On the mechanism of conductivity enhancement in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment

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Received 6 August 2004; received in revised form 22 September 2004; accepted 1 October 2004
Available online 22 October 2004

Abstract

The conductivity of a poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film is enhanced by more than 100-folds on adding some organic compounds into PEDOT:PSS aqueous solutions or by treating the PEDOT:PSS film with organic solvents, such as ethylene glycol (EG), 2-nitroethanol, methyl sulfoxide or 1-methyl-2-pyrrolidinone. The mechanism for this conductivity enhancement was studied through various chemical and physical characterizations. The PEDOT:PSS film which is soluble in water becomes insoluble after treatment with EG. This strongly suggests an increased interchain interaction among the PEDOT chains. Raman spectroscopy indicates that this increased interchain interaction results from conformational changes of the PEDOT chains, which change from a coil to linear or expanded-coil structure. The increased interchain interaction and conformation changes are further confirmed by the temperature dependence of conductivity and the electron spin resonance (ESR). It is found that EG treatment lowers the energy barrier for charge hopping among the PEDOT chains, lowers the polaron concentration in the PEDOT:PSS film by \(\sim 50\%\), and increases the electrochemical activity of the PEDOT:PSS film in NaCl aqueous solution by \(\sim 100\%\). Atomic force microscopy (AFM) and contact angle measurements show that the surface morphology of the PEDOT:PSS film changes as well after the EG treatment. Conductivity enhancement was also observed when other organic compounds were used, but it was strongly dependent on the chemical structure of the organic compounds, and observed only with organic compound with two or more polar groups. These experimental results support our proposal that the conductivity enhancement is due to the conformational change of the PEDOT chains and the driving force is the interaction between the dipoles of the organic compound and dipoles or charges on the PEDOT chains.

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Keywords: PEDOT:PSS; Conductivity; Solvent

1. Introduction

Recently, it was discovered that the conductivity of poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS, chemical structure in Scheme 1) film is enhanced by over 100-folds if a liquid or solid organic compound, such as methyl sulfoxide (DMSO), \(N,N\)-dimethylformamide (DMF), glycerol, or sorbitol, is added to the PEDOT:PSS aqueous solution [1–5]. This discovery is very important for fundamental studies and practical applications of conducting polymers, since PEDOT:PSS has become one of the most important conducting polymers, as, e.g., an important hole injecting and transporting material for organic light-emitting diodes (OLEDs) [6]. Aqueous PEDOT:PSS solution is commercially available. High-quality films can be easily formed on various substrates by conventional solution processing techniques, and they have excellent thermal stability and high transparency in the visible range. These merits render PEDOT:PSS a very promising candidate for various applications in electronic devices, such as flexible electrodes, buffer layers in OLEDs,
change is the interaction among the dipoles of the additive PEDOT chains and the driving force for the conformational enhancement is due to the conformational change of the PEDOT:PSS film. We proposed that the conductivity becomes very thin. Recently, through Raman spectroscopy that the insulating PSS layer around the conductive particles the EG reduces the conductive PEDOT:PSS particle size so positively charged PEDOT chains and negatively charged PSS chains, thus reducing the Coulomb interaction between them. Inganäs et al. observed conductivity enhancement when adding solid sorbitol into the PEDOT:PSS aqueous solution, but only after the film was baked at a high temperature [1]. They argued that the additive might act as a plasticizer to help reorient the PEDOT chains at high temperature. Jönsson et al. studied the effect of sorbitol and 1-methyl-2-pyrrolidinone (NMP) by X-ray photoelectron spectroscopy (XPS), and suggested that the conductivity is enhanced because the insulating PSS chains are washed away from the surface region of the PEDOT:PSS film during film formation, leaving a high-conductivity thin layer with a high amount of PEDOT chains on the surface [4]. Crispin et al. studied the conductivity enhancement by adding EG into PEDOT:PSS aqueous solution with XPS and AFM and proposed a modified scenario [5]. In this scenario, the EG reduces the conductive PEDOT:PSS particle size so that the insulating PSS layer around the conductive particles becomes very thin. Recently, through Raman spectroscopy of PEDOT:PSS film we proposed that the conductivity enhancement is due to the conformational change of the PEDOT chains and the driving force for the conformational change is the interaction among the dipoles of the additive and the dipole or charge on PEDOT chains in PEDOT:PSS film [16].

In this work, the conductivity enhancement mechanism was further studied by investigating the chemical structure of the additives and by studying the PEDOT:PSS film by various chemical and physical measurements. These experimental results provided further evidences for our proposed mechanism.

2. Experimental

The PEDOT:PSS films were formed on glass or silicon substrates by spin-coating or drop-casting the commercial PEDOT:PSS aqueous solution (Baytron P V4071, Bayer Corporation). The films were dried at 80 °C for 30–60 min in vacuum or in air before any further characterization.

