

ORIGINAL ARTICLE

Correlation between the hierarchical structure and electrical conductivity of PEDOT/PSS

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The correlation between the hierarchical structure and electrical conductivity of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) was investigated by means of X-ray photoelectron spectroscopy, wide-angle X-ray diffraction, conductive atomic force microscopy and the temperature dependence of the electrical conductivity. Upon adding 3% ethylene glycol (EG), the electrical conductivity at room temperature significantly increased from 3 to 175 S cm⁻¹, while a further increase in EG up to 20% resulted in a decrease in the electrical conductivity to 117 S cm⁻¹. It was found that the improvement in the electrical conductivity could be explained from the changes in the hierarchical structure; a decrease in the insulating PSS shell, crystallization of the PEDOT and aggregation of the PEDOT/PSS particles, which affect both the intra- and interparticle transport of charge carriers.

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INTRODUCTION

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonic acid) (PEDOT/PSS), commercially available in the form of an aqueous dispersion of colloidal particles, is one of the most successful conductive polymers with a hierarchical structure (Figure 1).^{1,2} The specific sequence of partially cationic ethylenedioxythiophene and anionic styrenesulfonic acid monomer units (primary structure) forms a polyion complex through electrostatic interactions (secondary structure), which disperses in water as a colloidal gel particle (tertiary structure). Therefore, the PEDOT/PSS colloidal gel particles can be shaped into thin coatings,^{3,4} fibers^{5,6} and thick films^{7,8} by a facile wet-process.

Interestingly, upon adding high-boiling-point solvents such as EG, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and *N,N*-dimethylformamide, the electrical conductivity rises remarkably by two orders of magnitude, which is namely a ‘solvent effect’.⁹ The highly conductive PEDOT/PSS has potential applications in flexible transparent electrodes of flat panel displays,^{3,10} touch panels¹¹ and solar cells¹² as an alternative to indium tin oxide. The mechanism by which the electrical conductivity improves has been thoroughly investigated using UV–vis–NIR spectroscopy,³ Raman spectroscopy,¹³ wide-angle X-ray diffraction (XRD),⁶ X-ray photoelectron spectroscopy (XPS),¹⁴ electron spin resonance spectroscopy¹⁵ and atomic force microscopy (AFM).¹⁶ Yang *et al.*¹³ suggested that PEDOT underwent a conformational change from a compact coil to an extended coil caused by treatment with EG and meso-erythritol, resulting in the observed increase in electrical conductivity. On the other hand, Jönsson *et al.*¹⁴ demonstrated that the thickness of the insulating PSS layer surrounding the PEDOT/PSS particles was reduced by the addition of solvents. This improved the contact between such particles and increased the

electrical conductivity. However, these studies only focused on one layer of the hierarchical structure such as the conformational change of the PEDOT (secondary structure) or the contact between the PEDOT/PSS particles (quaternary structure). This is insufficient to understand the solvent effect comprehensively because little is known about the correlation between the hierarchical structure and the electrical conductivity of the PEDOT/PSS.

In this study, we investigated the effect of EG on the hierarchical structure by means of XPS, XRD and conductive AFM techniques in order to elucidate the mechanism responsible for the improved conductivity in detail. From the results obtained, we can conclude that the decrease in the insulating PSS shell, the crystallization of PEDOT and the aggregation of PEDOT/PSS particles caused by the addition of EG are crucial for both the intra- and interparticle transport of charge carriers.

EXPERIMENTAL PROCEDURE

PEDOT/PSS was commercially available in the form of an aqueous dispersion of colloidal particles (Clevios P AG, Heraeus, Hanau, Germany). Free-standing films with a thickness of ~17 μm were prepared by casting the PEDOT/PSS dispersion containing different amounts of EG in a Teflon dish at 60 °C for 6 h. The film was then heated at 160 °C for 1 h in vacuum to remove the EG completely from the film. The electrical conductivity of the PEDOT/PSS film was measured by a normal four-probe method with a Lorester (MCP-T610, Mitsubishi Chemical Analytech, Chigasaki, Japan). The temperature dependence of the electrical conductivity was measured from 8 to 300 K at a constant heating rate of 1 K min⁻¹ using a cryostat (PS22, Nagase Techno-Engineering, Chuo, Japan). The XPS measurements were carried out with an Al Kα line (Quantera SXM, Physical Electronics, Chanhassen, MN, USA) on the thin films spin-coated on n-doped Si substrates. The XRD patterns were measured using an imaging plate (R-AXIS DS3C, Rigaku, Shibuya, Japan) at 40 kV and 30 mA with an exposure time of 1 h.

