

Electrical conductivity enhancement of spin-coated PEDOT:PSS thin film via dipping method in low concentration aqueous DMSO

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ABSTRACT: The electrical conductivity of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was enhanced by dipping the thin films prepared by spin coating technique in an aqueous DMSO solution. The low concentration range of DMSO in water between 0–5 vol % was studied in comparison with pure water and pure DMSO. It was found that the electrical conductivity dramatically increased as increasing the concentration of DMSO and reached the constant value of 350 S cm^{-1} at 2 vol % of aqueous DMSO solution. This could be explained by the conformational change of PEDOT chains from the coil structure to the linear or expanded coil structure as confirmed by Raman spectra. Further, white patches were obviously noticed on the surface of the films dipped in pure DMSO, indicating the phase separation of conductive PEDOT grains and associated PSS. The sulfur element of the dipped film surface was investigated by XPS. The XPS S2p core-level spectra displayed that the unassociated PSS was considerably removed from the surface of PEDOT:PSS films dipped in pure water and 2 vol % of aqueous DMSO solution, indicating that the presence of water in the solvents is important to prominently promote the washing effect. Finally, UV–Vis spectra revealed the improved transparency of the films probably owing to the decreased film thickness. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42108.

KEYWORDS: conducting polymers; morphology; structure; property relations

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INTRODUCTION

Recently, the electronics manufacturing industry has been rapidly growing due to the first discovery of conductive polymer in the mid-1970s and intense R&D activities since then. Conductive polymer plays a key role in achieving high performance and environmentally friendly electronic devices to replace the traditional metals like indium tin oxide (ITO). Among them, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is an intriguing conductive polymer that has been paid attention for many electronics applications, i.e., organic photovoltaic devices (OPVs), organic light emitting diodes (OLEDs), and chemiresistive sensors, because of its outstanding properties including high electrical conductivity, environmental stability, and high transparency.^{1–5} Generally, PEDOT is intrinsically insoluble in water; therefore, the incorporation of water-soluble insulating PSS leads to the enhancement of the dispersibility in an aqueous solution and some polar organic solvents due to the formation of the polyelectrolyte complex of PEDOT:PSS, resulting in better processibility on the flexible

substrates.⁶ Film forming techniques, i.e., drop casting and spin coating, have been performed to deposit the conductive materials owing to an ease to create the small scale of patterns. Unfortunately, the electrical conductivity of pristine PEDOT:PSS is relatively low ($\sim 0.3 \text{ S cm}^{-1}$), depending on the polymerization method,⁷ and thus the enhancement of the electrical conductivity is greatly necessary for the usage in advanced applications such as OPVs.

Many researchers have attempted to improve the electrical properties of the conductive polymers by straightforwardly adding or *in situ* chemical oxidative polymerization with conductive particles such as novel metals (gold and silver),^{8–10} multiwall carbon nanotubes (MWCNTs),^{11–13} and graphene.^{14,15} Without surface modification, the agglomeration of these nano-sized particles also resulted in poor electrical conductivity. Reddy and coworkers^{16,17} successfully prepared the spherical core-shell nanocomposites containing PEDOT coated onto the surfaces of MWCNTs and Fe_3O_4 by chemical oxidative polymerization in the micellar medium. It was found that the electrical

conductivity of these nanocomposites was considerably enhanced with increasing the particle loading. Moreover, it has been reported that the electrical conductivity can also be enhanced by acidic treatments, thermal annealing and chemical treatments.^{18,19} Concerning the environmental issue, acidic treatment was unsuitable because the used chemicals were hazardous and corrosive, which might damage the ITO electrodes. The thermal treatment was easy to conduct; however, the electrical conductivity was only slightly improved about one order of magnitude.²⁰ Direct addition of high boiling point organic solvents into PEDOT:PSS, also known as solvent doping method, increased the electrical conductivity of PEDOT:PSS more than 100 times when compared with unmodified PEDOT:PSS.^{21,22} The high boiling point (BP) organic solvents include dimethyl sulfoxide (DMSO; BP = 189°C), ethylene glycol (BP = 197°C), *N*-methylpyrrolidone (BP = 202°C), glycerol (BP = 290°C), and sorbitol (BP = 296°C).^{23,24} Secondly, the previous literatures mentioned that solvent doping method strongly affected the surface morphology of PEDOT:PSS thin films. The surface roughness dramatically increased as a result of the phase separation between the PEDOT matrix and excess PSS, resulting in aggregation of the conductive PEDOT grains and the formation of PSS-enriched layer on the top surface of thin films.^{25,26} Consequently, the surface roughness increased as a function of doping ratio and the electrical conductivity thus dropped significantly because it traps the charge carriers.^{27,28} Furthermore, removal of these solvents requires high temperature which is often in the range of the decomposition temperatures of PEDOT (150°C) and PSS (250°C), reducing the electrical properties and light transmittance of the prepared films.^{29,30} Hence, the surface roughness of the thin film as well as type and concentration of additional solvent are crucial to be controlled to enhance the physical properties and electrical conductivity of the PEDOT:PSS thin films.

