugated polymers has attracted much attention and emerged as a promising candidate for next-generation electronic devices because of their favorable processability, possibility of tailoring their structures and functions on the molecular scale, low cost, and reasonable stability. They have been studied for a variety of applications such as field-effect transistors, light-emitting diodes, memories, solar cells, electrochromic devices, electronic circuits, sensors, and other devices. Among various polymers explored for organic electronics, PEDOT is considered as one of the most important and widely used polymers due to its many advantages such as good transparency in the visible region, excellent stability, easy processing, and versatile derivatives. In particular, thin PEDOT layers have been very successfully in the field of organic photovoltaics and light-emitting diodes as a hole-transporting “buffer layer” between an active organic layer and the indium tin oxide (ITO) anode. Moreover, only PEDOT thin films have been examined as a transparent organic “conducting electrode” with an aim at replacing expensive but brittle inorganic counterparts, i.e., ITO glasses. It was recently reported that their bulk-scale conductivity can be varied anywhere between the one suitable for their use as a “buffer” layer and that for the “conducting” layer, and an underlying mechanism has been speculated and proposed on the basis of limited experimental data. In attempts to see microscopic structures and their effects on the bulk-scale conductivity, Kemerink and co-workers carefully used scanning tunneling microscopy (STM) on spin-coated thin PEDOT:PSS films. They suggested from their results that the PEDOT:PSS film has a sort of a lamellar structure with ellipsoid-shaped PEDOT-rich particles on the order of 5–50 nm in length separated by thin insulating PSS-rich regions. The STM studies, however, use a sharp conducting tip, which penetrates into the film through the insulating top layers of PSS-rich domains to probe both the topography of the surface and its conductivity. This would make it difficult to truly relate the surface morphology with the conductivity of the as-prepared film. On the other hand, the current-sensing AFM (CS-AFM) allows both the topographic and current images to be obtained concurrently without its tip having to penetrate into the sample. In addition, current−voltage (I−V) traces can be obtained on selected spots throughout the sample, which allows their electrical properties to be characterized. The technique has been used for studying various nanostructures such as single molecules, biomolecules, carbon nanotubes, self-assembled monolayers, quantum dots, and other nanostructures, as well as various organic thin films, in which its usefulness was shown by directly observing the inhomogeneity of electrical properties at single molecular levels or in nanometer scales. For the past few years, our group has successfully employed the CS-AFM technique for the study of electrodedeposited conducting polymer films of various doping levels and varied histories to see changes in local conductivity and their distributions. In contrast to the STM, CS-AFM can routinely provide information on the correlation between the morphology of the film and its characteristic current pathway over almost all the organic thin films irrespective of whether they are homogeneous or not in their conductivity. Therefore, the CS-AFM-based measurement is an ideal and unique technique for monitoring the conductivity of thin organic films at a nanometer scale and for investigating the underlying electrical conduction mechanisms. Only recently was there a brief report on the local conductivity of a thick (~1 μm) PEDOT:PSS film studied by the CS-AFM technique.

In this study, we use the CS-AFM to investigate changes in conductivity of PEDOT:PSS films at nanometer scales obtained by adding a few additives into PEDOT:PSS dispersions, which
had been reported to increase their bulk conductivities. The $I−V$ curves obtained at various spots of additive-treated films were compared with those of the pristine film. The pristine PEDOT:PSS films were also electrochemically doped, which was shown to increase the conductivity.

**Experimental Method**

An aqueous dispersion of the PEDOT:PSS mixture (Baytron P 4071 with the PEDOT: PSS ratio of 1:2.5) was purchased from H. C. Starck (Germany). Ethylenedioxithiophene (EDOT, Aldrich 99.8%, anhydrous), D-sorbitol (Aldrich, 99%), glycerol (Aldrich, 99%), ethylene glycol (Aldrich, 99%), and dimethyl sulfoxide (DMSO, Aldrich, 99.9%) were used as received. Lithium perchlorate (LiClO$_4$, Aldrich, 99.99%) was used after being dried in a vacuum oven at 110°C for 16 h. The PEDOT:PSS films were prepared by spin-coating the dispersion over a gold-on-silicon (with Cr adhesive layers, LGA films) substrate and then dried at 150°C for 30 min, resulting in a thin (∼100 nm) film. The dispersion was either used as received or used after an additive such as D-sorbitol, glycerol, ethylene glycol, or DMSO, had been added prior to its spin-coating.