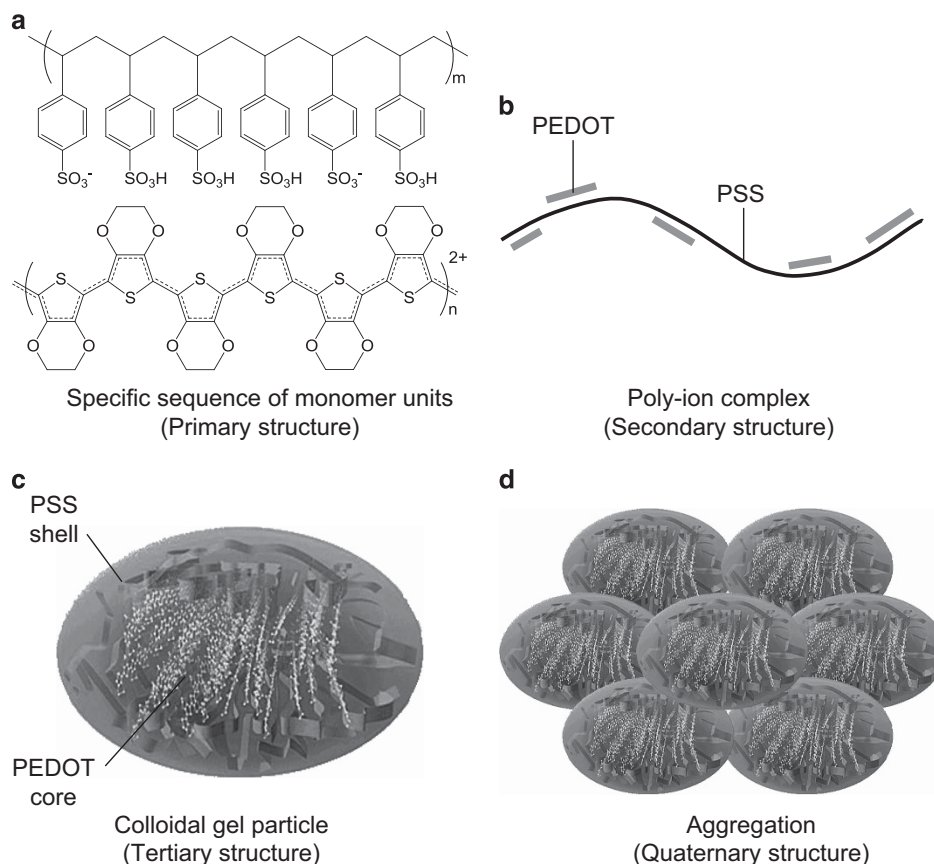


Figure 1 Hierarchical structure of PEDOT/PSS. (a) specific sequence of monomer units (primary structure), (b) poly-ion complex (secondary structure), (c) colloidal gel particle (tertiary structure) and (d) aggregation (quaternary structure). A full color version of this figure is available at *Polymer Journal* online.

The conductive AFM measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu, Kyoto, Japan) equipped with a conductive probe in contact mode under a bias voltage of 0.5 V.

RESULTS AND DISCUSSION

Electrical conductivity

A clear indication of the importance of EG in the improvement of the electrical conductivity is demonstrated in Figure 2. Upon adding 3% EG, the conductivity significantly increases by two orders of magnitude from 3 S cm^{-1} (pristine) to 175 S cm^{-1} (EG3), while a further increase in EG up to 20% results in a decrease in the conductivity to 117 S cm^{-1} (EG20). The lower electrical conductivities measured are ascribed to the low-conductivity PEDOT/PSS (Clevios P AG), which is the most popular grade used industrially in antistatic coatings. Indeed, the electrical conductivity of high-conductivity grade PEDOT/PSS (Clevios PH1000) was found to be as high as 5 S cm^{-1} (pristine) and 840 S cm^{-1} (EG3).

A similar solvent effect was observed for thin coatings of PEDOT/PSS, where the electrical conductivity of spin-coated thin films ($\sim 60 \text{ nm}$ thick) increased from 0.6 S cm^{-1} (pristine) to 45 S cm^{-1} (EG3). The values were relatively small compared with those of the free-standing thick films, which may result from the nonuniformity and/or structural defects of the thin films. Therefore, to clarify the intrinsic conductivity of PEDOT/PSS in the bulk state, the solvent effect on the hierarchical structure of the pristine, EG3 and EG20 thick films were comprehensively investigated.

