

Significant Conductivity Enhancement of Conductive Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) Films through a Treatment with Organic Carboxylic Acids and Inorganic Acids

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ABSTRACT Significant conductivity enhancement was observed on transparent and conductive poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) films after a treatment with organic and inorganic acids, including acetic acid, propionic acid, butyric acid, oxalic acid, sulfurous acid, and hydrochloric acid. The conductivity could be enhanced from 0.2 to over 200 S cm⁻¹, that is, by a factor of more than 1000. The conductivity enhancement was dependent on the structure of the acids and the experimental conditions during the treatment, such as the acid concentration and the temperature. The optimal temperature was in the range of 120 to 160 °C. The resistance dropped rapidly when a PEDOT:PSS film was treated with acid solution of high concentration, whereas it gradually increased and then decreased when it was treated with an acid solution of low concentration. The mechanism for this conductivity enhancement was studied by various chemical and physical characterizations. The temperature dependence of conductivity indicates that the energy barrier for charge hopping among the PEDOT chains become lower in the highly conductive PEDOT:PSS film after the acid treatment. The ultraviolet–visible–near-infrared (UV–vis–NIR) absorption spectroscopy, the X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) indicate the loss of polystyrene sulfonic acid (PSSH) chains from the PEDOT:PSS film after the acid treatment, and the atomic force microscopy (AFM) suggest conformational change of the polymer chains. Therefore, the conductivity enhancement is attributed to the loss of PSSH chains from the PEDOT:PSS film and the conformational change of the PEDOT chains, which are induced by the acids.

KEYWORDS: PEDOT:PSS • conducting polymer • conductivity • transparent • organic acid • inorganic acid

1. INTRODUCTION

Conducting polymers have been attracting strong attention since the discovery of conducting polyacetylene in the 1970s (1–3). They have important potential application in many areas, such as in electronic devices, supercapacitors, secondary batteries, to name a few. However, the application of early conducting polymers, such as polypyrrole and polythiophene, is severely affected by their poor processability, because they are intractable and insoluble in water and organic solvents when in the conductive state. Soluble conductive polyanilines were discovered more than ten years after the discovery of the conductive polyacetylene (4). Polyanilines doped with bulky anions can be dispersed in some organic solvents like *m*-cresol. A couple of years later, it was discovered that poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) with excess poly(styrene sulfonate acid) PSSH could be dispersed in water with good stability (5–7). The discovery of the water-dispersible PEDOT:PSS strongly facilitates the application of the conducting polymers. A conductive PEDOT:PSS

film could be prepared by a conventional solution processing of the PEDOT:PSS aqueous solution. In addition, the PEDOT:PSS film has high transparency in the visible range, high mechanical flexibility, and excellent thermal stability. Hence, PEDOT:PSS may be the most successful conducting polymer in terms of the commercial application. They can be used as the conductive wires in the electric circuits, or electrode of electronic devices. More importantly, they can be potentially used as the transparent electrode of optoelectronic devices. This renders PEDOT:PSS a good candidate to replace indium tin oxide (ITO) as the transparent electrode in optoelectronic devices. ITO has a problem mainly due to the limited source of indium on earth (8). However, currently as-prepared PEDOT:PSS films from the PEDOT:PSS aqueous solution like Baytron P solution are principally used as the buffer layer in optoelectronic devices due to the low conductivity of the as-prepared PEDOT:PSS films (9). The as-prepared PEDOT:PSS film prepared from the PEDOT:PSS aqueous solution usually has a conductivity below 1 S cm⁻¹, remarkably lower than ITO.

It is possible to enhance the conductivity of PEDOT:PSS to be comparable to that of ITO, since high conductivity has been observed on PEDOT doped with some small anions (10). Much effort has been made to enhance the conductivity

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of PEDOT:PSS. The early efforts focused on the change of the solvent for PEDOT:PSS. It was discovered that its conductivity could be enhanced by a factor of a few hundreds, from 1×10^{-1} to about 200 S cm^{-1} , through a treatment with a polar organic compound, such as ethylene glycol, glycerol, D-sorbitol, or dimethyl sulfoxide (DMSO) (11–17). Applications for these highly conductive PEDOT:PSS films as the transparent electrode of optoelectronic devices and counter electrode of dye-sensitized solar cells were demonstrated (18–25). Döbbelin et al. observed similar conductivity enhancement of PEDOT:PSS by adding ionic liquids into the PEDOT:PSS aqueous solution (26). Recently, we reported two approaches to significantly enhance the conductivity of PEDOT:PSS. One is to add anionic surfactants into the PEDOT:PSS aqueous solution (27). This approach can enhance the conductivity of PEDOT:PSS from 0.2 S cm^{-1} to about 80 S cm^{-1} . Another approach is to treat the PEDOT:PSS film with solution of some salts (28). The salt treatment can enhance the conductivity of PEDOT:PSS to about 140 S cm^{-1} .

In this manuscript, we report a new method to significantly enhance the conductivity of PEDOT:PSS. We found that the conductivity of the PEDOT:PSS film could be enhanced from 0.2 to over 200 S cm^{-1} , that is, by a factor of more than 1000, after a treatment with an organic or inorganic acid, such as acetic acid, propionic acid, butyric acid, oxalic acid, sulfurous acid, or hydrochloric acid. This is the first time to observe the conductivity enhancement on a conducting polymer through a treatment with weak acids. This method is different from the addition of hydrochloric acid into the PEDOT:PSS aqueous solution as reported by Aleshin et al. (29). The highest conductivity by their method is around 20 S cm^{-1} .

2. EXPERIMENTAL SECTION

Treatment of PEDOT:PSS Films. PEDOT:PSS aqueous solution (Baytron P, renamed as Clevis P, Item No. 1802705, Lot No. HCE07P107) was purchased from H.C. Starck. The polymer concentration was 1.3% by weight, and the weight ratio of PEDOT to PSS is 2.5. Other chemicals were purchased from Sigma-Aldrich. These materials were used without further purification. The PEDOT:PSS films were prepared by spin-coating the PEDOT:PSS aqueous solution on precleaned glass substrates of $1.3 \times 1.3 \text{ cm}^2$. The precleaning of the glass substrates was performed by rinsing with detergent, deionized (DI) water, acetone, and ethanol in sequence. The PEDOT:PSS films were dried at $110 \text{ }^\circ\text{C}$ on a hot plate for 30 min. The film thickness was ca. 130 nm. The PEDOT:PSS films were treated by solution of various acids, including acetic acid, propionic acid, butyric acid, oxalic acid, sulfurous acid, and hydrochloric acid. The treatment with an acid was performed by dropping $100 \mu\text{L}$ of acid solution on a PEDOT:PSS film on a hot plate at $140 \text{ }^\circ\text{C}$. The PEDOT:PSS films were dried after about 10 min. They were cooled down to room temperature, and then were rinsed with deionized water for three times. Finally, the polymer films were dried at $140 \text{ }^\circ\text{C}$ for about 10 min again. The preparation and acid treatment of the PEDOT:PSS films were carried out in air.

