Significant Conductivity Enhancement of Conductive Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) Films by Adding Anionic Surfactants into Polymer Solution

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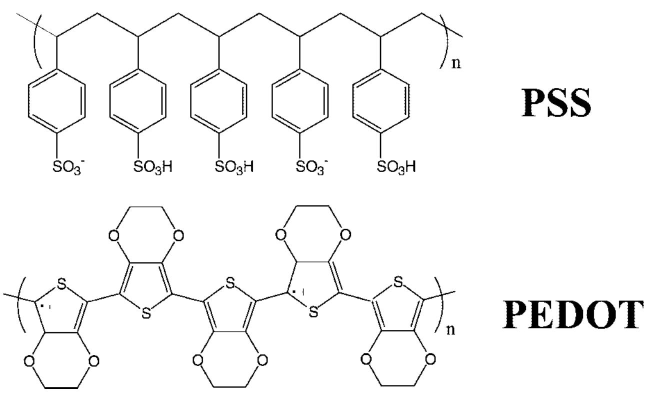
Introduction. Optoelectronic devices, including light-emitting diodes and photovoltaic cells, have strong application in many aspects. One electrode must be transparent for an optoelectronic device. Conventional transparent electrode materials are metal oxides, such as indium tin oxide (ITO). But these metal oxides have some problems in the optoelectronic application. One problem is the limitation of indium in earth.[1] Another problem is the rigidity of the metal oxides.[2] This rigidity badly affects the application of ITO in the flexible electronic devices, which are regarded as the next-generation electronic devices.[3–5] Hence, there is a strong demand for cheap and transparent thin films with high conductivity and high mechanical flexibility. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, chemical structure shown in Scheme 1) emerged as a promising conducting polymer to replace ITO in the optoelectronic application. It has many merits, including high transparency in the visible range, solution processability, high mechanical flexibility, and good thermal stability.[6–8]

Though PEDOT:PSS has been extensively used in the optoelectronic devices, it is usually used as the material for the buffer layer between the electrode and the active layer other than as the electrode material.[9] This is related to the low conductivity of PEDOT:PSS. The as-prepared PEDOT:PSS film obtained from the PEDOT:PSS aqueous solution usually has a conductivity lower than 1 S cm^{-1}, remarkably lower than ITO.[7] This low conductivity badly affects the application of PEDOT:PSS in many aspects. Much effort has been made to improve the conductivity of PEDOT:PSS. One method recently developed is to add a high-boiling-point polar organic compound into the PEDOT:PSS aqueous solution or treat the PEDOT:PSS film with polar solvent, such as ethylene glycol or dimethyl sulfoxide.[10–14] This method can enhance the conductivity of the PEDOT:PSS film by a factor of several hundred.

Here, we report a novel method to significantly enhance the conductivity of the PEDOT:PSS film by adding anionic surfactants into the PEDOT:PSS aqueous solution. The method is stimulated by the conductivity dependence of the conductive PEDOT film on the counteranions,[15,16] which are present in the conducting polymer to compensate the positive charges on the PEDOT chain. For example, PEDOT with *p*-toluenesulfonate as the counteranion (PEDOT:TsO) exhibits conductivity as high as 900 S cm^{-1}, which is significant higher than that of PEDOT:PSS. We discovered that the introduction of TsO anions into the PEDOT:PSS aqueous solution could significantly enhance the conductivity of PEDOT:PSS.

Scheme 1. Chemical Structure of PEDOT:PSS



Experimental Section. PEDOT:PSS (Baytron P, Item No. 1802705, Lot No. HCE07P107) was purchased from H.C. Starck, and all other chemicals were purchased from Sigma-Aldrich. These materials were used without further purification. Surfactant or salt was added into the PEDOT:PSS aqueous solution, and the solution was vigorously stirred overnight. The conducting polymer films were fabricated by spin-coating the polymer solution on the glass substrates, which were carefully precleaned by detergent, deion water, acetone, and ethanol. The films were dried by baking at 110 °C on a hot plate for 30 min.