Composition ratio (secondary structure)

The effect of EG on the secondary structure or the composition ratio between PEDOT and PSS was investigated by XPS. In general, XPS samples are prepared by spin-coating the PEDOT/PSS dispersion containing EG on a conductive substrate. However, it was difficult to obtain a uniform thin film of EG20 on an n-doped Si wafer because of the slow evaporation of EG and/or low PEDOT/PSS concentration. Therefore, XPS measurements were performed only on the pristine and EG3 thin films. As demonstrated in Figure 3, the XPS spectra of the pristine and EG3 films in the energy range of the S 2p signal showed well-defined peaks at ~ 169 and 165 eV assigned to the sulfur atoms of PSS and PEDOT, respectively.^{6,14} The peak at 169 eV , corresponding to the PSS, significantly decreased upon the addition of EG. The PSS to PEDOT ratio, calculated using the peak area, decreased from 2.9 (pristine) to 2.3 (EG3). Because the PSS to PEDOT ratio of the PEDOT/PSS particles (Clevios P AG) used in this study was ~ 2.5 ,¹⁰ the results suggest that excess PSS on the surface of the colloidal particles decreased, and the composition between PEDOT and PSS became more homogeneous. This is consistent with the results reported by Jönsson *et al.*¹⁷ They found that phase segregation occurred in the PEDOT/PSS system and that PSS was the predominant species on the surface. The shell surrounding the PEDOT/PSS particles consisting of the excess PSS was estimated to be $\sim 37 \text{ \AA}$ thick using XPS and ultraviolet photoelectron spectroscopy.¹⁷ Thus, the increased conductivity is associated with a decrease in the insulating PSS shell thickness covering the PEDOT/PSS particles, which improves

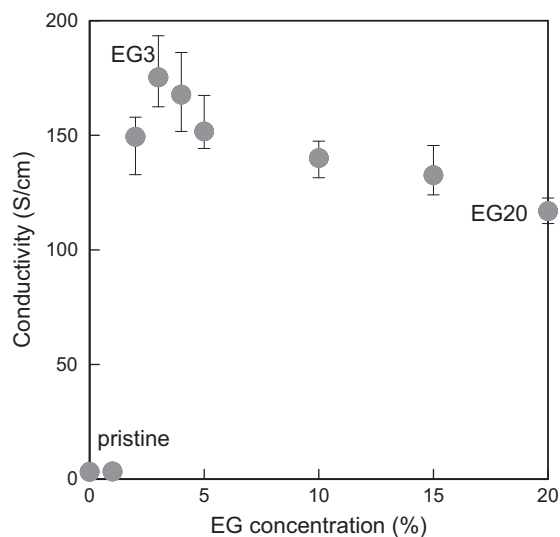


Figure 2 Dependence of the electrical conductivity of the PEDOT/PSS films on the EG concentration as measured by a four-probe method at room temperature. A full color version of this figure is available at *Polymer Journal* online.

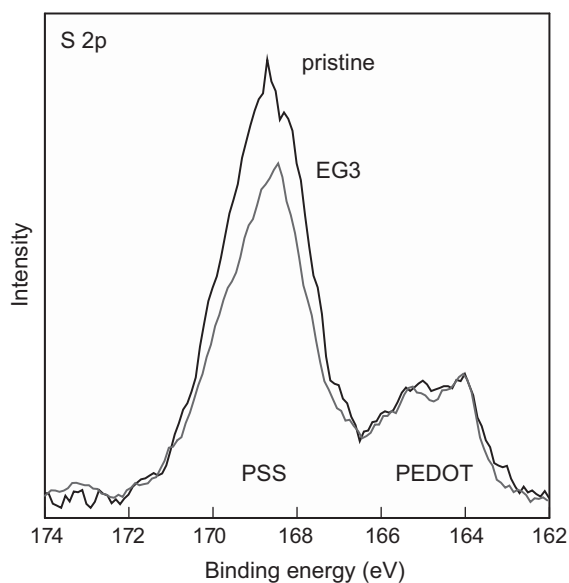


Figure 3 XPS spectra of pristine and EG3 films in the energy range of the S 2p signal. A full color version of this figure is available at *Polymer Journal* online.