Characterization of PEDOT:PSS Films. The conductivities of the dried PEDOT:PSS films before and after treatment were measured by the van der Pauw four-point probe technique with a Keithley 2400 source/meter. The electrical contacts were

made by pressing indium or putting silver paste on the four corners of each PEDOT:PSS film on glass substrate. For the transient resistances of the PEDOT:PSS films during the acid treatment, indium was pressed at the four corners of as-prepared PEDOT:PSS films, and a small amount of acid was dropped at the center of each sample. The acid was not in contact with indium. The transient resistances were recorded with a program-controlled Keithley 2400 source/meter with the step of 0.1 s. The temperature dependences of the resistivities of the PEDOT:PSS films were measured using a Janis Research VPF-475 dewar with liquid nitrogen as coolant and a Conductus LTC-11 temperature controller. The ultraviolet–visible–near-infrared (UV–vis–NIR) absorption spectra of the polymer films were taken with a Varian Cary 5000 UV–vis–NIR spectrometer. The samples for FTIR were prepared by dispersing polymers in KBr pellets, and the FTIR spectra were acquired with a Varian 3100 FT-IR spectrometer. The X-ray photoelectron spectra (XPS) were taken with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al K α X-ray source (1486.6 eV). The atomic force microscopic (AFM) images of the polymer films were acquired using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode, and the scanning electron microscopic (SEM) images were taken using Hitachi S-4100 scanning electron microscope. The thicknesses of the films were determined with an Alpha 500 step profiler.

3. RESULTS AND DISCUSSION

Conductivity Enhancement of PEDOT:PSS by Acid Treatment. The acid treatment of a PEDOT:PSS film was carried out by dropping an aqueous acid solution on the PEDOT:PSS film at $140 \text{ }^\circ\text{C}$ on a hot plate. Both organic acids, including acetic acid (CH_3COOH), propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$), butyric acid ($\text{CH}_3(\text{CH}_2)_2\text{COOH}$), and oxalic acid (HOCCOOH), and inorganic acids, including hydrochloric acid (HCl) and sulfurous acid (H_2SO_3), were used to treat the PEDOT:PSS films. Among them oxalic acid and sulfurous acid are biacid (biacid: an acid with two replaceable hydrogen atoms), whereas the rest are monoacid (monoacid: an acid with one replaceable hydrogen atom). The conductivities were measured on the dried PEDOT:PSS films with or without acid treatment. They were the same when indium or silver paste was used for the contact. In addition, there was no remarkable difference in the conductivity for the measurement in air or in vacuum. Both the organic and inorganic acids could significantly enhance the conductivity of the PEDOT:PSS films (Figure 1). The conductivity enhancement depended on the structure and concentration of the acids. The conductivity exhibited an “n” shape dependence on the acid concentration when the PEDOT:PSS films were treated with the organic monoacids. It was 0.2 S cm^{-1} for an as-prepared PEDOT:PSS film, and increased to 2 and 10 S cm^{-1} after the treatment with 0.1 and 1 M acetic acid, respectively. The maximum conductivity reached 190 S cm^{-1} when the concentration of acetic acid increased to 14 M. The conductivity then dropped with the further increase in acetic acid concentration. It was only 1.8 S cm^{-1} for a PEDOT:PSS film treated with 16 M acetic acid, which was pure acetic acid without the addition of water. Similar “n” dependence of the conductivity on the acid concentration was observed when a PEDOT:PSS film was treated with propionic acid or butyric acid. The maximum conductivities were 197 and 138 S cm^{-1} after the PEDOT:PSS films were

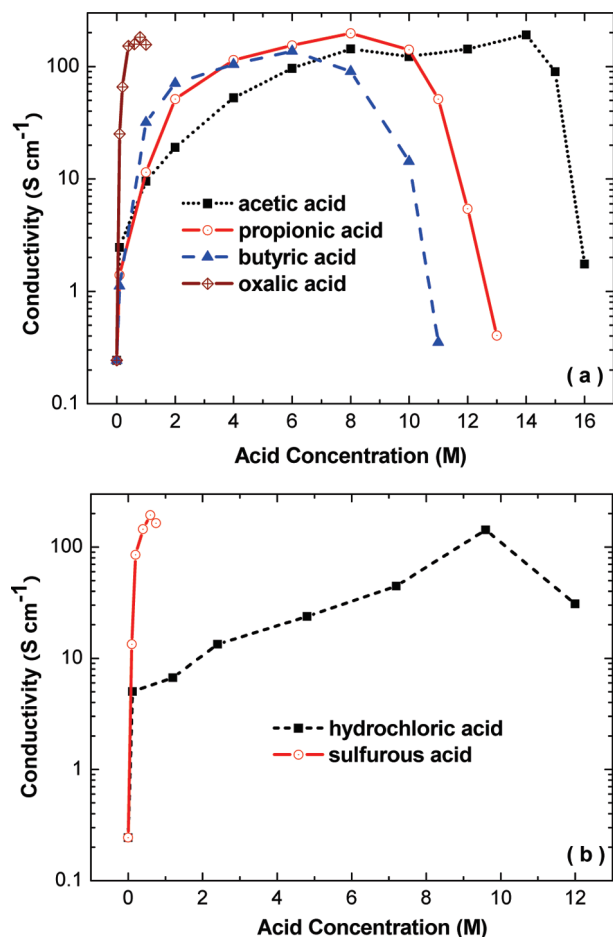


FIGURE 1. Conductivities of PEDOT:PSS films after treating with solutions of (a) organic and (b) inorganic acids of various concentrations. The organic acids are acetic acid, propionic acid, butyric acid, and oxalic acid, and the inorganic acids are sulfurous acid and hydrochloric acid.

treated with 8 M propionic acid and 6 M butyric acid, respectively. No salient conductivity enhancement was observed when a PEDOT:PSS film was treated with pure propionic acid (13 M) or pure butyric acid (11 M). Oxalic acid was a solid at room temperature, and its solutions with concentration below 1 M were used to treat PEDOT:PSS films. The maximum conductivity was 182 S cm^{-1} for the PEDOT:PSS film treated with 0.8 M oxalic acid.

