Conductivity Enhancement of PEDOT/PSS Films by Solvent Vapor Treatment

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Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) is a promising conductive polymer owing to its transparency, the high stability, and high conductivity. Previous studies have reported that the conductivity of PEDOT/PSS films increases on the addition of polar organic solvents to PEDOT/PSS water dispersion prior to film preparation. In this study, we report the conductivity enhancement in PEDOT/PSS films by solvent vapor treatment of the prefabricated film. In addition to dimethylsulfoxide, *N,N*-dimethylformamide and ethylene glycol, which are known effective additives for enhancing conductivity in PEDOT/PSS films prepared by solvent-addition method, methanol is also effective in enhancing conductivity by solvent vapor treatment. The conductivity of PEDOT/PSS films is enhanced from 5 to 384 S/cm after the solvent vapor treatment by methanol at 35°C. In this study, the effect of treatment conditions and the morphological changes after the vapor treatment have been investigated.

Key Words : PEDOT/PSS / conductivity enhancement / morphology

1 INTRODUCTION

Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) is a promising conductive polymer and has attracted considerable attention from researchers in both academia and industry.¹ Owing to its transparency, in contrast to polypyrroles and polyanilines, PEDOT/PSS can be used as a transparent electrode and a hole-transporting layer in organic light emitting devices. Bayer first commercialized a PEDOT/PSS water dispersion in 1994. In the dispersion, PSS acts both as a dopant for PEDOT and a dispersant in water. A drawback of PEDOT/PSS film prepared from the dispersion is its low conductivity relative to the widely used transparent indium-thin oxide electrode.

The conductivity of the generated PEDOT/PSS film increases on the addition of polar organic solvents into PEDOT/PSS water dispersion prior to the preparation of the film. Pettersson et al. reported significant enhancement in the conductivity of PEDOT films on addition of sorbitol or ethylene glycol into the PEDOT/PSS water dispersion.² Kim et al. reported a similar conductivity enhancement on addition of dimethylsulfoxide (DMSO) or *N,N*-dimethylformamide (DMF) to the dispersion.³ Generally, polar and high-boiling point solvents seem to be suitable for enhancing conductivity. In addition to solvent addition, similar conductivity enhancement was also observed when the prepared film was immersed in organic solvents.⁴ Ethylene glycol, ethanol, and methanol are reported to be effective in enhancing conductivity. However, the mechanism of enhancement in conductivity on the addition of organic compounds is not clear. Crispin et al. reported morphological and compositional changes on the surface of PEDOT/PSS films.⁵ Ouyang et al. reported similar morphological

changes and PEDOT chain reorientation.^{4b, 6} Nardes et al. demonstrated that, in PEDOT/PSS films prepared after addition of solvent to the dispersion, charge transport occurred via quasi 1D variable range hopping.⁷ Based on these reports, the added solvent seems to induce the phase separation of PEDOT/PSS domains and excess insulating PSS chains, which can be observed by atomic force microscope (AFM) measurements. Moreover, the reorientation of PEDOT chains from random coil-rich to quinoid-rich conformation has also been reported.⁶ The removal of excess PSS chains from the film surface has been stated as the reason for the observed conductivity enhancement when a film is immersed in organic solvents.^{4c} Recently, Takano et al. observed the formation of PEDOT nanocrystals in highly conductive PEDOT film by small and wide-angle X-ray scatterings using a synchrotron radiation source.^{4d}

In this study, we report the enhancement in conductivity of prefabricated PEDOT/PSS films by solvent vapor treatment. In addition to DMSO and amide solvents, methanol is observed to be effective in enhancing conductivity. Moreover, the effects of the solvent on the conductivity enhancement and morphological

Figure 1 Structure of PEDOT/PSS

changes induced by solvent vapor treatment are also investigated.

2 EXPERIMENTAL

2.1 Materials.

PEDOT/PSS water dispersion (Clevios P HC V4, H. C. Starck GmbH) was used as received. Reagent grade organic solvents (Kanto Chemical Co. Inc.) were used without purification. Each glass plate (1.5 cm×1.5 cm) was immersed in 2-propanol for 15 min, rinsed with methanol, and then dried under a flow of nitrogen. The glass plate was further cleaned by a UV ozone cleaner (Filgen UV253) to obtain a hydrophilic surface. PEDOT/PSS films were prepared on the cleaned glass plate by spin coating method (2000 rpm for 15 s and 3000 rpm for 15 s). The thickness of the films was 0.09-0.25 μm.

