Effect of pH on Structure and Conductivity of PEDOT/PSS

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Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) was synthesized by oxidative polymerization and pH dependence of structure and electrical conductivity of the cast films were investigated by means of UV-vis-NIR, XRD, AFM analyses, and four-point technique. It was found that the neutralization of PEDOT/PSS with NaOH decreased the absorption of bipolarons representing the PEDOT in the highly doped state and disrupted the π - π stacking of the PEDOT crystalline structure, which lowered the electrical conductivity by six orders of magnitude with increasing the pH from 1.7 to 13.

Key words: PEDOT/PSS, pH, Titration, Electrical conductivity, Crystallinity

1. INTRODUCTION

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS), which is commercially available in the form of aqueous dispersion as colloidal gel particles, is one of the most successful conducting polymers during the last two decades. The PEDOT/PSS has a hierarchical structure as shown in Fig.1. The sequence of monomer units of PEDOT and PSS (primary structure) forms a poly-ion complex between PEDOT cations and PSS anions through electrostatic interactions (secondary structure). The poly-ion complex disperses in water as a colloidal gel particle (tertiary structure) with a diameter of several tens nm where hydrophobic PEDOT molecules aggregate to form physical cross-links of the PSS chains, which contains water as high as 90-95 wt%. Therefore, the PEDOT/PSS colloidal gel particles can be shaped into various shapes such as thin coatings on various substrates, fibers, and free-standing thick films (quaternary structure), which can be applied to printed organic electronics. Because of its high electrical conductivity, transparency, and thermal stability, the PEDOT/PSS has been paid considerable attention for transparent electrodes of touch panels [1,2], flat panel displays [3,4], and solar cells [5] as an alternative of indium tin oxide (ITO) due to the drain problem of rare metals. However, the PSS is a strong acid ($\text{pH} < 2$) having hygroscopic and corrosive properties, which lowers lifetime and performance of the organic electronic devices [5]. Although the PSS can be neutralized with various bases, little is known about changes in structure and electrical conductivity of the resulting PEDOT/PSS.

In this study, PEDOT/PSS was synthesized by oxidative polymerization of EDOT in the presence of PSS and neutralized with NaOH. The pH dependence of structure and electrical conductivity of the resulting PEDOT/PSS were investigated by means of UV-vis-NIR, XRD, AFM analyses, and four-point technique.

Fig.1 Hierarchical structure of PEDOT/PSS.

2. EXPERIMENTAL

2.1 Synthesis of PEDOT/PSS

PEDOT/PSS was synthesized by oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) monomer in the presence of PSS. The EDOT (0.5 wt%) and PSS (1.5 wt%) were mixed in pure water containing $\text{Na}_2\text{S}_2\text{O}_8$ as an oxidant and the oxidative polymerization was carried out under vigorous stirring with a magic LAB (IKA) at 20 °C for 24 h. After polymerization, the resulting sodium and sulfate ions were removed by cation and anion exchange resins for 24 h and subsequently filtered. The PEDOT/PSS aqueous dispersion was neutralized with 5 N solution of NaOH.

2.2 Measurements

The electrical conductivity of films prepared by casting the PEDOT/PSS dispersions with different pHs was measured by a normal four-point method with a Lorester (MCP-T610, Dia Instruments). The UV-vis-NIR spectra of PEDOT/PSS thin films prepared by spin-coating at 3000 rpm were measured with a spectrophotometer (V-670, JASCO) in a range of wavelength between 400 and 2500 nm. The thickness of the PEDOT/PSS thin films were 125~142 nm evaluated by using a spectroscopic ellipsometer (FE-5000S,

Otsuka Electronics). The X-ray diffraction (XRD) patterns were measured using an imaging plate (R-Axis DS3C, Rigaku) at 40 kV and 30 mA with an exposure time of 30 min. Atomic force microscopic (AFM) measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu) equipped with a conductive probe, where height and current images were measured by tapping and contact modes (a bias of 0.2 V), respectively.

3. RESULTS AND DISCUSSION

3.1 Neutralization of PSS with NaOH

In the PEDOT/PSS colloidal gel particles, the PSS has two functions as (i) a dopant to compensate charges of the PEDOT cations and as (ii) a dispersant to stabilize the dispersion of insoluble PEDOT molecules in water [6]. Indeed, the PEDOT/PSS contains excess PSS (more than twice in molar ratio of PEDOT monomer unit), having a zeta potential of -80.6 mV [7]. Fig.2 shows a titration curve of the PEDOT/PSS with NaOH. The initial pH of the PEDOT/PSS dispersion is 1.7, indicative of a strong acid, due to the sulfonic acid groups of the excess PSS. A steep rise of the pH from 2.5 to 11.7 at the titration fraction from 0.8 to 1.2 clearly demonstrates the neutralization of a strong acid with a strong base, in which the sulfonic acid groups change to sodium sulfonate as shown in the inset of Fig.2. Interestingly, a color of the PEDOT/PSS dispersion changes from dark blue to ultramarine during the neutralization.

Fig.2 Titration curve of PEDOT/PSS with NaOH.