To overcome these problems, Yeo *et al.* proposed a polar-solvent vapor annealing, in which the solvent vapor only interacts with the surface of the PEDOT:PSS films.³¹ They suggested that the induced phase-separated morphology resulted in better connection of conductive grains while the surface roughness at the top layer of films was reduced substantially from 1.31 to 0.32 nm. Dropping the solvent on the prepared films gave the similar conductivity to vapor annealing.³² Alemu *et al.* has compared dropping, dipping, and a combination of these treatments with various alcohols in an attempt to enhance the electrical conductivity and light transmittance of the PEDOT:PSS films. It is suggested that dropping method exhibited higher electrical conductivity than dipping method; however, the films treated by dropping with methanol showed the serrated white lines of excess PSS on the film surface even if these defects can be easily removed by additional dipping. Unlike dropping and the sequential treatments, dipping method can improve the conformational structure of PEDOT and remove the excess PSS concurrently. Therefore, dipping method seems to be more convenient because it is a less-time consuming one-step post-treatment and the obtained electrical conductivity is not much different from the two-step post-treatment.

In this article, we fabricated PEDOT:PSS thin films on glass substrates by spin coating and subsequently dipping them into

a DMSO solution. The effect of the concentration of DMSO in an aqueous solution on the surface morphology, surface chemistry and electrical conductivity of the PEDOT:PSS thin films after the dipping process was investigated. The low concentration range of DMSO between 0 and 5 vol % was chosen.

EXPERIMENTAL

Materials

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) in an aqueous solution (Clevios PH 1000) was purchased from Heraeus GmbH, Germany. The solid content of PEDOT:PSS was 1.1 wt % and the weight ratio of PEDOT-to-PSS was 1 : 2.5. Dimethyl sulfoxide (DMSO) was bought from Sigma-Aldrich and used as received without further purification.

Sample Preparation

The commercial PEDOT:PSS material was filtered through a glass membrane with 0.45 μm pore size and spin coated (G3P-8 Spincoat, Cookson electronics equipment) at 1500 rpm for 40 s on the glass substrates, which were sequentially cleaned before use in an ultrasonic bath with detergent, deionized water, acetone, and isopropyl alcohol, respectively. Subsequently, drying was carried out on a hot plate at 150°C for 20 min in an ambient air. The prepared thin films were eventually dipped for 20 s in 5 mL of water or DMSO or an aqueous DMSO solution at various concentrations, ranged between 0 and 5 vol %, followed by drying on a hot plate at 150°C for 20 min.

Instruments

The electrical conductivity of the prepared PEDOT:PSS thin films was measured by a standard four-point probe technique using a Keithley Instruments 6221 DC and AC current source and a Keithley 2182A nanovoltmeter. Further, the electrical conductivity of pristine PEDOT:PSS films and all dipped films were recorded after being stored in the chamber at 25°C and 30%RH for 1 week in order to acquire the steady values. The electrical conductivity (σ) can be calculated as $\sigma = 1/(R_s T)$, where R_s is the sheet resistance obtained using the equation $R_s = (\pi/\ln 2)(V/I)$ and T is an average thickness of the thin films obtained from a stylus surface profiler (Veeco Dektak 6 M Stylus Profiler) with standard scan resolution of 0.1 μm/sample. All measurements were performed five times for each specimen.

The surface structure of the PEDOT:PSS films before and after dipping treatment was characterized by Fourier transform Raman spectrometer (Perkin Elmer, Spectrum GX) equipped with a diode pumped Nd/YAG laser. The Raman spectra were collected at 1064 nm excitation using a high-sensitivity InGaAs detector at room temperature.

The sulfur S2p core-level spectra of the surface of the thin films were recorded by a X-ray photoelectron spectroscopy (XPS) (Shimadzu, ESCA-3400) equipped with a nonmonochromatic Mg K α radiation (1253.6 eV) as an excitation source at a vacuum pressure less than 1×10^{-5} Pa.

The surface topography and morphology of PEDOT:PSS thin films were examined by atomic force microscopy (AFM) (Veeco) controlled by a Nanoscope IV in tapping mode and

scanning electron microscopy (SEM) (JEOL, JSM-6400) coupled with energy dispersive X-ray analysis (EDX) at an accelerating voltage of 15 kV. The EDX data was gathered to evaluate the elemental composition on the surface of the specimens. The particle size and shape of the dipped films were observed using a high-resolution transmission electron microscopy (HRTEM) (JEOL, JEM 2100) operating at an accelerating voltage of 300 kV and 0.23 nm point resolution.

The optical appearance was measured by ultraviolet spectroscopy (Cary 5000 UV-Vis-NIR Spectrophotometer).