2.2 Solvent vapor treatment of PEDOT/PSS films.

PEDOT/PSS film coated on glass plate was placed in a sample vial (50 mL). Organic solvent (1 mL) was slowly added to the sample vial, and then, the sample vial was sealed with a cap. The sample vial was immersed in a water bath maintained at 35°C. After 1 h, the film was dried under vacuum at 100°C for 30 min, and then at 200°C for 5 min.

2.3 Preparation of PEDOT/PSS films by solvent addition method.

A small amount of an organic solvent (0.1-20 vol%) was added to the PEDOT/PSS water dispersion. The mixture was stirred for 1 min, and then spin-coated onto a glass plate. The PEDOT/PSS film was dried under vacuum at 100°C for 30 min and then at 200°C for 5 min.

2.4 Measurements

The resistance of the film was measured by a four-point probe method using a Loresta-GP with a MCP-TP06P probe (Mitsubishi Chemical Co.). The resistance of the film was determined by the average of at least 8 data points. A constant resistivity correction factor (4.532) was employed for the calculation of the conductivity (S/cm). The thickness of the film was determined by a laser microscope VK-X200 (Keyence, Japan). The film prepared on the glass plate was partially removed and the difference in the height between the coated PEDOT/PSS film and the bare glass surface was measured to determine the thickness of the film. Tapping mode AFM observations were performed with a NanoNavi S-image SPM system (SII, Japan) using a cantilever with a force constant of ca. 15 N/m. Laser microscopic images were obtained using a laser microscope VK-X200 (Keyence, Japan).

3 RESULTS AND DISCUSSION

The addition of polar organic solvents such as DMSO, DMF and ethylene glycol to PEDOT/PSS water dispersion effectively to enhances the conductivity of the subsequently prepared PEDOT/PSS film. In this study, the cast film of PEDOT/PSS is prepared from the pristine water dispersion. The pristine PEDOT film has a low conductivity (ca. 5 S/cm). Exposure of the pristine film to solvent vapors at 35°C for 1 h leads to changes in conductivity and morphology of the PEDOT/PSS film. In Table 1, the effect of different solvents in enhancing the conductivity of PEDOT/PSS films is shown. Significant enhancement in conductivity is observed when DMSO, DMF, *N*-methyl-2-pyrrolidone (NMP) or methanol is used as the organic solvent. On the other hand,

Table 1 Conductivity of PEDOT/PSS films after solvent vapor-treatment at 35°C for 60 min.

Solvent	Conductivity (S/cm) ^{a)}
Dimethyl sulfoxide (DMSO)	364 ^{b)}
<i>N,N</i> -dimethylformamide (DMF)	326
<i>N</i> -methyl-2-pyrrolidone (NMP)	236
Methanol	384 ^{b)}
Ethylene glycol	240
Ethanol	179
H ₂ O	28.1
Nitromethane	17.2
Propylene carbonate	17.0
Acetonitrile	16.9
Chloroform	16.6
Acetone	15.2
Tetrahydrofuran (THF)	12.0
Air (no solvent)	13.1

^{a)} Average of 5 independent samples.

^{b)} Average of 10 independent samples.

polar solvents such as nitromethane and propylene carbonate are not very effective in enhancing conductivity. Solvent vapor treatment using non-polar solvents is also ineffective. Although DMSO, DMF, and NMP are reported to be effective additives, methanol has been reported to be an ineffective additive for enhancing the conductivity of PEDOT/PSS. In this study, it is revealed that methanol can also effectively enhance conductivity in PEDOT films when introduced via solvent vapor treatment.

Figure 2 shows the effect of concentration of the organic solvent on conductivity of PEDOT/PSS films that are prepared by the solvent-addition method. In agreement with the previously reported results, the conductivity of the films increase with an increase in the amount of the additive (DMSO). Maximum conductivity is observed when the concentration of DMSO is ca. 15 vol%. The dependence of conductance on the amount of DMSO is similar to that observed in the reported data.⁸ However, contrary to the results from solvent vapor treatment, no enhancement in the conductivity of the films was observed on methanol addition in

Figure 2 Effect of the concentration of the organic solvent on the conductivity enhancement of PEDOT/PSS films prepared by solvent-addition method.

the measured range. Clearly, methanol enhances conductivity only when introduced via solvent vapor treatment. Recently, Alemu et al. reported the conductivity enhancement in a PEDOT/PSS film after its immersion in methanol.^{4c} The removal of the insulating PSS from the film, in addition to changes in morphology and conformation are proposed as the cause for the conductivity enhancement. The solvent vapor treatment used in this study precludes the removal of the insulating PSS. In the films prepared by solvent addition method, the methanol added to the water dispersion may volatilize quickly during the preparation of film. However, in solvent vapor treatment, the prefabricated PEDOT/PSS film makes contact with methanol vapor. Therefore, the methanol-vapor-induced morphological and conformational changes may possibly cause the observed enhancement in conductivity.