An electrochemical cell with a three-electrode configuration was used for both electrochemical deposition of PEDOT and doping of spin-coated PEDOT films. Gold-on-silicon electrodes were annealed by a hydrogen flame and used as the working electrode (exposed diameter: 5.7 mm). A platinum gauze and a silver wire were used as counter and pseudo-reference electrodes, respectively. PEDOT films were grown potentiostatically in an acetonitrile solution containing 0.10 M LiClO$_4$ and 0.10 M LiClO$_4$ by applying 1.20 V for 15 s using an EG&G model 273 potentiostat–galvanostat. After the electrochemical synthesis, the films were rinsed with acetonitrile and dried at room temperature. All solutions were purged with N$_2$ for 30 min prior to each experiment. The PEDOT film thickness was determined to be about 300 nm from the cross-sectional view of the SEM image.

The contact mode AFM (PicoSPM, Molecular Imaging Inc.) with a current-sensing module, commonly known as a current-sensing AFM, was used to simultaneously obtain topographical, deflection, and current images. The platinum–iridium (PtIr) coated cantilevers (spring constant, 0.25 N/m) were obtained from Nanosensors (Neuchatel, Switzerland). The load force was maintained below 10 nN to avoid damages of the tip and samples. A bias voltage between the substrate (Au) and the conducting cantilever (which is grounded) was 100 mV during all imaging experiments.

**Results and Discussion**

Figure 1 shows a schematic diagram of the current-sensing AFM for simultaneously obtaining a two-dimensional topography and current image over an organic thin film. In this study, thin PEDOT:PSS films (∼100 nm) were prepared by spin-casting a commercial dispersion, Baytron P with or without an additive, on gold-on-silicon electrodes, and their typical topography and corresponding currents flowing vertically through the film were imaged by contacting a conductive tip with the film surface and applying a small bias voltage (100 mV) between the tip and the substrate while the tip was being horizontally scanned over the film. The vertical conductivity obtained at each point resolved by the AFM tip would be more relevant in evaluating the electrical properties of the PEDOT:PSS layer than the typical lateral conductivity obtained using the four-probe technique as the vertical charge flow actually occurs in real electronic devices.

Figure 2 shows typical topographic (a), deflection (b), and current (c) images simultaneously obtained from a spin-coated pristine PEDOT:PSS film. In the topographic image (Figure 2a), a relatively flat surface (rms roughness: 0.78 nm, Table 1) was observed with a granular morphology, in which smaller grains appear to have been aggregated into larger ones. In the two-dimensional current image obtained at a bias voltage of 100 mV (Figure 2c), bright spots, at which currents flow vertical to the film surface from the tip to the substrate, are seen to be randomly scattered throughout the wide insulating dark surroundings. Under the conditions used in this experiment, this random pattern of the current flow was observed reproducibly in all pristine films tested and no strong correlation was found between the bright conducting spots and morphological features; this observation indicates that (1) well-connected PEDOT-rich grains, which must be responsible for the conducting pathway, are distributed randomly and (2) PSS-abundant regions are dominant at the surface/bulk, which appear to block the current from flowing. Both of these parameters appear to affect the random current-flowing pattern through the film. The maximum current flowing at bright spots in the image scanned was less than ∼40 nA at an applied bias voltage of 100 mV, and the average current value measured over the whole scanned surface (Figure 1c) was 0.61 ± 0.32 nA. The average vertical conductivity, $\kappa$, across the PEDOT film scanned was obtained using the following equation:

$$\kappa = \left(\frac{1}{R}\right) \frac{l}{A}$$

where $l$ is the film thickness, $A$ is the contact area of the probing tip with the sample surface, and $R$ is the vertical resistance obtained for the film between the gold substrate and the tip via current measurement at the applied bias potential. The film thickness (∼100 nm) was measured using the AFM across a line scratched out prior to the experiment. The contact area of the probe with the film was calculated using the Hertz theory. Conductivities thus calculated for the scanned surfaces are summarized in Table 1. In the case of the pristine film (Figure 2c), the average vertical conductivity was measured to be about 0.20 (S/cm), which places the film in a typical range of a moderately doped semiconducting state. This is about one-fifth of the reported bulk-scale lateral conductivity (∼1 S/cm); the differences between the vertical and the bulk-scale lateral conductivities can be explained by the well-known anisotropic conductivities of PEDOT:PSS films and also by the fact that the film surface has higher fraction of the PSS component. This rather low conductivity reflects a low population of heavily doped regions.
used for the treatment of materials or their surfaces to reduce or eliminate buildup of static electricity generally caused by the triboelectric effect.

Recently, there have been interesting reports on the enhancement of the conductivity of the PEDOT:PSS film by more than an order of magnitude upon addition of polyalcohols or polar solvents to the PEDOT:PSS solution prior to spin coating.12,23,26 The mechanism for this enhancement in conductivity of the PEDOT:PSS film is still controversial. To see if the films behave in the same manner at a microscopic level as well, the additives used in the previous studies were added to the PEDOT:PSS solution, and their effects on the conductivity of the resulting PEDOT:PSS film were studied using CS-AFM under the same conditions as shown in Figure 2. Figure 3 shows a typical set of topographic, deflection, and current images from a PEDOT:PSS film spin-casted after adding 3 wt % sorbitol to the pristine PEDOT:PSS dispersion. In the morphological image, the aggregates became more pronounced with an overall increase in the surface roughness (rms roughness increased from 0.78 to 1.12 nm, Table 1), although the surface grains are smaller. This implies that added sorbitol affects the final conformational arrangement of the PEDOT:PSS chains and thus their aggregated grains. The effect of additives on the current flow through the film was more dramatic; the currents increased by more than an order of magnitude from a few tens to several hundreds of nanoamperes and the population of conducting spots also increased significantly (Figure 3c). The average current on the scanned surface was determined to be $47.4 \pm 25.4 \text{ nA}$, which is almost 2 orders of magnitude greater than that of the pristine PEDOT:PSS film ($0.61 \pm 0.32 \text{ nA}$, Figure 2c). A similar behavior was observed for other additives such as glycerol, ethylene glycol, and DMSO (Supporting Information, Figures 1–3) although changes in both the morphology and the currents were somewhat different depending on a specific additive used; this is another evidence that the interaction between different additives and PEDOT:PSS chains plays important roles in determining the final morphology of as-prepared films, leading to a favorable pathway for improved charge transport through the film. The additive molecules have hydrophilic hydroxide groups attached to a hydrophobic alkyl chain and would thus help disperse PEDOT and PSS chains by aligning their hydrophobic chain along the more hydrophobic back chains of the polymers. The fact that sorbitol with a longer saturated carbon chain than other smaller alcohols and DMSO improves the electrical characteristics of the composite film more efficiently than other additives supports this. PEDOT chains would be better dispersed without being self-coiled and surrounded by large amounts of PSS counter chains (2.5 times) even though the PEDOT–PSS concentration would remain practically constant before and after addition of the additive. This would lead to a film on which the conducting spots are more densely and evenly distributed.

The average conductivity through the sorbitol-treated film (Figure 3c) was calculated to be $15.4 \pm 8.2 \text{ S/cm}$, which is about 2 orders of magnitude higher compared to that of pristine film ($0.20 \pm 0.10 \text{ S/cm}$). This is in good agreement with reports from other groups on the bulk conductivity of PEDOT:PSS films obtained upon addition of the additives.12,13c,26 The mechanism for the enhancement of the conductivity after the additive-treatment is still under debate. Several proposed mechanisms include: (1) a screening effect between the positive PEDOT and negative PSS chains by the additives,26d (2) washing away the insulating PSS-rich parts from the surface during the process