The organic acids used in the treatment are carboxylic acids, and they are weak acids as indicated by their pK_a values (Table 1). Weak acids are usually not used for the conductivity enhancement of conducting polymers, since many conducting polymers exhibit conductivity decreases after treating with solution of high pH value (30–34). To the best of our knowledge, this is the first time to observe significant conductivity enhancement by treating a conducting polymer with weak organic acids.

The PEDOT:PSS films were also treated with inorganic acids, and significant conductivity enhancement was observed as well (Figure 1b). The maximum conductivities were 142 and 193 S cm^{-1} for the PEDOT:PSS films after treating with 9.6 M hydrochloric acid and 0.6 M sulphurous acid, respectively. It is worth pointing out that our approach to treating the PEDOT:PSS film with acid solution is different

from that adding acid into the PEDOT:PSS aqueous solution as reported by Aleshin et al. (29). They reported that the highest conductivity was 20 S cm^{-1} by adjusting the pH value of the PEDOT:PSS aqueous solution to 1 with HCl.

Effect of Temperature during Treatment on Conductivity Enhancement. Besides the structure and concentration of the acids, the temperature during the acid treatment also affected the conductivity. Figure 2a shows the conductivities of the PEDOT:PSS films after treating with the organic acids with the optimal concentration. The conductivity of the PEDOT:PSS films was about 140 S cm^{-1} after the treatment with 14 M acetic acid at 80°C . It increased with the increase of the temperature during the treatment and reached the maximum value of 210 S cm^{-1} after treating at 160°C . This maximum conductivity is higher than the conductivity of the as-prepared PEDOT:PSS film by a factor of more than 1000. The conductivity then decreased with the further increase in temperature during the acid treatment. The optimal temperature corresponding to the maximum conductivity enhancement shows some variation with the organic acids, but it is in the range of $120\text{--}160^\circ\text{C}$ for the treatment with these organic acids.

The temperature during the acid treatment also affected the conductivity of the PEDOT:PSS films treated with inorganic acids, and the optimal temperature corresponding to the maximum conductivity was in the temperature range of $120\text{--}160^\circ\text{C}$ as well. As shown in Table 1, the six acids used in this study have different boiling points. It indicates that the optimal treating temperature is not determined by the boiling point of the acid. For example, the optimal temperature is around 160°C for the treatment with acetic acid whose boiling point is 118°C , whereas it is around 120°C for the treatment with propionic acid whose boiling point is 141°C . It is interesting to find that the optimal temperature for the acid treatment of PEDOT:PSS coincides with that by a treatment with salts (28). Hence, the effect of the temperature during the acid treatment on the conductivity of the PEDOT:PSS film may be related to the thermal properties of the PEDOT:PSS film.

Transient Resistances during Acid Treatment of PEDOT:PSS. The resistances of the PEDOT:PSS films were monitored by the four-point van der Pauw technique during the acid treatment (Figure 3). The configuration for the resistance measured is schematically shown in the inset of Figure 3a. Indium (In) was pressed at the four corners of the PEDOT:PSS film to facilitate the electrical contact. A small amount of acid was dropped at the center of each sample, and the acid did not contact indium during the measurement. Because the acid treatment was performed after the press of the indium at the four corners, the areas of the PEDOT:PSS film under indium were not treated by the acids, that is, the parts of the PEDOT:PSS film under indium kept the high resistance during the acid treatment. This is why the resistance decrease shown in Figure 3 is less than in Figure 1. Thus, the absolute transient resistances were not very meaningful but their change during the acid treatment provided important information for the under-

Table 1. pK_a and Physical Parameters of Acids Used in This Study

acid	pK_a^a	melting point ($^{\circ}C$)	boiling point ($^{\circ}C$)
hydrochloric acid HCl	-8.0	-27.3 (38% solution)	110 $^{\circ}C$ (20% solution)
sulfurous acid H_2SO_3	$pK_{a1} = 1.9, pK_{a2} = 7.0$	Release SO_2 when heated	
oxalic acid $HOOC-COOH$	$pK_{a1} = 1.23, pK_{a2} = 4.28$	182–190	150 (sublimation)
acetic acid CH_3COOH	4.75	16.6	118
propionic acid CH_3CH_2COOH	4.87	-22	141
butyric acid $CH_3CH_2CH_2COOH$	4.82	-7.9	164

^a $pK_a = -\log K_a$, where K_a is the acid dissociation constant.

standing of the acid treatment. To make sure that the resistance change during the acid treatment is not due to any possible interaction between acid and indium, gold (Au) was evaporated to replace indium at the four corners of the samples for the transient resistance study. The change in the resistances with time was quite similar to the samples with indium.

Figure 3a presents the transient resistances of the PEDOT:PSS films during the treatment with acetic acid solutions of different concentrations, 0.8 M and 14 M. The transient resistance exhibited dependence on the acid concentration. The resistance immediately decreased when the

PEDOT:PSS film was treated with 14 M acetic acid, whereas it increased and then gradually decreased with 0.8 M acetic acid. These results suggest that there may be two processes during the acid treatment. One is the conductivity enhancement due to the acid, another is the conductivity decrease as the result of polymer swelling in water. Water can penetrate into PEDOT:PSS, which gives rise to the decrease of the interchain interaction among the PEDOT:PSS chains and the increase of the resistance (Figure 3b). The conductivity enhancement due to the acid was dominant when acetic acid of high concentration was used, whereas the polymer swelling affected the resistance before the drying of water when the PEDOT:PSS film was treated with acetic acid of low concentration. Similar transient resistance was