the contact between the conductive PEDOT domains and enhances the transport of charge carriers.^{6,10}

Crystallinity (tertiary structure)

The XRD patterns of various PEDOT/PSS films with different EG concentrations are shown in Figure 4. The Debye–Scherrer ring at a $2\theta = 26^\circ$ ($d = 3.4 \text{ \AA}$) assigned to the (020) plane of an orthorhombic unit cell of PEDOT¹⁸ became more apparent as the EG concentration increased. This clearly indicates that the PEDOT molecules are partially crystallized (tertiary structure) during the film formation, leading to an increase in the crystallinity and crystallite size of the

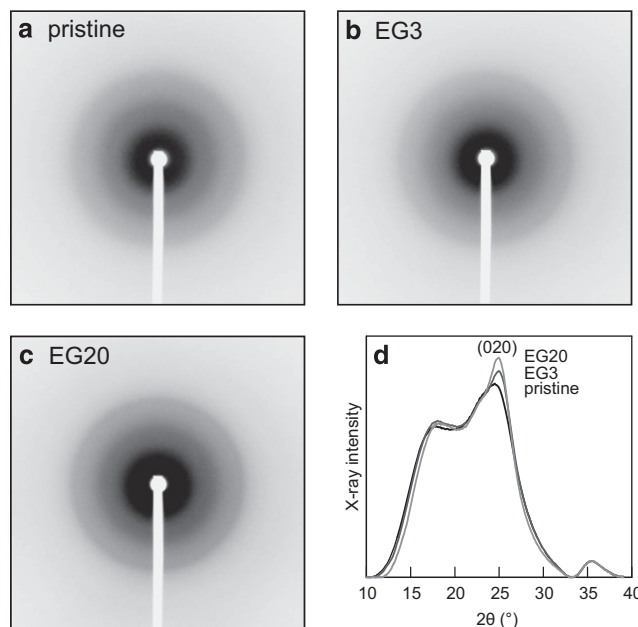


Figure 4 XRD spectra of (a) pristine, (b) EG3 and (c) EG20 films measured using an imaging plate and (d) XRD profiles for various films. A full color version of this figure is available at *Polymer Journal* online.

PEDOT nanocrystals.^{6,19} It is expected that EG, a high-boiling-point organic solvent with a high dielectric constant, will decrease the electrostatic interactions between the PEDOT cations and PSS anions by a screening effect. This may induce a spontaneous stacking of the linear and planar PEDOT molecules, which favors the formation of a crystalline phase.

Surface morphology (quaternary structure)

Figure 5 shows the effect of EG on the morphology (quaternary structure) of the PEDOT/PSS films. One can see that numerous particles with diameters of several tens of nanometers are densely packed, forming the pristine and EG3 films with a surface roughness (R_a) of 1.3 and 2.1 nm, respectively. On the other hand, in the EG20 film, larger grains loosely aggregate with structural defects such as holes and cracks where the R_a increases to 3.6 nm. Crispin *et al.*²⁰ observed elongated islands because of phase segregation upon the addition of diethylene glycol in AFM images. They also concluded that the addition of diethylene glycol reduced the amount of excess PSS on the PEDOT/PSS particles by phase segregation. The current images, reflecting local conductivity in the thickness direction, clearly show that the highly conductive domains (bright area) are randomly and loosely distributed in the less conductive matrices (dark area) in the film. It should be noted that the highly conductive domains significantly increase in size and in number with an increasing EG concentration.

Carrier transport properties

To clarify the effect of EG on the carrier transport properties in more detail, the temperature dependence of the conductivity was measured, and the results are shown in Figure 6. The conductivity of the pristine, EG3 and EG20 films gradually increases as the temperature (T) is increased from 8 to 300 K, which is characteristic of semiconducting materials. According to the nearest-neighbor hopping model,²¹ the temperature dependence of conductivity (σ) can be