The conductivities of the polymer films were measured by the Van der Pauw four-point probe technique with a Keithley 2400 source/meter. The electrical contacts were made by pressing indium or putting silver paste on the four corners of the 1 cm × 1 cm polymer film on glass substrate. The samples for FTIR were prepared by dispersing PEDOT:PSS powder in KBr pellet, and the FTIR spectra were taken by a Varian 3100 FT-IR spectrometer. The AFM images of the polymer films were acquired using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode.

Results and Discussion. High-quality polymer films were obtained by spin-coating the PEDOT:PSS aqueous solution added with sodium *p*-toluenesulfonate (TsONa). This modified polymer is denoted with PEDOT:PSS(TsO). The introduction of TsONa into the PEDOT:PSS aqueous solution significantly enhanced the conductivity of the PEDOT:PSS film. Figure 1 shows the conductivities of the PEDOT:PSS(TsO) films. The conductivity of the film depended on the molar ratio of TsONa to the PEDOT repeating unit. At first, the conductivity of the PEDOT:PSS film rapidly increased with the increasing TsONa additive. It was 0.16 S cm^{-1} for the PEDOT:PSS film and increased to 25.4 S cm^{-1} when the molar ratio of the TsONa additive to the PEDOT repeating unit of PEDOT:PSS was 1.4. Then, the conductivity enhancement became less remarkable with the further increasing TsONa. The maximum conductivity of the PEDOT:PSS(TsO) film obtained was 37 S cm^{-1} at a molar ratio of 2.2. This maximum conductivity is higher than that of the PEDOT:PSS film by a factor of 234.

Significant enhancement in the conductivity of the PEDOT:PSS film was also observed, when another anionic surfactant, such as sodium dodecyl sulfonate (SDS) or dodecylbenzenesulfonic acid sodium salt, was added. The data are shown in Figure 1 as well. In fact, the highest conductivity of 80 S cm^{-1} was observed on a PEDOT:PSS(SDS) film. This conductivity is 500 times as high as that of the PEDOT:PSS film. This conductivity enhancement is comparable to the effect of the high-boiling-point polar compound on the conductivity of the PEDOT:PSS film.[10–14]

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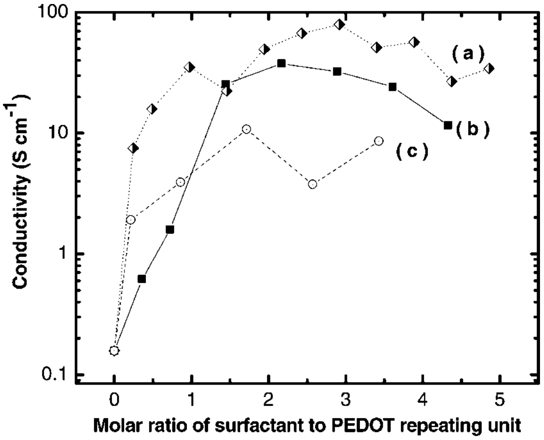

Figure 1. Variation of the conductivity of the PEDOT:PSS(surfactant) film with the molar ratio of the anionic surfactant to the PEDOT repeating unit. The additives are (a) SDS, (b) TsONa, and (c) dodecylbenzenesulfonic acid sodium salt.

The conductivity enhancement mechanism due to the anionic surfactant is different from that due to the high-boiling-point polar compound, since these surfactants have structures remarkably different from those polar compounds. In addition, the conductivity enhancement due to the anionic surfactant was observed even for the conducting polymer films dried in vacuum at room temperature, which was much lower than the melting point of the anionic surfactant. Subsequently heating these dried PEDOT:PSS films added with anionic surfactant at a high temperature did not further increase the conductivity. This is remarkably different from the conductivity enhancement of the PEDOT:PSS film due to the high-boiling-point polar compound, which requires a heating process at a temperature higher than the melting point of the polar compound for the conductivity enhancement.[13]