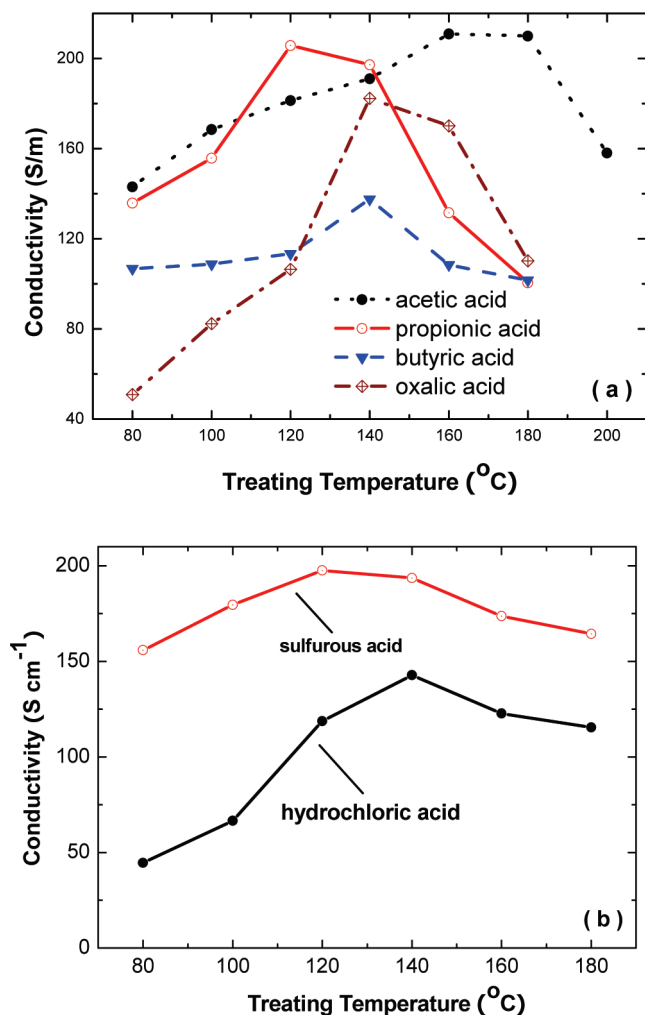


FIGURE 2. Dependence of the conductivities of PEDOT:PSS films on the temperature during the treatment with (a) organic acids and (b) inorganic acids.

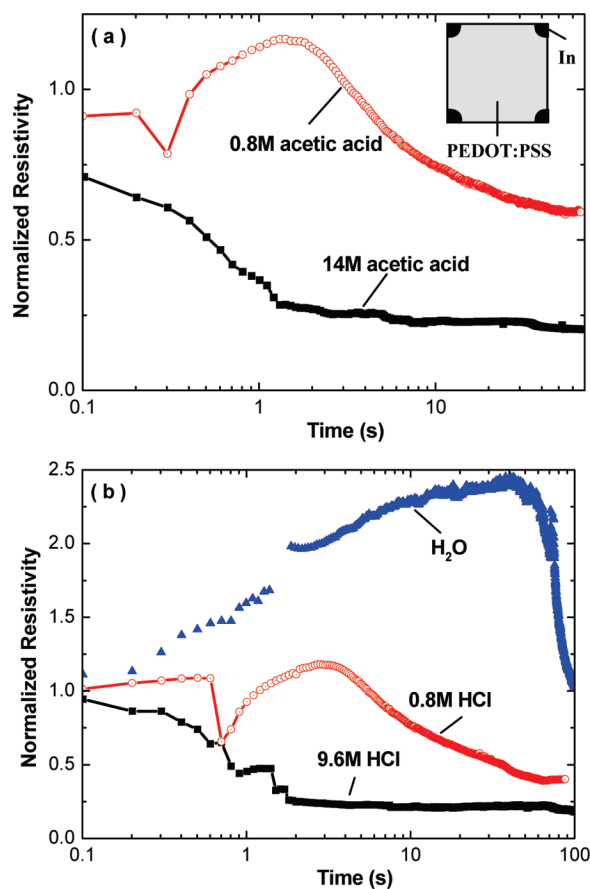


FIGURE 3. Transient resistances of PEDOT:PSS films during the treatment with (a) acetic acid and (b) hydrochloric acid of different concentrations. The transient resistances of PEDOT:PSS during water treatment is also shown in (b). The resistances were normalized to the resistance of the as-prepared PEDOT:PSS film. The inset in a shows the configuration for the resistance measurements.

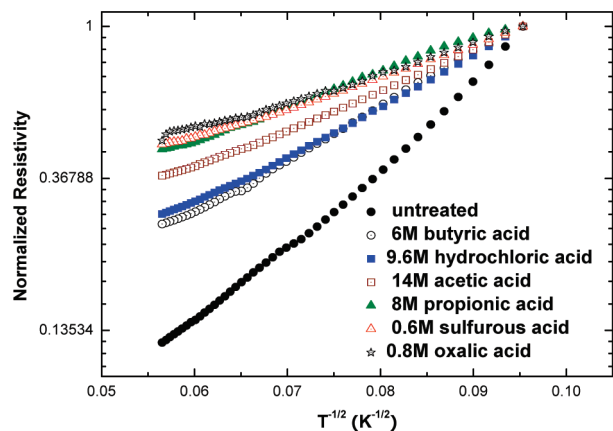


FIGURE 4. Temperature dependence of the normalized resistivities of untreated and acid-treated PEDOT:PSS films. The resistivities were normalized to the resistivity of the corresponding PEDOT:PSS film at 110 K. The acids for the treatment are indicated.

observed when the PEDOT:PSS film was treated with other organic acids.

As mentioned above, these organic acids are weak acid. There is low proton concentration in these acid solutions. To understand the effect of the proton concentration on the transient resistance of the PEDOT:PSS film during the acid treatment, we monitored the transient resistance of the PEDOT:PSS film during the treatment with HCl solutions of different concentrations. The transient resistances were quite similar to that with acetic acid solutions of different concentrations. Rapid resistance decrease was observed when the PEDOT:PSS film was treated with 9.6 M HCl solution, while the transient resistance gradually increased then gradually decreased with 0.8 M HCl solution. The proton concentration in 0.8 M HCl solution should be higher than in 14 M acetic acid solution. Therefore, the proton concentration is not directly related to the transient resistance during the acid treatment.