RESULTS AND DISCUSSION

Electrical Conductivity Enhancement of PEDOT:PSS Thin Films via Dipping Method

The electrical conductivity of pristine PEDOT:PSS and dipped PEDOT:PSS films is shown in Figure 1. The pristine PEDOT:PSS film has low electrical conductivity of $\sim 0.3 \text{ S cm}^{-1}$. Dipping in pure water leads to a slight increase in electrical conductivity to 1.8 S cm^{-1} possibly because of the physical removal of excess insulating PSS layer from the surface of the thin films, which is consistent with the work done by De Longchamp *et al.*³³ Interestingly, the electrical conductivity of the PEDOT:PSS films dipped in aqueous DMSO solutions is steadily improved at lower concentration of DMSO and then approaches the constant value of 350 S cm^{-1} at 2 vol % of DMSO in solution, which is similar to those dipped in pure DMSO in our study (as displayed in a dashed line). These results imply that the use of a low concentration aqueous DMSO solution with the dipping method shows the more practical process because this technique is easier and requires shorter operating time than that of doping method with DMSO, and only a small amount of high-boiling point DMSO is incorporated.

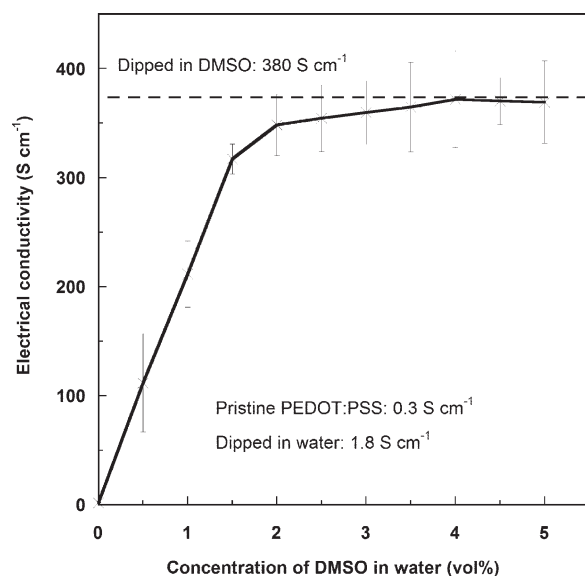


Figure 1. The electrical conductivity of PEDOT:PSS films dipped in various DMSO concentrations. The dash line represents the electrical conductivity of the film dipped in pure DMSO.

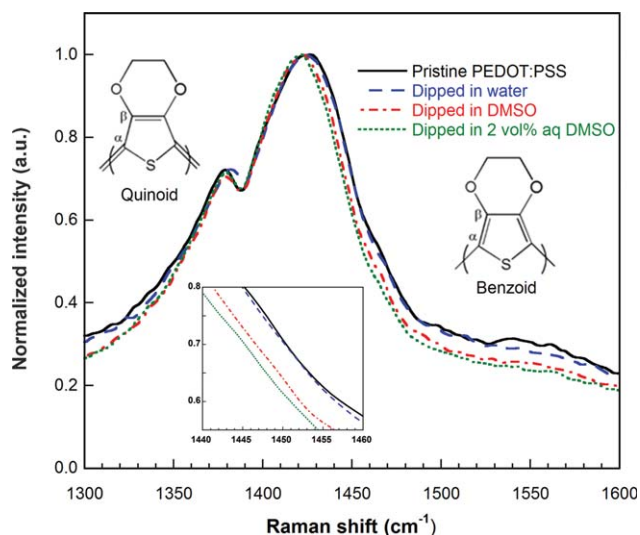


Figure 2. Raman spectra of pristine PEDOT:PSS film and dipped PEDOT:PSS films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Raman Spectroscopy

The molecular structure at the surface of pristine PEDOT:PSS and dipped PEDOT:PSS films are investigated by Raman spectroscopy as depicted in Figure 2. All samples display the band between 1300 and 1600 cm^{-1} , corresponding to the stretching vibration of carbon atoms on thiophene rings of PEDOT chains. The strong intensity at $\sim 1427 \text{ cm}^{-1}$ represents the $C_{\alpha}-C_{\beta}$ stretching vibration in favor of a quinoid structure, whereas the shoulder at $\sim 1448 \text{ cm}^{-1}$ is assigned to the stretching of $C_{\alpha}=C_{\beta}$ as to be favorable to a coil-like benzoid structure. In case of dipping in pure DMSO and aqueous DMSO solutions, the intensity of the benzoid structure is weakened and the band is red-shifted and becomes narrower, indicating that the PEDOT chains transform from a coil structure to a linear or expanded-coil structure.³⁴ It is expected that this conformational change is responsible for the enhanced electrical conductivity upon dipping in pure DMSO and aqueous DMSO solutions because the linear interchain interaction declines the energy barrier of the PEDOT chains, facilitating the charge delocalization along the π -conjugated PEDOT backbones.³⁵ On the other hand, the intensity of the films dipped in pure water demonstrates an insignificant change in comparison with that of pristine PEDOT:PSS films, suggesting that the benzoid-quinoid transformation rarely takes place. Therefore, a slight increase (~ 6 times) in the conductivity of films after treatment with pure water could be contributed to the washing effect of unassociated PSS rather than the conformational change.