The conductivity enhancement is not due to chemical structure change of PEDOT:PSS, since the anionic surfactants are mild chemical compounds. The FTIR study also indicates that they did not change the chemical structure of PEDOT:PSS. Compounds other than anionic surfactant were added into the PEDOT:PSS aqueous solution as well. Though high conductivity was reported for PEDOT doped with small inorganic anions,[16] no conductivity enhancement was observed for the PEDOT:PSS films casted from the PEDOT:PSS aqueous solution added with sodium chloride. This suggests that the ionic strength in the solution does not play a role for the conductivity enhancement, though it usually affects the structure and dispersion of many polymer ions in water.[17,18] Since sodium chloride and TsONa have the same cation species, that is, the sodium cation, the effect of anionic surfactant on the conductivity of the PEDOT:PSS film must be due to the anion. Nonionic and cationic surfactants were also investigated as the additives into the PEDOT:PSS aqueous solution. When polyoxyethylene(12) tridecyl ether, a nonionic surfactant, was added, the maximum conductivity enhancement was only by a factor of about 20. On the other hand, the conductivity almost did not change when tetraoctylammonium bromide, which was a cationic surfactant, was added. Therefore, significantly conductivity enhancement took place only when an anionic surfactant was added into the PEDOT:PSS aqueous solution.

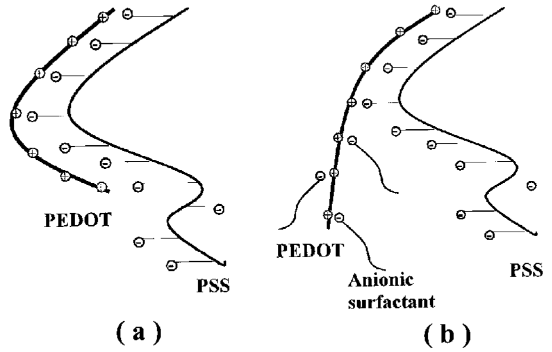

Figure 2. Schematic structure of a PEDOT segment and a PSS segment in water (a) without and (b) with the addition of anionic surfactant. The long thick curve with positive signs represents a PEDOT segment, the long thin curve with pendant short lines and minus signs stands for a PSS segment, and short curve with minus sign at one end is for the anionic surfactant.

On the basis of these experimental results, a mechanism is proposed for the conductivity enhancement by adding anionic surfactant into the PEDOT:PSS aqueous solution. The molar ratio of the PEDOT repeating unit to the PSS repeating unit is 1:1.9 for our PEDOT:PSS; that is, the PSS units far exceed the PEDOT units. Figure 2a shows the schematic structure of a PEDOT segment and a PSS segment in water. The PEDOT segment, which has positive charges, is bound to the PSS segment, which has negative charges, by the Coulombic attraction between them. The excess PSS units, which do not interact with PEDOT, are solvated by water, giving rise to good dispersion of PEDOT:PSS in water.[19] The PSS chain adopts a coiled conformation in water, and the PEDOT chain has to follow the coiled conformation of PSS chain. The chemical structure of PEDOT:PSS as shown in Scheme 1 suggests that PEDOT does not match with PSS perfectly. In fact, the length of the PEDOT repeating unit, 3,4-ethylenedioxythiophene, is longer than that of the PSS repeating unit, styrenesulfonate. Thus, the PEDOT segment must distort, and the distortion results into the localization of the positive charges in the PEDOT chain. The distortion of the PEDOT chain may be the reason for the lower conductivity of PEDOT:PSS than the PEDOT with small-size anions as the counteranions. After the anionic surfactant is introduced into the PEDOT:PSS aqueous solution, the anionic surfactants can replace PSS$^-$ as the counteranions to PEDOT (Figure 3b). Hence, the distortion structure of the PEDOT chain disappears. This conformational change results into the enhanced conductivity of the polymer films with anionic surfactant.

The proposed mechanism is evidenced by the stability of PEDOT:PSS in water. The polymer solution became less stable after the addition of the anionic surfactant, but it was noticeable only after 1 week. The effect of the surfactant on the conformation of the PEDOT:PSS is supported by the AFM study of the PEDOT:PDSS films as well. Figure 3 shows the AFM images of the PEDOT:PSS and PEDOT:PSS(SDS) films on glass substrates. The two films exhibited remarkably different morphologies. It is also possible that some PSS chains that surround the PEDOT:PSS globules in the polymer film might disappear after the addition of the anionic surfactant. It can also contribute to the conductivity enhancement and the morphological change of the polymer film.[12,20]