| TABLE 1: Data Set of Different PEDOT Films Shown in Figures 2, 3, 5 and 6, Including RMS Roughness and Average Current/Conductivity from Topography and Current Images, Respectively |
|---------------------|---------------------|---------------------|---------------------|
| Figure | rms roughness (nm) | Average current (nA) | Average conductivity (S/cm) |
| pristine PEDOT | 2 | 0.78 | 0.61 ± 0.32 | 0.20 ± 0.10 |
| sorbitol-treated PEDOT | 3 | 1.12 | 47.4 ± 25.4 | 15.4 ± 8.2 |
| electropolymerized PEDOT | 5 | 52.6 | 479 ± 209 | 467 ± 203 |
| pristine PEDOT doped electrochemically | 6 | 2.24 | 5.03 ± 3.94 | 1.63 ± 1.28 |

*a The conductivity values were calculated as described in the text.
of film formation,\textsuperscript{23a} (3) conformational changes from the coil to the expanded coil or a linear structure due to dipole interactions,\textsuperscript{12} and (4) the additive-induced self-organization of the PEDOT-rich grains into 1-D aggregates for easier hopping of charge carriers.\textsuperscript{13c} As described above, our observations (Figure 2c vs Figure 3c; also vide infra) support the last mechanism. Though it is difficult to verify the above-proposed explanations on the molecular level with CS-AFM data alone, the nanoscale current images and vertical conductivities obtained here from the AFM method are consistent with the expected changes in electrical properties induced by the additives; the well-connected vertical pathway for charge percolation was established more densely over the entire surface after the addition of additives.

The drastic changes in conductivity of the PEDOT:PSS films upon addition of additives can also be displayed more clearly by comparing \(I-V\) curves obtained at various spots in the CS-AFM images. The typical \(I-V\) curves obtained at more insulating (dark) and conducting (bright) spots from the pristine and its sorbitol-treated PEDOT:PSS films are shown in Figure 4a–d; the \(I-V\) curves were taken while scanning the bias voltage from \(-3\) to \(+3\) V, which can be compared with each other for their electronic properties of different spots in the current images. The current detected was nearly zero at a bias.

![Figure 3.](image-url) Concurrently obtained AFM images of typical topography (a), deflection (b), and current (c) for a spin-coated sorbitol-treated PEDOT:PSS film and their cross-sectional analyses. The amount of added sorbitol was 3 wt \%.}

![Figure 4.](image-url) Representative current–voltage curves measured at more insulating (dark) (a) and conducting (bright) (b) spots shown in Figure 2c while those shown in (c) and (d) were taken from dark and bright spots in Figure 3c, respectively. Typical \(I-V\) curves obtained from two different semiconducting states of electropolymerized polypyrrole films are shown in (e) and (f).
voltage of 100 mV in dark areas of the image as can be seen in Figure 4a,c while some currents (1–40 nA) were observed at brighter spots as shown in Figure 4b,d. Generally, the current flowing over the entire bias range was about 1 order of magnitude larger at a bright spot than at a dark one. While almost all the data points (256 × 256) in the current image shown in Figure 2c displayed different electronic states by showing different $I$–$V$ curves, the average conductivity obtained from all these curves fell into a lightly doped semiconducting state with its conductivity of 0.20 ± 0.10 S/cm. One distinctive feature of $I$–$V$ curves shown in Figure 4a–c was their shapes, not the magnitudes of currents in contrast to the ones observed normally from the electrodeposited polypyrrole (PPy) film (Figure 4e,f) and other data reported previously.22a–c In these $I$–$V$ curves, many current spikes are seen beyond about ±1.5 V (a few more examples are shown in the Supporting Information, Figure 4). These spikes were much more severe for the pristine film than for as-electrodeposited (Figure 4f) and reduced (Figure 4e) PPy films. While the currents and the curve shapes are very similar within a ±1 V range for both the pristine PEDOT:PSS and electrodeposited PPy films during the voltage scan, many current spikes are seen when the voltage goes beyond about ±1.5 V. The differences shown in curve shapes between the two films clearly indicate that the electronic states for charge transport must be significantly different from each other. The composition and doped states are rather homogeneous throughout the film when produced by electrochemical growth from monomer and electrolyte solutions, with the homogeneity maintained during and after the dedoping process for electrodeposited films. For the spin-coated PEDOT:PSS films, however, their microscopic compositions are not homogeneous, resulting in an inhomogeneous distribution of PEDOT throughout the film, which appears to be highly dependent upon their preparation conditions as well as original solution compositions. The nanoscopically inhomogeneous mixing of PEDOT and PSS components could generate different electronic states at different spots of the film, leading to a discrete density of states (DOS) for the observed current spikes in Figure 4a,c. This inhomogeneity might also have caused the asymmetric $I$–$V$ curve with higher currents at one polarity than at the other, as observed in Figure 4a–c. After 3 wt % sorbitol is added to the PEDOT:PSS dispersion, highly conducting bright spots are more homogeneously dispersed among insulating dark ones (Figure 3c). A typical $I$–$V$ curve (Figure 4c) taken at insulating dark points in Figure 3c was very similar to the one in Figure 4a, indicating that the electronic states of the dark areas shown in both Figures 2c and 3c are almost the same. However, the slope of the $I$–$V$ curve obtained at bright spots (Figure 3c) increased remarkably near 0 V and the electronic state changed to a highly doped semiconducting state judging from $I$–$V$ traces shown in Figure 4d. The curve shape shown here closely resembles that of a highly doped, electrodeposited conducting polymer.22 The drastic increase in slopes of $I$–$V$ curves indicates that a vertical electrical pathway is now well-defined for charge transport and connected by virtue of additives, as in electrodeposited polymer films.