XPS Analysis

The washing effect of the unassociated PSS from PEDOT:PSS surface after dipping process is evaluated by comparing the XPS sulfur S2p core-level spectra, as demonstrated in Figure 3. The XPS spectra of all samples reveal the main peak between 169.8 and 168.5 eV , which is associated with the sulfur atoms of the complex PSS fragments containing poly(styrene sulfonic acid) (PSSH) and anionic polyelectrolyte poly(sodium styrene

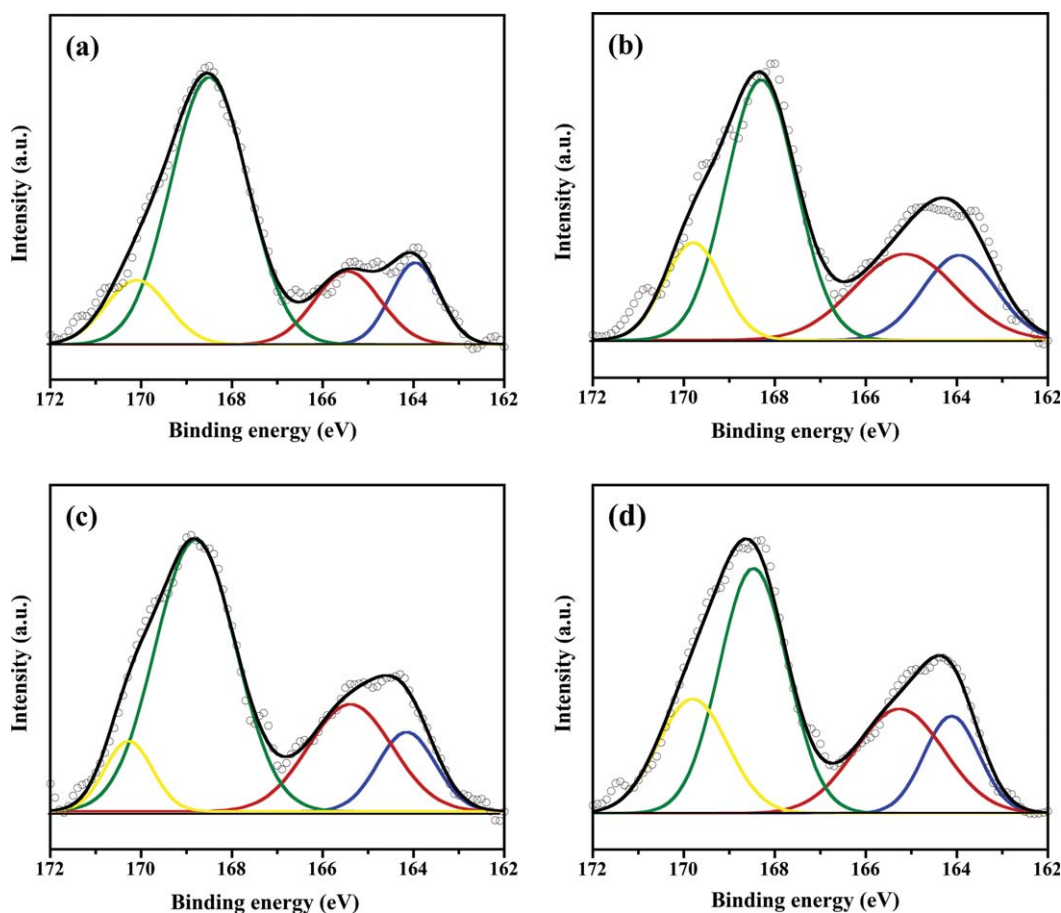


Figure 3. XPS S2p core-level spectra of (a) pristine PEDOT:PSS film and PEDOT:PSS films dipped in (b) water, (c) DMSO, and (d) 2 vol % of aqueous DMSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfonate) (PSSNa).³⁶ The formation of PSSNa can possibly be explained by the presence of $\text{Na}_2\text{S}_2\text{O}_8$ as the oxidizing agent upon the polymerization of PEDOT.³⁷ Further, the S2p contribution peak is deconvoluted into 2 peaks at 164.1 and 165.3 eV which are corresponding to the spin-split components of the sulfur atoms of the PEDOT chains. The area ratio of PSS to PEDOT is calculated to estimate the content of remaining PSS after the surface treatment; in addition, it is found that the area ratio for pristine PEDOT:PSS film is 3.17, meanwhile the ratios are 1.79, 1.94, and 1.74 for the films dipped in water, DMSO, and 2 vol % of aqueous DMSO, respectively. In other words, the existence of water in the used solvents is of great importance to remove the PSS by the dipping method. The XPS results also indicate that the surface composition is significantly changed after the dipping process. Namely, a great loss of insulating PSS fraction from the film surface can be described through the fact that the phase separation of unassociated PSS causes the enrichment of PSS on the film surface which is washed away by solvents upon dip-treatment, leading to a decreased film thickness and enhanced electrical conductivity. The removal of insulating PSS from the surface of dipped films results in an increase in electrical conductivity, which is consistent with the previous work done by Kang *et al.* in which the influence of PEDOT:PSS ratio on the electrical conductivity of

nanocomposites was investigated.³⁸ Moreover, it is worth mentioning that the removal of PSS is an advantage of the dipping technique because PSS acid exhibits hygroscopic property; the film surface containing a PSS layer can absorb water which could reduce the stability of the film in moist condition and electronics performance over time.