The Raman spectra of the polymer films were taken in a back scattering configuration using a Renishaw 1000 Raman system with a 632.8 nm HeNe laser as the excitation source. The laser power was 0.2 mW and the resolution was 1 cm

-1. The room temperature conductivity of the polymer films was measured by the four-point probe technique using a Keithley 2400 Source Meter. The temperature dependence of the resistivity was determined using a Janis Research VPF-475 dewar with liquid nitrogen as coolant and a Conductus LTC-11 temperature controller. Electron spin resonance (ESR) was measured using a Bruker ER-200D X-band spectrometer. Atomic force microscope (AFM) images were obtained from a Digital Instruments NanoScope III equipped with an extender module box operating in tapping mode under ambient condition. The contact angle was measured with a March Instruments contact angle meter. The UV–Vis absorption spectra were taken using a Varian Cary 50 Conc spectrophotometer. Thick PEDOT:PSS films on glass substrates were used for the XPS and X-ray diffraction measurements. The dipole moments of 1,4-ethylidioxythiophene and thiophene were calculated by the semiempirical PM3 method provided by the HyperChem 7.5 program.

Cyclic voltammetry (CV) measurements were carried out with a Bioanalytical System CV-50W Voltammetric Analyzer in 0.1 M NaCl solution with a Pt disc coated with PEDOT:PSS film as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. The PEDOT:PSS film was coated by dropping PEDOT:PSS aqueous solution on the 1.6 mm diameter Pt disc, which was then dried in vacuum at 80–120 °C. After measuring the CVs, the PEDOT:PSS film was immersed in EG for 3 min and subsequently dried in vacuum at 80 °C. Then, CVs were carried out on this EG-treated PEDOT:PSS film again. In situ UV–Vis-NIR absorption spectra were taken by combining the BAS Voltammetric Analyzer with a Shimadzu UV-3101PC UV–Vis-NIR scanning spectrometer. An indium tin oxide (ITO) glass substrate (Colorado Concept Coatings LLC, surface resistivity...
25 Ω/□) coated with a PEDOT:PSS film was used as the working electrode. The reference and counter electrodes were the same as those for the CV measurements.

3. Results and discussion

3.1. EG treatment, solubility and Raman spectroscopy of PEDOT:PSS film

Other than the conductivity enhancement observed for a PEDOT:PSS film by adding EG into the PEDOT:PSS aqueous solution, conductivity enhancement was also observed after a dried PEDOT:PSS film was immersed in EG for a few minutes. The conductivity of PEDOT:PSS film was enhanced from 0.4 to 200 S/cm. (PEDOT:PSS treated with EG is henceforth denoted as EG-PEDOT:PSS). This conductivity enhancement was observed for the EG-PEDOT:PSS film dried in vacuum or by heating at 80–100°C. Hence, the post baking process does not play a role for the conductivity enhancement.

The EG treatment affects the solubility of the PEDOT:PSS film in water: the dried PEDOT:PSS film could be re-dispersed homogeneously in hot water at 100°C, while the EG-PEDOT:PSS film becomes insoluble. This solubility change indicates the increase of the interchain interaction after the treatment. Since a dried PEDOT:PSS is insoluble in EG, presumably, the increase of the interchain interaction should be attributed to the effect of EG on the conformation of the polymer chains.

The effect of the conformation of the PEDOT chains in the PEDOT:PSS film before and after the EG treatment was studied by Raman spectroscopy (Fig. 1). It exhibits similar change as that by adding EG into the PEDOT:PSS aqueous solution [16]: the band between 1400 and 1500 cm⁻¹, which corresponds to the stretching vibration of Cₓ = Cₓ on the five-member ring of PEDOT [17–19], shifts to red and becomes narrow. This Raman spectroscopic study indicates that the resonant structure of PEDOT chain changes from a benzoid to a quinoid structure (Scheme 2).

The benzoid structure may be the favorite structure for a coil conformation, while the quinoid structure may be the favorite structure for a linear or expanded-coil structure. Therefore, we proposed that both coil and linear or expanded-coil conformations exist in a PEDOT:PSS film (Scheme 3), and the coil conformation turns into linear or expanded-coil conformation after the conductivity enhancement. It is understandable that the interaction among the PEDOT chains of linear conformation will be stronger than that among the PEDOT chains of coil conformation.