PEDOT films can also be prepared on a conducting substrate via electrochemical oxidation of EDOT monomers.23 Considering that a different electrical property of a π-conjugated conducting polymer would result from its different preparation method, it would be instructive to compare the nanoscale electrical properties of the PEDOT films prepared by two different methods, one by spin-coating of chemically prepared PEDOT and the other by direct electropolymerization of EDOT. Figure 5 shows topographic (a) and current (b) images as well as an $I$–$V$ curve (c) obtained at a bright spot of a PEDOT film potentiostatically prepared at 1.2 V on a gold-on-silicon substrate from an acetonitrile solution containing 0.1 M EDOT monomer. A much rougher surface with an rms roughness of 52.6 nm was obtained when compared with spin-casted films (Figures 2 and 3). However, the roughness of electrodeposited polymer films is highly dependent on the film deposition parameters used; a much smoother film can be obtained by changing the electrodeposition conditions.23 Also, currents higher than 1 µA, which is the maximum value our current amplifier can handle, were observed even at a low bias voltage of 100 mV over almost
the entire surface of the film (see the cross-section analysis). Such a high conductivity has been observed in many conducting polymers with a highly doped state when prepared by the electrochemical polymerization method.22 The protruded regions in the topography correspond well with highly conducting areas in the current image. This is a very common feature observed in electrodeposited films as more conducting (or better doped) spots grow faster than less conducting ones during the electrolysis, forming a mountain-like morphology for the grains of the film.22 When compared with spin-coated PEDOT films shown above (Figures 2c and 3c), the electropolymerized PEDOT film shows much denser bright spots due to more homogeneous generation of doping sites during the electrochemical growth. The average current was about 10 times greater than that of the sorbitol-treated film, the most conductive of all additive-treated films. When \( I-V \) curves were obtained over a highly conducting spot in the current image shown in Figure 5b, very steep slopes of 10 000–35 000 nA/V were observed around 0 V (Figure 5c), whereas the slopes were in a range of 3000–9000 nA/V for conducting spots on the sorbitol-treated film (Figure 4d). The conductivity calculated from the average value of the slopes (conductance) across the scanned surface shown in Figure 5b was 467 (±203) S/cm, which places the film in a metallic state (≥10² S/cm) while the sorbitol-treated PEDOT:PSS film was in a highly doped semiconducting state (15.4 ± 8.2 S/cm).25a The nanoscale conductivity of 467 S/cm, which was obtained by CS-AFM measurements, is comparable with a bulk-scale value (650 S/cm) measured on an electropolymerized PEDOT film by an in situ method using two platinum band electrodes.25c On the basis of the comparison of nanoscale and bulk conductivities of electrochemically prepared PEDOT films, the vertical charge flow through the spin-coated, additive-treated PEDOT films may not be as efficient as that through the electrodeposited films due both to the poor homogeneity of the conducting areas and the low conductivity through the PEDOT/PSS chains. Further studies are now in progress to find some critical parameters for increasing the density of conducting areas and conductivities throughout PEDOT:PSS films.