Figure 3 shows the effect of the time of exposure to methanol vapors on the conductivity of PEDOT/PSS films. The enhancement in conductivity is observed within minutes of exposure to methanol vapors. The effect of the temperature of exposure on the conductivity is shown in Figure 4. In the

Figure 3 Effect of time of exposure to methanol vapors on the conductivity of PEDOT/PSS films.

Figure 4 Effect of the temperature of exposure on the conductivity of PEDOT/PSS films.

case of methanol, a temperature dependent increase in the conductivity of PEDOT/PSS films is observed with temperature from 384 to 647 S/cm. On the other hand, the effect of the temperature of exposure is negligible in the case of DMSO. It is clear that the amount of methanol vapor gives great influence on the conductivity enhancement of PEDOT/PSS films.

Topography and phase images of the PEDOT/PSS films are shown in Figures 5 and 6. A higher density of small grains is observed in the topography of films treated with DMSO vapors (Figure 5c) when compared with that in pristine film (Figure 5a). More noticeable changes are observed in the phase images (Figures 5b and 5d). Interconnected domains are clearly observed in DMSO vapor-treated films (Figure 5d). The topography and phase images of DMSO vapor-treated films (Figure 5c and 5d) are similar to those of DMSO-added films (Figure 5e and 5f); therefore, similar morphological changes are possibly induced by solvent vapor treatment and solvent addition. Dark regions in the phase images are due to the presence of a relatively soft material, presumably, the excess PSS material. Bright areas attributed to PEDOT-rich domains are interconnected with each other. The observed clear phase separation between insulating

Figure 5 Topography (left) and phase images (right) of the PEDOT/PSS films; panels a) and b): untreated, panels c) and d): DMSO vapor-treated, and panels e) and f): DMSO-added.

PSS materials and the interconnected PEDOT-rich domains can enhance the conductivity of PEDOT/PSS films. Figure 6 shows the topography and phase images of pristine (6a and 6b), methanol vapor-treated (6c and 6d), and methanol-added (6e and 6f) PEDOT/PSS films. Similar to Figure 5c and 5e, the number of small grains increased in Figure 6c. Moreover, the phase image (Figure 6d) showed interconnected domains. This observation suggests that similar phase separation of insulating PSS and PEDOT-rich domains is induced by the methanol vapor treatment. On the other hand, the topography (Figure 6e) and the phase image (Figure 6f) of the methanol-added film are similar to those of untreated films (Figures 6a and 6b). This indicates that methanol vapors induce the phase separation of PEDOT-rich domains and the excess insulating PSS chains, resulting in enhancement of the conductivity of PEDOT/PSS films.

Figure 7 shows the laser microscopic images of PEDOT/PSS films, allowing us to investigate their macroscopic morphologies. Noticeable morphological changes are observed for the DMSO vapor-treated films (Figure 7c) while such differences are not observed for the DMSO-added film (Figure 7b). The difference in height from the lower to higher domains in DMSO vapor-treated

Figure 7 Macroscopic morphology of the PEDOT/PSS films measured by laser microscopy; a) untreated, b) DMSO added, c) DMSO vapor-treated, and d) methanol vapor-treated.

film is $0.13\mu\text{m}$, which amounts to 56% of the thickness of the film ($0.23\mu\text{m}$). Swelling the film by DMSO vapor might lead to an uneven surface. A partially uneven morphology is also observed for the methanol vapor-treated film (Figure 7d). A relatively smaller difference in height between lower and higher domains ($0.03\mu\text{m}$, 14%) is also observed. Note that no noticeable morphological differences between untreated and DMSO-added films are observed.

4 Conclusion

Conductivity of PEDOT/PSS films is significantly enhanced by solvent vapor treatment. In addition to the polar and high boiling-point solvents, such as DMSO and ethylene glycol, methanol vapors are also effective in enhancing conductivity. Methanol vapors can induce morphological and conformational changes in PEDOT/PSS films, which result in enhanced conductivity. Interconnected PEDOT-rich domains are clearly observed in the highly conductive films by AFM measurements. Laser microscopic images indicate that exposure of films to DMSO vapors can lead to the formation of uneven surface in the PEDOT/PSS films. Use of inexpensive and volatile methanol in solvent vapor treatment can be a cost-effective method process for enhancing the conductivity of prefabricated PEDOT/PSS films.

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Figure 6 Topography (left) and phase images (right) of the PEDOT/PSS films; panels a) and b) untreated, panels c) and d) methanol vapor-treated, and panels e) and f) methanol-added.

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