3.2. Temperature dependence of conductivity

Charge hopping among the polymer chains is believed to be the dominant conduction mechanism in almost all conducting polymers [20–22]. An increased interchain interaction should facilitate charge hopping among the conductive PEDOT chains. This point is addressed by the conductivity measurements of the PEDOT:PSS films from 295 K to liquid nitrogen temperature. As Fig. 2 shows, the solvent treatment significantly affects the temperature dependence of the conductivity. This temperature dependence fits the one-dimensional variable range hopping (VRH) mechanism [23,24]:

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

where \( T_0 = 16/k_B N(E_F) L_{||} L_{\perp}^2 \) is the energy barrier between localized states, \( N(E_F) \) is the density of the states at the Fermi level, and \( L_{||} (L_{\perp}) \) is the localization length in the parallel (perpendicular) direction. The fitted \( T_0 \) values are 2927, 2243, 1153 and 903 K for the untreated, NMP-, DMSO- and EG-PEDOT:PSS films, respectively. At room temperature the conductivity is \( \sigma(295 \text{ K}) \approx 0.4, 46, 143 \) and 200 S/cm for the untreated, NMP-, DMSO- and EG-PEDOT:PSS films, respectively. Note that \( T_0 \) decreases with increasing \( \sigma(295 \text{ K}) \). This behavior suggests a lower energy barrier among the PEDOT chains and a longer localization length of the charge. Hence, it is consistent with an increased interchain interaction and the proposed conformational changes.

3.3. Electron spin resonance (ESR)

ESR measurements were carried out to study the EG effect on the nature of the charge carriers in the PEDOT:PSS films. As Fig. 3 shows, the integrated ESR intensity decreases by \( \sim 50\% \) following EG treatment. Since a polaron has a spin of 1/2 while a bipolaron is spinless [25], the results suggest that roughly half of the polarons in the PEDOT:PSS film pair to bipolarons. A polaron corresponds
to a positive charge on a unit while a bipolaron corresponds
to two positive charges delocalized over several units.
Clearly, the transition from polarons to bipolarons is due to
the conformational change from coil to linear or expanded-coil structure so that the charge becomes more delocalized
on the PEDOT chains.

3.4. Electrochemical characterization

The effect of solvent on the electrochemical behavior of
the PEDOT:PSS films was studied by CV and in situ UV–Vis-NIR absorption spectroscopy in a 0.1 M NaCl aqueous
solution with Ag/AgCl as the reference electrode (Fig. 4).
The PEDOT:PSS films exhibit redox behavior at a potential
higher than $-0.2\ \text{V}$ vs Ag/AgCl before the treatment and an
additional redox behavior between $-0.2$ and $-0.7\ \text{V}$. The
integrated current doubled after the EG treatment. These
changes were always observed by changing the scan rate
from 5 to 200 mV/s. The change of the redox behavior is
similar to the redox behavior change from irregular
poly(3-dodecylthiophene) to regioregular poly(3-dodecyl-
thiophene) [26]. The dependence of the CVs of 3-sub-
stituted-polythiophene in aqueous solution on the
hydrophilicity of the substituted group was observed as
well [27]. The doping degree of the PEDOT:PSS film does
not change after the EG treatment. Therefore, the change in
the redox behavior should be attributed to the EG effect on
the conformation of the PEDOT chains.

![Scheme 2. Scheme of transformation of the PEDOT chain from the benzoid to the quinoid structure. The ‘dot’ and ‘plus’ represents the unpaired electron and positive charge on the PEDOT chain, respectively.](image)

![Scheme 3. Schematic conformation of a PEDOT chain in untreated PEDOT:PSS. The PEDOT chain has coil conformation at region (a) and (c), and linear conformation at region (b).](image)

![Fig. 2. Temperature dependence of the normalized resistance of PEDOT:PSS films treated with (a) untreated, (b) NMP, (c) DMSO, and (d) ethylene glycol (EG). The resistances are normalized to that at 100 K.](image)
electrochemically reduced, the film has a low conductivity and the electron transfer between the PEDOT chains with coil conformation and electrode becomes difficult, so that the PEDOT chains cannot be completely reduced electrochemically. After the coil structure transforms to the linear or expanded-coil structure by the EG treatment, the PEDOT chains can be completely reduced.

3.5. AFM and contact angle measurements

The morphology of the untreated and treated PEDOT:PSS film was studied with AFM. The AFM pictures of the film change significantly, with appearance of some large domains, after the EG treatment (Fig. 7). This change is due to the conformational change and the resultant increased interchain interaction. The contact angle of water on untreated PEDOT:PSS is 10–12°, which increases to 20–22° on the EG-PEDOT:PSS. Hence, the surface becomes more hydrophobic after the EG treatment.