Temperature Dependence of Resistivities. The conductivity enhancement suggests the change in the conduction mechanism of the PEDOT:PSS films after the acid treatment. The resistivities of the untreated and acid-treated PEDOT:PSS films were investigated from room temperature down to 110 K to understand the effect of the acid treatment on the conduction mechanism (Figure 4). The resistances of the untreated and acid-treated PEDOT:PSS films increased with lowering temperature. The resistivity-temperature relationships can be fitted by the one-dimensional variable range-hopping (VRH) mechanism (35, 36)

$$R(T) = R_0 \exp \left[\left(\frac{T_0}{T} \right)^{1/2} \right]$$

where $T_0 = 16/k_B N(E_F) L_{||} L_{\perp}^2$ is the energy barrier between localized states with $N(E_F)$ being the density of the states at the Fermi level and $L_{||}$ (L_{\perp}) being the localization length in the parallel (perpendicular) direction. The T_0 values obtained by fitting the temperature dependences of the resistances of the PEDOT:PSS films are 2660, 1211, 1011, 639, and 405

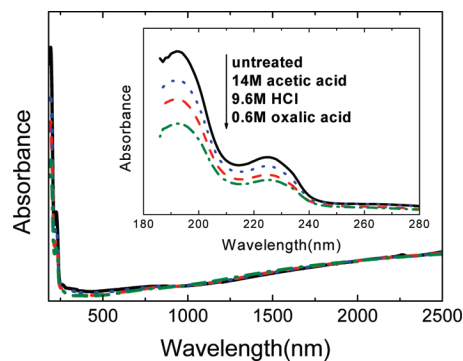


FIGURE 5. UV-vis-NIR absorbance spectra of PEDOT:PSS films before and after the treatment with 14 M acetic acid, 9.6 M hydrochloric acid, and 0.6 M oxalic acid.

K for the untreated, propionic acid-, HCl-, acetic acid-, and sulfurous acid-treated PEDOT:PSS films, respectively. These T_0 values are consistent with the conductivities of these PEDOT:PSS films at room temperature, which are 0.2, 138, 143, 191, and 194 $S \text{ cm}^{-1}$ for the untreated, propionic acid-, HCl-, acetic acid-, and sulfurous acid-treated PEDOT:PSS films, respectively. These suggest that the acid treatment can lower the energy barrier and increase the localization length of the charges.

Spectroscopies of PEDOT:PSS Films. The PEDOT:PSS films treated with acids were studied through various chemical and physical characterizations. The UV-vis-NIR absorption spectra of a PEDOT:PSS film before and after the treatment are shown in Figure 5. The absorbance at the wavelength above 500 nm almost did not change, whereas a decrease in the absorbance in the UV range could be observed after the acid treatment. The PEDOT:PSS films treated by other acids showed a similar change in the absorption. The transparency of the PEDOT:PSS film did not change after the acid treatment, though its conductivity increases significantly.

The two absorption bands in the UV range from 180 to 260 nm originate from PSS in PEDOT:PSS (12). The decrease in the absorption of these bands suggests that some PSS chains leave the PEDOT:PSS film after the acid treatment. On the other hand, no remarkable change was observed in the whole wavelength range from 180 to 2500 cm^{-1} when the PEDOT:PSS films were treated with pure propionic acid (13 M) or pure butyric acid (11 M). As discussed above, these pure organic acids did not remarkably affect the conductivity of the PEDOT:PSS film. Thus, the conductivity enhancement is related to the PSS loss after the acid treatment.

The PEDOT:PSS before and after treatment with various acids were studied by the FTIR spectroscopy as well (Figure 6). No significant difference was observed on the FTIR spectra for the PEDOT:PSS films after the acid treatment. The organic acids have a strong absorption band at about 1708 cm^{-1} characteristic of the stretching of the carbonyl group C=O (37, 38). The absence of such a band in the FTIR spectra of the PEDOT:PSS films treated with organic acids suggest that no organic acid remains in the PEDOT:PSS films after the treatment. There may be no HCl and sulfurous acid in PEDOT:PSS as well, because they vaporize or decompose

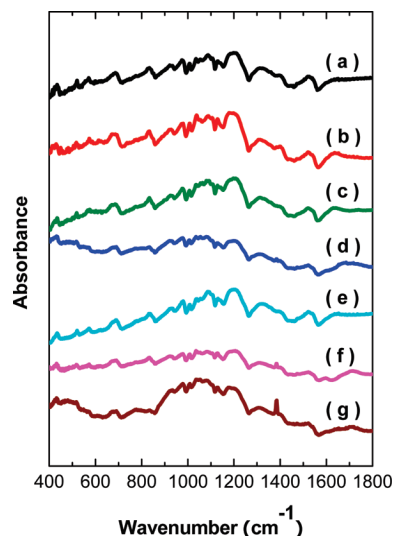


FIGURE 6. FTIR spectra of (a) untreated PEDOT:PSS and PEDOT:PSS treated with aqueous solution of (b) 9.6 M HCl, (c) 0.6 M sulfurous acid, (d) 0.8 M oxalic acid, (e) 14 M acetic acid, (f) 8 M propionic acid, and (g) 6 M butyric acid.

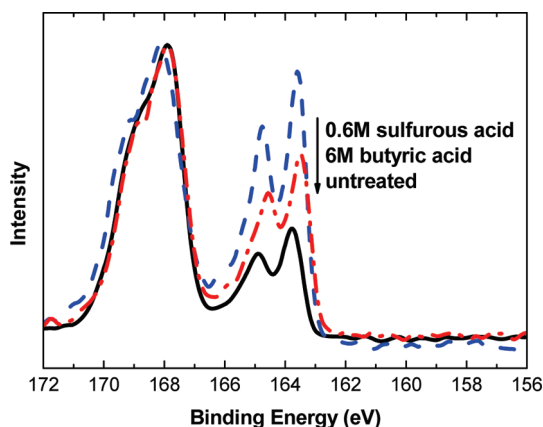


FIGURE 7. S_{2p} XPS of PEDOT:PSS films untreated and treated with 0.6 M sulfurous acid and 6 M butyric acid.

after the vaporization of water during heating. In fact, no Cl signal was detected when the HCl-treated PEDOT:PSS film was studied by XPS.

The loss of PSS from the PEDOT:PSS film after the acid treatment is further confirmed by the XPS of the PEDOT:PSS films (Figure 7). The two XPS bands with binding energy between 166 and 172 eV originate from the sulfur atoms in PSS, whereas the two XPS bands with binding energy between 162 and 166 eV are due to the sulfur atoms in PEDOT (39, 40). The S_{2p} XPS band of PEDOT relative to that of PSS increased for the PEDOT:PSS films after the acid treatment. This also suggests the loss of PSS from the PEDOT:PSS films after the acid treatment.

Morphology of PEDOT:PSS Films. The morphology of the PEDOT:PSS films was studied by AFM before and after acid treatment. Figure 8 shows the AFM images of an untreated PEDOT:PSS film and highly conductive PEDOT:PSS films treated with various acids. The as-prepared PEDOT:PSS film was very smooth, and it became rough after it became highly conductive after the acid treatment. The roughness was 1.06 nm for the as-prepared PEDOT:PSS film,

and it increased to 3.70, 1.91, and 2.71 nm, after treating with HCl, oxalic acid, and propionic acid, respectively. Small domains appeared for the PEDOT:PSS film treated with 9.6 M HCl solution, and entangled wires with diameters in tens of nanometers could be observed on the PEDOT:PSS films after treating with 0.6 M sulfurous acid, 0.8 M oxalic acid, 14 M acetic acid or 8 M propionic acid. The AFM image of the PEDOT:PSS film treated with 6 M butyric acid was quite similar to that treated with 8 M propionic acid. The change in the AFM image of the PEDOT:PSS film after the acid treatment suggests that conformational change of the polymer chains.

The morphology of the PEDOT:PSS films after treating with pure propionic acid and pure butyric acid were also studied by AFM (Figure 9). These films were quite smooth and similar to the AFM image of the as-prepared PEDOT:PSS film. These AFM images are consistent with the conductivity of the PEDOT:PSS films after the acid treatment.

Mechanism for Conductivity Enhancement. The experimental results indicate at least two reasons for the conductivity enhancement of the PEDOT:PSS film by the acid treatment. One is the loss of the PSS chains from the PEDOT:PSS film, and another is the conformational change of the polymer chains. The leave of the PSS chains from the PEDOT:PSS film could be clearly observed on the PEDOT:PSS film after drying of the acid solution. Figure 10 shows the SEM images of PEDOT:PSS films treated with 8 M propionic acid and 6 M butyric acid, respectively. The particles with submicrometer size appeared on the PEDOT:PSS films after the drying of the acids, and they can be washed away with water. Presumably, these particles are made of PSSH. It is interesting to point out that such particles could not be observed on the PEDOT:PSS films when they were treated with pure organic acids. This is consistent with the observation on the UV–vis–NIR absorption and XPS of the PEDOT:PSS films after acid treatment. Hence, the leave of the PSSH chains from the PEDOT:PSS film must be related to the dissociation of the acids in water. There is almost no dissociation for pure propionic acid or pure butyric acid, so that they can not give rise to the loss of the PSSH chains from the PEDOT:PSS films and negligible change in the conductivity of the PEDOT:PSS film. This was further confirmed by the fact that a PEDOT:PSS film treated with acetone solution of 14 M acetic acid, 8 M propionic acid, or 6 M butyric acid did not exhibit a conductivity increase. This is also because that these acids almost do not dissociate in acetone.

However, the conductivity enhancement of PEDOT:PSS by acid treatment may not be determined by the proton concentration in solution. The proton concentrations of the six acids with different concentrations were determined by a pH meter at room temperature as shown in Figure 11. The conductivity enhancement of the PEDOT:PSS film after acid treatment is not consistent with the proton concentration of the acid solutions. The proton concentration of 1.2 M HCl aqueous solution is higher than all other acid solutions at all the concentrations, whereas the conductivity of the PEDOT:PSS film treated with 1.2 M HCl aqueous solution is just

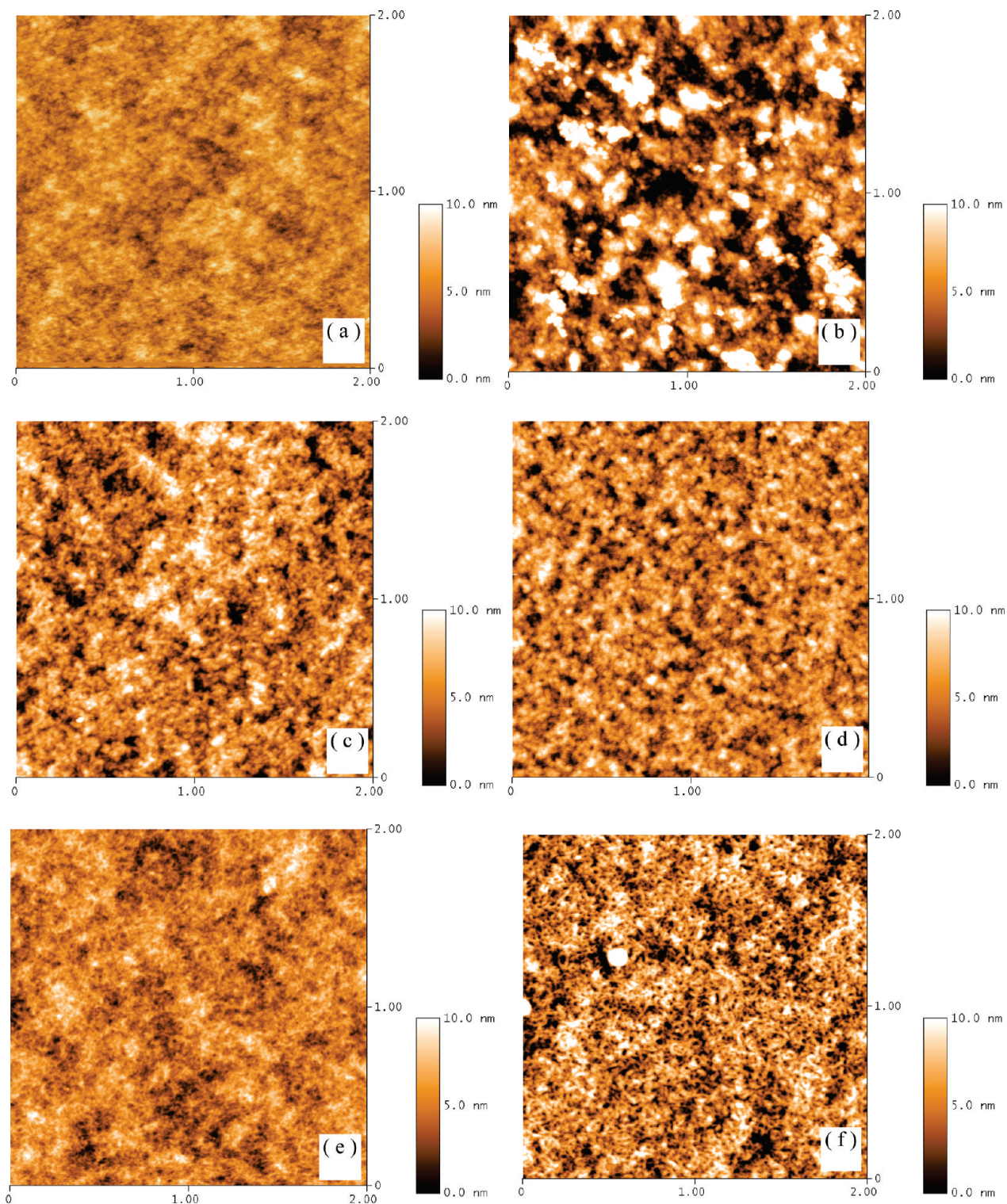


FIGURE 8. AFM images of PEDOT:PSS films (a) untreated and treated with (b) 9.6 M HCl, (c) 0.6 M sulfurous acid, (d) 0.8 M oxalic acid, (e) 14 M acetic acid, and (f) 8 M propionic acid. The unit for the AFM images is micrometers.

about 6.7 S cm^{-1} . The transient resistance of the PEDOT:PSS film during the acid treatment also suggests that proton concentration may not be the only reason for the conductivity enhancement, because the resistance change of the PEDOT:PSS film when treated with 0.8 M HCl solution is similar to that with 0.8 M acetic acid, though the two solutions have quite different proton concentrations. These results indicated that the conductivity enhancement could

not be attributed to protonation of the PEDOT chains. This is further confirmed by the observations that there was no conductivity enhancement when a PEDOT:PSS film was treated with a polymer acid, such as PSSH or poly(carboxylic acid).

On the basis of the experimental results and the above discussion, we propose the following mechanism for the conductivity enhancement of PEDOT:PSS film by the acid

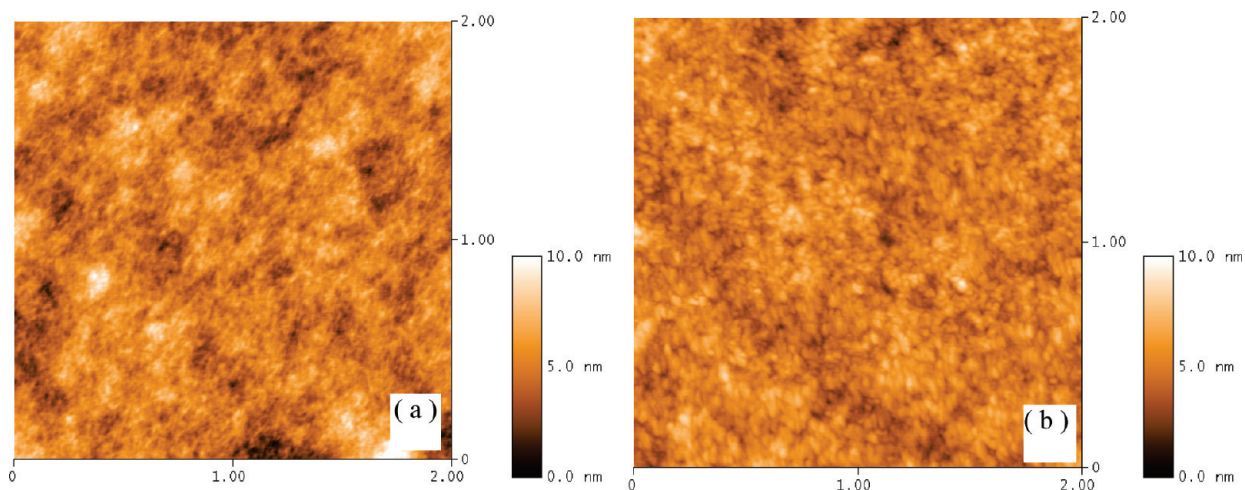


FIGURE 9. AFM images of PEDOT:PSS films treated with (a) 13 M propionic acid and (b) 11 M butyric acid. The unit for the AFM images is μm .

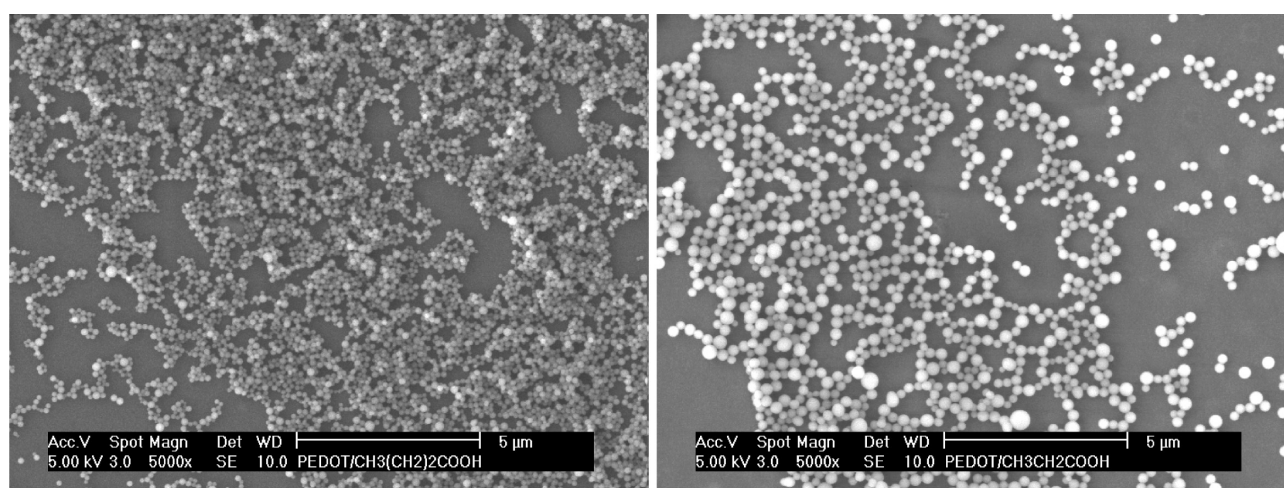


FIGURE 10. SEM images of PEDOT:PSS films treated with (a) 8 M propionic acid and (b) 6 M butyric acid.

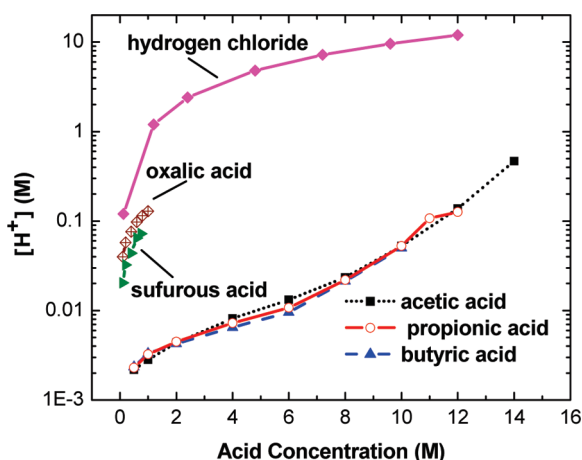
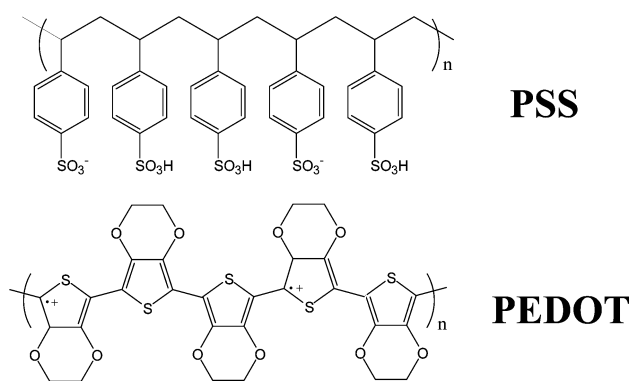


FIGURE 11. Proton concentrations of acids with different concentrations.

treatment. The acids can lower the interaction between PEDOT and PSS, resulting into the PSS loss from the PEDOT:PSS films. In addition, the PSSH loss from the PEDOT:PSS film may be related to the temporary replacement of the PSS anions by the acid anions. When an acid solution is dropped on the PEDOT:PSS film, the acid anions may penetrate into the PEDOT:PSS film and replace some PSS as the counter-

anions. The interaction between the positively charged PEDOT chains and the acid anions is probably stronger than that between PEDOT and PSS. Consequently, the protons of the acid are transferred to PSS, so that PSS becomes PSSH and leaves the PEDOT:PSS film as the result of the disappearance of the Coulombic interaction between PEDOT and PSSH. The presence of the acid anions in the PEDOT:PSS film may be temporary, because no acid anions were observed after the treatment. As indicated in Scheme 1, most of the styrene sulfonate groups of PSS are in the acid structure other than the anion structure, that is, there are lots of protons in PSS of PEDOT:PSS. Some PSS chains still remain in PEDOT:PSS, and some protons of these PSS chains may transfer from the PSS chains to the acid anions. These protons form acids with the acid anions, and the acids vaporize or decompose during heating. Consequently, PEDOT:PSS has fewer PSS chains inside and has no acid anions after the acid treatment. The acid plays a role to help the leave of some PSS chains from the PEDOT:PSS film. It is understandable that the PEDOT chains experience a change in the conformation. This conformational change together with the loss of insulating PSS account for the

Scheme 1. Chemical Structure of PEDOT:PSS



conductivity enhancement of the PEDOT:PSS film after the acid treatment.

This proposed mechanism can interpret the experimental results. The conductivity enhancement of the PEDOT:PSS film through the acid treatment is not due to protonation of the PEDOT chains but the acid-assisted PSS leave. This accounts for the fact that the acetic acid-treated PEDOT:PSS film can have even higher conductivity than the HCl-treated PEDOT:PSS film. The weak acids may be more effective than strong acids in assisting the leave of the PSS chains from the PEDOT:PSS chains, because the anions of the weak acids may have even stronger interaction with the positively charged PEDOT than that of strong acids, similar to the interaction between the anions and proton.

This mechanism can account for the negligible conductivity enhancement for the PEDOT:PSS film treated with acetone solution of organic acids or pure organic acids. The dissociation of the organic acids is difficult when acetone is used as the solvent or they are pure acids, so that the anion concentration in the solution is quite low. The anions with low concentration can not effectively replace some PSS as the counteranions in PEDOT:PSS, so that they can not assist the leave of the PSS chains from the PEDOT:PSS and give rise to negligible change in the conductivity of the PEDOT:PSS film.

The effect of the treatment temperature during the conductivity enhancement can be understood in terms of this proposed mechanism as well. The leave of the PSS chains and the conformational change of the PEDOT chains are related to the thermal properties of PEDOT:PSS. We believe that 140 °C could be higher than the glass-transition temperature of PEDOT:PSS, though no thermal transition was observed on the differential scanning calorimetry (DSC) of PEDOT:PSS. At such a high temperature, the segments of the polymer chains can have rotational and translational motion so that the PSSH chains can move out from the PEDOT:PSS film, and the PEDOT chains can have conformational change. These processes may become more difficult at lower temperature, leading to less-remarkable conductivity enhancement. The lesser conductivity enhancement observed at temperatures higher than 160 °C may be due to degradation of PEDOT:PSS.

4. CONCLUSIONS

The conductivity of the PEDOT:PSS films can be significantly enhanced by a treatment with various acids, including acetic acid, propionic acid, butyric acid, oxalic acid, sulfurous acid, and hydrochloric acid. The conductivity enhancement from 0.2 to over 200 S cm⁻¹, that is, by a factor of more than 1000, was observed. The structure of the acids and the experimental conditions during the treatment, such as the acid concentration and the temperature, affected the conductivity enhancement. The optimal temperature was in the range of 120–160 °C. The conductivity enhancement is attributed to acid-assisted PSSH loss from the PEDOT:PSS film and conformational change of the PEDOT chains. To the best of our knowledge, this is the first time significant conductivity enhancement has been observed by treating a conducting polymer with weak acids.

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