Surface Morphology and Elemental Composition

The surface morphology of PEDOT:PSS films coated on the glass substrates is observed by SEM. The surfaces of pristine PEDOT:PSS films [Figure 4(a)] and PEDOT:PSS films treated with pure water [Figure 4(b)] are relatively smooth; however, the crinkles on the film surface are clearly detected in case of pure water as indicated by inserted arrows which might be due to the peeling off of the film upon immersion. These defects damage the surface of the PEDOT:PSS films, resulting in lower electrical conductivity, and thus the immersion time is of great importance to optimize the films' properties. It is worth noting that dipping the films in pure water for a long immersion time (~ 1 min) leads to a loss of almost PEDOT:PSS films from the glass substrates. In addition, the insulating PSS layer on the film surface is also washed away as confirmed by the XPS spectra; however, the significant change on the surface morphology by this incident is not noticed by the SEM images. As displayed in

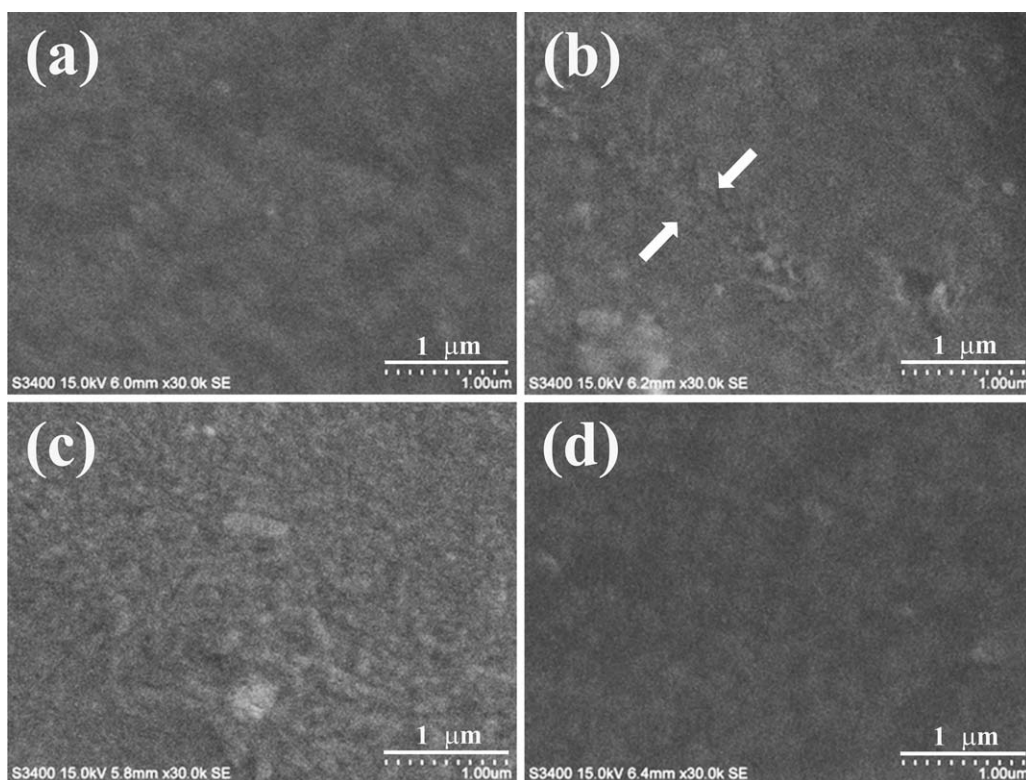


Figure 4. SEM images of (a) pristine PEDOT:PSS films and PEDOT:PSS film dipped in (b) water, (c) DMSO, and (d) 2 vol % of aqueous DMSO solution.

Figure 4(c), the films dipped in pure DMSO show the swelling of conductive PEDOT grains. The good film forming surface is obtained after being dipped in 2 vol % of aqueous DMSO solution [Figure 4(d)]. The aqueous DMSO is a suitable solvent for the dipping method because PEDOT:PSS film can be prepared without any defects.

Although the films dipped in pure DMSO give the highest electrical conductivity, the white patches as defects are clearly found on the whole film surface as illustrated in Figure 5(a). Moreover, these white patches are not observed on the films dipped in 2 vol % of aqueous DMSO as illustrated in Figure 5(c). To describe the phenomenon, the elemental composition around the white patches is measured by an energy dispersive X-ray (EDX) analysis. The bright spots in the EDX images represent the sulfur atoms. The EDX result shown in Figure 5(b) reveals that the borders of the white patches specifically contain the sulfur atoms of the aggregated PSS phase separated from the associated PEDOT chains with the uniform PSS dispersion in inner and outer regions of the white patches.³⁹ This indicates the phase separation between the excess PSS and PEDOT matrix. Furthermore, these white patches can be easily removed by rinsing with water, corresponding to the absent white patches on the PEDOT:PSS films dipped in pure water and 2 vol % of aqueous DMSO solution. As displayed in Figure 5(d), the surface of the films dipped in 2 vol % of aqueous DMSO solution shows a well uniform dispersion of sulfur atoms. Normally, the hydrophilic nature of DMSO molecules decreases the interchain interaction between conductive PEDOT-rich

grains and the insulating PSS-rich shell and it is able to dissolve some unassociated PSS phase from the film surface.³¹ Nonetheless, the washing efficiency using pure DMSO might be lower than using pure water, as shown in the calculation of the area ratio in the XPS results depicted in Figure 3. As a consequence, PSS was incompletely washed away by pure DMSO and the remaining PSS caused a formation of white patches.