3.6. Effect of organic compounds on the conductivity of PEDOT:PSS film

The conductivity enhancement of the PEDOT:PSS films is strongly dependent on the properties and structure of the organic compounds. As mentioned above, conductivity enhancement is always observed when EG, which is a liquid at room temperature, is used. When a solid compound such as meso-erythritol (melting point 123 °C) or 1,2,4-benzene-triol (melting point 140 °C) is added to the PEDOT:PSS aqueous solution, the conductivity enhancement is observed.
only after the PEDOT:PSS film is baked at 150 °C for 30 min. No conductivity enhancement was observed for the film dried at room temperature. These results suggest that the conductivity enhancement occurs only when the additive is in a liquid state.

The conductivity enhancement is strongly dependent on the chemical structure of the organic compounds. Table 1 lists the effect of various organic compounds. When a compound with only one polar group, such as acetonitrile, nitromethane, or methyl alcohol was used, no conductivity enhancement was observed, despite these compounds’ high dielectric constant. This provides strong evidence that the organic compounds do not play a role in charge screening, an effect proposed by Kim et al. [2]. The organic compounds that do enhance the conductivity significantly have a common feature: they have two or more polar groups on each molecule. Hence we propose that the driving force for the conformational change of the PEDOT chains is the interaction between the dipole of one polar group of the organic compound and the dipoles or the positive charges on the PEDOT chains. Calculations using HyperChem 7.1 indicate that the dipole moment of 1,4-ethyldioxythiophene ($\mu = 1.87$ D) is much larger than that of thiophene (Scheme 4). Another polar group of the organic compound may form a hydrogen bond to PSS chains so that the organic compound can stay in the polymer film and in close proximity to the PEDOT chain. Though DMSO has only one polar group, it probably still keeps a strong dipole moment close enough to the PEDOT chains so that the dipole–dipole or dipole–charge interaction can take place after the formation of a hydrogen bond with PSS.

The mechanism proposed in this paper is similar to secondary doping of polyaniline [28–31], but the difference is significant as well: As studied by several groups, including ours, the PEDOT:PSS film remains in the amorphous state following the EG treatment. In
comparison, polyaniline films crystallize after secondary doping. This difference may result from solvent effects occurring at different stages in these two polymers. The solvent affects the conformation of the polyaniline chains even when they are dispersed in solvent so that ordering of the polyaniline chains can take place during film formation. In contrast, solvent affects the conformation of the PEDOT chains only when the film has already been formed, and it has no effect on the conformation of the PEDOT chains when they are in aqueous solution, so the PEDOT chains cannot order during film formation.

Though the mechanism of the conductivity enhancement of PEDOT:PSS film is similar to that of polyaniline, the effect on the absorption spectrum is remarkably different. Significant effect due to the secondary doping has been observed on polyaniline film in UV–Vis-NIR absorption spectrum [28], while not much difference was observed for PEDOT:PSS film before and after the EG treatment. This can be attributed to the amount of bipolaron in the conducting polymer film. Bipolarons are already present in the untreated PEDOT film, as evidenced by the strong absorption in the infrared range, since some polymer chains have a linear or expanded-coil conformation. This strong band may hide the effect of the conformational change on the absorption spectrum. In contrast, the conformation for a low-conductivity polyaniline film is dominated by the coil structure, so that there is no absorption band corresponding to the bipolaron. After the secondary doping, the conformation of the polyaniline chains changes into the linear or expanded-coil structure, leading to the formation of bipolarons. Therefore, the UV–Vis-NIR absorption spectrum of polyaniline film changes significantly.

4. Conclusions

The present study on the conductivity enhancement of PEDOT:PSS films which results from adding organic compounds to PEDOT:PSS aqueous solution or treating the PEDOT:PSS film with an organic solvent indicates a
mechanism different from those proposed previously. Following EG treatment, the PEDOT:PSS films become insoluble in water. This suggests an increased interchain interaction. Raman spectroscopy indicates that the PEDOT chains transform from the benzoid to the quinoid structure following EG treatment. This transformation of the resonant structure suggests a conformational change of the PEDOT chains from the coil structure into expanded-coil or linear structure. The increased interchain interaction and conformational change were confirmed by the temperature dependence of the conductivity of the PEDOT:PSS film, ESR measurements, and electrochemical characterizations. AFM and contact angle measurements indicated changes in the morphology of the PEDOT:PSS films following EG treatment. Conductivity enhancement was observed only when organic compounds with two or more polar groups in a molecule were used. We propose that the driving force for the conformational changes in the PEDOT chains is the interaction between the dipole of one polar group of the organic compound and the dipoles or the charges on the PEDOT chains.

Acknowledgements

The authors are indebted to Dr Qibing Pei of SRI for valuable discussion and comments on the manuscript. This research was supported by AFOSR (F49620-03-1-0101) and ONR (N00014-01-1-0855). Ames Laboratory is operated by Iowa State University for the US Department of Energy under Contract W-7405-Eng-82. The work in Ames was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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