3.2 Electronic structure of PEDOT

To evaluate structural changes of the PEDOT by adding NaOH, UV-vis-NIR spectra of PEDOT/PSS thin films (125~142 nm thick) were measured and the results are shown in Fig.3. At pH = 1.7 the spectrum shows a small shoulder around 800 nm, representing the band gap of PEDOT (1.5 eV), while a free-carrier tail of bipolarons in the NIR region clearly indicates the PEDOT in the highly doped state [8-10]. An increase of the pH by adding NaOH decreases the strong absorption in the NIR region whereas the absorption at 900 nm

corresponding to a sub-band gap of the bipolarons [11,12] increases. The isosbestic point around 1100 nm demonstrates the equilibrium of two different states of the PEDOT. In fact, the spectral change of the PEDOT is reversible: when HCl solution is added to decrease the pH, the spectrum recovers to the original one. Here, the pH dependence of the spectral change is not associated with reduction of the PEDOT, which arises from the facts that NaOH has no reducibility and PEDOT in the neutral or reduced state shows a strong absorption at 600 nm due to the π - π^* transition [10,13].

Fig.3 UV-vis-NIR spectra of PEDOT/PSS thin films with various pHs.

Fig.4 Equilibrium between (a) polaron and (b) bipolaron of PEDOT.

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changes between polaron and bipolaron of PEDOT molecules (Fig.4) [14]. The replacement of H^+ with Na^+ may unstabilize the bipolarons by local environmental changes of the PEDOT cations, which can shift the equilibrium from bipolarons to polarons.

3.3 Electrical conductivity

A clear indication of the importance of pH on electrical conductivity is demonstrated in Fig.5. The conductivity of the PEDOT/PSS pristine film (pH = 1.7) measured by a four-point method is 6×10^{-2} S/cm which remarkably rises by three orders of magnitude and reaches 270 S/cm by adding 5 wt% of ethylene glycol (EG5). As reported previously, this can be associated with (i) removal of the insulating PSS from the surface of the colloidal particles and (ii) crystallization of PEDOT molecules which improve both intra- and inter-particle transfer of charge carriers [15-17]. In other words, the increase of electrical conductivity is attributed to an enhancement of the carrier mobility since the EG does not affect the carrier concentration. Indeed, the UV-vis-NIR spectra of the PEDOT/PSS were substantially the same regardless of the EG [3]. We should emphasize here the conductivity of both pristine and EG5 films gradually decreases with increasing the pH and drops at pH > 11, where the conductivity change of the EG5 film is six orders of magnitude in the pH range between 1.7 and 13.

Fig.5 Effect of pH on electrical conductivity of various films prepared by casting PEDOT/PSS dispersion (pristine) and PEDOT/PSS dispersion containing 5 wt% of ethylene glycol (EG5).

3.4 Crystalline structure

In order to clarify the effect of structural change on electrical conductivity in more detail, XRD measurements were performed on EG5 films and the results are shown in Fig.6. It is known that PEDOT molecules in the amorphous state partly change into crystalline state by adding EG during the film formation [15,16]. The Debye-Scherrer ring at $2\theta = 26^\circ$ ($d = 3.4 \text{ \AA}$), corresponding to a diffraction from (020) planes of an orthorhombic unit cell, represents a π - π stacking of the PEDOT molecules [18]. It is noted that the diffraction

peak decreases with increasing the pH, where the diffraction profile at pH = 12 is similar to that of the amorphous pristine film. The results clearly demonstrate that the neutralization with NaOH lowers the crystallinity of the PEDOT.

Fig.6 XRD patterns of EG films at different pH of (a) 1.7, (b) 7, and (c) 12 measured using an imaging plate and (d) XRD profiles of various films.

Fig.7 AFM (left) and current (right) images for EG films at different pH of (a) 1.7, (b) 7, and (c) 12. Scale bars are 500 nm.

3.5 Surface morphology and local conductivity

Figure 7 shows AFM and current images of the PEDOT/PSS films with different pHs. It is found that the surface roughness (R_s) is less dependent on the pH to be 1.3~1.4 nm, indicating high stability of dispersion in water without gelation or precipitation of the PEDOT/PSS colloidal gel particles even at pH = 12. In contrast, the current image, reflecting the local conductivity in the thickness direction, strongly depends on the pH. At pH = 1.7 highly conductive domains (bright area) densely and randomly distribute in the less conductive matrices (dark area), where transport of charge carriers between such the highly conductive domains may lead to the higher bulk conductivity. On the other hand, at pH = 7 the highly conductive domains decrease in number and size and almost covered with the less conductive dark area at pH = 12. The results demonstrate that the neutralization of PEDOT/PSS with NaOH lowers the local conductivity, which is in good agreement with the pH dependence of the bulk conductivity as shown in Fig.5.

4. CONCLUSIONS

In conclusion, we found that the pH was crucially important for both structure and electrical conductivity of the PEDOT/PSS films. The neutralization with NaOH decreased the absorption of bipolarons representing the PEDOT in the highly doped state and disrupted the π - π stacking of the PEDOT crystalline structure, which was responsible for decreasing the electrical conductivity. Although the pH dependence of conductivity was similar to polyaniline [19], a further investigation was necessary to clarify the detailed mechanism by means of ESR, Raman, and terahertz spectroscopic analyses [20]. The results indicated the possibility to control the carrier transport properties of the PEDOT/PSS by pH, which could provide a new class of conducting and semiconducting PEDOT materials for organic electronic devices such as sensors and transistors. Furthermore, neutral and highly conductive PEDOT/PSS dispersion has attracted considerable attention not only from the fundamental viewpoints for understanding the relation between hierarchical structure and carrier transport at the molecular level but also from the practical use to improve the lifetime and performance of the organic electric devices.

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