Effect of Solvents on the Surface Topography of PEDOT:PSS Thin Films

The average thickness of PEDOT:PSS thin films is obtained by a surface profiler measured at five different positions per sample. Pristine PEDOT:PSS films have an average thickness of 1130 Å. After surface treatment, all dipped samples exhibit a decreased film thickness to approximately 940 Å (17% reduction) because the unassociated PSS-enrich layer on the film surface was washed away upon the dipping process.⁴⁰

Additionally, the surface topography and the root mean square (RMS) roughness (R_q) are recorded by tapping mode atomic force microscopy (AFM) as illustrated in Figure 6. It is pointed out that the R_q values of PEDOT:PSS after dipping in water and 2 vol % of aqueous DMSO solution are in a same order of magnitude as that of pristine PEDOT:PSS films, ranging between 2.4 and 2.6 nm. It should be mentioned that the measured R_q values exclude the surface of the white patches. Conversely, the R_q value obviously increases to 4.2 nm for the PEDOT:PSS films dipped in DMSO since it induces the phase separation and the conformational change from the benzoid

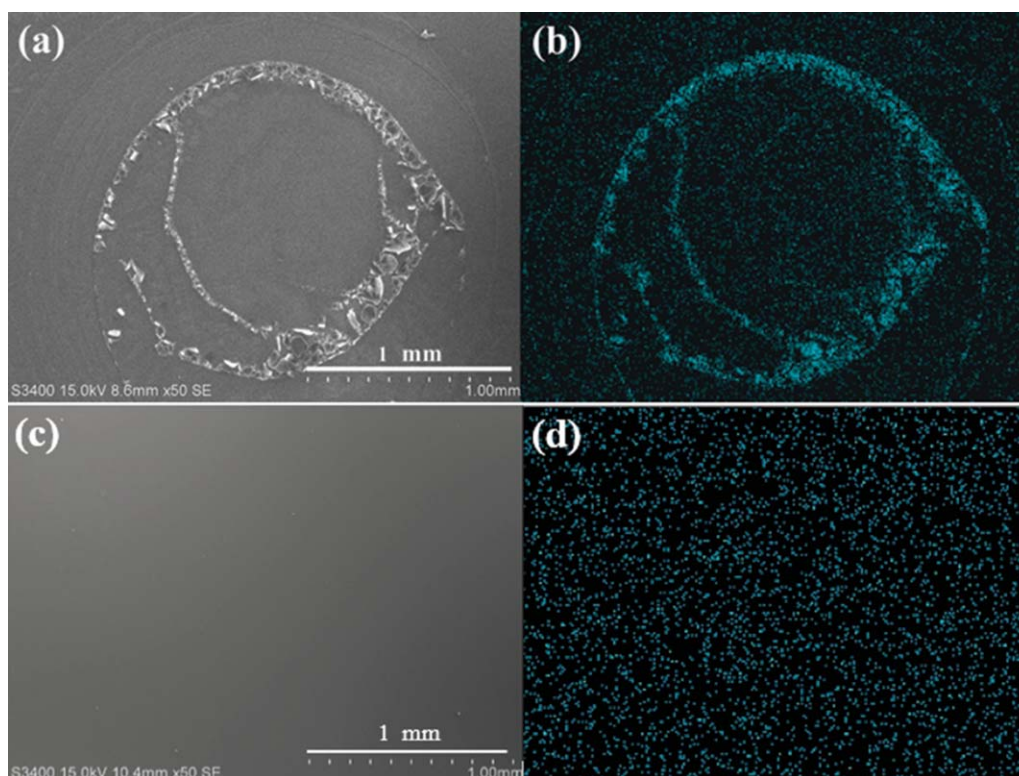


Figure 5. SEM/EDX images of (a, b) white patches on the surface of the films dipped in pure DMSO and (c, d) surface of the films dipped in 2 vol % of aqueous DMSO solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure to the quinoid structure, as early discussed in the Raman results (reference to Raman spectroscopy, Figure 2). Furthermore, the dipping method leads to a swelling of the

PEDOT:PSS grains and the removed excess insulating PSS layer.⁴¹ According to the previous literatures, the aggregation and the growth of conductive PEDOT grains usually detected in the