This proposed mechanism can interpret the experimental results well. PSS can be regarded as a polymer anionic surfactant, which stabilizes the PEDOT chains in water. A cationic surfactant can interact with the negatively charged PSS other than the positively charge PEDOT, so that the cationic surfactants cannot replace PSS as the counteranions to PEDOT. Sodium chloride is not a surfactant, so that the chloride anions cannot replace PSS as well. Hence, both the anionic surfactant and sodium chloride have no effect on the conductivity of PEDOT:PSS. Nonionic surfactant may affect the PEDOT and

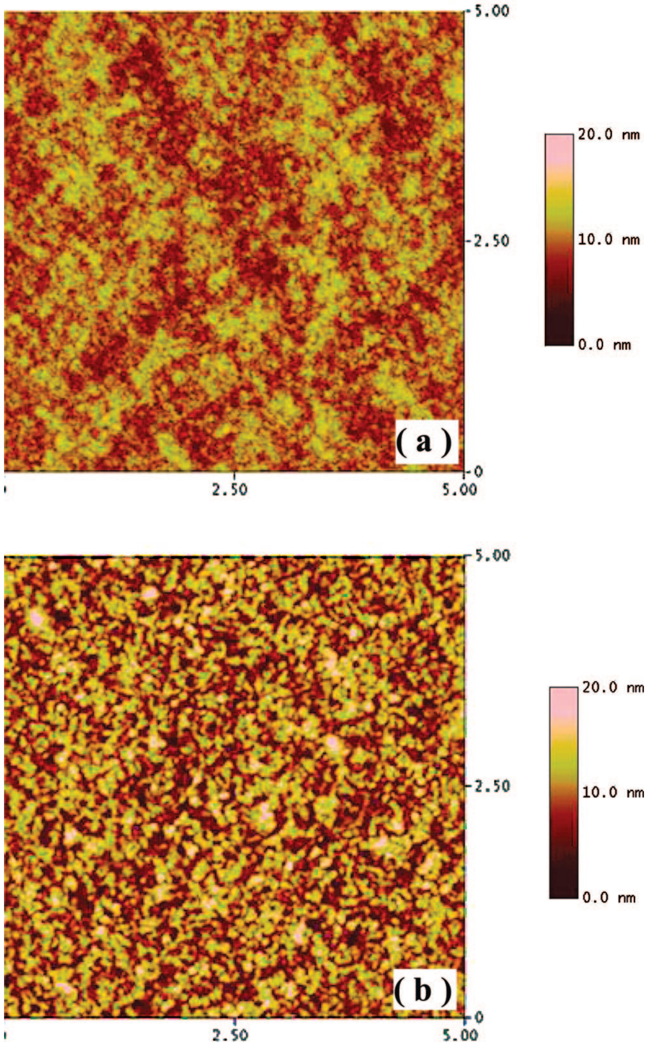

Figure 3. AFM images of (a) a PEDOT:PSS film and (b) a PEDOT:PSS(SDS) film with the molar ratio of SDS to the PEDOT repeating unit being 2.5. The unit for the AFM images is μm.

PSS chain structures in water, but its effect may not strong since it cannot become the counteranions to PEDOT, resulting into a moderate conductivity enhancement.

Though anion exchange has been reported between the conducting polymer film and the surrounding solution when an insoluble conducting polymer film is immersed into a salt solution, the conductivity of the conducting polymer film does not remarkably increase.[21,22] In our method, the introduction of the new anions into the conducting polymer is by adding them into the conducting polymer solution. To our best knowledge, this is the first time to observe the conductivity enhancement by an anion introduction into the conducting polymer solution. This provides a new approach to improve the conductivity of the conducting polymers.

In conclusion, the conductivity of the PEDOT:PSS film can be significantly enhanced by adding anionic surfactant into the PEDOT:PSS aqueous solution. Conductivity enhancement by a factor of 500 was observed. The conductivity enhancement was attributed to the effect of the anionic surfactant on the conformation of the conductive PEDOT chains. The PEDOT chain has to follow the structure of the PSS chain in water, giving rise to the distortion structure of the PEDOT chain. The anionic surfactant replaces PSS as the counteranions to PEDOT in water, so that the distortion structure of the PEDOT chain disappears. This conformational change in the PEDOT chain results into the significant enhancement in the conductivity of the PEDOT:PSS film.

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