Electrochemical or chemical doping is the most popular method for increasing the conductivity of \( \pi \)-conjugated organic materials.25 To see the effect of electrochemical doping on the nanoscale conductivity of the spin-casted PEDOT:PSS film, we oxidized it at an applied voltage of 0.8 V (vs Ag wire) for 15 min in an ACN solution containing 0.1 M LiClO₄. As a result of the doping process, the surface roughness increased by about 3 times (Table 1) with the grain size decreased and the shape more rounded (Figure 6a,b). Those changes must have been caused by the insertion of perchlorate anions into the polymer matrix, which would induce changes in the internal structures. The current flowing at bright spots also increased by about an order of magnitude to a few hundreds of nanoamps as in the case of addition of additives (Figure 3c and Figures 1–3 in the Supporting Information). One interesting point is that the density of conducting spots did not undergo an increase after the electrochemical doping process. This observation indicates that the doping process occurred effectively only through relatively well-connected, conducting spots but not in the surrounding insulating regions. When the additive-treated films were electrochemically doped, the charge flow through conducting spots was also enhanced more in the same way as in the pristine film. Therefore, electrochemical doping can be considered as a general method for increasing the conductivity of chemically prepared PEDOT:PSS films at conductive spots.

Conclusions

We have demonstrated that a few additives, which have been known to increase the bulk conductivities of PEDOT:PSS films, were shown to increase the nanoscale vertical current flows and the density of conductive spots as well on the film surface by affecting the final distribution and arrangement of PEDOT:PSS chains and their grains. The \( I-V \) curves acquired at insulting (dark) spots over both pristine and additive-treated PEDOT:PSS films showed many irregular current spikes when the bias potentials went above/below ±1.5 V, which reflects the non-continuous density of states for the charge flow due to the
inhomogeneous distribution of PEDOT and PSS chains. On the other hand, $I$–$V$ curves showed smoother and steeper shapes at conducting (bright) spots upon additive treatment, as observed in a highly doped semiconducting state of electropolymerized conducting polymer films. Compared with electropolymerized PEDOT films, the additive-treated PEDOT:PSS films showed rather inhomogeneous current pathways and densities of conducting spots. A new insight acquired from the series of spatially resolved CS-AFM observations is that the conductivity of the conducting spots on the additive-treated PEDOT:PSS films could be varied by electrochemically doping them but their populations were not. Thus, the enhancement in conductivity due to electrochemical doping does not result from the increase in population of conductive spots but from heavier doping of those already conductive spots. This indicates that the density of the conducting spots introduced during the film preparation process is simply determined by whether or not an additive was used and which additive was used. This is because the additive such as sorbitol not only affects interactions between PEDOT$^+$ and PSS$^-$ ion pairs but also makes them better dispersed in water although the PEDOT$^+$–PSS$^-$ concentration would remain constant or even smaller after addition of the additive. This leads to a film, on which the conducting spots are more densely and evenly distributed, resulting in higher conductivity due to the formation of well-connected conducting domains and their higher population.

Finally, it should be pointed out that electrochemically prepared films display much better electrical characteristics in comparison to the films obtained by spin-coating chemically doped PEDOT at the expense of the smoother morphology of the latter. Thus, the electrochemical doping process is suggested as an effective option to significantly enhance the conductivity of PEDOT:PSS films even though they have been chemically doped to make the PEDOT$^+-$PSS$^-$ ion pairs prior to the preparation of the dispersions.

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Supporting Information Available: Topography, deflection, and current images. $I$–$V$ curves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes