HIGHLY CONDUCTIVE
POLY(3,4-ETHYLENEDIOXYTHIOPHENE):POLY(STYRENESULFONATE) (PEDOT:PSS) FILMS AND THEIR APPLICATION IN POLYMER PHOTOVOLTAIC DEVICES

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DEVICES

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Summary

New transparent conductive materials are urgently needed to replace indium tin oxide (ITO) as the transparent electrode of optoelectronic devices. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a quite promising candidate as the next-generation transparent electrode in optoelectronic devices. However, as-prepared PEDOT:PSS from its aqueous solution suffers a problem of low conductivity of <1 S/cm. It is important to significantly enhance the conductivity of PEDOT:PSS. This study aims at developing novel and effective methods to achieve highly conductive PEDOT:PSS films, understanding the mechanism for the conductivity enhancement, and demonstrating the application of these highly conductive PEDOT:PSS films as the transparent electrode of polymer photovoltaic cells (PVs).

Four novel methods have been developed to significantly enhance the conductivity of PEDOT:PSS in this study. The first approach is to significantly enhance the conductivity of PEDOT:PSS films through a treatment with solution of a certain salt. Conductivity enhancement by a factor of about 1000 was observed. The conductivity enhancement depended on the softness parameter of cations and the concentration of the salts in solution. The anions of the salts can also affect the
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In order to avoid metal ion in PEDOT:PSS that can diffuse into the active layer of organic electronic devices and deteriorate the devices, zwitterions were used to replace the salts in the first method to treat the PEDOT:PSS film. The conductivity of PEDOT:PSS films could be significantly enhanced to close to 100 S/cm through a treatment with aqueous solution of a zwitterion. The zwitterions can effectively induce a charge screening between PEDOT and PSS and consequently lead to the significant conductivity enhancement, while their large size and Coulombic interactions make the ion diffusion in the PEDOT:PSS films difficult. Polymer PVs with the zwitterion-treated PEDOT:PSS films as the transparent electrode were demonstrated, and the photovoltaic efficiency as high as 2.48% was achieved under AM 1.5G illumination.

The third way is to significantly enhance the conductivity of PEDOT:PSS by carboxylic acids and inorganic acids. The conductivity of the PEDOT:PSS film could be enhanced to over 200 S/cm, that is, by a factor of more than 1000. The conductivity enhancement is attributed to acid-assisted PSSH loss from the PEDOT:PSS film and conformational change of the PEDOT chains. Polymer PVs with the acid-treated PEDOT:PSS films as the transparent electrode were
demonstrated and the photovoltaic efficiency as high as 2.53% was achieved.

The forth method is to treat PEDOT:PSS films with cosolvents of water and common organic solvents like ethanol, acetone, isopropyl alcohol, and tetrahydrofuran (THF). Conductivity enhancement from 0.2 S/cm to 103 S/cm was observed. The conductivity enhancement is attributed to the preferential solvation of PEDOT:PSS by the cosolvents. The preferential solvation induces the departure of the insulator PSSH chains from the PEDOT:PSS film, aggregation of PSSH segments in the PEDOT:PSS film, and the conformational change of the PEDOT chains from coiled to linear. The cosolvent-treated PEDOT:PSS films were quite smooth. They were used as the transparent electrode of polymer PVs. Photovoltaic efficiency close to 3% was achieved.
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Chapter 1

Introduction

The enthusiasm for research on PEDOT:PSS is driven by both a fundamental interest in the structure and properties of conducting polymers and their promising practical applications. This chapter will briefly introduce the historical development and electronic structure on conducting polymers followed by a detailed description on the electrical properties of PEDOT:PSS and its applications in polymer photovoltaic devices. The objectives of my research work and the outline of this thesis will be presented in the end.

1.1 A brief overview of conducting polymers

1.1.1 Historical background of conducting polymers

Conducting polymers have been attracting strong interest since the discovery of
conducting polymers by Shirakawa, MacDiarmid, and Heeger in 1977, who were awarded the Nobel Prize in Chemistry in 2000 for this discovery [1,2]. The early study on conducting polymers was focusing on polyacetylenes (PAs). PA is a conjugated polymer and is an insulator in the neutral state. It becomes highly conductive in the oxidized or reduced state (Figure 1.1). The conductivity of the oxidized PAs can be as high as $10^5$ S/cm, comparable to that of copper. Conducting polymers should have wide application as metallic plastics. Nevertheless, the oxidized PAs degrade readily in air. They are infusible and insoluble in solvents, making it difficult to process them. These drawbacks severely impede their application. People have been searching for conducting polymers that are highly conductive, stable and easily processable. Conducting polymers with heteroatom, such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTs), have good stability when in the conductive state (Figure 1.2) [3]. But they are still intractable because they are insoluble and cannot melt. A breakthrough in developing processable conducting polymers was made in 1993 as reported by Cao et al., who discovered that conductive PANI can be dispersed in some organic solvents like m-cresol [4]. This discovery enables conductive PANI to be processed by solution processing. But PANI prepared by solution processing usually has a low conductivity of around $10^1$ S/cm. The green color of PANI also affects its application in some areas. In addition, the toxic solvent used for dispersing PANI brings health and environmental concerns. A breakthrough was made by Bayer AG, a couple of years later, which reported water-dispersable poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). When
excess poly(styrene sulfonate acid) PSSH is used with PEDOT, PEDOT can be dispersed in water with good stability [5-7]. Uniform PEDOT:PSS films can be readily fabricated from the PEDOT:PSS aqueous solution by coating. Moreover, PEDOT:PSS has good thermal stability and high transparency in the visible range. Today, PEDOT:PSS becomes the most important conducting polymer in terms of the commercial application.

\[
\text{[CH]}_n + \frac{3x}{2} \text{I}_2 \rightarrow [\text{CH}]_n^{x^+} + x\text{I}_3^- \quad \text{Oxidative doping}
\]

\[
[\text{CH}]_n + x\text{Na} \rightarrow [\text{CH}]_n^{x^-} + x\text{Na}^+ \quad \text{Reductive doping}
\]

**Figure 1.1** Oxidative and reductive doping of PA.

trans-polyacetylene (t-PA)  
Polythiophene (PT)  
Polypyrrole (PPy)  
Poly(ethylenedioxythiophene) (PEDOT)  
Polyaniline (PANI)

**Figure 1.2** Chemical structures of some well-known conducting polymers.
Conducting polymers have been attracting great attention in the past decade due to their advantages of light weight, high mechanical flexibility, and simple solution processing. In addition, their electronic properties can be tuned by manipulating the chemical structure, the alignment of polymer chains, and doping conditions [8]. The solution processability is crucial for the application of conducting polymers in many areas. Besides the conventional coating, such as drop casting and spin coating, inkjet printing and stamp printing were also developed to process conducting polymers. These methods can produce conducting polymers with desirable pattern at a low fabrication cost. Compared with inorganic conducting polymers, conducting polymers have high mechanical flexibility. They are thus particularly important for the flexible electronics devices that are regarded as the next-generation electronic devices.

1.1.2 Electrical properties of conducting polymers

Conjugated polymers are usually insulator when in the neutral state. Their conductivity can be significantly increased after the oxidation or reduction. The oxidation or reduction results into the positive or negative charges on the conjugated polymers, which are compensated by the counter ions. Thus, the oxidation or reduction of conducting polymers is called doping as well. But this doping is different from the doping of inorganic semiconductor in nature. For example, the undoped conjugated polymer such as polypyrrole, polyacetylene, etc, has only a conductivity
of around $10^{-10}$ to $10^{-8}$ S/cm. After doping, the conductivity can approach around $10^2$-$10^5$ S/cm. It is higher than that of inorganic semiconductors and comparable to that of many metals (Figure 1.3) [1,3,9,10].

![Figure 1.3 Conductivities of conducting polymers and other materials, reproduced from [9].](image)

The conduction mechanism of conducting polymers is different from that of metals and inorganic semiconductors. It is related to the conjugated $\pi$ orbitals along the main chain. The two $p_z$ orbitals of two neighbour atoms form into a bonding ($\pi$) orbital and an antibonding ($\pi^*$) orbital. The electrons on the $\pi$ orbitals are mobile and delocalize. The $\pi$ and $\pi^*$ orbitals interact and form two continuous bands, the valence and the conduction bands. Take PA as an example, there should be band gap between the valence band and conduction band for a neutral PA, if the chemical bonds along the PA chain are uniform with equivalent bond length. However, the stable structure for PA is the one with different bond lengths. One is short like the C=C bond, while
another is long as the C-C bond. The inequivalent bond lengths along the main chains give rise to a band gap of about 1.5 eV for neutral PA. Consequently, neutral PA has a very low conductivity.

There are a few solitons in neutral PA when the $2p_z$ orbital of a C atom does not participate in the conjugated $\pi$ orbital (Figure 1.4). A soliton has a discrete energy level between the conduction and valence bands. A soliton delocalizes over 12 CH units and are mobile. The soliton concentration in PA significantly increases after doping. Those solitons are positively or negatively charged when PA is in the oxidized and reduced state, respectively. When the soliton concentration is higher enough as the result of high doping degree, the solitons interact with each other and form a soliton band between the conduction and valence band. Finally, the soliton band becomes broad enough to overlap with the conduction and valence band. Therefore, PA becomes metallic.

Figure 1.4 Illustration and electronic states of soliton in PA, adapted from [12,13].
Solitons are the charge carriers for the conducting polymers with high symmetry like PA. The charge carriers in other conducting polymers with low symmetry are polarons and bipolarons. Use polypyrrole as an example (Figure 1.5). Polypyrrole in the neutral state is an insulator with a band gap between the conduction and valence bands. When polypyrrole is oxidized, electrons are taken away from the conjugated \( \pi \) orbital. That will leave an unfilled \( p_z \) orbital of one C atom and a \( p_z \) orbital with an unpair electron of another C atom. These two \( p_z \) orbitals interact through the conjugated \( \pi \) orbital between them and form two discrete energy levels between the conduction and the valence bands. These discrete energy levels are polaron level. Polaron is a charge carrier associated with a lattice distortion. The polaron state is symmetrically located about 0.5 eV from the band edges in polypyrrole [13]. Polarons are the main charge carriers for conducting polymers like polypyrrole at a low doping degree.

![Figure 1.5 Illustration and electronic states of polaron in polypyrrole, adapted from [12,13].](image)
The polarons interact with each other when the polaron concentration becomes high in polypyrrole as the result of high doping degree. The coupling of two polarons result into the formation of a bipolaron, which has two positive charges while no unpaired electrons (Figure 1.6). The bipolarons have continuous band structure. The bipolarons are located symmetrically 0.75 eV from the band edges in polypyrrole [13]. With continued doping, bipolaron states form into two continuous bipolaron bands. The width of the bipolaron bands in highly doped polypyrrole is about 0.4 eV [13]. The band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very heavily doped polymer, it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity.

![Figure 1.6 Illustration and electronic states of bipolaron in polypyrrole, adapted from [12,13].](image)

The formation of unfilled bipolaron states after doping can be observed by optical spectra in low energy range. The Optical absorption spectra of ClO₄-doped polypyrrole as a function of dopant concentration are shown in Figure 1.7. At low
doping, three absorptions at 0.7, 1.4, and 2.1 eV are attributed, as discussed before, to the presence of polarons. The absorption at 3.2 eV is attributed to the bandgap transition. At intermediate doping, the 1.4 eV absorption associated with transitions between the polaron levels disappears. At very high doping, two wide optical absorptions peaking at 1.0 and 2.7 eV are present, in agreement with the existence of two bipolaron bands. The bandgap transition has shifted to higher energy, 3.6 eV.

Figure 1.7 Optical absorption spectra of ClO₄-doped polypyrrole as a function of dopant concentration, The dopant level increases from the bottom curve (almost neutral polypyrrole) to the top curve (33 mol% doping level), reproduced from [13].
1. Introduction

1.2 Background and development of PEDOT:PSS

1.2.1 Background of PEDOT:PSS

PEDOT is a derivative of polythiophene and is usually prepared by polymerization of ethylenedioxythiophene (EDOT). Conductive PEDOT can be prepared by electrochemical or chemical polymerization. PEDOT doped with small anions are insoluble in any solvent. However, when excess PSS is used as the counter anion for the PEDOT by chemical oxidation, the polymer, PEDOT:PSS (chemical structure shown in Figure 1.8), can be dispersed in water. The PEDOT chains are attached to the PSS chains through the Coulomnic interaction. They are stabilized by the excess PSS.

![Figure 1.8](image-url) The schematic picture of the morphology of PEDOT:PSS and its chemistry structure. Left: the top view of the morphology of a thin film of PEDOT:PSS particles, surrounded by a thin PSS-rich surface layer. PEDOT chains are displayed as short bars. Right: chemical structure of the species present in the film, reproduced from [17].
**Figure 1.8** illustrates the schematic microscopic structure of a PEDOT:PSS film prepared from PEDOT:PSS aqueous solution. There is core/shell structure. The PEDOT:PSS core is surrounded by a PSS-rich shell. PEDOT:PSS used in this research has a PSS/PEDOT weight ratio of 2.5 in solution, that is, the molar ratio of the repeating unit of PEDOT to that of PSS is 1:1.8. The excess PSS is used to stabilize PEDOT in water. The hydrophilic PSS chains form micelles with the hydrophobic PEDOT chains inside. This structure in water is conserved in the PEDOT:PSS films. The PEDOT:PSS films are composed of grains with diameters of about 50 nm [17-21]. The conductive PEDOT is rich in the core while the insulating PSS is rich in the shell of a grain. The shell has a thickness of about 5-10 nm. This insulator shell blocks the charge transport across the grains, which is considered as one of the reason for the low conductivity of < 1 S/cm observed on PEDOT:PSS films prepared from the PEDOT:PSS aqueous solution. In addition, the PEDOT and PSS chains are bonded by the Coulombic attraction. There is a stress in the polymer chains owing to the mismatch between the PEDOT and PSS chains, so that the PEDOT chains adopt a coiled structure, which results into the localization of the positive charges (**Figure 1.9**). This is another reason account for the low conductivity of PEDOT:PSS. Therefore, approaches which lower the amount of PSS in the PEDOT:PSS film and/or reduce the stress in PEDOT:PSS can improve the conductivity of PEDOT:PSS.
1.2.2 Charge transport properties of PEDOT:PSS

Charge hopping among the polymer chains is believed to be the dominant conduction mechanism in almost all conducting polymers including PEDOT:PSS [22,23]. This can be revealed by the temperature dependence of the conductivity. Mott et al. [24] developed a variable range hopping (VRH) model to describe electron conduction in amorphous materials that is well applicable to conducting polymers. The VRH model can be expressed as:

\[ R(T) = R_0 \exp \left( \frac{T_0}{T} \right)^{\alpha} \]  

where \( R_0 \) is the resistance at infinite temperature, and \( \alpha \) the exponent that in standard VRH theory is equal to \( 1/(1+D) \), where \( D \) is dimensionality of the system. \( T_0 = 16/k_B N(E_F)L_{\parallel}/L_{\perp}^2 \) is the energy barrier between localized states, \( N(E_F) \) is the density of the states at the Fermi level, and \( L_{\parallel} \) (\( L_{\perp} \)) is the localization length in the parallel (perpendicular) direction.

In general, fitting of the temperature-dependence of the resistivities using VRH
model provides valuable information for not only the nature of the charge transport mechanism but also the dimensionality of the system [25-28].

1.2.3 Development of PEDOT:PSS

Nowadays, PEDOT:PSS becomes one of the most successful conducting polymer in terms of the commercial application due to its merits. PEDOT:PSS films have a high transparency in the visible range, high mechanical flexibility, and excellent thermal stability. This renders PEDOT:PSS a good candidate to replace indium tin oxide (ITO) as the transparent electrode in optoelectronic devices. ITO has a severe of the scarce indium on earth [29-31]. However, as-prepared PEDOT:PSS from PEDOT:PSS aqueous solution suffers a problem of low conductivity. An as-prepared PEDOT:PSS film fabricated from its aqueous solution usually has a conductivity below 1 S/cm, which is remarkably lower than ITO [7,32]. Hence, it is important to significantly enhance the conductivity of PEDOT:PSS films.

It is highly possible to significantly enhance the conductivity of PEDOT:PSS, since the PEDOT polymers doped with small anions can exhibit conductivities close to 1000 S/cm, which is comparable to that of ITO [6,33,34]. Much effort has been made in improving the conductivity of PEDOT:PSS, and several approaches have been reported to significantly improve the conductivity 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 from 0.8 to 80 S/cm, when PEDOT:PSS solution was mixed with organic solvents, such as ethylene glycol, sorbitol, diethylene glycol, N,N-dimethyl formamide, N-methylpyrrolidone, or dimethyl sulfoxide [25,26,35-39]. The screening effect due to the polar solvent, reducing the Coulomb interaction between PEDOT$^+$ and PSS$^-$ chains, plays an important role for the conductivity enhancement. However, the PEDOT:PSS solution usually become unstable after adding organic solvents. Thus, researchers have focused on the methods to treat PEDOT:PSS films with these polar organic compounds. These methods are immersing PEDOT:PSS film in polar solvents or spin-coating polar solvents on the pristine PEDOT:PSS film [40-42]. The conductivity could be enhanced by a factor of a few hundreds, from $1 \times 10^{-1}$ to about 200 S/cm. The conductivity enhancement is due to the conformational change of the PEDOT chains and the formation of longer conduction paths of PEDOT-PSS domains enabled by phase segregation. Besides the polar organic compounds, the introduction of ionic liquids [43] or anionic surfactants [44] into the PEDOT:PSS aqueous solution or treating the PEDOT:PSS with dichloroacetic acid (DCA) [45] can also significantly enhance the conductivity of PEDOT:PSS. Thus, there is still room for the further improvement of the conductivity of the PEDOT:PSS film.
1.3 Applications for PEDOT:PSS in polymer photovoltaic devices

Highly conductive PEDOT:PSS can replace ITO as the transparent electrode of optoelectronic devices. This application was demonstrated in polymer photovoltaic cells. Today, solar cells become one of the most focused research areas due to energy crisis and environmental problems. Polymer-based organic photovoltaic systems hold the promise for a cost-effective, lightweight and large-area solar energy conversion platform, which could benefit from simple solution processing of the active layer. Since the bulk-heterojunction photovoltaic cells were first reported in 1995 [46], there have been tremendous progresses in this exciting field in the past 15 years and the power conversion efficiencies (PCEs) of polymer PVs have been increasing continuously over the last few years and reached 6-8% [47-55].

A typical polymer PV is composed of an active layer, a buffer layer, anode and cathode terminals. Figure 1.10 schematically illustrates the device structure of a typical polymer PV and the morphology of the active layer. PEDOT:PSS films are usually used as buffer layer to flatten the ITO surface and tailor the work function of the anode for active layer. The energy conversion process has four fundamental steps in the commonly accepted mechanism [56,57]: 1) Absorption of light and generation of excitons, 2) exciton diffusion to the Donor-Acceptor interface and subsequent dissociation into free electron and hole, 3) transport of free charge carriers to respective electrodes, 4) charge collection at the respective electrode.
Figure 1.10 Schematic illustration of a polymer PV device, with a magnified area showing the bicontinuous morphology of the active layer, reproduced from [56].

Figure 1.11 The typical current-voltage characteristics for dark and light current in a polymer PV illustrate the important parameters for such devices, reproduced from [56].
The most meaningful and direct characterization of a polymer PV is to measure the current (I)-voltage (V) curve under both dark and illumination conditions. The I-V curve is obtained by sweeping the voltage in the suitable range of a device and simultaneously recording the current output. Figure 1.11 shows a typical I-V characteristic of a polymer PV. The dash curve represents the I-V behavior of a PV in dark; while the solid curve is the I-V curve recorded under illumination. There are a few important parameters obtained from these curves. $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open circuit voltage, $J_m$ and $V_m$ are the current and voltage at the maximum power point, and $FF$ is the fill factor, which is defined as the ratio of maximum power and the product of $V_{oc}$ and $J_{sc}$. It describes the “squareness” of the I-V curve and is expressed as:

$$FF = \frac{(J_m)(V_m)}{(J_{sc})(V_{oc})} \quad (1.2)$$

Finally, the power conversion efficiency (PCE) is defined, both simplistically as the ratio of power out ($P_{out}$) to power in ($P_{in}$), as well as in terms of the relevant parameters derived from the current–voltage relationship:

$$PCE = \frac{P_{out}}{P_{in}} = FF \frac{(J_{sc})(V_{oc})}{P_{in}} \quad (1.3)$$

Therefore, the improvement of PCE depends on the continuous improvement of these parameters ($J_{sc}$, $V_{oc}$ and $FF$).

Besides the efficiency, the flexibility and the low cost are decisive for the future commercial success of polymer PVs. A printing or coating based vacuum free deposition scheme for ultimately all layers of the PVs would be a strong advantage.
over conventional inorganic crystalline or thin film technologies. However, most PVs as well as other optoelectronic devices incorporate a ITO electrode harnessing its good transparency (typically $T \geq 90\%$) and high conductivity (typically $\sigma \geq 4000$ S/cm) [29-31]. The high and increasing indium price and the high mechanical brittleness of ITO question the use of this anode material for future low cost and flexible PVs.

Therefore, PEDOT:PSS film with improved conductivity is quite promising as a next-generation transparent electrode material. There have been many demonstrations of utilizing PEDOT:PSS as a replacement to ITO as the transparent electrode in the conventional device architecture.

In particular, polymeric PVs using anodes made of PEDOT:PSS and PEDOT:PSS modified with sorbitol or glycerol treatment on a glass substrate have been reported, which demonstrated the possibility of using flexible polymer anodes in plastic solar cells [58]. Later, PEDOT:PSS doped with sorbitol and vapour-phase polymerized PEDOT have been reported as anode material for polymer PVs. However, the devices exhibited PCE lower than 1% [59]. Polymer PVs using the PEDOT:PSS films treated with EG as the anode have higher performance (PCE = 1.5%) [42]. Most recently, the PCE of polymers PVs using PEDOT:PSS films modified by DCA has reached 2.12% [45]. In addition, to further enhance conductivity of PEDOT:PSS anode in a device, a metallic Ag grid is introduced to PEDOT:PSS film [60]. This newly developed PEDOT:PSS-based transparent anode is successfully applied onto flexible substrates. Moreover, polymer PVs using PEDOT:PSS films as both bottom and top electrodes
have been demonstrated. Semi-transparent inverted solar cells fabricated with ITO as the cathode and PEDOT:PSS as the top anode electrode were demonstrated showing efficiencies of ~2.51% while replacement of both ITO and Ag with PEDOT:PSS as both the cathode and anode show efficiencies of ~0.47% [61]. Although most of the above-mentioned studies have successfully demonstrated the possibility of substituting the ITO with PEDOT:PSS in polymer PVs, the efficiencies of devices remained low - less than 3% - compared with those of current devices (~4%). Thus, further efforts should be devoted to the production of ITO-free devices with high efficiency-comparable to those of ITO-based devices.

1.4 Objectives and outline of this thesis

The objective of this study is to develop novel and effective methods to achieve highly conductive PEDOT:PSS films so that they can be used as the transparent electrode in optoelectronic devices, understand the mechanisms for the conductivity enhancements, demonstrate the application of these highly conductive PEDOT:PSS films as the transparent electrode of polymer photovoltaic cells (PVs). Four novel methods have been developed in this research work to significantly enhance the conductivity of PEDOT:PSS. The understanding in the mechanisms for the conductivity enhancement provides guidance for developing highly conductive polymers.
There are six chapters in this thesis. Chapter 1 (this chapter) provides the general background for conducting polymers and the development of PEDOT:PSS.

The four methods developed in this research work are presented in 4 chapters following the first chapter. The first method is reported in chapter 2 to significantly enhance the conductivity of the PEDOT:PSS. The PEDOT:PSS films are treated with an aqueous solution of a certain salt. The effect of metal ion and anion on the conductivity enhancement was discussed. The mechanism for the conductivity enhancement was studied by various characterizations.

The second method is to treat the PEDOT:PSS films with zwitterions, which is presented in Chapter 3. The zwitterion treatment can produce significant conductivity enhancement of PEDOT:PSS films as well. Besides the investigation in the mechanism for the conductivity enhancement, polymer PVs with the zwitterion-treated PEDOT:PSS films as the transparent electrode were demonstrated.

The conductivity of PEDOT:PSS can be significantly enhanced through a treatment with an organic or inorganic acid. This is presented in Chapter 4. The mechanism for the conductivity enhancement was interpreted based on various chemical and physical characterizations. Polymer PVs with the acid-treated PEDOT:PSS films as the transparent electrode were also demonstrated.

The forth method is introduced in Chapter 5. The conductivity of PEDOT:PSS films is significantly enhanced by cosolvents. The preferential solvation of PEDOT:PSS by water and organic solvent of the cosolvents is proposed as the main reason for the conductivity enhancement. The cosolvent-treated PEDOT:PSS films
were used as the transparent electrode of polymer PVs as well.

The thesis is summarized in Chapter 6 with proposed future research.
Chapter 2

Salt-induced significant conductivity enhancement of PEDOT:PSS films

2.1 Introduction

The conductivity of conjugated polymer is greatly improved by the oxidation or reduction, that generate positive or negative charges on polymers. The charges on the conducting polymer chain are neutralized by the counterions in the polymer. Thus, the conducting polymers can be viewed as conjugated polycations or polyanions considering from the chemical structure. Though tremendous research has been carried out on the conducting polymers and non-conjugated polyions [62,63], the idea of considering the conducting polymers as polyions has been rarely explored [47,67]. This new viewpoint on the conducting polymers can help to understand the structure and develop new approaches to improve the properties of the conducting polymers. For example, factors affecting the structure and properties of non-conjugated polyions may have an effect on the electronic properties and structure of conducting polymers.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

as well. Bear this in mind, we studied the salt effect on the structure and properties of the conducting PEDOT:PSS. Because PEDOT:PSS is a polyelectrolyte complex of conjugated polycation (PEDOT) and non-conjugated polyanion (PSS), and it is well known that the structure and properties of the non-conjugated polyelectrolyte complex is strongly affected by salt [62-66].

In this chapter, conductivity enhancement of PEDOT:PSS film through a treatment with aqueous solutions of various salts was studied. Conductivity enhancement by a factor of more than 1000 was observed when CuBr₂ or InI₃ aqueous solution was used. The metal ion effect and the anion effect on the salt-induced conductivity enhancement of PEDOT:PSS were investigated to understand the mechanism for the salt-induced conductivity enhancement of PEDOT:PSS.

2.2 Experimental procedure

PEDOT:PSS aqueous solution (Clevios™ P, Item No. 1802705, Lot No. HCE07P107) was purchased from H.C. Starck. The concentration of PEDOT:PSS was 1.3% by weight, and the weight ratio of PSS to PEDOT was 2.5. All other chemicals were purchased from Sigma-Aldrich. These materials were used without further purification.

PEDOT:PSS films were prepared by spin-coating the PEDOT:PSS aqueous solution on 1.3 × 1.3 cm² glass substrates. The substrates were pre-cleaned by
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

detergent, de-ionized (DI) water, acetone and isopropyl alcohol in sequence. The PEDOT:PSS films were dried at 110 °C on a hot plate for 30 min. The film thickness was about 130 nm. The treatment with a salt solution was performed by dropping 150 µL aqueous solution of a 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 down to room temperature in air and rinsed with de-ionized water three times. Then, they were dried at 140 °C again. The film thickness was ca. 110 nm after the treatment.

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 on the four corners of each PEDOT:PSS film on glass substrate. Indium was used as probe tip due to the negligible contact resistance. The UV–Vis–NIR absorption spectra of the polymer films were taken with a Varian Cary 5000 UV–Vis–NIR spectrometer. The X-ray photoelectron spectra (XPS) were taken with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al Ka X-ray source (1486.6 eV). 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 atomic force microscopic (AFM) images of the polymer films were obtained using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode. The thicknesses of the films were determined with an Alpha 500 step profiler. The temperature dependences of the resistivities of the untreated and salt-treated 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 highly conductive PEDOT:PSS films on glass were used as the bottom electrode of polymer PVs. The active layer was formed by spin coating a chlorobenzene solution consisting of 17 mg ml\(^{-1}\) poly(3-hexylthiophene) P3HT and 17 mg ml\(^{-1}\) [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (chemical structure shown in Figure 2.1) at 500 rpm for 1 min in a glove box filled with N\(_2\). It was dried at room temperature for 20 min, and then annealed at 120 °C for 10 min in the glove box. The P3HT:PCBM layer had a thickness of 200 nm. The top electrode was fabricated by thermally depositing a layer of LiF of 0.5 nm in thickness and subsequently a layer of Al of 110 nm in thickness in a vacuum of 10\(^{-7}\) mbar. Each polymer PV had an active area of 0.11 cm\(^2\). The polymer PVs were encapsulated in the glove box with a UV-curable epoxy and glass sheets and then taken out for the photovoltaic study. The photovoltaic performance of the devices was measured with a computer-programmed Keithley 2400 source/meter. The light source was a Newport’s Oriel class A solar simulator, which simulated the AM1.5G sunlight (100 mW cm\(^{-2}\)) and was certified to the JIS C 8912 standard.

![Chemical structure of P3HT and PCBM](image)
2.3 Results and discussion

2.3.1 Metal ion effect on conductivity enhancement

2.3.1.1 Conductivity Enhancement of PEDOT:PSS Films through CuCl$_2$ Treatment

Aqueous solutions of AgNO$_3$ and chloride salts with various metal ions, including CuCl$_2$, 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, and it significantly increased after a treatment with CuCl$_2$ solution at 140 °C, as shown in Figure 2.2. 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 after the treatment with 0.074 M CuCl$_2$ solution and reached 139.7 S/cm after the treatment with 0.74 M CuCl$_2$ solution. This latter conductivity is almost 700 times higher than that of the as-prepared PEDOT:PSS film.
Figure 2.2 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.

The conductivity enhancement of the PEDOT:PSS films also depended on the temperature during the treatment with the CuCl$_2$ aqueous solution. Figure 2.3 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 for the PEDOT:PSS films after the treatment at 80 °C and increased to 47 S/cm after the treatment at 160 °C. The conductivity then dropped to 40 S/cm 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 [121].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

![Graph showing the dependence of conductivity on treating temperature.](image)

**Figure 2.3** Dependence of the conductivity of treated PEDOT:PSS films on treating temperature. The solution is 0.074 M CuCl$_2$ aqueous solution.

### 2.3.1.2 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 2.4**. 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 π-π* transitions of the benzene rings...
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

of PSS [35]. The decreasing absorption indicates the decrease of PSS in PEDOT:PSS after the CuCl₂ solution treatment.

\textbf{Figure 2.4} UV-Visible-NIR absorbance spectra of PEDOT:PSS films before (solid curve) and after the treatment with 0.1 M MgCl₂ (dashed dotted curve), 0.1 M NaCl (dotted curve), and 0.1 M CuCl₂ (dashed curve) solution.

This change in the composition of the PEDOT:PSS film after the treatment was confirmed by XPS (\textbf{Figure 2.5}). The bands with binding energy higher than 166.6 eV are the S₂p bands of the sulfur atoms in PSS, and the two bands with low binding energy are the S₂p bands of the sulfur atoms in PEDOT [20,66]. The S₂p intensity of PEDOT relative to that of PSS increases after the CuCl₂ 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
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

was treated with organic solvents [36,37]. 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.

![Graph showing XPS spectra](image)

**Figure 2.5** S$_{2p}$ XPS spectra of untreated PEDOT:PSS (solid curve) and PEDOT:PSS treated with 0.37 M CuCl$_2$ solution (dashed curve).

The chemical structure of PEDOT:PSS was studied by the FTIR spectroscopy as well (Figure 2.6). 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
Salt-induced significant conductivity enhancement of PEDOT:PSS films

structure but due to the compositional change after the treatment.

![FTIR spectra](image)

**Figure 2.6** FTIR spectra of untreated PEDOT:PSS (a) and PEDOT:PSS treated with aqueous solution of CuCl₂ (b), InCl₃ (c), AgNO₃ (d), NaCl (e), and MgCl₂ (f). The concentrations were 0.1 M for all the solutions.

The PEDOT:PSS films were further characterized with AFM (**Figure 2.7**). The untreated PEDOT:PSS film had a smooth surface. The surface became quite rough with the appearance of big domains after the CuCl₂ 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 [28, 41].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

2.3.1.3 Mechanism for Conductivity Enhancement

The results suggest that the conductivity enhancement of the PEDOT:PSS film by the treatment with CuCl₂ 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 at room temperature [68], much lower than the conductivity observed on the CuCl₂-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 CuCl₂-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 CuCl₂ treatment.

Figure 2.7 AFM images of PEDOT:PSS films, which were (a) untreated and (b) treated with 0.74 M CuCl₂ solution. The unit for the AFM images is μm.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

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 2.8 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 the observation by DeLongchamp et al. on the impedance of the PEDOT:PSS films after rinsed with water [69]. 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.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

![Ac Impedance spectra of untreated (solid curve) and CuCl₂-treated (dashed curve) PEDOT:PSS films. |Z| is the modulus of the impedance. The modulus of CuCl₂-treated PEDOT:PSS was lower than that of untreated by about two orders in magnitude. The modulus presented in the plot were normalized with respect to the modulus at 10 Hz for both films.](image)

The conductivity enhancement cannot be attributed to the increase of the doping degree in PEDOT:PSS, since CuCl₂ 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 CuCl₂ solution is even lower than that in the PEDOT:PSS aqueous solution. In fact, the pH value of the 0.074 M CuCl₂ 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 [23].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

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 [69]. Thus, the conductivity enhancement should be related to the salt.

Other salts including AgNO₃, InCl₃, LiCl, NaCl, MgCl₂, and NiCl₂ were also investigated to treat the PEDOT:PSS films. Figure 2.9 shows the effects of InCl₃ 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 InCl₃ aqueous solution, and the conductivity enhancement depended on the InCl₃ concentration. These results are similar to that with the CuCl₂ 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 2.1. 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 CuCl₂, InCl₃, and AgNO₃. These salts can significantly enhance the conductivity of the PEDOT:PSS film. The second group includes LiCl, NaCl, NiCl₂, and MgCl₂. These salts give rise to only slight conductivity enhancement or even do not affect the conductivity.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

![Figure 2.9](image.png)

Figure 2.9 Variations of the conductivity of treated PEDOT:PSS films with InCl₃ concentration (solid squares) and NaCl concentration (open circles) in aqueous solutions.

Table 2.1 Conductivity of PEDOT:PSS films after treated with 0.1 M solutions of various salts.

<table>
<thead>
<tr>
<th>salt</th>
<th>softness parameter of metal ion⁹</th>
<th>softness parameter of anion⁹</th>
<th>conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO₃</td>
<td>+0.18</td>
<td>+0.03</td>
<td>7.4</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>+0.38</td>
<td>-0.09</td>
<td>29.0</td>
</tr>
<tr>
<td>InCl₃</td>
<td>+0.48</td>
<td>-0.09</td>
<td>95.5</td>
</tr>
<tr>
<td>LiCl</td>
<td>-1.02</td>
<td>-0.09</td>
<td>0.6</td>
</tr>
<tr>
<td>NaCl</td>
<td>-0.75</td>
<td>-0.09</td>
<td>1.5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>-0.41</td>
<td>-0.09</td>
<td>0.2</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>-0.11</td>
<td>-0.09</td>
<td>0.3</td>
</tr>
</tbody>
</table>

⁹The softness parameter values were obtained from [70,71].
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 crosslinking of the PSS chains as proposed by Ghosh et al. [67]. 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 [68].

The PEDOT:PSS films treated with aqueous solutions of these salts were characterized as well. The UV-vis-NIR absorption spectroscopy also indicated the PSS loss after the treatment, as shown in Figure 2.4. 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 2.6; 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 2.1. 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\(^{2+}\)
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

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 defined as the difference of enthalpy change between ionization and hydration (Figure 2.10). It is related to the binding energy of this ion to other species [70,71]. 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. The metal ions with positive softness parameter may effectively reduce the Coulombic interaction between PEDOT 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.

\[
\sigma_A(M^{m+}) = \left[ \sum_{i=1}^{m} I_i + \Delta_{\text{hyd}} H_i^0 \right] / m \\
\sigma_B(X^{x-}) = \left[ -EA + \Delta_{\text{hyd}} H_x^0 \right] / x
\]

**Figure 2.10** Definition of softness parameter of cations (\( \sigma_A \)) and anions (\( \sigma_B \)) [70,71].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

![Figure 2.11 Schematic structure of PEDOT:PSS before and after CuCl₂ treatment.](image)

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. CuCl₂ is used as an example to explain the mechanism (Figure 2.11). Cu²⁺ and Cl⁻ ions penetrate into the PEDOT:PSS film, and the Cu²⁺ ions bind to the PSS anions during the treatment. The Cu²⁺ 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 [62-65], 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 CuCl₂ 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 the treatment
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

of the PEDOT:PSS film with a polar organic solvent [36,37].

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 Cu²⁺ or In³⁺, 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 [7,44]. In contrast, a metal ion with negative softness parameter, such as Na⁺ or Mg²⁺ or Ni²⁺, 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.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

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

Figure 2.12 AFM images of PEDOT:PSS films after treated with (a) water, (b) 0.1 M InCl$_3$, (c) 0.1 M AgNO$_3$, (d) 0.1 M MgCl$_2$ (treating temperature is 140°C), and (e) 0.1 M CuCl$_2$ (treating temperature is 80°C). The unit for the AFM images is μm.
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 2.7, 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 2.12. 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. No obvious domains can be observed on the surface of PEDOT:PSS film treated with CuCl$_2$ at 80$^\circ$C (Figure 2.12(e)). 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. [67]. They observed conductivity enhancement on blends of PEDOT:PSS in a non-conjugated 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
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

blends up to but not higher than that of pure PEDOT:PSS, that is, less than 1 S/cm. Hence, it 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 [25,28,35,38-41] or ionic liquid [43] or anionic surfactant [44] into the PEDOT:PSS aqueous solution.

2.3.2 Anion effect on conductivity enhancement

Though the role of the metal ions on the conductivity enhancement was well studied, it is unknown whether the anion of the salt affects the conductivity enhancement. Table 2.2 listed the conductivities of the PEDOT:PSS films after treated with 0.1 M and 1 M aqueous solutions of cupric (Cu$^{2+}$) and indium (In$^{3+}$) salts with various anions. These results indicate that the anions significantly affected the conductivity of PEDOT:PSS. The conductivity of the PEDOT:PSS film increased to 74.3 S/cm after it was treated with 0.1 M CuBr$_2$ aqueous solution, while it was only 5.1 S/cm after treated with 0.1 M CuSO$_4$ aqueous solution. In addition, the conductivity just slightly increased to 1.1 S/cm after it was treated with 0.1 M Cu(CH$_3$COO)$_2$ aqueous solution. The remarkable difference was observed on the conductivities of the PEDOT:PSS films treated with various 1 M Cu$^{2+}$ aqueous solutions as well. The anion effect on the
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

conductivity enhancement was also observed when the PEDOT:PSS films were treated with solutions of various In$^{3+}$ salts.

The results presented in Table 2.2 indicate that I$_3^-$ and Br$^-$ salts give rise to the most significant conductivity enhancement. In fact, the conductivity of the PEDOT:PSS film was enhanced from 0.2 S/cm to 220 S/cm and 264.8 S/cm after treatments with 2 M CuBr$_2$ aqueous solution and 2 M InI$_3$ aqueous solution, respectively. The latter conductivity is higher than that of the as-prepared PEDOT:PSS film by a factor of more than 1300.

Table 2.2 Conductivities of PEDOT:PSS films after a treatment with 0.1 M and 1 M aqueous solutions of various salts.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Softness parameter of cation$^a$</th>
<th>Softness parameter of anion$^a$</th>
<th>Conductivity$^b$ (S cm$^{-1}$)</th>
<th>Conductivity$^c$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$</td>
<td>+0.38</td>
<td>-0.38</td>
<td>5.1</td>
<td>33.4</td>
</tr>
<tr>
<td>Cu(CH$_3$COO)$_2$</td>
<td>+0.38</td>
<td>-0.22</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Cu(ClO$_4$)$_2$</td>
<td>+0.38</td>
<td>-0.3</td>
<td>57.1</td>
<td>127.8</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>+0.38</td>
<td>-0.09</td>
<td>29.0</td>
<td>168.7</td>
</tr>
<tr>
<td>CuBr$_2$</td>
<td>+0.38</td>
<td>+0.17</td>
<td>74.3</td>
<td>187.5</td>
</tr>
<tr>
<td>InCl$_3$</td>
<td>+0.48</td>
<td>-0.09</td>
<td>95.5</td>
<td>136.0</td>
</tr>
<tr>
<td>InBr$_3$</td>
<td>+0.48</td>
<td>+0.17</td>
<td>145.9</td>
<td>152.0</td>
</tr>
<tr>
<td>InI$_3$</td>
<td>+0.48</td>
<td>+0.5</td>
<td>177.5</td>
<td>191.6</td>
</tr>
</tbody>
</table>

$^a$The softness parameter values were obtained from [70,71].
$^b$Treated with 0.1 M solution.
$^c$Treated with 1 M solution.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

The conductivities of the salt-treated PEDOT:PSS films were plotted against the softness parameters of the anions of the salts (Figure 2.13(a)). The conductivities of the PEDOT:PSS films treated with 0.1 M aqueous solutions of various sodium (Na\(^+\)) salts were presented as well. Two conclusions were obtained from Figure 2.13(a). The first conclusion is that the dominant factor for the salt-induced conductivity enhancement is the metal ions of the salts. No remarkable conductivity enhancement was observed for PEDOT:PSS treated with Na\(^+\) salts, whose anions have softness parameters varied from -0.38 to 0.5, while significant conductivity enhancement was observed for that treated with solutions of Cu\(^{2+}\) and In\(^{3+}\) salts. The second conclusion is that the anion effect on the conductivity enhancement is inconsistent with the softness parameters of the anions. For example, ClO\(_4^-\) had a softness parameter lower than Cl\(^-\), while the 0.1 M Cu(ClO\(_4\))\(_2\)-treated PEDOT:PSS films exhibited a conductivity higher than the 0.1 M CuCl\(_2\)-treated PEDOT:PSS film. The CuSO\(_4\)-treated PEDOT:PSS films had a conductivity higher than the Cu(CH\(_3\)COO)\(_2\)-treated PEDOT:PSS films as well, though SO\(_4^{2-}\) has a softness parameter lower than CH\(_3\)COO\(^-\). This is different from the effect of the metal ions on the conductivity enhancement of PEDOT:PSS, for which the conductivity enhancement is consistent with the softness parameters of the metal ions [72].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

Figure 2.13 Conductivities of PEDOT:PSS films treated with 0.1 M solutions of salts (a) Conductivities versus softness parameters of anions, and (b) Conductivities versus pKₐ values of acids corresponding to the anions. The softness parameters are obtained from [70,71]. The pKₐ value for SO₄²⁻ is the pKₐ of sulfuric acid. The straight line in (b) is a linear fitting of the data.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

Presumably, the inconsistence of the conductivity enhancement with the softness parameter of the anions is because only the enthalpy change is taken into account in the softness parameter [70,71]. Thus, the softness parameters can provide only a rough estimation for the association of an ion with other species. As we proposed, the salt treatment of the PEDOT:PSS films involves three processes: the dissociation of the salt, the association of the metal ions with PSS\(^-\), and the association of the anions with PEDOT\(^+\). The reason for the consistence of the softness parameters with the effect of metal ions on the conductivity enhancement of PEDOT:PSS is that the entropy change for the association of the metal ions with PSS\(^-\) is close since all the metal ions have similar sizes. This becomes different for the anion effect on the conductivity enhancement of PEDOT:PSS. The entropy changes can be quite different for different anions, particularly multi-atom anions like SO\(_4\)^\(^{2-}\) and CH\(_3\)COO\(^-\). Hence, the softness parameters are too rough to estimate the processes involving the anions. We turn to other parameters characteristic of the association of the anion with cation. The dissociation of the salts may be linearly related to the dissociation constants of the acids corresponding to the anions, since the association of metal ions with organic ligands is proportional to the association of metal ions with hydroxide [73]. The value of the acid dissociation \(K_a\) for an acid HA, which defined as

\[
\text{HA} \rightarrow \text{H}^+ + \text{A}^-, \quad K_a = [\text{A}^-][\text{H}^+]/[\text{HA}], \quad \text{and} \quad \text{p}K_a = - \log K_a,
\]

can provide more accurate information for the dissociation of the anion A\(^-\) with other species. We plotted the conductivity enhancement against the p\(K_a\) values of the corresponding acids of the anions (Figure 2.13(b)). The conductivities of the
salt-induced significant conductivity enhancement of PEDOT:PSS films

Salt-treated PEDOT:PSS films are consistent with the pK\text{a} values of the anions. The conductivity enhancement became more significant for the anions with lower pK\text{a} values. The logarithm of the conductivity almost linearly decreases with the increasing pK\text{a} value. The best fitting of this linear relationship indicates

\[ \log \sigma = 0.78 - 0.127pK\text{a}. \]

The relationship between the anion effect on the conductivity enhancement of PEDOT:PSS and the acid association constants of the anions is consistent with the mechanism we proposed. The association of the metal ions with PSS\(^-\) can be roughly described in terms of the softness parameters of the metal ions, while the softness parameters of the anions cannot provide accurate information for the dissociation of the salts and association of the anions with PEDOT\(^+\). The latter two processes involve the anions from the salt. The metal ions and PEDOT\(^+\) compete for the anions during the treatment. A high dissociation constant for a salt, or a low association constant for the metal ions with the anions, benefits the association of the anions with PEDOT\(^+\). Consequently, more significant conductivity enhancement can be obtained for the salts with anions of lower pK\text{a} values.

The three processes during the salt treatment of PEDOT:PSS result into the weakening of the Coulombic attraction between PEDOT\(^+\) and PSS\(^-\), the replacement of the PSS\(^-\) chains with small anions from the salt as the counter anions of PEDOT\(^+\), and the loss of PSS chains from the PEDOT:PSS films. Grain structure has been observed for the as-prepared PEDOT:PSS films with a PSS-rich shell and PEDOT-rich core for each grain [18-21]. The removal of some PSS chains, which are
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

insulator, can effectively reduce the shell thickness, which will benefit the charge transport through the PEDOT:PSS film. Moreover, the PEDOT$^+$ chains will experience a conformational change during the salt treatment. All these contribute to the conductivity enhancement of the PEDOT:PSS films. The anion exchange between the salts and PEDOT:PSS is different from the anion exchange observed on conducting polymers doped with small anions, in which no conductivity change was usually observed [74,75].

2.3.2.1 PSS loss from PEDOT:PSS and presence of small ions in PEDOT:PSS

![Figure 2.14](image)

**Figure 2.14** UV-Visible absorption spectra of PEDOT:PSS films untreated and treated with 1 M CuSO$_4$, CuCl$_2$ and CuBr$_2$. 
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

As discussed above, the anions from the salts affect the loss of PSS chains from the PEDOT:PSS film. This is evidenced by the absorption spectroscopy and XPS of the PEDOT:PSS treated with Cu$^{2+}$ salts with various anions. Figure 2.14 presents the absorption spectra of the treated and untreated PEDOT:PSS films in the UV range. The two bands with the absorption maxima at 193 nm and 225 nm are the absorption due to PSS [33]. The decreasing intensity of the two bands suggests the loss of some PSS chains from the PEDOT:PSS films after the treatment with the Cu$^{2+}$ salts. Some PSS chains left during DI water wash. In terms of these absorption spectra, the PSS loss increases with the treatment salts at this sequence: CuSO$_4$-treated $<$ CuCl$_2$-treated $<$ CuBr$_2$-treated PEDOT:PSS.

![Figure 2.14 Absorption Spectra of PEDOT:PSS](image)

**Figure 2.14** Absorption Spectra of PEDOT:PSS films untreated and treated with 1 M CuSO$_4$, CuCl$_2$ and CuBr$_2$.

![Figure 2.15 XPS Spectra of PEDOT:PSS](image)

**Figure 2.15** S$_{2p}$ XPS spectra of PEDOT:PSS films untreated and treated with 1 M CuSO$_4$, CuCl$_2$ and CuBr$_2$. 
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

The PSS loss from the PEDOT:PSS films during the salt treatment is also confirmed by the S\textsubscript{2p} XPS of the salt-treated PEDOT:PSS films (Figure 2.15). The XPS bands with binding energies below and above 166 eV arise from the sulfur atoms in PEDOT and in PSS, respectively [20,66]. The intensity ratio of these XPS bands are related to the PSS loss from the PEDOT:PSS films. The PSS loss from PEDOT:PSS was observed in the XPS of the PEDOT:PSS films treated with polar solvents as well. The S\textsubscript{2p} XPS intensity ratio of PEDOT to PSS increases after the salt treatment, and it increases at the sequence: untreated < CuSO\textsubscript{4}-treated < CuCl\textsubscript{2}-treated < CuBr\textsubscript{2}-treated PEDOT:PSS. This is consistent with the absorption spectra of the salt-treated PEDOT:PSS films. These results can be interpreted in terms of the dissociation of the salts. A salt with higher dissociation gives rise to higher ion concentration, which can more effectively screen the Coulombic attraction between PEDOT and PSS chains, so that more PSS chains are removed from the PEDOT:PSS film during the salt treatment.

When salts of Cu\textsuperscript{2+} or In\textsuperscript{3+} that has positive softness parameter are used to treat the PEDOT:PSS, the metal ions can associate with PSS\textsuperscript{-} in PEDOT:PSS. This can result into the presence of the small anions from the salts into the PEDOT:PSS films. This is supported by the FTIR spectroscopy and XPS of the salt-treated PEDOT:PSS films. PEDOT:PSS films treated with salts of multi-atom anions, such as CuSO\textsubscript{4} and Cu(ClO\textsubscript{4})\textsubscript{2} were studied by the FTIR spectroscopy, since the multi-atom anions have IR-active vibrational bands. Figure 2.16 shows the FTIR spectra of the untreated and CuSO\textsubscript{4}-treated PEDOT:PSS films, CuSO\textsubscript{4} and poly(styrenesulfonic acid) (PSSH).
Two vibrational bands at 661 and 603 cm\(^{-1}\) due to SO\(_4^{2-}\) were observed in the FTIR spectrum of the CuSO\(_4\)-treated PEDOT:PSS film. This suggests the presence of the SO\(_4^{2-}\) anions in the PEDOT:PSS films after the treatment with CuSO\(_4\) solution.

The PEDOT:PSS films treated with salts of mono-atom anion, such as CuCl\(_2\) and InI\(_3\), were investigated by XPS. XPS signals of Cu\(^{2+}\), Cl\(^{-}\) and In\(^{3+}\) were detected in the PEDOT:PSS films treated with these salts. This also indicates the presence of the salts in the PEDOT:PSS films after the salt treatment.

![FTIR spectra](image)

**Figure 2.16** FTIR spectra of (a) untreated PEDOT:PSS, (b) PEDOT:PSS treated with 0.1 M CuSO\(_4\), (c) CuSO\(_4\) and (d) PSSH.

### 2.3.2.2 Morphology and conduction mechanism of PEDOT:PSS films

The loss of some PSS chains and the presence of salt in the PEDOT:PSS film can
affect the film morphology. This is revealed by the AFM study of the salt-treated PEDOT:PSS films (Figure 2.17). An as-prepared PEDOT:PSS film was quite smooth with a roughness of 1.06 nm. It became rough for the PEDOT:PSS film treated with 0.1 M CuSO₄ solution and quite rough for the one treated with 0.1 M CuBr₂ or 0.1 M InI₃ solution. The roughnesses were 1.86 nm, 2.59 nm, and 3.00 nm for the PEDOT:PSS films treated with 0.1 M CuSO₄, 0.1 M CuBr₂ and 0.1 M InI₃ solutions, respectively. The increase in the roughness is due to the increasing grain size after the salt treatment. The grain size increases at the sequence of untreated < CuSO₄-treated < CuBr₂-treated < InI₃-treated PEDOT:PSS. The increasing gain size can be attributed to the loss of some PSS chains from the PEDOT:PSS films.

Figure 2.17 AFM images of PEDOT:PSS films (a) untreated and treated with 1 M (b) CuSO₄, (c) CuCl₂ and (d) CuBr₂. The unit for the AFM images is µm.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

As discussed in Chapter 1, the conductivity of PEDOT:PSS film is dominated by charge hopping among the PEDOT chains. The increased grain size can facilitate the charge hopping across the grains. Effect of the salt treatment on the conduction mechanism was investigated by characterizing the temperature dependence of resistivities of the PEDOT:PSS films before and after the treatment with various salts. The resistivities of the PEDOT:PSS films treated with various solutions of 1 M Cu\(^{2+}\) salts was studied from 300 K down to 110 K (Figure 2.18). The temperature dependences of the resistivities can be fitted by the one-dimensional variable range hopping (VRH) mechanism as discussed in Chapter 1.2.2 [24-28]

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

The parameter \(\alpha\) is 1/2 in one-dimensional system. \(T_0\) values can be calculated from the slope of the linear fit of the curves in Figure 2.18. The \(T_0\) value remarkably changed for the PEDOT:PSS film after the salt treatment. It was 2660 K for the untreated PEDOT:PSS film, and it decreased to 974 K, 407 K and 359 K for the PEDOT:PSS films treated with 1 M CuSO\(_4\), CuCl\(_2\) and CuBr\(_2\), respectively. The \(T_0\) values are consistent with the conductivities of these PEDOT:PSS films at room temperature, which are 0.2, 33, 169 and 188 S/cm for the untreated, CuSO\(_4\)-treated, CuCl\(_2\)-treated and CuBr\(_2\)-treated PEDOT:PSS films, respectively. Therefore, the conductivity enhancement of the PEDOT:PSS film by the salt treatment can be attributed to the lowering energy barrier. The lowering energy barrier suggests that the salt treatment may increase the localization length, since an increase in localization length usually cause a lower energy barrier for carrier hoping [24-28].
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

Figure 2.18 Temperature dependences of the normalized resistances of PEDOT:PSS films. (a) Untreated and treated with 1 M (b) CuSO₄, (c) CuCl₂ and (d) CuBr₂. The resistances are normalized to that at 110 K.

The anions of the salts can affect the dynamic process of the salt treatment, since they affect the dissociation of the salts and the association of the anions with PEDOT⁺. This was studied by monitoring the resistance of the PEDOT:PSS films during the treatment with various salts (Figure 2.19(a)). The configuration for the resistance measured is schematically shown in the inset of Figure 2.19(b). Indium (In) was pressed at the four corners of a PEDOT:PSS film to facilitate the electrical contact. Because the salt treatment was performed with indium at the four corners of each PEDOT:PSS film, the areas of the PEDOT:PSS film under indium were not treated by the salts, that is, the parts of the PEDOT:PSS film under indium kept the high resistance during the salt treatment. This is why the resistance decrease shown in
Figure 2.19(a) is less than in Table 2.2. Though the absolute transient resistances were not very meaningful, their change during the salt treatment provided important information for the dynamic process during the salt treatment.

Figure 2.19(a) presents the transient resistances of the PEDOT:PSS films during the treatment with 1 M CuSO₄ and 1 M CuBr₂ aqueous solutions. The resistance immediately decreased when the PEDOT:PSS film was treated with 1 M CuBr₂ solution, while it increased then gradually decreased when treated with 1 M CuSO₄ solution. The transient resistances are affected by two processes. One process is the swollen of the polymer chains by water, which gives rise to the decrease in the interchain charge transport and the increase in the resistance, as shown in Figure 2.19(b). Another process is the salt-induced resistivity decrease. The second process is the dominant process for the treatment with CuBr₂ aqueous solution, while the dominant process shifts from the first process to the second process for the treatment with CuSO₄ aqueous solution. The different transient resistances of the PEDOT:PSS films treated by the two salts can be attributed to the effect of the anions on the dissociation of the salts and association with PEDOT⁺.
Figure 2.19 Transient resistances of PEDOT:PSS films during the treatments. (a) 1 M CuBr₂ and 1 M CuSO₄ and (b) water. The resistances were normalized to the resistance of the as-prepared PEDOT:PSS film. The inset in (b) shows the configuration for the resistance measurements.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

2.3.3 Application of highly conductive PEDOT:PSS in polymer PVs

These highly conductive PEDOT:PSS films were used to replace ITO as the transparent anode of polymer PVs. Figure 2.20 presents the transmittance spectra of salt-treated PEDOT:PSS films in the visible range. The transmittance of the 110 nm-thick PEDOT:PSS films are around 81% at 550 nm. The work functions of the salt-treated PEDOT:PSS films were around 5.4 eV as determined by ultraviolet photoelectron spectroscopy (UPS), which was even higher than that (5.2 eV) of the untreated PEDOT:PSS film. This high work function can help the hole collection in polymer PVs. The architecture of the polymer PVs is illustrated in the inset of Figure 2.21(b). There is no ITO in these PVs. The salt-treated PEDOT:PSS films with a thickness of 110 nm were used as the transparent anode. The untreated PEDOT:PSS films were used as the anode of polymer PVs for comparison. The current density (J)-voltage (V) curves of these polymer PVs are presented in Figure 2.21. The photovoltaic parameters, including the short-circuit current (J_sc), open-circuit voltage (V_oc), fill factor (FF), and power conversion efficiency (PCE), are summarized in Table 2.3.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

![Graph showing transmittance of 110nm-thick salt-treated PEDOT:PSS film.

**Figure 2.20** Transmittance of 110nm-thick salt-treated PEDOT:PSS film.

**Table 2.3** Photovoltaic performances of polymer PVs with salt-treated or untreated PEDOT:PSS films as the anode.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Conductivity</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl$_2$-PEDOT:PSS</td>
<td>168.7</td>
<td>2.85</td>
<td>0.52</td>
<td>0.29</td>
<td>0.43</td>
</tr>
<tr>
<td>CuBr$_2$-PEDOT:PSS</td>
<td>187.5</td>
<td>6.62</td>
<td>0.52</td>
<td>0.31</td>
<td>1.08</td>
</tr>
<tr>
<td>Untreated PEDOT:PSS</td>
<td>0.2</td>
<td>0.49</td>
<td>0.60</td>
<td>0.31</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Figure 2.21 J-V characteristics of polymer PVs glass|PEDOT:PSS|P3HT:PCBM|LiF|Al in dark and under illumination. The PEDOT:PSS films treated with (a) normal salts and (b) untreated were used as the anode. The inset in (b) shows the architecture of the polymer PVs.
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

The devices using untreated PEDOT:PSS anode exhibited a photovoltaic efficiency of 0.09% which can be attributed to the low conductivity of the polymer anode. The photovoltaic performance of the polymer PVs with the CuCl$_2$- and CuBr$_2$-treated PEDOT:PSS films was much higher than that of the device with the untreated PEDOT:PSS film, due to the PEDOT:PSS anode have higher conductivities. However, the PCE of these polymer PVs are only 0.43% and 1.08%. In addition, the dark currents of the polymer PVs with the CuCl$_2$- and CuBr$_2$-treated PEDOT:PSS films are high. This can be attributed to the presence of the small ions in the salt-treated PEDOT:PSS films. It has been realized that the presence of small ions in PEDOT:PSS can deteriorate the performance of the polymer light-emitting diodes and polymer PVs [76,77]. The migration of metal ions in to the active layer can cause a high leakage current or electrical shorting of the device.

2.4 Conclusions

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 more than 1000 was observed when CuBr$_2$ or InI$_3$ aqueous solution was used.

The conductivity enhancement depends on the concentration and the soft parameter of the cations of the salts. Salts, whose cations have positive soft parameter,
2. Salt-induced significant conductivity enhancement of PEDOT:PSS films

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.

The anions of the salts also affect the salt-induced conductivity enhancement of the PEDOT:PSS film. Conductivity enhancement by a factor of more than 1000 was observed when CuBr$_2$ or InI$_3$ aqueous solution was used, while it became less significant and negligible when CuSO$_4$ and Cu(CH$_3$COO)$_2$ aqueous solutions were used. The anion effect on the conductivity enhancement of PEDOT:PSS is related to the competition of two processes, the dissociation of the salts and the association of the anions with PEDOT$^+$. A salt with a higher dissociation benefits the loss of more PSS chains from the PEDOT:PSS film after the salt treatment, so that it results in more significant conductivity enhancement.
Chapter 3

Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

3.1 Introduction

Chapter 2 of this thesis reports a novel and effective method to significantly enhance the conductivity of PEDOT:PSS through a treatment with a salt, such as CuCl$_2$ or InCl$_3$ [72,78]. The conductivity enhancement was attributed to the loss of PSSH from the PEDOT:PSS films and the conformational change of the PEDOT chains as the result of the ion-induced charge screening between PEDOT and PSS. Conductivity enhancement by a factor of more than 1000 was observed. However, the photovoltaic performances of the polymer PVs with these salt-treated PEDOT:PSS anodes were not good due to the ion diffusion in the films. In fact, a high leakage current caused by the metal ion diffusion from PEDOT:PSS into the organic layer was observed [76,77].
Therefore, we use zwitterions to solve this problem. A zwitterion is a compound that has both the cation and anion in one molecule, and the cationic and anionic charges are immobile. This unique characteristic renders zwitterions important applications, such as surfactants [79], detergents [80], and in rechargeable lithium batteries [81-83] and drug delivery [84,85]. Their interesting structure stimulates us to study the zwitterion effect on the structure and properties of PEDOT:PSS.

In this chapter, we reports the significant conductivity enhancement of PEDOT:PSS films through a treatment with aqueous solutions of zwitterions. The zwitterions can effectively induce a charge screening between PEDOT and PSS and consequently lead to significant conductivity enhancement, while their large size and coulombic interactions make it difficult to diffuse in the PEDOT:PSS films. We also demonstrated high-performance polymer PVs with the zwitterion-treated PEDOT:PSS films as the transparent electrode.

### 3.2 Experimental procedure

The PEDOT:PSS films were prepared by spin-coating the PEDOT:PSS aqueous solution on \(1.3 \times 1.3 \text{ cm}^2\) glass substrates, which were pre-cleaned by detergent, de-ionized (DI) water, acetone and isopropyl alcohol in sequence. The PEDOT:PSS films were dried at 110 °C on a hot plate for 30 min. The film thickness was ca. 130 nm. The treatment with a zwitterion solution was performed by dropping 150 μL
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

aqueous solution of a zwitterion on a PEDOT:PSS film on a hot plate at 140 °C. The film dried after about 5 min. The zwitterion-treated PEDOT:PSS films were cooled to room temperature in air and successively rinsed with DI water three times. Then, they were dried at 140 °C for 5 min again. The film thickness was ca. 110 nm after the treatment.

The characterization of zwitterion-treated PEDOT:PSS films and the fabrication of polymer PVs are the same as that of salt-treated PEDOT:PSS films in Chapter 2.

3.3 Results and discussion

3.3.1 Zwitterion-induced conductivity enhancement of PEDOT:PSS films

Three zwitterions, 1-(N,N-dimethylcarbamoyl)-4-(2-sulfoethyl)pyridinium hydroxide (DMCSP), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDMAP), and N,N-dimethyl-N-[3-(sulfooxy)propyl]-1-nonanaminium hydroxide (DNSPN), were used to treat PEDOT:PSS films. Their chemical structures are shown in Figure 3.1. The positive charge is located on a nitrogen atom, and the negative charge is present as SO$_3^-$ or SO$_4^{2-}$ in these zwitterions. Zwitterions present in PEDOT:PSS should diffuse slowly due to their bulky size and the coulombic interactions with the
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

positively charged PEDOT and negatively charged PSS chains.

![Chemical structure of DMCSP, DDMAP and DNSPN.](image)

**Figure 3.1** Chemical structure of DMCSP, DDMAP and DNSPN.

Significant conductivity enhancement was observed on the PEDOT:PSS films after the treatment with solutions of these zwitterions. The conductivity enhancement depends on the structure of the zwitterions. The conductivity was 0.2 S/cm for an as-prepared PEDOT:PSS film. It increased to 5.9, 49.2 and 57.7 S/cm after the PEDOT:PSS films were treated with 0.01 M solutions of DMCSP, DDMAP and DNSPN, respectively. The lower conductivity enhancement by a treatment with DMCSP than with the other two zwitterions may be related to the rigid aromatic ring in DMCSP.

The conductivity enhancement is also affected by the concentration of the zwitterion solutions (**Figure 3.2**). Significant conductivity enhancement was observed even at a low concentration of the zwitterions. The highest conductivities were 81.2 and 92.4 S/cm for PEDOT:PSS after treatment with 3 M DMCSP and 0.5 M DNSPN, respectively (the highest concentrations used for these two zwitterions). The concentration effect of the zwitterions on the conductivity of PEDOT:PSS is quite
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

similar to that found through treatment with a normal salt like CuCl₂ or InCl₃ [72].

The concentration effect of DDMAP on the conductivity of PEDOT:PSS was not studied, because DDMAP solutions became viscous even at a low concentration and were difficult to wash away from the PEDOT:PSS films.

Figure 3.2 Variations of the conductivities of treated PEDOT:PSS films with concentrations of DNSPN (□) and DMCSP (●). The inset shows the conductivity at low concentration of zwitterions.

Besides the structure and the concentration of the zwitterions, the temperature during the treatment also affected the conductivity. Figure 3.3 shows the dependence of the conductivity of the PEDOT:PSS films treated with 3 M DMCSP on the treatment temperature from 80 up to 200 °C. The conductivity increased with increasing treatment temperature from 80 to 140 °C, then dropped when the
temperature was further increased to 200 °C. The conductivity drop may be related to
the degradation of PEDOT:PSS at such a high temperature. The optimal temperature
for the zwitterion treatment of PEDOT:PSS is 140 °C, which coincides with that by a
treatment with salts [72,78]. It is believed that the effect of the temperature during the
treatment on the conductivity of the PEDOT:PSS film is related to the thermal
properties of the PEDOT:PSS film.

![Graph](image)

**Figure 3.3** Dependence of the conductivity of 3 M DMCSP-treated PEDOT:PSS films on the
temperature during the treatment.

This research work to enhance the conductivity of PEDOT:PSS with zwitterions
is different from that reported by Bhandari et al. [86]. They reported the
electrochromism of PEDOTs doped with electrochromic zwitterionic viologen, which
was induced into PEDOTs during the electrochemical polymerization of the monomer
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

and was used to enhance the electrochromic properties of PEDOTs. To the best of our knowledge, this is the first time to observe the significant conductivity enhancement of PEDOT:PSS films induced by zwitterions.

3.3.2 Mechanism for zwitterion-induced conductivity enhancement

The mechanism for the conductivity enhancement though the zwitterion treatment was studied by various chemical and physical characterizations. The UV-Vis-NIR absorption spectra of untreated- and zwitterion-treated PEDOT:PSS films are shown in Figure 3.4. The decrease in the absorption intensity of two bands in the UV range, which originate from PSS, after the zwitterion treatment indicates the decrease of the PSSH amount in PEDOT:PSS. The results are similar to that with the salt treatments [72,78].

The PSS decrease is confirmed by the observation of PEDOT:PSS precipitation after adding 300 mL 3M DMCSP into 500 mL PEDOT:PSS aqueous solution. The stable dispersion of PEDOT:PSS in water is due to the presence of excess PSSH. When the zwitterion induces the leaving of some PSSH from PEDOT:PSS, PEDOT becomes unstable and precipitates.
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

![UV-Vis-NIR absorption spectra of PEDOT:PSS films](image)

**Figure 3.4** UV-Vis-NIR absorption spectra of PEDOT:PSS films: untreated and treated with 3, 0.5 and 0.01 M DDMAP.

The decreasing PSSH amount in PEDOT:PSS can facilitate the charge transport across the conjugated PEDOT chains. As Lang et al. pointed out, there is a core–shell structure in an as-prepared PEDOT:PSS film [18]. The core rich in conductive PEDOT is surrounded by a shell rich in insulating PSSH. The decreasing PSSH amount will reduce the thickness of the insulating shell. Consequently, the interchain charge transport will be improved. This is confirmed by the temperature dependences of the resistivities of the PEDOT:PSS films before and after the treatment. The resistivities of the PEDOT:PSS films were measured from 300 down to 110 K (Figure 3.5). The temperature dependences of the resistivities can be fitted by the one-dimensional variable range hopping (VRH) model (Eq. (2.1)). The $T_0$ value remarkably decreased
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

for the PEDOT:PSS film after the zwitterion treatment. It was 2660 K for the untreated PEDOT:PSS film, and decreased to 1191, 858 and 288 K for the PEDOT:PSS films treated with 0.01 M DDMAP, 3 M DMCSP and 0.5 M DNSPN, respectively. The $T_0$ values are consistent with the conductivities of these PEDOT:PSS films at room temperature, which are 0.2, 49.2, 81.2 and 92.4 S/cm for the untreated, DDMAP, DMCSP and DNSPN treated PEDOT:PSS films, respectively. Obviously, $T_0$ decreases with the increasing conductivity which suggests that the zwitterion treatment lowers the energy barrier for the charge transport across the conductive PEDOT chains and increases the localization length.

![Figure 3.5](image)

**Figure 3.5** Temperature dependences of the normalized resistances of PEDOT:PSS films untreated (●) and treated with DDMAP (△), DMCSP (■) and DNSPN (◇). The resistances are normalized to that of the corresponding PEDOT:PSS films at 110 K.
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

The morphology of the PEDOT:PSS films was studied by AFM before and after the zwitterion treatment. As shown in Figure 3.6, an untreated PEDOT:PSS film was quite smooth with a roughness of 1.06 nm. The surface became rougher after the zwitterion solution treatment. The roughnesses were 4.59, 3.02 and 2.39 nm for the PEDOT:PSS films treated with DNSPN, DMCSP and DDMAP, respectively. This suggests the conformational change of the polymer chains during the zwitterion treatment.

Figure 3.6 AFM images of PEDOT:PSS films (a) untreated and treated with (b) 0.5 M DNSPN, (c) 3 M DMCSP and (d) 0.01 M DDMAP. The unit for the AFM images is µm.
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

The conformational change of the PEDOT chains after the zwitterion treatment was further studied by Raman spectroscopy. Figure 3.7 shows the Raman spectra of untreated and 3 M DMCSP-treated PEDOT:PSS films. The PEDOT:PSS films treated with DNSPN and DDMAP were also studied by Raman spectroscopy. The spectra are similar to that of the DMCSP-treated Raman spectrum, and so are not shown. The Raman band between 1400 and 1500 cm\(^{-1}\), which corresponds to the stretching vibration of the C=C bonds of PEDOT [87-89], is red-shifted and becomes narrower after the DMCSP treatment. This change is similar to that of PEDOT:PSS by a treatment with ethylene glycol [41] and indicates that some PEDOT chains change from a benzenoid to a quinoid structure.

![Figure 3.7 Raman spectra of PEDOT:PSS films untreated (solid) and treated with 3 M DMCSP (dashed).](image-url)
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

The electrochemical activity of the PEDOT:PSS film is quite sensitive to its conductivity [41]. The zwitterion-treated PEDOT:PSS films were investigated by cyclic voltammetry (CV) in a 0.1 M NaCl aqueous solution (Figure 3.8). The CVs of the DNSPN- and DDMAP-treated PEDOT:PSS films are similar to that of the DMCSP-treated PEDOT:PSS film and are not shown. The PEDOT:PSS film exhibited electrochemical activity only at potentials higher than -0.2 V before the treatment, while additional electrochemical activity appeared at potentials below -0.2 V after the DMCSP treatment. The change in the electrochemical behavior is similar to that of PEDOT:PSS treated with ethylene glycol [41]. It can be attributed to the decreasing PSSH amount and the conformational change of the PEDOT chains after the treatment.

![Cyclic voltammograms of PEDOT:PSS films untreated (solid) and treated with 3 M DMCSP (dashed).](image)

**Figure 3.8** Cyclic voltammograms of PEDOT:PSS films untreated (solid) and treated with 3 M DMCSP (dashed).
The dynamic process of the zwitterion treatment was studied by monitoring the resistances of the PEDOT:PSS films during the treatment (Figure 3.9). The configuration for the resistance measured is schematically shown in the inset of Figure 3.9. Indium (In) was pressed at the four corners of each PEDOT:PSS film to facilitate the electrical contact. The areas of the PEDOT:PSS films under indium were not treated by the zwitterions, so that the value of the transient resistances was not very meaningful. However, their change provided important information for the dynamic process during the zwitterion treatment. The transient resistances of the PEDOT:PSS film treated with 1 M CuBr$_2$ aqueous solution were also presented for comparison. The resistance immediately decreased when the PEDOT:PSS film was treated with 1 M CuBr$_2$ or 0.5 M DNSPN solution. This indicates that the dynamic process of zwitterion treatment is similar to the treatment with a simple salt [78]. Two processes occurring during the treatment can affect the transient resistance of the PEDOT:PSS film. One is the water-induced swelling of the PEDOT:PSS film. This will lower the inter-PEDOT interactions and lead to the increase of the resistance. Another is the resistance decrease induced by the salt or a zwitterion. The hump observed for the transient resistances upon treatment with 3 M DMCSP suggests that the resistance decrease during the DMCSP treatment is slower than during the DNSPN treatment. On the other hand, the big hump for the transient resistances through the treatment with 0.01 M DDMAP may be related to the low DDMAP concentration. The resistance increases at the beginning is due to the water-induced swelling of the polymer chains, while the zwitterion-induced resistance decrease takes
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

place after the evaporation of water.

![Figure 3.9](image)

**Figure 3.9** Transient resistances of PEDOT:PSS films during the treatment with (a) 0.5 M DNSPN, (b) 1 M CuBr₂, (c) 3 M DMCSP and (d) 0.01 M DDMAP. The resistances were normalized to that of the PEDOT:PSS films before the treatments. The inset shows the configuration for the resistance measurements.

The experimental results indicate that the mechanism for the conductivity enhancement of PEDOT:PSS by the zwitterion treatment is similar to that by the treatment with a simple salt such as CuBr₂ or InCl₃ [72,78]. A zwitterion can have coulombic interactions with both the positively charged PEDOT and negatively charged PSS, so that it can effectively screen the coulombic attraction between PEDOT and PSS (**Figure 3.10**). The decrease in the coulombic attraction between PEDOT and PSS can give rise to the PSSH loss from the PEDOT:PSS film and the
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

conformational change of the PEDOT chains. These changes in the compositions and structure of PEDOT:PSS result into the conductivity enhancement.

Figure 3.10 Schematic structures of PEDOT:PSS before and after zwitterion treatment.

3.3.3 Application of highly conductive PEDOT:PSS in polymer PVs

PEDOT:PSS used in the electronic devices usually has an electronic purity to minimize the diffusion of small ions. Zwitterions are difficult to diffuse or drift under electrical field due to their bulky size and the presence of both positive and negative charges in the same molecule. The ionic conductivity of zwitterions should be significantly lower than for small normal ions in conducting polymers. The zwitterion-treated PEDOT:PSS films were then used as the transparent electrode of polymer PVs. The work functions of the zwitterion-treated PEDOT:PSS films were around 5.3 eV as determined by ultraviolet photoelectron spectroscopy (UPS), which was even higher than that (5.2 eV) of the untreated PEDOT:PSS film. This high work
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

function can help the hole collection in polymer PVs. Figure 3.11 presents the transmittance spectra of zwitterion-treated PEDOT:PSS films in the visible range. The transmittance of the 110 nm-thick PEDOT:PSS films are above 85% at 550 nm.

![Figure 3.11 Transmittance of 110nm-thick zwitterion-treated PEDOT:PSS film.](image)

The architecture of the polymer PVs is the same as that of PVs using salt-treated PEDOT:PSS anode discussed in Chapter 2. The active layer of the devices was a blend film of P3HT and PCBM, and the cathode was LiF/Al. The current density (J)-voltage (V) curves of these polymer PVs are presented in Figure 3.12. The photovoltaic parameters, including the short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE), are summarized in Table 3.1. The polymer PVs with CuCl₂ and CuBr₂-treated PEDOT:PSS films were listed for comparison.
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

Figure 3.11 $J-V$ characteristics of polymer PVs glass|PEDOT:PSS|P3HT:PCBM|LiF|Al in dark and under illumination. The PEDOT:PSS films were treated with zwitterions.

Table 3.1 Photovoltaic performances of polymer PVs with zwitterion- or salt-treated PEDOT:PSS films as the anode.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Conductivity (S/cm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$PCE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMCSP-PEDOT:PSS</td>
<td>81.2</td>
<td>7.00</td>
<td>0.60</td>
<td>0.30</td>
<td>1.24</td>
</tr>
<tr>
<td>DDMAP-PEDOT:PSS</td>
<td>49.2</td>
<td>8.51</td>
<td>0.57</td>
<td>0.43</td>
<td>2.08</td>
</tr>
<tr>
<td>DNSPN-PEDOT:PSS</td>
<td>92.4</td>
<td>8.25</td>
<td>0.55</td>
<td>0.40</td>
<td>1.79</td>
</tr>
<tr>
<td>CuCl$_2$-PEDOT:PSS</td>
<td>168.7</td>
<td>2.85</td>
<td>0.52</td>
<td>0.29</td>
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<td>CuBr$_2$-PEDOT:PSS</td>
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<td>0.31</td>
<td>1.08</td>
</tr>
</tbody>
</table>
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

The photovoltaic performance of these polymer PVs is strongly affected by the PEDOT:PSS anode. Though the PEDOT:PSS films treated with CuCl\textsubscript{2} and CuBr\textsubscript{2} had higher conductivities than that treated with the zwitterions, the OPVs with the latter exhibited saliently better photovoltaic efficiency than that with the former. In addition, the dark currents of the polymer PVs with the zwitterion-treated PEDOT:PSS films are remarkably lower than that of the polymer PVs with the CuCl\textsubscript{2}- and CuBr\textsubscript{2}-treated PEDOT:PSS films. This can be attributed to the presence of the small ions in the salt-treated PEDOT:PSS films [72,78].

The photovoltaic stability of the polymer PVs is also dependent on the PEDOT:PSS anode. The polymer PVs encapsulated with glass sheets were put in air and tested after 24 h. The photovoltaic efficiency of the PVs with the DMCSP-treated PEDOT:PSS anode decreased by 13% after 24 h, whereas that with the CuCl\textsubscript{2}-treated PEDOT:PSS anode exhibited a decreased in the photovoltaic efficiency of 42% under the same experimental conditions. The different stability can be attributed to the ion diffusion of small ions such as Cu\textsuperscript{2+} and Cl\textsuperscript{-} from the PEDOT:PSS film into the active P3HT:PCBM layer. Similar ion diffusion is however difficult for the zwitterions.
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

It seems that the photovoltaic efficiencies of the polymer PVs are inconsistent with the conductivities of the zwitterion-treated PEDOT:PSS films. The DDMAP-treated PEDOT:PSS film has a conductivity lower than the PEDOT:PSS films treated with the other two zwitterions, whereas the polymer PV with the DDMAP-treated PEDOT:PSS anode has the highest photovoltaic efficiency. This can be attributed to the different morphologies of the PEDOT:PSS films treated with different zwitterions. Device performance depends not only on the conductivity of anode but also on the roughness of the anode surface [90,91]. Though the PEDOT:PSS film treated by DDMAP has the lowest conductivity among the
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

PEDOT:PSS films treated with the three zwitterions, it has the smoothest surface as revealed by AFM as shown in Figure 3.6. This is further confirmed by putting a MoO₃ layer of 6 nm in thickness as the buffer layer between a zwitterion-treated PEDOT:PSS film and the active P3HT:PCBM layer. Such a buffer layer can make the electrode surface smoother and help the charge collection [92-94], The performance of the devices was improved after adding the MoO₃ buffer layer (Figure 3.13). The polymer PVs with PEDOT:PSS films treated with the three zwitterions exhibited quite similar photovoltaic performance. The device with the DDMAP-treated PEDOT:PSS film as the anode exhibited the highest photovoltaic performance: $J_{sc}$ of 9.49 mA cm⁻², $V_{oc}$ of 0.56 V, $FF$ of 0.47, and PCE of 2.48%. The PCEs of the OPVs with DMCSP- and DNSPN-treated PEDOT:PSS films as the anode were significantly improved to 2.22% and 2.28%, respectively.

3.5 Conclusions

The conductivity of PEDOT:PSS films could be significantly enhanced to close to 100 S/cm through a treatment with aqueous solutions of zwitterions. The mechanism for the conduction enhancement is attributed to the zwitterion-induced charge screening. The zwitterions effectively screen the coulombic attraction between the PEDOT and PSS chains, resulting in PSSH loss from the PEDOT:PSS film and the conformational change of PEDOT chains. The zwitterion-treated PEDOT:PSS films
3. Highly conductive PEDOT:PSS films prepared through a treatment with zwitterions

have a low ion diffusion due to the bulky size and the two opposite charges in the same molecule of the zwitterion. They are more suitable to replace ITO as the anode of PVs than PEDOT:PSS films treated with normal salts. Photovoltaic efficiency as high as 2.48% was achieved on the P3HT:PCBM PVs with zwitterion-treated PEDOT:PSS films as the anode.
Chapter 4

Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

4.1 Introduction

In 1998, Aleshin et al. reported that the conductivities of PEDOT:PSS films were dependent on the pH value of the solutions from which the films were cast [23]. They improved the conductivity of PEDOT:PSS film by altering the pH value of the PEDOT:PSS aqueous solution using hydrochloric acid (HCl) and sodium hydroxide (NaOH). It was shown that the conductivity increased from pH=3 and peaked at pH=1.2. The highest conductivity obtained was approximately 20 S/cm. When the pH value was further increased, the conductivity of PEDOT:PSS started to decrease and finally fell to $5.5 \times 10^{-2}$ S/cm at pH = 12.2. Therefore, we study the acid effect on the
conductivity enhancement of PEDOT:PSS.

In this chapter, we report a new method to significantly enhance the conductivity of PEDOT:PSS. The conductivity of the PEDOT:PSS film could be enhanced from 0.2 to over 200 S/cm, 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. [23].

### 4.2 Experimental procedure

The PEDOT:PSS films were prepared by spin-coating the PEDOT:PSS aqueous solution on 1.3 × 1.3 cm² glass substrates, which were pre-cleaned by detergent, de-ionized (DI) water, acetone and isopropyl alcohol in sequence. The PEDOT:PSS films were dried at 110 °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 μL of acid solution on a PEDOT:PSS film on a hot plate at 140 °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 °C for about 10 min again. The preparation and acid treatment of the PEDOT:PSS films were carried out in air.

The characterization of acid-treated PEDOT:PSS films and the fabrication of polymer PVs are the same as that of salt-treated PEDOT:PSS films in Chapter 2.

4.3 Results and discussion

4.3.1 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 °C on a hot plate. Both organic acids, including acetic acid (CH₃COOH), propionic acid (CH₃CH₂COOH), butyric acid (CH₃(CH₂)₂COOH), and oxalic acid (HOOCCOOH), and inorganic acids, including hydrochloric acid (HCl) and sulfurous acid (H₂SO₃), 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
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

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 4.1). 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 for an as-prepared PEDOT:PSS film, and increased to 2 and 10 S/cm after the treatment with 0.1 and 1 M acetic acid, respectively. The maximum conductivity reached 190 S/cm 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 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 after the PEDOT:PSS films were 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 for the PEDOT:PSS film treated with 0.8 M oxalic acid.

**Figure 4.1** 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

The organic acids used in the treatment are carboxylic acids, and they are weak acids as indicated by their $pK_a$ values (Table 4.1). 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 [74,95-98]. 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.

Table 4.1 $pK_a$ and physical parameters of acids used in this study.

<table>
<thead>
<tr>
<th>acid</th>
<th>$pK_a^{a}$</th>
<th>melting point ($^\circ$C)</th>
<th>boiling point ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>-8.0</td>
<td>-27.3</td>
<td>110 ($^\circ$C)</td>
</tr>
<tr>
<td>H$_2$SO$_3$</td>
<td>$pK_{a1} = 1.9$, $pK_{a2} = 7.0$</td>
<td>Release SO$_2$ when heated</td>
<td></td>
</tr>
<tr>
<td>HOOC$_2$COOH</td>
<td>$pK_{a1} = 1.23$, $pK_{a2} = 4.28$</td>
<td>182-190</td>
<td>150 (sublimation)</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>4.75</td>
<td>16.6</td>
<td>118</td>
</tr>
<tr>
<td>CH$_3$CH$_2$COOH</td>
<td>4.87</td>
<td>-22</td>
<td>141</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$COOH</td>
<td>4.82</td>
<td>-7.9</td>
<td>164</td>
</tr>
</tbody>
</table>

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

The PEDOT:PSS films were also treated with inorganic acids, and significant conductivity enhancement was observed as well (Figure 4.1(b)). The maximum conductivities were 142 and 193 S/cm 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. [23]. They reported that the highest conductivity was 20 S/cm by adjusting the pH value of the PEDOT:PSS aqueous solution to 1 with HCl.

**4.3.1.1 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 4.2(a) 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 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 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 120-160 °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 120-160 °C as well. As shown in Table 4.1, 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 [72,78]. 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![Graph showing the conductivity of PEDOT:PSS films treated with sulfuric acid and hydrochloric acid.](image)

**Figure 4.2** Dependence of the conductivities of PEDOT:PSS films on the temperature during the treatment with (a) organic acids and (b) inorganic acids.

### 4.3.1.2 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 4.3**). The configuration for the resistance measured is schematically shown in the inset of **Figure 4.3**(a). 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 4.3 is less than in Figure 4.1. Thus, the absolute transient resistances were not very meaningful but their change during the acid treatment provided important information for the understanding 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![Graph](image.png)

**Figure 4.3** 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 shows the configuration for the resistance measurements.

**Figure 4.3** (a) 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 4.3(b)). 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 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

4.3.1.3 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 4.4). 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 (Eq. (2.1)). The $T_0$ value obtained by fitting the temperature dependences of the resistances of the PEDOT:PSS films are 2660, 1211, 1011, 639, and 405 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/cm 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![Graph showing normalized resistivity vs. T^1/2](image)

**Figure 4.4** 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.

4.3.1.4 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 4.5**. 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![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.](image)

**Figure 4.5** 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.

The two absorption bands in the UV range from 180 to 260 nm originate from PSS in PEDOT:PSS [35]. 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.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

**Figure 4.6** 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.

The PEDOT:PSS before and after treatment with various acids were studied by the FTIR spectroscopy as well (**Figure 4.6**). 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 [99,100]. 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 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.

![Graph showing XPS of PEDOT:PSS films untreated and treated with different acids](image)

**Figure 4.7** $S_{2p}$ XPS of PEDOT:PSS films untreated and treated with 0.6 M sulfurous acid and 6 M butyric acid.

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 4.7). 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 [20,66]. 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
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

the loss of PSS from the PEDOT:PSS films after the acid treatment.

4.3.1.5 Morphology of PEDOT:PSS films

The morphology of the PEDOT:PSS films was studied by AFM before and after acid treatment. Figure 4.8 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.

Figure 4.8 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 μm.

The morphology of the PEDOT:PSS films after treating with pure propionic acid and pure butyric acid were also studied by AFM (Figure 4.9). These films were quite smooth and similar to the AFM image of the as-prepared PEDOT:PSS film. These
4.4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

AFM images are consistent with the conductivity of the PEDOT:PSS films after the acid treatment.

Figure 4.9 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.

4.3.2 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 4.10 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.

![Figure 4.10 SEM images of PEDOT:PSS films treated with (a) 8 M propionic acid and (b) 6 M butyric acid.](image)

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 4.11. The conductivity enhancement of the
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

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 about 6.7 S/cm. 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).

![Figure 4.11 Proton concentrations of acids with different concentrations.](image-url)
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 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. 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
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
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

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.

4.3.3 Application of highly conductive PEDOT:PSS in polymer PVs

The acids used are easily removed from the PEDOT:PSS films by heating and no ions remain on the film. Hence, they are more suitable as the transparent electrode of optoelectronic devices than salt-treated PEDOT:PSS films. The work functions of the acid-treated PEDOT:PSS films were around 5.3 eV as determined by ultraviolet photoelectron spectroscopy (UPS), which was even higher than that (5.2 eV) of the untreated PEDOT:PSS film. This high work function can help the hole collection in polymer PVs. Figure 4.12 presents the transmittance spectra of acid-treated PEDOT:PSS films in the visible range. The transmittance of the 110 nm-thick PEDOT:PSS films are around 82% at 550 nm.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![Transmittance of 110nm-thick acid-treated PEDOT:PSS film.](image)

**Figure 4.12** Transmittance of 110nm-thick acid-treated PEDOT:PSS film.

The architecture of the polymer PVs is the same as that of PVs using salt-treated PEDOT:PSS anode discussed in Chapter 2. The active layer of the devices was a blend film of P3HT and PCBM, and the cathode was LiF/Al. The current density (J)-voltage (V) curves of these polymer PVs are presented in Figure 4.13. The photovoltaic parameters, including the short-circuit current (J\textsubscript{sc}), open-circuit voltage (V\textsubscript{oc}), fill factor (FF), and power conversion efficiency (PCE), are summarized in Table 4.2. The photovoltaic efficiencies of the polymer PVs with the acid-treated PEDOT:PSS films were reached 2.53% under AM 1.5 G illumination, which was much higher than that of the devices with salt- and zwitterion treated PEDOT:PSS film.
4. Significant conductivity enhancement of PEDOT:PSS films through a treatment with organic carboxylic acids and inorganic acids

![Graph showing J-V characteristics of polymer PVs glass|PEDOT:PSS|P3HT:PCBM|LiF|Al in dark and under illumination. The PEDOT:PSS films were treated with 14 M acetic acid and 6 M butyric acid, respectively.](image)

**Figure 4.12** $J-V$ characteristics of polymer PVs glass|PEDOT:PSS|P3HT:PCBM|LiF|Al in dark and under illumination. The PEDOT:PSS films were treated with 14 M acetic acid and 6 M butyric acid, respectively.

<table>
<thead>
<tr>
<th>Anode Conductivity</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid-PEDOT:PSS</td>
<td>190</td>
<td>8.18</td>
<td>0.56</td>
<td>0.51</td>
</tr>
<tr>
<td>butyric acid-PEDOT:PSS</td>
<td>138</td>
<td>8.68</td>
<td>0.56</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Table 4.2** Photovoltaic performances of polymer PVs with acid-treated PEDOT:PSS films as the anode.
4.4 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, 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 that significant conductivity enhancement has been observed by treating a conducting polymer with weak acids. Photovoltaic efficiency as high as 2.53% was achieved on the P3HT:PCBM PVs with acid-treated PEDOT:PSS films as the anode.
Chapter 5

PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

5.1 Introduction

One of the methods reported to improve the conductivity of PEDOT:PSS film is to add a polar organic compound with high boiling point, such as ethylene glycol or dimethyl sulfoxide (DMSO), into PEDOT:PSS aqueous solution [25,26,35-42]. Similar conductivity enhancement was also observed when a PEDOT:PSS film was treated with such an organic compound. The organic solvent was the sole reason for the conductivity enhancement, while water did not contribute to the conductivity enhancement in these methods. In addition, the conductivity did not change remarkably when a organic solvent with a low boiling point like acetone, ethanol, iso-propyl alcohol (IPA), acetonitrile (ACN), or tetrahydrofuran (THF), was added into the PEDOT:PSS aqueous solution.
In this chapter, we report the significant conductivity enhancement observed on PEDOT:PSS films through a treatment with a cosolvent of water and an organic solvent like methanol, ethanol, IPA, ACN, acetone, or THF. The conductivity enhancement by the cosolvent treatment was attributed to the preferential solvations of the PEDOT and PSS chains with the cosolvents. The organic solvents and water in the cosolvents preferentially solvate the hydrophobic PEDOT and hydrophilic PSSH, respectively. The organic solvents used in this research are easy to be removed and recycled due to their low boiling points, and the cosolvent-treated PEDOT:PSS films are quite smooth, which is good for the application as the electrode of many electronic devices. We also demonstrated the application of these highly conductive PEDOT:PSS films as the transparent electrode of polymer photovoltaic cells (PVs).

5.2 Experimental procedure

The PEDOT:PSS films were prepared by spin-coating the PEDOT:PSS aqueous solution on $1.3 \times 1.3$ cm$^2$ glass substrates, which were pre-cleaned by detergent, de-ionized (DI) water, acetone and isopropyl alcohol in sequence. The PEDOT:PSS films were dried at 110 °C on a hot plate for 30 min. The film thickness was ca. 130 nm. The treatment with a cosolvent was performed by dropping 100 μL cosolvent on a PEDOT:PSS film on a hot plate at 140 °C. The film dried after about 5 min.

The characterization of acid-treated PEDOT:PSS films and the fabrication of
polymer PVs are the same as that of salt-treated PEDOT:PSS films in Chapter 2.

5.3 Results and discussion

5.3.1 Cosolvent-induced conductivity enhancement of PEDOT:PSS films

The conductivity of PEDOT:PSS film was significantly enhanced after the treatment with a cosolvent of water and an organic solvent like methanol, ethanol, IPA, ACN, acetone or THF (Figure 5.1). For example, the conductivity of the PEDOT:PSS film increased from 0.2 S/cm to 79 S/cm after a treatment with a cosolvent of 80% ACN-20% water (the percentages refer to the volume fractions). The conductivity depended on the volume fraction of the organic solvents in the cosolvents. At first, it increased with the increasing volume fraction of the organic solvents in the cosolvents. Maximum conductivities were observed at volume fractions of 70-90%, slightly changing with different organic solvents. Then, the conductivity decreased with the further increase in the volume fraction of the organic solvents in the cosolvents.
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

Figure 5.1 Conductivities of PEDOT:PSS films after treated with cosolvents of water and organic solvents. The organic solvents are (a) methanol, ethanol, IPA, and (b) ACN, acetone, and THF.
The conductivity did not change too much when a PEDOT:PSS film was treated with water or a neat organic solvent. It slightly increased to 0.4 S/cm and 0.6 S/cm after the PEDOT:PSS films were treated with neat ACN and water, respectively. In addition, when an organic solvent like methanol, ethanol, IPA, ACN, acetone or THF was added into the PEDOT:PSS aqueous solution, no conductivity enhancement was observed. These results indicate that the cosolvent-induced conductivity enhancement of PEDOT:PSS is different from the treatment with a polar solvent of high boiling point like ethylene glycol or DMSO, on which the conductivity is significantly enhanced either by directly adding the solvent into the PEDOT:PSS aqueous solution or treating a PEDOT:PSS film with a neat organic solvent [25,41].

The conductivity enhancement is dependent on the chemical structure of the organic solvents in the cosolvents. The maximum conductivity of PEDOT:PSS reached 73 S/cm after treated with a cosolvent of 80% ethanol-20% water, while it was only 42 S/cm with 80% IPA-20% water. The six organic solvents can be classified into two groups in terms of their chemical structure (Table 5.1). The alcohols, including methanol, ethanol and IPA, are in the first group. ACN, acetone and THF do not have an OH group, and they belong to the second group. There is no remarkable difference in the conductivity enhancement with the two groups of organic solvents. Hence, OH group is not a requisite in organic solvent for the conductivity enhancement. Some physical properties of the organic solvents are listed in Table 5.1 to identify the factors affecting the conductivity enhancement. In general, the maximum conductivities are consistent with the dielectric constants of the organic
solvents. A cosolvent with an organic solvent of high dielectric constant like ACN or ethanol generally give rise to a conductivity enhancement higher than that of low dielectric constant like THF or IPA.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>Dielectric constant [a]</th>
<th>Boiling point (°C)</th>
<th>Absolute viscosity (cp)</th>
<th>Conductivity (S cm⁻¹) [b]</th>
<th>Conductivity (S cm⁻¹) [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>CH₃OH</td>
<td>32.6</td>
<td>64</td>
<td>0.6</td>
<td>14.8</td>
<td>69.7</td>
</tr>
<tr>
<td>ethanol</td>
<td>CH₃CH₂OH</td>
<td>22.4</td>
<td>78</td>
<td>1.1</td>
<td>1.5</td>
<td>72.7</td>
</tr>
<tr>
<td>IPA</td>
<td></td>
<td>18.3</td>
<td>82</td>
<td>2.0</td>
<td>1.9</td>
<td>42</td>
</tr>
<tr>
<td>ACN</td>
<td></td>
<td>37.5</td>
<td>82</td>
<td>0.4</td>
<td>0.4</td>
<td>78.9</td>
</tr>
<tr>
<td>acetone</td>
<td></td>
<td>20.6</td>
<td>56</td>
<td>0.3</td>
<td>1.2</td>
<td>47.1</td>
</tr>
<tr>
<td>THF</td>
<td></td>
<td>7.6</td>
<td>66</td>
<td>0.6</td>
<td>0.4</td>
<td>40.9</td>
</tr>
<tr>
<td>water</td>
<td>H₂O</td>
<td>79.7</td>
<td>100</td>
<td>0.9</td>
<td>0.6</td>
<td>/</td>
</tr>
</tbody>
</table>

[a] The dielectric constant values of neat solvents obtained from Ref. [103]. [b] Conductivity of PEDOT:PSS after treated with a neat solvent. [c] Conductivity of PEDOT:PSS after treated with a cosolvent of water and organic solvent.

The temperature during the treatment also affected the conductivity. As shown in Figure 5.2, the optimal temperatures corresponding to the highest conductivity enhancement were in the temperature range of 120-180 °C. The conductivity was increased to 103 S/cm for the PEDOT:PSS film treated with cosolvent of 80% ACN-20% water at 180 °C. The optimal temperatures are much higher than the boiling points of both water and the organic solvents. The boiling points of the
cosolvents are not higher than the boiling point of neat water [104]. The optimal temperatures coincide with that by a treatment with a salt, a zwitterions or an acid [72,78,101,102]. The optimal temperature increased from acetone to methanol to ethanol and ACN, which is consistent with the boiling points of these organic solvents. This indicates that the low boiling point of the organic solvents may be the reason for the high volume fraction of the organic solvents required in the optimal cosolvents corresponding to the maximum conductivity enhancement. In addition, the conductivity of a PEDOT:PSS film was enhanced to 73 S/cm after a treatment with a cosolvent of 80% ethanol-20% water. It further increased to 84 S/cm if the treated PEDOT:PSS film was treated with the cosolvent of 80% ethanol-20% water again.

![Conductivity vs. Treating Temperature](image_url)

**Figure 5.2** Variations of the conductivities of cosolvent-treated PEDOT:PSS films with the temperature during the treatments with cosolvents of 80% organic solvents-20% water. The organic solvents are indicated in the figure.
The dynamic process of the cosolvent treatment was studied by monitoring the resistances of the PEDOT:PSS films during the treatments (Figure 5.3). The configuration for the resistance measurement is schematically presented in the inset of Figure 5.3(b). Indium (In) was pressed at the four corners of each PEDOT:PSS film at room temperature, which was used to facilitate the electrical contact. A solvent or cosolvent was dropped at the center of a PEDOT:PSS film at 160 °C. It did not touch the indium at the corners, so that the areas of the PEDOT:PSS film under indium were not treated by the cosolvents. The value of the transient resistances was not very meaningful. But their change provided important information for the dynamic change during the cosolvent treatment.

![Graph](image-url)
Figure 5.3 Transient resistances of PEDOT:PSS films during treatments with (a) neat water, neat ethanol and cosolvents of ethanol-water and (b) neat ethanol, neat ACN, 80% ethanol-20% water, and 80% ACN-20% water at 160 °C. The volume fractions of the organic solvents in the cosolvents are indicated in figure. The resistances were normalized to the resistance of the as-prepared PEDOT:PSS film. The inset in (b) shows the configuration for the resistance measurements.

Figure 5.3(a) presents the transient resistances of PEDOT:PSS films during the treatments with water, ethanol, and cosolvents of ethanol-water. A big hump was observed on the transient resistances during the treatment with neat water or ethanol. The resistance firstly increased and finally fell. The hump width for the water treatment was saliently larger than for the ethanol treatment. The transient resistances also exhibited a hump but some significant differences could be observed, when a cosolvent of 20% ethanol-80% water was used. The resistance increase was less than with the neat water or ethanol treatment, and the hump width was between the
treatments with neat water and ethanol. The transient resistance at first decreased and then exhibited a small hump when the volume fraction of ethanol was increased to 50% in the cosolvent. No hump was observed on the transient resistances of the PEDOT:PSS film treated with a cosolvent of 80% ethanol-20% water. The resistance increases during the treatments can be attributed to weakening inter-PEDOT chains as the result of the swelling of the PEDOT:PSS films with the solvents, that is, the solvation of the polymer chains. The faster resistance increase during the neat ethanol treatment than during the neat water treatment suggests that the solvation of the polymer chains with ethanol is faster than with water. Presumably, this is related to the preferential solvations of hydrophobic PEDOT chains and hydrophilic PSSH chains by the solvents. The preferential solvation does not suggest the separation of the two components of the cosolvent but PEDOT or PSS is surrounded dominantly by one component [105]. In terms of polarities of water and ethanol, ethanol preferentially solvates PEDOT, whereas water preferentially solvates PSSH. The ethanol solvation of the PEDOT chains can immediately affects the charge transport, while the water solvation of PSSH can affect the charge transport only after it can weaken the inter-PEDOT interaction. The significant change of the transient resistances from the neat solvent treatment to the cosolvent treatment can be attributed to the synergetic effects by both ethanol and water.

Cosolvents with other organic solvents also showed a similar effect on the transient resistances of PEDOT:PSS during the treatments. Figure 5.3(b) illustrates the transient resistances of PEDOT:PSS during the treatments with two cosolvents,
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

80% ethanol-20% water and 80% ACN-20% water. The transient resistances during the treatments with the neat solvents are presented as well for comparison. The resistance hump during the treatment with neat ethanol was narrower than with neat ACN. But the transient resistances during the treatments with the two cosolvents have almost the same behavior.

5.3.2 Characterization of PEDOT:PSS films

The PEDOT:PSS films before and after the cosolvent treatment were characterized to understand the mechanism for the conductivity enhancement. At first, they were studied by the UV-Vis-NIR absorption spectroscopy. A cosolvent treatment remarkably affected the absorption only in the UV range (Figure 5.4). This is similar to the effect of the treatment of PEDOT:PSS with polar solvent of high boiling point on the absorption [58]. The intensity of two absorption bands that originate from PSS dropped after a treatment with a cosolvent. This intensity decrease cannot be attributed to the loss of PSSH from the PEDOT:PSS films, because the cosolvents were removed from the PEDOT:PSS films by heating and the treated PEDOT:PSS films were not rinsed with any solvent. Thus, the absorption drop should be due to a solvent-induced change in the morphology of the PEDOT:PSS films. This conclusion was interpreted by a simple model in the following.
As shown in Figure 5.5, the light absorption \( A \) is determined by the intensities of the incident \( I_{in} \) and transmitted \( I_{out} \) lights in terms of the Beer-Lambert law,

\[
A = -\log_{10}(I_{out}/I_{in}) = \alpha l,
\]

where \( \alpha \) and \( l \) are the absorption coefficient and the thickness of the sample, respectively, when a sample uniformly covers the substrate as in Figure 5.5(a). The absorbance changes when the sample coverage is not uniform. Simply assume that the sample of the same volume covers only half of the substrate, the thickness of the sample will increase to \( 2l \) (Figure 5.5(b)), and the intensity of the transmitted light will become

\[
I_{out}' = (0.5 + 0.5 \times 10^{-2\alpha l}) I_{in}.
\]
Thus, \( \frac{I_{\text{out}}'}{I_{\text{out}}} = 0.5 \times (10^{\alpha l} + 10^{-\alpha l}) \). \( \alpha l > 0 \), leading to \( 10^{\alpha l} + 10^{-\alpha l} > 2 \), consequently \( I_{\text{out}}' > I_{\text{out}} \).

This simple model can be used to understand the cosolvent effect on the absorption of PEDOT:PSS. When the PSSH chains uniformly disperse in a PEDOT:PSS film, the light absorption can be modeled as in Figure 5.5(a). When PSSH chains aggregate, their dispersion becomes non-uniform, and its light absorption can be somewhat modeled as in Figure 5.5(b). Thus, the absorption decrease of PEDOT:PSS after a cosolvent treatment suggests the aggregation of the PSSH chains.

![Figure 5.5 Light transmittances through a substrate with a sample covering (a) the whole and (b) half of the substrate. The white and the gray rectangles are for the substrate and the sample, respectively. The solid and broken arrows stand for the incident and the transmitted lights, respectively.](image)

The aggregation of the PSS chains is confirmed by the scanning electron microscopy (SEM) of PEDOT:PSS (Figure 5.6). Sometimes, white patches visible in eye appeared on some cosolvent-treated PEDOT:PSS films. These patches could be rinsed away with water, and they had sulphur atoms as indicated by energy-dispersive X-ray spectroscopy (EDX). This phenomenon was also observed after the acid
treatment [102]. Presumably, these patches are made of PSSH, which indicates that the cosolvents can induce the phase separation of some PSSH chains from PEDOT:PSS films. The phase separation of PSSH chains is the result of the PSSH aggregation. The PSS chains remaining in the PEDOT:PSS film can aggregate as well.

The smooth areas of the PEDOT:PSS films free of the white patches were further characterized with atomic force microscopy (AFM) in the height mode. As shown in Figure 5.7, both the untreated and cosolvent-treated PEDOT:PSS films were quite smooth. The roughnesses were 1.06 nm, 1.271 nm, 1.124 nm, and 1.268 nm for the untreated and 80% ethanol-20% water-treated, 80% acetone-20% water-treated, and 80% THF-20% water-treated PEDOT:PSS films, respectively. These results are different from the treatment of the PEDOT:PSS films with a polar organic solvent of high boiling point, which gives rise to a remarkable increase in the roughness of the PEDOT:PSS film [41]. Though the film roughness almost did not change, some
differences in the AFM images could be observed.

![AFM images of PEDOT:PSS films](image)

**Figure 5.7** AFM height images of PEDOT:PSS films (a) untreated and after treated with (b) 80% ethanol-20%water, (c) 80% acetone-20%water, and (d) 80% THF- 20%water. The unit for the AFM images is μm. All the images have the sample height scale.

The loss of PSS chains and the morphological change can affect the charge transport across the PEDOT chains. This was studied by the temperature dependences of the resistivities of untreated and treated PEDOT:PSS films. The resistivities of the PEDOT:PSS films were measured from 313 K down to 110 K (**Figure 5.8**). The temperature dependences of the resistivities can be fitted by the one-dimensional variable range hopping (VRH) model (**Eq. (2.1)**) The $T_0$ value obtained by remarkably decreased for the PEDOT:PSS film after a cosolvent treatment. It was
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

2660 K for the untreated PEDOT:PSS film, and it decreased to 1648, 1250, and 860 K for the PEDOT:PSS films treated with cosolvents of 80% acetone-20% water, 80% methanol-20% water, and 80% ethanol-20% water, respectively. The \( T_0 \) values are consistent with the conductivities of these PEDOT:PSS films at room temperature, which are 0.2, 47.1, 69.7 and 73/S cm for the untreated, 80% acetone-20% water, 80% methanol-20% water, and 80% ethanol-20% water-treated PEDOT:PSS films, respectively. Obviously, \( T_0 \) decreases with the increasing conductivity. It suggests that the cosolvent treatment lowers the energy barrier for the charge transport across the PEDOT chains and increases the localization length.

Figure 5.8 Temperature dependences of the normalized resistances of PEDOT:PSS films (a) untreated and treated with a cosolvent of (b) 80% acetone-20% water, (c) 80% methanol-20% water, and (d) 80% ethanol-20% water. The resistances are normalized to that of the corresponding PEDOT:PSS films at 110 K.

The electrochemical activity of a PEDOT:PSS film is quite sensitive to chain
conformation [41]. The cosolvent-treated PEDOT:PSS films were investigated by CV in a 0.1 M NaCl aqueous solution with Ag/AgCl as the reference electrode. Figure 5.9 presents the CVs of PEDOT:PSS films treated with a cosolvent of 80% ethanol-20% water and untreated film. The CVs of PEDOT:PSS films treated with other cosolvents are similar to that of the PEDOT:PSS film treated with the cosolvent of 80% ethanol-20% water, and so they are not shown. The PEDOT:PSS film exhibited electrochemical activity only at potential higher than -0.2 V before the treatment, while additional electrochemical activity appeared at the potential range below -0.2 V after the treatment. The change in the electrochemical behavior is similar to that of PEDOT:PSS treated with ethylene glycol and zwitterion [41,101]. It can be attributed to the decreasing PSSH shell and the conformational change of the PEDOT chains after the cosolvent treatment.

![Figure 5.9 Cyclic voltammograms of PEDOT:PSS films untreated (dashed curve) and treated with 80% ethanol-20% water (solid curve).](image-url)
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

5.3.3 Mechanism for cosolvent-induced conductivity enhancement

The above results indicate that a cosolvent treatment induces the detachment of PSS from PEDOT or conformational change of PSSH and facilitates the inter-PEDOT chain charge transport. On the other hand, the conductivity was not remarkably enhanced when a PEDOT:PSS film was treated with neat water or a neat organic solvent. Directly adding any of these organic solvents into the PEDOT:PSS aqueous solution does not result into a significant conductivity enhancement. A mechanism account for the cosolvent-induced conductivity enhancement should provide a reasonable explanation for all these results.