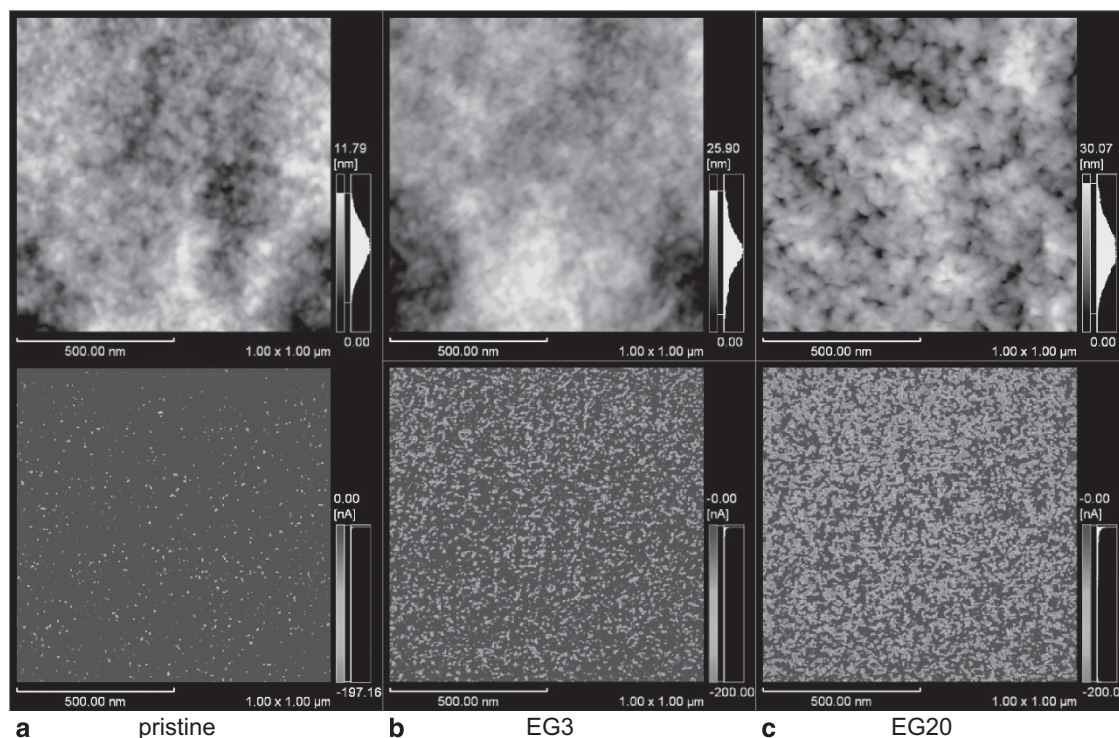


Figure 5 AFM height images (top) and current images measured under a bias voltage of 0.5 V (bottom) for (a) pristine, (b) EG3 and (c) EG20 films. A full color version of this figure is available at *Polymer Journal* online.

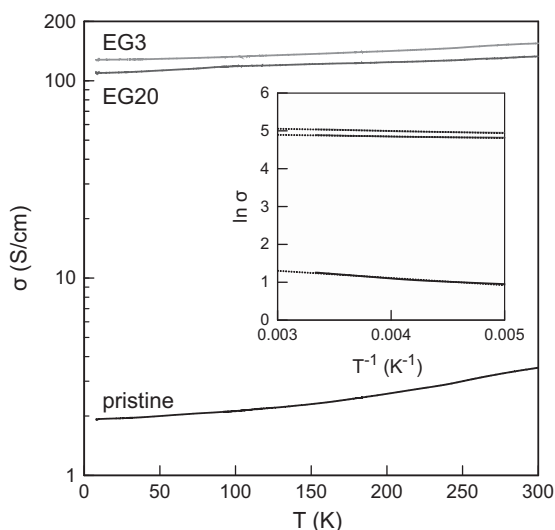


Figure 6 Temperature dependence of the electrical conductivity of pristine, EG3 and EG20 films as measured by a four-probe method from 8 to 300 K at a constant heating rate of 1 K min⁻¹. A full color version of this figure is available at *Polymer Journal* online.

described by

$$\sigma = \sigma_0 \exp[-(E_a/k_B T)] \quad (1)$$

where σ_0 is the conductivity factor, k_B is the Boltzmann constant and E_a is the activation energy. From the inset in Figure 6, it can be seen that the pristine, EG3 and EG20 films show a linear relationship

