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Salt-Induced Charge Screening and Significant Conductivity Enhancement of Conducting Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)

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ABSTRACT: This article reports a novel method to significantly enhance the conductivity of conducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films through a treatment with aqueous solutions of various salts, such as copper(II) chloride. Conductivity enhancement by a factor of about 700 was observed. Many salts were investigated, and the conductivity enhancement depended on the softness parameter of cations and the concentration of the salts in solution. A salt like copper(II) chloride or indium chloride, whose cation has positive softness parameter, could enhance the conductivity of the PEDOT:PSS film by 2 orders in magnitude, while other salt like sodium chloride or magnesium chloride, whose cation has negative softness parameter, gave rise to negligible effect on the conductivity. The mechanism for the conductivity enhancement was studied by various characterizations. It is attributed to PSS loss from the PEDOT:PSS film, and conformational change of PEDOT chains resulted from the salt-induced charge screening between PEDOT and PSS.

Introduction

Flexible electronic devices, which usually use organic or polymeric materials as the active component, has attracted strong attention due to the low device fabrication cost and the high mechanical flexibility of these materials.[1] Though organic or polymeric materials are quite successful to be used as the active materials of the electronic devices, such as light-emitting diodes, photovoltaic cells, and transistors, the success is limited for them as the electrode of the devices. New flexible materials are urgently needed as the electrode of flexible electronic devices. Materials, including conducting polymers,[2] carbon nanotubes,[3] graphenes,[4] and charge-transfer organic conductors,[5] have potential as the electrode of the electronic devices. Among them, conducting polymers are highly promising. Today, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, chemical structure shown in Scheme 1) become the most successful conducting polymer in terms of the commercial application due to the merit it has.[2b] PEDOT:PSS can be dispersed in water, and its films can be readily prepared through a conventional solution processing. A PEDOT:PSS film has high transparency in the visible range, high mechanical flexibility, and excellent thermal stability. These render PEDOT:PSS an excellent candidate as the electrode, particularly as the transparent electrode to replace indium tin oxide (ITO) in optoelectronic devices. However, the current application of PEDOT:PSS is principally used as the buffer layer in optoelectronic devices.[6] This is related to the low conductivity of the as-prepared PEDOT:PSS films. The as-prepared PEDOT:PSS film obtained from PEDOT:PSS aqueous solution usually has conductivity below 1 S cm^{-1}, remarkably lower than ITO.

It is important to develop PEDOT:PSS films with high conductivity. Several methods were recently reported to enhance the conductivity of the PEDOT:PSS film from 10^{-1} to 10^{2} S cm^{-1}. The first method is to add a high boiling point polar organic compound into the PEDOT:PSS aqueous solution or treat the PEDOT:PSS film with a polar solvent, such as ethylene glycol or dimethyl sulfoxide.[7] The second approach is to introduce an ionic liquid into the PEDOT:PSS aqueous solution.[8] The third way is to add an anionic surfactant into the PEDOT:PSS aqueous solution.[9] These methods can enhance the conductivity of the PEDOT:PSS film to 10^{2} S cm^{-1}, and high-performance electronic devices using the highly conductive PEDOT:PSS as the electrode were demonstrated as well.[10] Here, we report another method to significantly enhance the conductivity of the PEDOT:PSS through a treatment with aqueous solutions of salts. The conductivity can be enhanced by a factor of up to 700 and reaches 10^{2} S cm^{-1}.

Experimental Section

Treatment of PEDOT:PSS Films. PEDOT:PSS (Baytron P, Item No. 1802705, Lot No. HCE07P107) was purchased from H.C. Starck, and 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 1.3 × 1.3 cm^{2} glass substrates. The films were dried at 110 °C on a hot plate for 30 min. The film thickness was ca. 130 nm. The treatment with a salt solution was performed by dropping 150 μL aqueous solution of salt on a PEDOT:PSS film on a hot plate at 140 °C. The film dried after about 5 min. The salt-treated PEDOT:PSS films were cooled to room temperature in air and rinsed with deionized water for three times to wash away the salt then were dried at 140 °C again.

Characterization of PEDOT:PSS Films. The conductivities of the polymer films 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 the PEDOT:PSS film on glass substrate. The UV−vis−NIR absorption spectra of the polymer films were taken with a Varian Cary 5000 UV−vis−NIR spectrometer. The atomic force microscopic (AFM) images of the polymer films were acquired using a Veeco NanoScope IV

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Multi-Mode AFM with the tapping mode. The X-ray photoelectron spectroscopy (XPS) spectra were taken with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al Kα X-ray source (1486.6 eV). The ac impedance spectra were obtained using an SI 1260 impedance analyzer. The samples for FTIR were prepared by dispersing polymers in KBr pellets, and the FTIR spectra were taken with a Varian 3100 FT-IR spectrometer. The thicknesses of the films were measured with an Alpha 500 step profiler.

Results and Discussion

Conductivity Enhancement of PEDOT:PSS Films through $CuCl_2$ Treatment. Aqueous solutions of salts, including $CuCl_2$, $AgNO_3$, $InCl_3$, LiCl, NaCl, $MgCl_2$, and $NiCl_2$, were used to treat the PEDOT:PSS films. At first, the results after the treatment with $CuCl_2$ aqueous solution were presented and discussed as an example to explain the salt effect on the conductivity of the PEDOT:PSS film. The conductivity of an as-prepared PEDOT:PSS film was 0.2 S cm^{-1}, and it significantly increased after a treatment with $CuCl_2$ solution at 140 °C, as shown in Figure 1. The logarithmic conductivity linearly increased with the logarithmic concentration of $CuCl_2$ in solution. The conductivity of the PEDOT:PSS film increased to 26.3 S cm^{-1} after the treatment with 0.074 M $CuCl_2$ solution and reached 139.7 S cm^{-1} after the treatment with 0.74 M $CuCl_2$ solution. This latter conductivity is almost 700 times as high as that of the as-prepared PEDOT:PSS film.

The conductivity enhancement of the PEDOT:PSS films also depended on the temperature during the treatment with the $CuCl_2$ aqueous solution. Figure 2 shows the conductivity of the PEDOT:PSS films with the treating temperature from 80 to 180 °C. At first, the conductivity increased with increasing treating temperature from 80 up to 160 °C. It was 3 S cm^{-1} for the PEDOT:PSS films after the treatment at 80 °C and increased to 47 S cm^{-1} after the treatment at 160 °C. The conductivity then dropped to 40 S cm^{-1} when the temperature was further increased to 180 °C. The conductivity drop may be related to the degradation of PEDOT:PSS at such a high temperature.

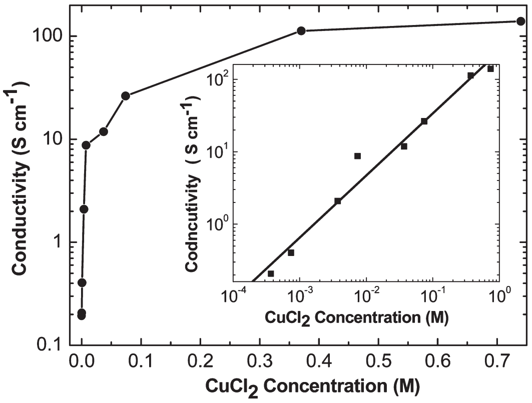
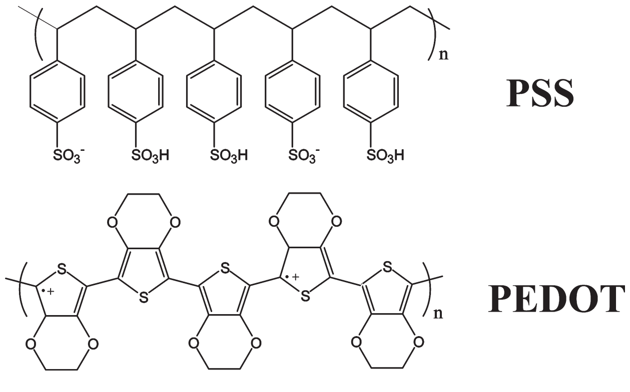


Figure 1. Variation of the conductivity of treated PEDOT:PSS films with $CuCl_2$ concentration. The inset plots the same data with the $CuCl_2$ concentration in logarithmic scale. The straight line in the inset is the linear fitting of the data.

Scheme 1. Chemical Structure of PEDOT:PSS



Characterization of PEDOT:PSS Films. No remarkable change was observed in the appearance of the PEDOT:PSS films to the eye after the treatment with $CuCl_2$ solution, and the PEDOT:PSS films remained highly transparent. The UV−vis−NIR absorption spectra of a PEDOT:PSS film before and after the treatment with 0.074 M $CuCl_2$ at 140 °C are shown in Figure 3. The absorption in the low-energy region below 2.5 eV, which is related to the collective electron oscillation on PEDOT, almost does not change after the treatment, while the intensity of the two absorption bands between 5 and 7 eV decreases. The latter two bands at the high-energy range correspond to the $\pi-\pi^*$ transitions of the benzene rings of PSS.[7b] The decreasing absorption indicates the decrease of PSS in PEDOT:PSS after the $CuCl_2$ solution treatment.

This change in the composition of the PEDOT:PSS film after the treatment was confirmed by XPS (Figure 4). The bands with binding energy higher than 166.6 eV are the S_{2p} bands of the sulfur atoms in PSS, and the two bands with low binding energy are the S_{2p} bands of the sulfur atoms in

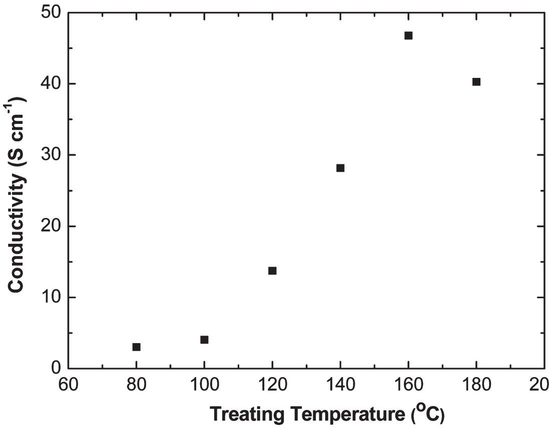


Figure 2. Dependence of the conductivity of treated PEDOT:PSS films on treating temperature. The solution is 0.074 M $CuCl_2$ aqueous solution.

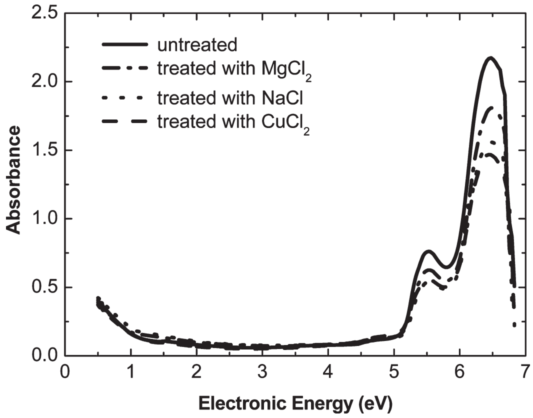


Figure 3. UV−vis−NIR absorbance spectra of PEDOT:PSS films before (solid curve) and after the treatment with 0.1 M $MgCl_2$ (dashed dotted curve), 0.1 M NaCl (dotted curve), and 0.1 M $CuCl_2$ (dashed curve) solution.

PEDOT.[11] The S_{2p} intensity of PEDOT relative to that of PSS increases after the $CuCl_2$ solution treatment. This suggests the loss of PSS from the PEDOT:PSS film, which is consistent with the UV−vis−NIR absorption spectra. PSS loss from PEDOT:PSS was also observed after it was treated with organic solvents.[7c,7e] Besides the intensity, the S_{2p} bands of PEDOT shift to high binding energy by about 0.1 eV, which suggests that the $CuCl_2$ solution treatment also affects the electronic structure of PEDOT in the PEDOT:PSS film.

The chemical structure of PEDOT:PSS was studied by the FTIR spectroscopy as well (Figure 5). No remarkable difference could be observed on the FTIR bands of PEDOT:PSS after the $CuCl_2$ treatment. Thus, the treatment of the PEDOT:PSS films with $CuCl_2$ aqueous solution did not affect the chemical structure. The change in the UV−vis−NIR absorption and XPS spectra is not due to the change in the chemical structure but due to the compositional change after the treatment.

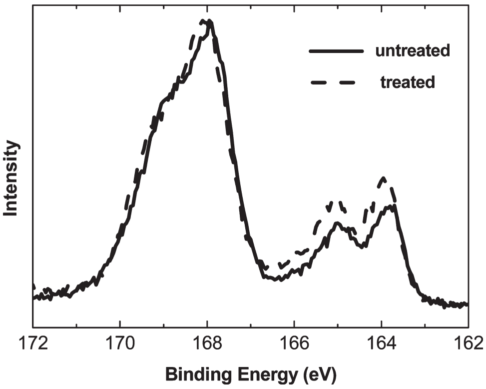


Figure 4. S_{2p} XPS spectra of untreated PEDOT:PSS (solid curve) and PEDOT:PSS treated with 0.37 M $CuCl_2$ solution (dashed curve).

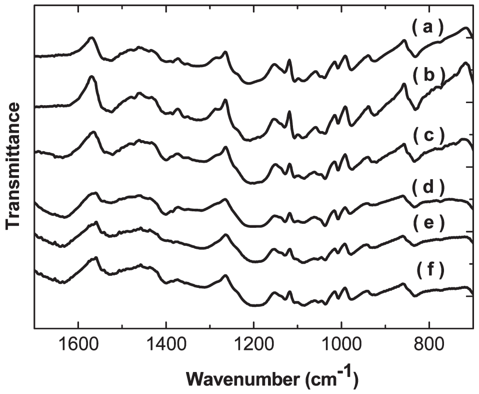


Figure 5. FTIR spectra of untreated PEDOT:PSS (a) and PEDOT:PSS treated with aqueous solution of $CuCl_2$ (b), $InCl_3$ (c), $AgNO_3$ (d), NaCl (e), and $MgCl_2$ (f). The concentrations were 0.1 M for all the solutions.

The PEDOT:PSS films were further characterized with AFM (Figure 6). The untreated PEDOT:PSS film had a smooth surface. The surface became quite rough with the appearance of big domains after the $CuCl_2$ solution treatment. The morphological change of the PEDOT:PSS film suggests the conformational change of the polymer chains during the treatment. The surface morphological change of the PEDOT:PSS films is similar to that of the PEDOT:PSS films treated with a polar organic solvent of high boiling point.[7d,7g]

Mechanism for Conductivity Enhancement. Our results suggest that the conductivity enhancement of the PEDOT:PSS film by the treatment with $CuCl_2$ solution is not related to the ionic conductivity though some ions might remain in the PEDOT:PSS film after the treatment. The highest ionic conductivity observed for polymers is below 10^{-2} S cm^{-1} at room temperature,[12] much lower than the conductivity observed on the $CuCl_2$-treated PEDOT:PSS films. The ionic conduction in a polymer may become higher if water is absorbed into the polymer. The ionic conductivity may contribute to the conductivity enhancement of the PEDOT:PSS films, which may absorb water from the aqueous solution during the treatment or the moisture in air. To investigate this possibility, the $CuCl_2$-treated PEDOT:PSS films were evacuated under vacuum overnight. Then, they were transferred into a drybox filled with nitrogen for the conductivity testing. These films exhibited the same conductivity as tested in air just after the $CuCl_2$ treatment.

The ac impedance spectra of the PEDOT:PSS films before and after the treatment were measured to verify whether the conductivity enhancement originates from the ionic conductivity. The impedance of the PEDOT:PSS film decreased by 2 orders in magnitude after the $CuCl_2$ treatment in the frequency range from 10 to 10^4 Hz. The impedances normalized to that at 10 Hz are shown in Figure 7 to understand the change of the impedance after the treatment. The untreated PEDOT:PSS film exhibited a relaxation process in the impedance at the frequency above 10^4 Hz, while the relaxation disappeared in the frequency range from 10 to 10^6 Hz for the $CuCl_2$-treated PEDOT:PSS film. This change is similar to

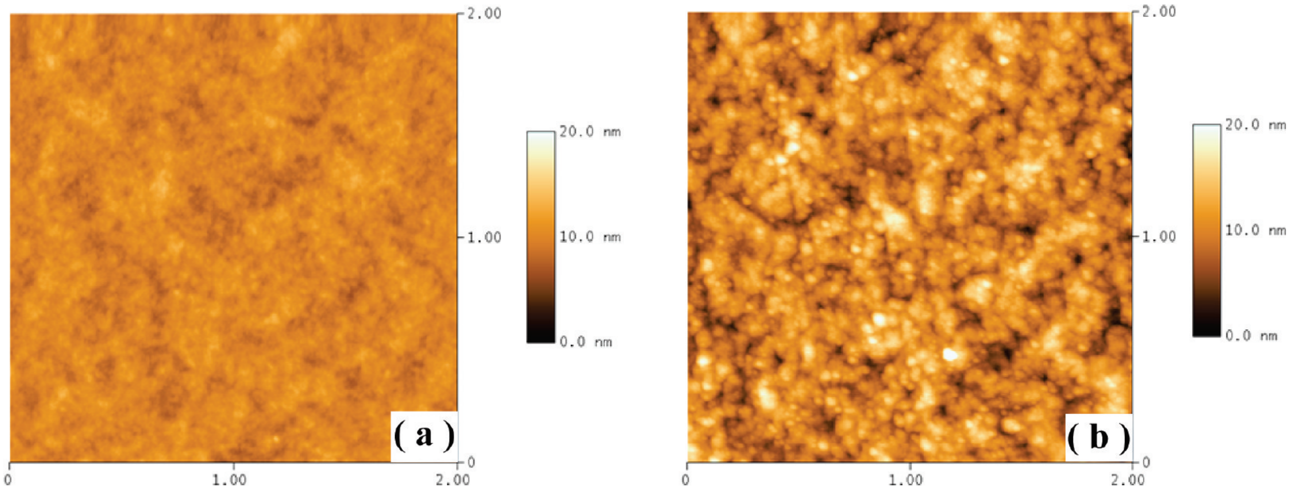


Figure 6. AFM images of PEDOT:PSS films, which were (a) untreated and (b) treated with 0.74 M $CuCl_2$ solution. The unit for the AFM images is μm.

the observation by DeLongchamp et al. on the impedance of the PEDOT:PSS films after rinsed with water.[13] They contributed the impedance change after rinsing the PEDOT:PSS films with water to the washing away of some PSS chains. Thus, the change in the impedance of our PEDOT:PSS film after the $CuCl_2$ treatment may be related to the PSS loss from the PEDOT:PSS film as well. Moreover, the insensitivity of the impedance to the frequency in the low-frequency range indicates that the conductivity enhancement cannot be attributed to ionic conductivity.

The conductivity enhancement cannot be attributed to the increase of the doping degree in PEDOT:PSS, since $CuCl_2$ is a mild salt and cannot oxidize PEDOT:PSS, which is already in the oxidized state. This is also supported by the FTIR spectra, which indicates no change in the chemical structure of PEDOT:PSS after the treatment. Furthermore, the protonation mechanism can be excluded for the conductivity enhancement by the fact that the proton concentration in $CuCl_2$ solution is even lower than that in the PEDOT:PSS aqueous solution. In fact, the pH value of the 0.074 M $CuCl_2$ solution was 3.9, which was higher than the pH value (pH = 2) of the PEDOT:PSS aqueous solution. A study by Aleshin et al. also suggested that the conductivity of the PEDOT:PSS film is insensitive to a low proton concentration.[14]

Though PSS loss can occur for a PEDOT:PSS film after a treatment with water, water is unlikely to be the principal factor for the significant conductivity enhancement observed in our experiments. As reported by DeLongchamp et al., the conductivity increased by only 50% after the PEDOT:PSS films were treated with water.[13] Thus, the conductivity enhancement should be related to the salt.

Other salts including $AgNO_3$, $InCl_3$, LiCl, NaCl, $MgCl_2$, and $NiCl_2$ were also investigated to treat the PEDOT:PSS films. Figure 8 shows the effects of $InCl_3$ and NaCl treatments on the conductivity of the PEDOT:PSS films. Significantly conductivity enhancement of 2 orders in magnitude was observed for the PEDOT:PSS films after the treatment with $InCl_3$ aqueous solution, and the conductivity enhancement depended on the $InCl_3$ concentration. These results are similar to that with the $CuCl_2$ treatment. In contrast, the NaCl treatment resulted into only slight conductivity enhancement. The conductivities of the PEDOT:PSS films after being treated with solution of various salts are listed in Table 1. The conductivity enhancement showed dependence on the nature of the salts. On the basis of the conductivity enhancement, the salts can be classified into two groups. The first group includes $CuCl_2$, $InCl_3$, and $AgNO_3$. These salts can significantly enhance the conductivity of the PEDOT:PSS film. The second group includes LiCl, NaCl, $NiCl_2$, and $MgCl_2$. These salts give rise to only slight conductivity enhancement or even do not affect the conductivity.

These results indicate that the metal ions of the salts play a key role while their valence is not important for the conductivity enhancement. Thus, the mechanism for the conductivity enhancement cannot be attributed to ionic cross-linking of the PSS chains as proposed by Ghosh et al.[15] They reported conductivity enhancement for polymer blends, such as PEDOT:PSS in poly(vinylpyrrolidone) (PVP) matrix, when bivalent cations, such as Mg^{2+}, were added into aqueous solution of polymer blends, while no conductivity enhancement for pure PEDOT:PSS added with Mg^{2+}. The dependence of the conductivity enhancement on the nature of the salts also evidences that the conductivity enhancement is not due to the ionic conductivity, since an ion with small size and monovalence usually has high ionic conductivity in polymer.[12]

The PEDOT:PSS films treated with aqueous solutions of these salts were characterized as well. The UV−vis−NIR

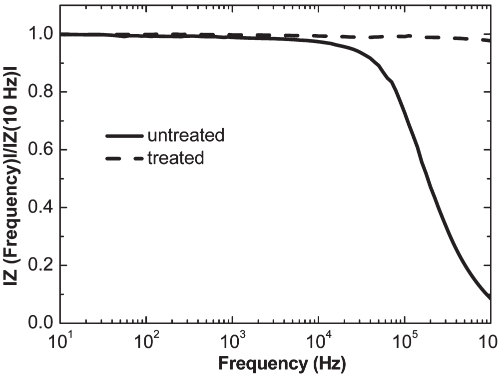


Figure 7. Ac impedance spectra of untreated (solid curve) and $CuCl_2$-treated (dashed curve) PEDOT:PSS films. |*Z*| is the modulus of the impedance. The modulus of $CuCl_2$-treated PEDOT:PSS was lower than that of untreated PEDOT:PSS by about 2 orders in magnitude. The moduli presented in the plot were normalized with respect to the modulus at 10 Hz for both films.

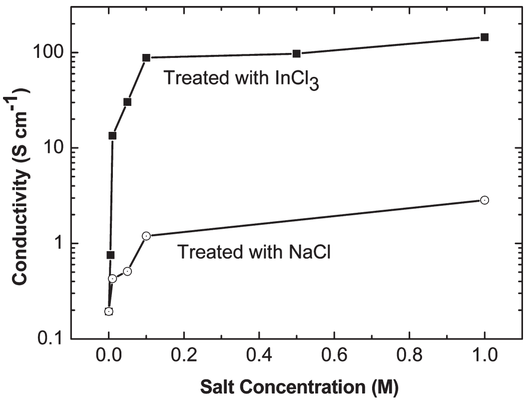


Figure 8. Variations of the conductivity of treated PEDOT:PSS films with $InCl_3$ concentration (solid squares) and NaCl concentration (open circles) in aqueous solutions.

Table 1. Conductivity of PEDOT:PSS Films after Treatment with 0.1 M Solution of Various Salts

salt	softness parameter of metal ion[a]	softness parameter of anion[a]	conductivity (S cm^{-1})
$AgNO_3$	+0.18	+0.03	7.4
$CuCl_2$	+0.38	−0.09	29.0
$InCl_3$	+0.48	−0.09	95.5
LiCl	−1.02	−0.09	0.6
NaCl	−0.75	−0.09	1.5
$MgCl_2$	−0.41	−0.09	0.2
$NiCl_2$	−0.11	−0.09	0.3

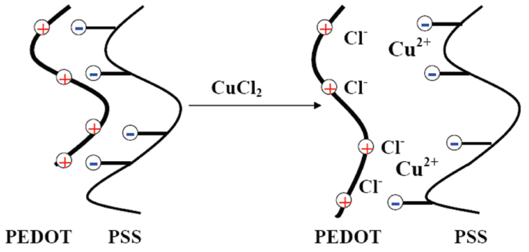
[a] The softness parameter values were obtained from ref 16.

absorption spectroscopy also indicated the PSS loss after the treatment, as shown in Figure 3. This is not surprising since PEDOT:PSS is a polyelectrolyte and salt can reduce the interaction between polycations and polyanions. PEDOT:PSS after treated with 0.1 M aqueous solution of various salts exhibited the same FTIR spectrum as the untreated PEDOT:PSS, as shown in Figure 5; that is, the chemical structure of PEDOT:PSS did not change after the treatment.

It is interesting to find that the conductivity enhancement of the PEDOT:PSS film is related to the softness parameter of the metal ions, as shown in Table 1. Cu^{2+}, Ag^{+}, and In^{3+} have positive softness parameters. Their salts can significantly enhance the conductivity of the PEDOT:PSS film. On the other hand, Li^{+}, Na^{+}, Mg^{2+}, and Ni^{2+} have negative softness parameters. Their salts have a less significant effect on the conductivity of the PEDOT:PSS film. The softness parameter of an ion is related to the binding energy of this ion to other species.[16] A cation with a negative (or positive) softness parameter is a hard (or soft) Lewis acid. Thus, the values for the softness parameters of cations are related to the binding strength between the cations and PSS. This indicates that the conductivity enhancement of the PEDOT:PSS film by the salt solution treatment is related to the binding of the metal ions to the PSS anions in PEDOT:PSS.

On the basis of these results, we propose the following mechanism for the conductivity enhancement of the PEDOT:PSS film by the salt solution treatment. $CuCl_2$ is used as an example to explain the mechanism (Scheme 2).

Scheme 2. Schematic Structure of PEDOT:PSS before and after $CuCl_2$ Treatment



Cu^{2+} and Cl^{-} ions penetrate into the PEDOT:PSS film, and the Cu^{2+} ions bind to the PSS anions during the treatment. The Cu^{2+} and Cl^{-} ions in the PEDOT:PSS film screen the charges on PEDOT and PSS, since salt can induce charge screening and conformational change on polyelectrolyte complexes,[17] and PEDOT:PSS, which has positively charged PEDOT chains and negatively charged PSS chains, can be considered as a polyelectrolyte complex. The charge screening weakens the Coulombic attraction between PEDOT and PSS. Consequently, some PSS chains leave the film when the $CuCl_2$ concentration is high. Moreover, the PEDOT conformation changes as a result of the weakening attraction between PEDOT and PSS and the leave of some PSS chains. This PEDOT conformational change and the loss of the insulating PSS are account for the conductivity enhancement of the PEDOT:PSS film. The PSS loss from PEDOT:PSS was also reported for

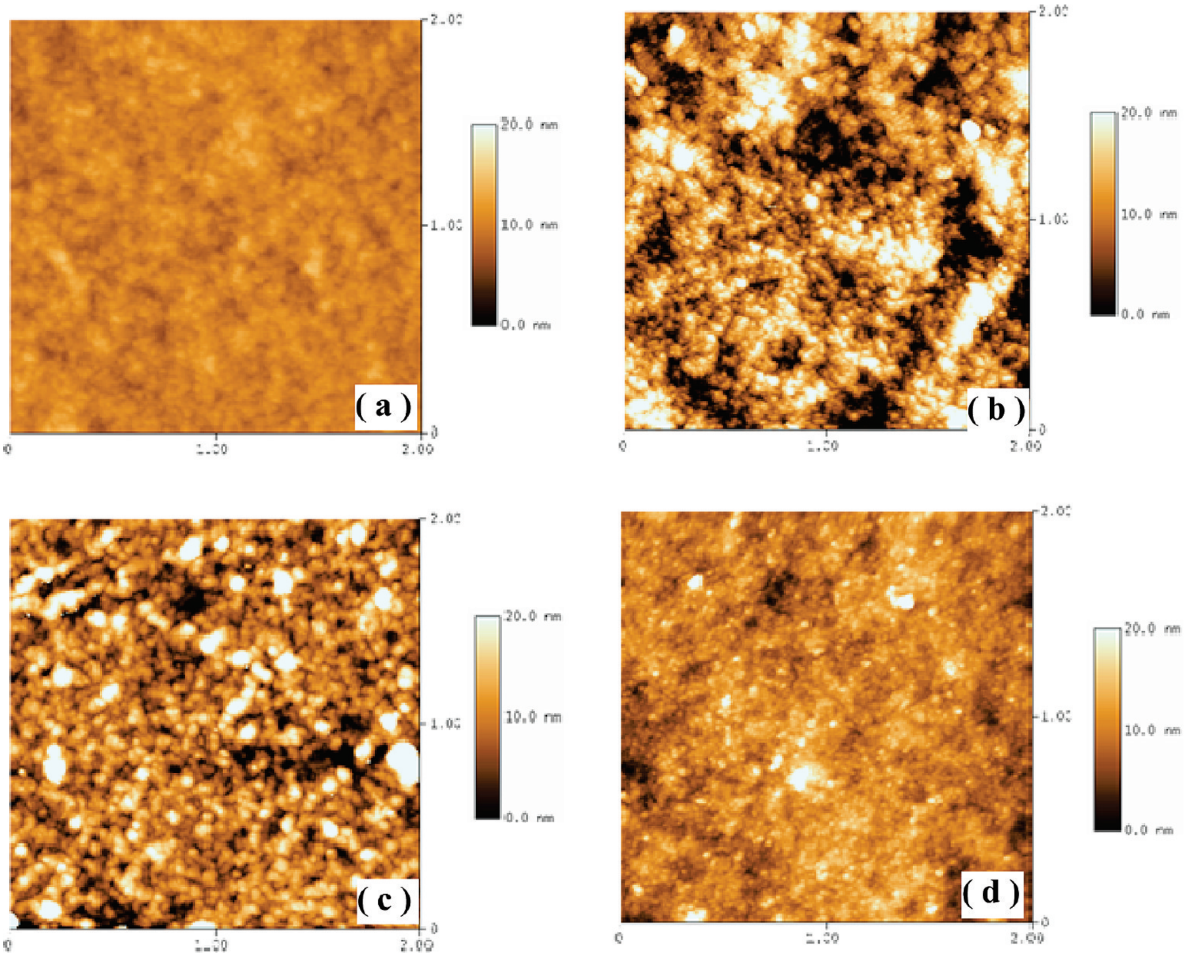


Figure 9. AFM images of PEDOT:PSS films after treated with (a) water, (b) 0.1 M $InCl_3$, (c) 0.1 M $AgNO_3$, and (d) 0.1 M $MgCl_2$ aqueous solution. The unit for the AFM images is μm.

the treatment of the PEDOT:PSS film with a polar organic solvent.[7c,7e]

The binding of the metal ions to the PSS anions is important for the conductivity enhancement of PEDOT:PSS. A metal ion with positive softness parameter, such as Ag^+ or Cu^{2+} or In^{3+}, can strongly bind to PSS, which results in replacement of some PSS anions by Cl^- ions as the counterions for PEDOT. Consequently, the conformation of the PEDOT chain changes, and the conductivity of the PEDOT:PSS film significantly increases since PEDOT doped with small anions like Cl^- has a higher conductivity than PEDOT:PSS.[2b,9] In contrast, a metal ion with negative softness parameter, such as Na^+ or Mg^{2+} or Ni^{2+}, are difficult to bind to PSS, so that the replacement of PSS by small anions like Cl^- as the counteranion for PEDOT does not happen and the conductivity of PEDOT:PSS does not change significantly.

This mechanism indicates that the conductivity enhancement is due to not only the PSS loss but also the conformational change of the PEDOT chains during the treatment. The conformational change of the PEDOT chains is suggested by the change of the AFM images of the PEDOT:PSS film before and after the treatment. Besides the AFM images of the untreated and $CuCl_2$-treated PEDOT:PSS films presented in Figure 6, we also obtained the AFM images of the PEDOT:PSS films treated by water and other salts in the first and second groups. Some of them are presented in Figure 9. The AFM image almost did not change after the treatment of the PEDOT:PSS film with water, while it became remarkably different with appearance of domains after the treatment with aqueous solution of various salts. The domain for the PEDOT:PSS film treated with the salts in the first group was bigger than that treated with the salts in the second group. Thus, the salts in the two groups have different effects on the conformation of the polymer chain during the treatment. Obviously, the conformational change of the PEDOT chains becomes easier at higher temperature. This is the reason for the higher conductivity enhancement of the PEDOT:PSS film after being treated with the $CuCl_2$ solution at higher temperature.

This research work is fundamentally different from that reported by Ghosh et al.[15] They observed conductivity enhancement on blends of PEDOT:PSS in a nonconjugated water-soluble polymer matrix by adding bivalent cations, such as Mg^{2+}, into the aqueous solution of the polymer blends and attributed the conductivity enhancement to the formation of a network of conducting PEDOT:PSS in an insulating polymer matrix, arising from the physical cross-linking of the PSS chains by bivalent metal ions. Their method could increase the conductivity of the polymer blends up to but not higher than that of pure PEDOT:PSS, that is, less than 1 S cm^{-1}. Hence, our observation is the first time to observe ion-induced charge screening and significant conductivity enhancement for a pure conducting polymer film. Our method is also different from previous methods to enhance the conductivity of the PEDOT:PSS film, such as the addition polar organic compound[7] or ionic liquid[8] or anionic surfactant[9] into the PEDOT:PSS aqueous solution.

Conclusions

In conclusion, a novel method was developed to significantly enhance the conductivity of the PEDOT:PSS film through a treatment with solution of a certain salt. Conductivity enhancement by a factor of about 700 was observed. The conductivity enhancement depends on the concentration and the soft parameter of the cations of the salts. Salts, whose cations have positive soft parameter, can significantly enhance the conductivity of the PEDOT:PSS film, while the ones whose cations have negative soft parameter have negligible effect. The conductivity enhancement is attributed to the PSS loss from the PEDOT:PSS film and the conformational change of PEDOT resulted from the ion-induced screening effect of the charges on PEDOT and PSS.

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