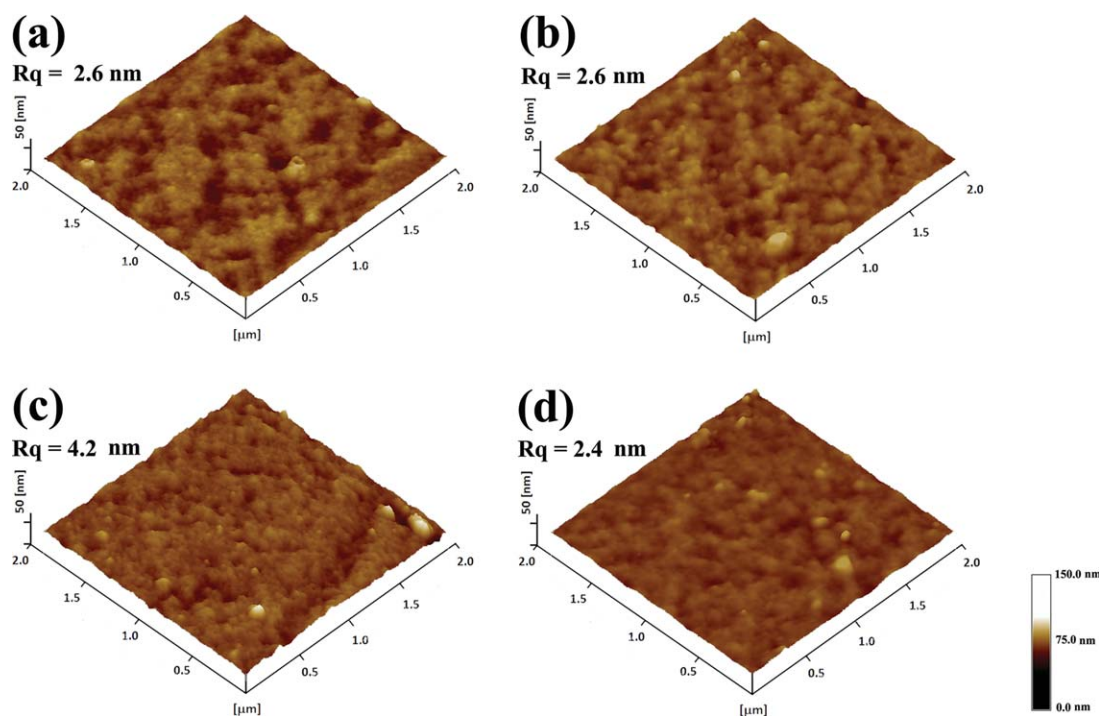


Figure 6. Tapping mode AFM topography of (a) pristine PEDOT:PSS films; and PEDOT:PSS films dipped in (b) water, (c) DMSO, and (d) 2 vol % of aqueous DMSO solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

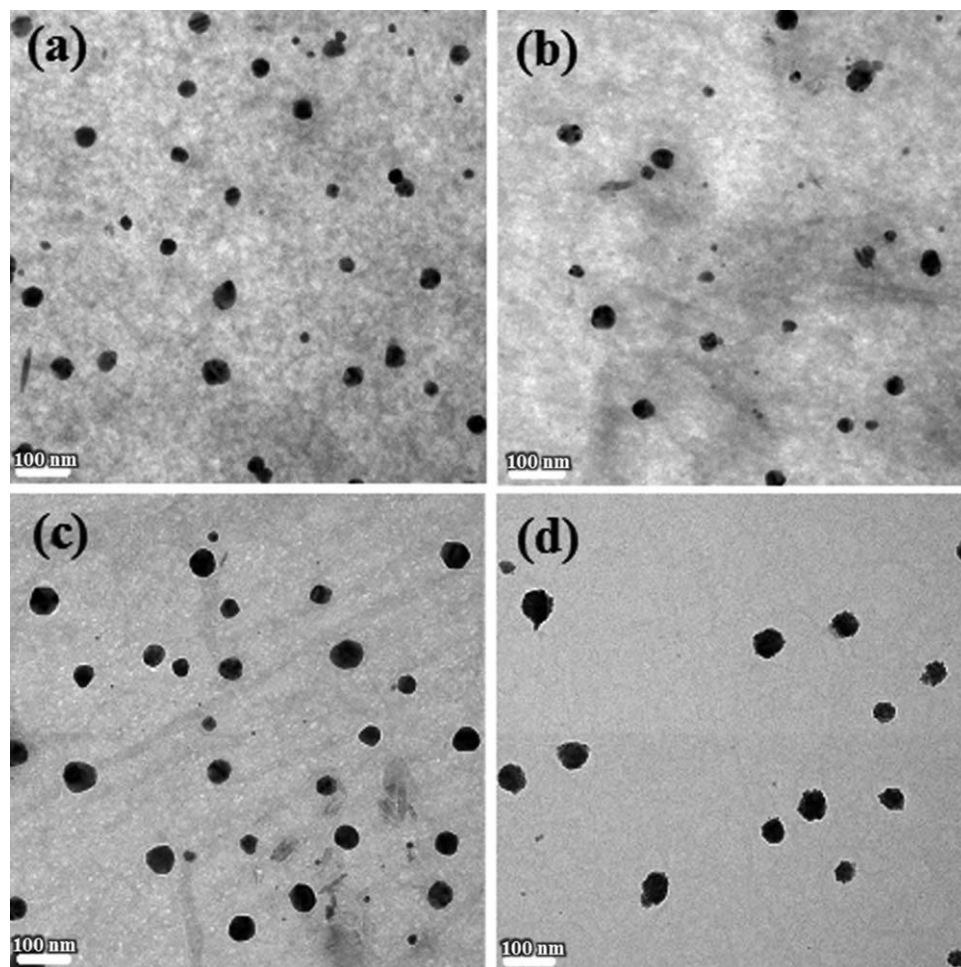


Figure 7. HRTEM images of (a) pristine PEDOT:PSS films; and PEDOT:PSS films dipped in (b) water, (c) DMSO, and (d) 2 vol % of aqueous DMSO solution.