between $\ln \sigma$ and T^{-1} within the temperature range of 200–300 K. This observation demonstrates that the transport of charge carriers can be described by the nearest-neighbor hopping model, which is a simple Arrhenius thermally activated process. Thus, the mechanism by which the solvent affects the hierarchical structure and electrical conductivity of the PEDOT/PSS particles is considered to occur as shown in Figure 7. The E_a for the pristine film was calculated to be 20 meV (Table 1), which demonstrates that the transport of charge carriers between the amorphous PEDOT molecules surrounded by the insulating PSS shell is unfavorable, which is responsible for the low conductivity of the pristine film (Figure 7a). It is noted that the E_a significantly decreased to 5.1 meV for the EG3 film, which reveals that the large number of highly conductive domains form conductive paths for charge-carrier hopping within the film, as indicated in Figure 5b. Indeed, the crystallization of the PEDOT molecules, as well as the decrease in the insulating PSS shell thickness, may enhance both the intra- and interparticle transport of charge carriers, leading to the highest conductivity in the EG3 film (Figure 7b).²² However, the E_a for the EG20 film slightly increases to 6.2 meV, although the highly conductive domains remarkably increase in size and in number as shown in Figure 5c. This is ascribed to the morphological defects, including holes and cracks, because of phase segregation. These defects are unfavorable for the transport of charge carriers between the highly conductive domains. Consequently, the bulk conductivity of the EG20 film decreases (Figure 7c). On the other hand, post-treatment with other solvents is also effective for the improvement of conductivity. We previously demonstrated that dip-treatment of PEDOT/PSS microfibers in EG for 3 min significantly increased the electrical conductivity from 11 to 195 S cm⁻¹, but it decreased R_a from 5.1 to 4.1 nm,⁶ which was explained by the crystallization of PEDOT molecules and washing away of the

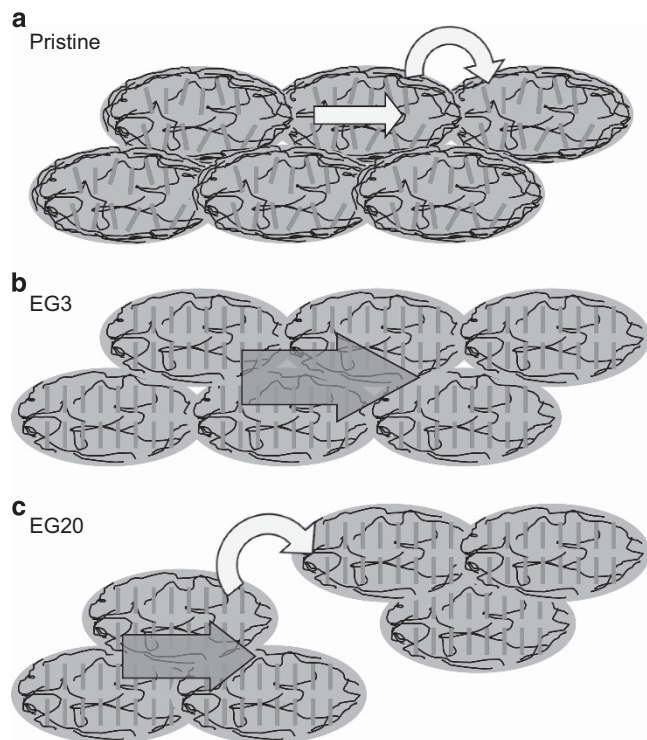


Figure 7 Schematic illustration of the possible mechanism to explain the correlation between the hierarchical structure and transport of charge carriers for (a) pristine, (b) EG3 and (c) EG20 films. A full color version of this figure is available at *Polymer Journal* online.

Table 1 Conductivity factor (σ_0), conductivity at 300 K ($\sigma_{300\text{K}}$) and activation energy (E_a) for pristine, EG3 and EG20 films

Film	σ_0 (S cm^{-1})	$\sigma_{300\text{K}}$ (S cm^{-1})	E_a (meV)
Pristine	19	4	20
EG3	217	161	5.1
EG20	198	133	6.2

insulating PSS shell with the EG. Thus, we can conclude from our results that the hierarchical structure including the composition ratio between PEDOT and PSS (secondary structure), the crystallinity of PEDOT (tertiary structure), and the surface morphology (quaternary structure) is crucial for the improvement of the PEDOT/PSS electrical conductivity.

CONCLUSION

The solvent effect on the improvement of electrical conductivity was investigated in terms of the changes in the hierarchical structure of PEDOT/PSS films. The results of the XPS, XRD and conductive AFM measurements clearly demonstrate that the decrease in the insulating PSS shell thickness surrounding the particles, crystallization of PEDOT molecules and aggregation of the particles caused by EG had a predominant role in the improvement of both the intra- and

interparticle transport of charge carriers and electrical conductivity in the bulk state.

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