There is excess PSSH in PEDOT:PSS aqueous solution to enable a stable dispersion in water because water is a bad solvent for the hydrophobic PEDOT chains. PEDOT chains attach to a PSSH chain through the Coulombic attraction. PEDOT:PSS is a polyelectrolyte, and the conformation of polyelectrolytes in solvents has been extensively studied [108-111]. On the base of the literature, we believe that the conformation of a PSSH chain attached with PEDOT chains can have a necklace conformation. There are principally two types of conformations for the PSS segments because of the different Coulombic interactions and the polymer/water interactions. The Coulombic repulsions among the PSS anions for the PSS segments attached with PEDOT are screened by the positive charges on PEDOT, so that these PSS segments together with attached PEDOT chains have a coiled conformation. The PSSH segments form blobs to prevent the contact of PEDOT from water, leading to
minimum interactions between PEDOT and water (Figure 5.10(a)). On the other hand, the PSSH segments without PEDOT attached dissociate into PSS anions and protons. These PSS segments adopt a linear conformation to minimize the Coulombic repulsions among the PSS anions. They serve as the strings between blobs. Moreover, the PSS anions in the shell of each blob try to repulse it away from other blobs. Hence, the blobs try to have separations as far as possible to lower the Coulombic repulsions among them. This necklace structure, which is similar to that proposed by Lang et al., [18] is conserved in the as-prepared PEDOT:PSS film from the aqueous PEDOT:PSS solution.

![Conformations of PEDOT:PSS](image)

Figure 5.10 Conformations of PEDOT:PSS (a) before and (b) after a cosolvent treatment. The thin and thick curves stand for PSS and PEDOT chains, respectively

When an as-prepared PEDOT:PSS film is treated with a cosolvent like ethanol-water, the hydrophobic PEDOT and hydrophilic PSSH chains are preferentially solvated with ethanol and water, respectively [105]. The PEDOT chains
are surrounded dominantly by an organic solvent, while the PSS chains by water, and PEDOT and PSS are separated by the colvent. The solvents solvating the two polymer chains effectively screen the Coulombic attraction between PEDOT and PSS. Consequently, the Coulombic repulsions among the positive (or negative) charges in the PEDOT (or PSS) chain become the dominant factor for the chain conformation, so that both PEDOT and PSS change to the linear or extended-coil conformation. Figure 5.10(b) schematically illustrates this conformation, which is similar to the conformation of PEDOT:PSS after a treatment with ethylene glycol [41]. We also need to point out that only some PEDOT chains change to the linear or extended-coil conformation after the treatment, because no ordered structure was observed by the X-ray diffraction study of the cosolvent-treated PEDOT:PSS films. The linear PEDOT chains can have stronger inter-chain interactions, which can help the inter-chain charge transport. Obviously, the screening of the Coulombic attraction between PEDOT and PSS is affected by the dielectric constant of the organic solvent. This can explain the more significant conductivity enhancement by a cosolvent with an organic solvent of higher dielectric constant.

Besides solvating the PEDOT chains, the presence of an organic solvent in water lowers the dissociation of PSSH into PSS anion and proton [112,113]. Thus, the Coulombic repulsions among the PSS anions in the same polymer chain are greatly reduced, giving rise to the conformational change of the PSSH segments without PEDOT attached from a linear to coiled conformation (Figure 5.10(b)). These PSSH segments aggregate, that is, the dispersion of PSSH in the PEDOT:PSS film becomes
non-uniform. The coiled PSSH segments can facilitate the phase separation of PSSH chains from the PEDOT:PSS film. Moreover, a less dissociated PSSH chain experiences much less Coulombic attraction with PEDOT when it leaves from a PEDOT:PSS film.

The preferential solvations of both the PEDOT and PSSH chains by organic solvent and water are important for the conformational changes of the polymer chains and the phase separation of PSSH from PEDOT:PSS. A neat solvent like ethanol, IPA, ACN, acetone or THF can not effectively solvate PSSH, so that it can not give rise to a significant conductivity enhancement. Methanol seems an exception as the conductivity of PEDOT:PSS can be improved to 13 S/cm after a neat methanol treatment though it is less significant than its cosolvent with water. Compared with other organic solvents, methanol is closer to water. It may solvate both the PEDOT and PSS chains, so that some conductivity enhancement even occurs when the PEDOT:PSS film is treated with neat methanol. On the other hand, a water treatment of a PEDOT:PSS film did not result into significant conductivity enhancement, because water could not solvate the hydrophobic PEDOT chains. When a cosolvent-treated PEDOT:PSS film was treated with water again, the conductivity decreased by about 30%. This is attributable to partially reverse conformational changes of the PEDOT and PSS chains caused by the solvation of PSSH with water.
The cosolvent-induced conformational changes of the PEDOT and PSS chains are supported by the AFM phase images of PEDOT:PSS films before and after a
cosolvent treatment (Figure 5.11). There are remarkable differences in the AFM phase images before and after the cosolvent treatments. As pointed out by Crispin et al. and Hsiao et al. [37,40], the bright regions in an AFM phase image are hard domains corresponding to PEDOT, whereas the dark regions denote the soft structure arising from excess PSS. The PEDOT domains appearing as separate domains in the AFM phase image of the untreated PEDOT:PSS film become continuous, whereas the segregation of dark PSS domains turns to be remarkable after the cosolvent treatment. The cosolvent-induced changes in the AFM phase image evidence the conformational changes of both PEDOT and PSS.

The reason that directly adding these organic solvents into the PEDOT:PSS aqueous solution does not induce a conductivity enhancement can be attributed to the difficulty for these organic solvents to enter the blobs rich in PEDOT because the shell of the blobs has already been solvated with water before the solvent addition. This becomes different for the PEDOT:PSS film which has no solvent prior to the solvent treatment. The organic solvents can diffuse into the PEDOT:PSS film as fast as water since they have comparable viscosities as presented in Table 5.1, so that both the PEDOT and PSS chains can be almost simultaneously solvated by different solvents.

The effect of the temperature during the treatment on the conductivity enhancement can be understood as the activation energy for the PSSH phase separation from PEDOT:PSS and the conformational change of PEDOT. At least the penetration of the organic solvents into the PEDOT-rich domain needs to overcome a
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certain energy barrier. This is evidenced by the effect of adding organic solvent into PEDOT:PSS aqueous solution. No conductivity enhancement and no polymer precipitation were observed when ethanol was added into PEDOT:PSS aqueous solution at room temperature. But conductivity slightly enhanced when the PEDOT:PSS aqueous solution added with ethanol was heated to 90 °C and processed at such a high temperature. In addition, polymer precipitation was observed after the solution was cooled down to room temperature. The polymer precipitation can be attributed to the screening of the Coulombic attraction between PEDOT and PSS as the result of the preferential solvation, because PEDOT is not stable in ethanol.

The effect of the temperature during the cosolvent treatment of PEDOT:PSS is different from the treatment with an organic solvent of high boiling point like ethylene glycol or dimethylsulfoxide (DMSO), on which significant conductivity enhancement can occur even at room temperature [42,58,106,107,114,115]. This indicates that the activation energy of the cosolvent treatment is higher. The energy barrier for DMSO to penetrate into the PEDOT-rich domains may be quite low, as evidenced by the precipitation of PEDOT:PSS after the addition of DMSO at room temperature. Besides the penetration of solvent into the PEDOT-rich domains, the phase separation of PSSH from PEDOT:PSS and the conformational change of PEDOT can affect the conductivity enhancement as well. These two processes are affected by the Coulombic interactions between PEDOT and PSS, the interaction of PSSH with solvent, and the thermal properties of PEDOT:PSS.
5.3.4 Application of high-conductivity PEDOT:PSS in polymer PVs

The organic solvents used in the cosolvents are much easier to be removed from the PEDOT:PSS films by heating than the polar organic solvents of high boiling point like ethylene glycol and DMSO. Furthermore, the cosolvent-treated PEDOT:PSS films are quite smooth. The white patches observed on some cosolvent-treated PEDOT:PSS films can be readily rinsed away with water. Hence, they are suitable as the transparent electrode of optoelectronic devices [40,42,45,61,106,107,114-120].

The thermal stability of PEDOT:PSS film is important to the device performance. The conductivity of the cosolvent-treated PEDOT:PSS film has no obvious change under heating at 80°C within 3 days (Figure 5.12). Figure 5.13 presents the transmittance spectra of cosolvent-treated PEDOT:PSS films in the visible range. The transmittance of the 130 nm-thick PEDOT:PSS film are about 89% at 550 nm. The transmittance are higher than 90% in the wavelength below 500 nm, and decrease a little but still higher than 80% at the wavelength over 550 nm. The work functions of the cosolvent-treated PEDOT:PSS films were around 5.3 eV as determined by ultraviolet photoelectron spectroscopy (UPS), which was even higher than that (5.2 eV) of the untreated PEDOT:PSS film. This high work function can help the hole collection in polymer PVs. The current density ($J$)-voltage ($V$) curves of these OPVs are presented in Figure 5.14. The $J$-$V$ curve of a control device with an untreated PEDOT:PSS film as the anode was presented as well. The photovoltaic parameters, including the short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), and power
conversion efficiency (PCE), are summarized in Table 5.2. The photovoltaic efficiencies of the polymer PVs with the cosolvent-treated PEDOT:PSS films were higher than 2.5% and close to 3% under AM 1.5 G illumination, which was much higher than that of the control device with the untreated PEDOT:PSS film.

Figure 5.12 Conductivity stability of 80% ethanol-20% water treated PEDOT:PSS film under heating at 80°C.
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

Figure 5.23 Transmittance of 130nm-thick cosolvent-treated PEDOT:PSS film.

Figure 5.13 $J-V$ characteristics of polymer PVs glass|PEDOT:PSS|P3HT:PCBM|LiF|Al in dark and under illumination. The PEDOT:PSS films were treated with cosolvents of 80% ethanol-20% water and 80% ACN-20% water, respectively.
5. PEDOT:PSS films with high conductivities induced by preferential solvation with cosolvents

### Table 5.2 Photovoltaic parameters and efficiencies of polymer PVs with untreated and cosolvent-treated PEDOT:PSS films as the anode.

<table>
<thead>
<tr>
<th>PEDOT:PSS anode</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol-water treated</td>
<td>72.7</td>
<td>8.99</td>
<td>0.61</td>
<td>0.52</td>
<td>2.87</td>
</tr>
<tr>
<td>ACN-water treated</td>
<td>78.9</td>
<td>7.84</td>
<td>0.63</td>
<td>0.51</td>
<td>2.51</td>
</tr>
</tbody>
</table>

### 5.4 Conclusions

The conductivity of the as-prepared PEDOT:PSS film was significantly enhanced by a treatment with a cosolvent of water and a common organic solvent like methanol, ethanol, IPA, ACN, acetone or THF. Conductivity enhancement from 0.2 S/cm to more than 100 S/cm was observed on PEDOT:PSS through a cosolvent treatment. The conductivity enhancement is attributed to the preferential solvations of the PEDOT and PSS chains with the cosolvents, which induces the phase separation of PSSH chains from the PEDOT:PSS film, the aggregation of the PSSH segments in the PEDOT:PSS film, and the conformational changes of the PEDOT chains. The cosolvent-treated PEDOT:PSS films are quite smooth and have high work functions. They are suitable to replace ITO as the transparent electrode of optoelectronic devices. Polymer PVs with the cosolvent-treated PEDOT:PSS films exhibited high photovoltaic performance. Photovoltaic efficiency close to 3% was achieved under AM1.5G illumination.
Chapter 6

Concluding remarks

6.1 Summary of results

In the thesis, four novel and effective methods were developed to significantly enhance the conductivity of PEDOT:PSS films. The conductivities of the PEDOT:PSS films treated with four methods and the efficiencies of the devices using these treated PEDOT:PSS films as anode are summarized in Table 6.1. The mechanisms for the conductivity enhancements were investigated, and the application of these highly conductive PEDOT:PSS films as the transparent electrode of polymer PVs were demonstrated. The major results are summarized as follows:

1) The first method was developed to significantly enhance the conductivity of PEDOT:PSS films through a treatment with solution of a certain salt. Conductivity enhancement by a factor of more than 1000 was observed when CuBr$_2$ or InI$_3$ aqueous solution was used. 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. The anions of the salts also affect the salt-induced conductivity enhancement of the PEDOT:PSS film. The anion effect on the conductivity enhancement of PEDOT:PSS is related to the competition of two processes, the dissociation of the salts and the association of the anions with PEDOT$^+$. A salt with a higher dissociation benefits the loss of more PSS chains from the PEDOT:PSS film after the salt treatment, so that it results into more significant conductivity enhancement.

(2) The second approach is to enhance the conductivity of PEDOT:PSS films through a treatment with aqueous solutions of zwitterions. The conductivity of PEDOT:PSS films could be significantly enhanced to close to 100 S/cm. The mechanism for the conduction enhancement is attributed to the zwitterion-induced charge screening. The zwitterions effectively screen the coulombic attraction between the PEDOT and PSS chains, resulting in PSSH loss from the PEDOT:PSS film and the conformational change of PEDOT chains. The zwitterion-treated PEDOT:PSS films have a low ion diffusion due to the bulky size and the two opposite charges in the same molecule of the zwitterion. They are more suitable to replace ITO as the anode of PVs than
PEDOT:PSS films treated with normal salts. Photovoltaic efficiency as high as 2.48% was achieved on the P3HT:PCBM PVs with zwitterion-treated PEDOT:PSS films as the anode.

(3) The third way is to enhance the conductivity of the PEDOT:PSS films by a treatment with various acids, including acetic acid, propionic acid, butyric acid, oxalic acid, sulfuric acid, and hydrochloric acid. The conductivity enhancement from 0.2 to over 200 S/cm, 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.

(4) The forth method is to treat PEDOT:PSS films with cosolvents. Conductivity enhancement from 0.2 S/cm to 103 S/cm was observed. The conductivity enhancement is attributed to the preferential solvations of the PEDOT and PSS chains with the cosolvents, which induce the phase separation of PSSH chains from the PEDOT:PSS film, the aggregation of the PSSH segments in the PEDOT:PSS film, and the conformational changes of the PEDOT chains. The cosolvent-treated PEDOT:PSS films are quite smooth and have high work
functions. They are suitable to replace ITO as the transparent electrode of optoelectronic devices. Polymer PVs with the cosolvent-treated PEDOT:PSS films exhibited high photovoltaic performance. Photovoltaic efficiency close to 3% was achieved.

Table 6.1 Conductivities of the PEDOT:PSS films treated with four methods and PCE values of the devices using these PEDOT:PSS films as anode.

<table>
<thead>
<tr>
<th>Method</th>
<th>Conductivity (S cm(^{-1}))</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>salt treatment</td>
<td>265</td>
<td>1.08</td>
</tr>
<tr>
<td>zwitterion treatment</td>
<td>92</td>
<td>2.08</td>
</tr>
<tr>
<td>acid treatment</td>
<td>210</td>
<td>2.53</td>
</tr>
<tr>
<td>cosolvent treatment</td>
<td>103</td>
<td>2.87</td>
</tr>
</tbody>
</table>

6.2 Future work

This thesis presents several methods on the conductivity enhancement of PEDOT:PSS films. The materials and the mechanisms for the conductivity were investigated by various experiments. The understanding acquired in this study provide guidance to further improve the conductivity of PEDOT:PSS film. Based on the understanding, the following ideas are proposed for future study:

(1) The mechanism for the conductivity enhancement presented in the thesis indicates that the conductivity can be affected by several factors, such as charge
screening, chain conformation, and interchain interaction. The conductivity of PEDOT:PSS film will be further improved if new materials or new methods could be found to further reduce the Coulombic attraction between the charge on PEDOT chains and the counter ions (PSS⁻), to get a planner chain conformation, and to further enhance the interchain interaction.

(2) The methods reported in the thesis can enhance the conductivity of PEDOT:PSS film by a factor of 1000. It is plausible that these methods should be applicable to other conducting polymers as well. Further study is needed to apply the methods to other conducting polymers, such as PANI, to further our knowledge and application of the methods on conductivity enhancement in conducting polymers.

(3) The application of these highly conductive PEDOT:PSS films as the transparent electrode of polymer PVs were demonstrated in the thesis. However, the polymer PVs were fabricated on glass substrate. It will be interesting if a flexible substrate is used to realize flexible ITO-free polymer PVs. Moreover, the potential applications of these highly conductive PEDOT:PSS films in other fields, such as the electrode of field-effect transistors, can be explored in the future.
Bibliography


[96] Li Y. Prog. Chem. 2002;14:207.