conventional solvent doping are not observed in the dipping method in our study. The possible explanation could be that the doped solvents decline the interchain interaction of the excess PSS and the conductive grains as well as induce the aggregation of PEDOT:PSS grains during mixing before coating on the substrates.⁴² In the dipping process, PEDOT:PSS is deposited on the substrates and subsequently dipped in the prepared solvents. It is informed that the phase separation and conformation of PEDOT chains occur when the films have already been formed but the conductive grains cannot be re-dispersed and diffused freely, yielding the unaltered conductive grain size.⁴³

Figure 7 demonstrates the HRTEM images of the PEDOT:PSS films dipped in various solvents, compared to that of the pristine PEDOT:PSS films. All samples demonstrate highly uniform dispersion of PEDOT-rich grains (black dots) whose mean particle size is ~ 43.5 nm in the PEDOT:PSS films. In case of dipping, the less segregation of PEDOT-rich grains on the as-prepared films is observed which could be due to the immobility of the PEDOT chains when compared with PEDOT-rich grains in the PEDOT:PSS aqueous solution directly mixed with DMSO solvent.

UV-Vis Spectroscopy

Figure 8 illustrates the UV-Vis spectra of pristine PEDOT:PSS and PEDOT:PSS films dipped in various solvents. The

maximum light transmittance at wavelength of 399 nm of pristine PEDOT:PSS is approximate 74.7% and it increases to 77.6, 75.6, and 75.4% for the PEDOT:PSS films dipped in water,

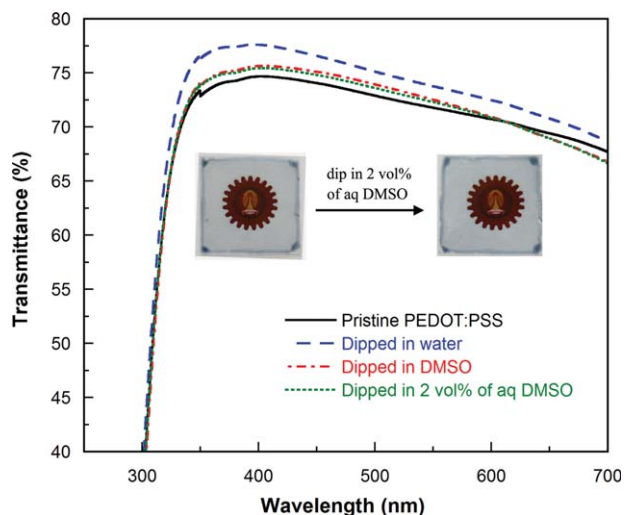


Figure 8. Transmittance as a function of wavelength of pristine PEDOT:PSS and dipped PEDOT:PSS films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMSO and 2 vol % of aqueous DMSO, respectively. Further, the percent transmittance relatively depends on the thickness of the films. Namely, the structure of PEDOT:PSS is a pancake-like particle surrounded by a PSS shell and the unassociated PSS phase presents on the top layer. Upon dipping, the unassociated PSS top layer was washed away, yielding the thinner films showing higher light transmittance.

CONCLUSIONS

In summary, the effect of a low concentration aqueous DMSO solution on the electrical conductivity, surface chemistry, and surface morphology of treated PEDOT:PSS films via dipping technique has been investigated. The conductivity monotonically increases with increasing DMSO concentration and reaches a constant value of 350 S cm^{-1} (more than 1000 times compared with that of pristine PEDOT:PSS) at 2 vol % of aqueous DMSO, which is close to that of films dipped in pure DMSO. The Raman spectra show that the conductivity enhancement is attributed to the conformational change from a coil structure to a linear or expanded-coil structure, yielding the higher charge mobility on the PEDOT chains. Moreover, the XPS S2p core-level spectra indicate that the washing effect of the unassociated PSS-rich layer is more pronounced for treatment with solvents composed of water, while pure DMSO barely removes total PSS layer leading to the aggregation of the PSS phase in the form of white patches. Furthermore, dipping the films in aqueous DMSO results in good film forming without any defects like crinkles in those dipped in water and white patches in those dipped in pure DMSO. It is pointed out by UV-Vis spectra that the transparency of dipped PEDOT:PSS films increases owing to the decreased film thickness as a result of the washing effect. Finally, it is worth noting that aqueous DMSO is the appropriate solvent for the dipping method in this study because only a small amount of high boiling point DMSO is involved, which is beneficial for removal upon heating.

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