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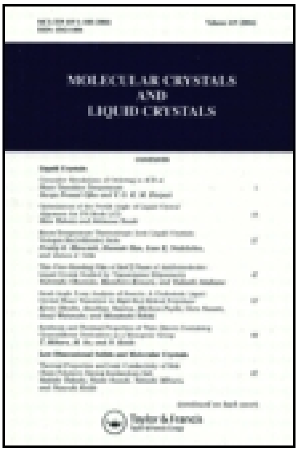

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# Improvement of Electrical Conductivity of Poly(3,4-ethylenedioxythiophene) (PEDOT) Thin Film

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# Improvement of Electrical Conductivity of Poly(3,4-ethylenedioxythiophene) (PEDOT) Thin Film

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*In order to improve the electrical conductivity of* in-situ *polymerized poly(3,4-ethylenedioxythiophene) (PEDOT) thin film, we investigated the effect of doping level and co-dopant on the electrical conductivity. Doping level of PEDOT thin film was determined by X-ray photoelectron spectroscopy (XPS) and it was found that the higher doping level led to higher electrical conductivity. We also used several kinds of co-dopants such as methanesulfunic acid, naphthalenesulfonic acid and p-toluenesulfonic acid to increase the conductivity of PEDOT. When methanesulfonic acid was used as co-dopant, electrical conductivity of PEDOT thin film increased up to 1,500 S/cm. It is considered that the enhanced conductivity resulted from higher interchain conduction or more expanded chain structure due to small dopant size of methanesulfunic acid.*

**Keywords** Co-dopant; doping level; electrical conductivity; in-situ polymerization; PEDOT

## 1. Introduction

Flexible displays have been widely studied over the last several years. One of the key issues for flexible display materials is developing the transparent electrodes having good mechanical flexibility, electrical conductivity, optical transmittance, thermal stability and productivity. Recently, Indium Tin Oxide (ITO) has been extensively used in organic electronics and photovoltaics as the transparent electrode because of its low surface resistivity [1–3]. However, high cost of production and high temperature process are demerits of ITO as transparent electrodes [4,5].

Electrically conductive polymers such as polyaniline, polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT) are possible candidates to replace the ITO in flexible electronics and displays. Among the electrically conductive polymers, PEDOT has received great attention owing to its high electrical conductivity and environmental stability [6–8].

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Many studies using PEDOT have been carried out in diverse research areas including sensors, solar cells, organic field-effect transistors (OTFTs) [9–11]. However, low electrical conductivity compared to ITO is drawback of PEDOT, so the electrical conductivity of PEDOT must be much further increased. Many researches were reported to enhance the conductivity of PEDOT films by forming nanocomposites with metal nanoparticle or by changing alcohol solvents [12–14].

In this study, we report a simple *in-situ* polymerization procedure to fabricate PEDOT thin film with high electrical conductivity. We investigated the effect of doping level of PEDOT on the electrical conductivity. To increase the electrical conductivity of PEDOT thin film, we also studied the effect of co-dopants including methanesulfonic acid, naphthalenesulfonic acid and *p*-toluenesufonic acid on the electrical conductivity of PEDOT thin film.

## 2. Experimental

### *2.1.* In-situ ***Polymerization of PEDOT Thin Film***

PEDOT thin film was fabricated using 3,4-ethylenedioxythiophene (EDOT) (Clevios$^{TM}$, M V2) as a monomer and ferric p-toluenesulfonate (FTS) (Clevios$^{TM}$, CE 40) as an oxidant and dopant source via *in-situ* polymerization. Typical procedure is as following. Monomer solution was prepared by dissolving 1.4 mmol of EDOT, 0.02 g of poly(vinyl pyrrolidone) (PVP) (Sigma Aldrich, Mw. 360,000) as the matrix polymer and 1.4 mmol of pyridine (Sigma Aldrich, 99.8%) as the polymerization retardant in 2 ml of 1-butanol (Sigma Aldrich, 99.8%). 45% oxidant solution was prepared by adding FTS-hexahydrate (Sigma Aldrich, technical grade) into the FTS (Clevios$^{TM}$, CE 40) solution. The monomer and oxidant solutions were then mixed, where mole ratio of FTS to EDOT was 1:2.3. The mixed solution was spin-coated onto glass substrate at 2,000 rpm for 15 sec and subsequently baked at 70°C for 30 min. The resulting PEDOT film was then washed with methanol to remove the residual reactants and dried in a convection oven at 70°C for 30 min.

### *2.2. Fabrication of PEDOT Thin Film with Co-dopants*

Methanesulfonic acid (MSA) (Sigma Aldrich, 99.5%), 2-naphthalenesulfonic acid (NSA) (Sigma Aldrich, 70%) and p-toluenesulfonic acid monohydrate (PSA) (Sigma Aldrich, 98.5%) were used as co-dopants. Chemical structures of the co-dopants are shown in Fig. 1. In order to incorporate the co-dopant, NSA, PSA or MSA were dissolved in the FTS solution before mixing it with the monomer solution. Polymerization process was same as the above. The molar ratio of co-dopants to EDOT ranged from 0.1 to 1.0.

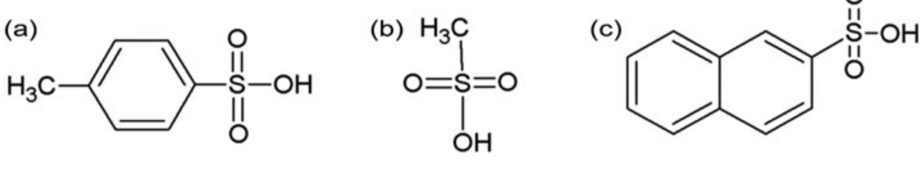

**Figure 1.** Chemical structures of (a) p-toluenesufonic acid, (b) methanesulfonic acid and (c) naphthalenesulfonic acid.

### *2.3. Characterization of PEDOT Thin Film*

Electrical conductivity of PEDOT thin films were measured with four-point probe (Dong Ah Trade & Tech Corp.) connected to the FLUKE 45 Dual Display Multimeter (Fluke Corporation) and the YOKOGAWA 2553 Single Output DC supply (Yokogawa Electric Co., Ltd.). Thickness of PEDOT film was measured by the Alpha-step IQ surface profiler (KLA Tencor). Optical transmittance of PEDOT film was measured using UV-Visible spectrophotometer (Agilent 8453). X-ray photoelectron spectroscopy analysis (XPS) (VG Microtech ESCA20000) was performed to obtain the doping level of PEDOT thin film.

## 3. Results and Discussion

### *3.1. Effect of Doping Level on the Electrical Conductivity of PEDOT Thin Film*

PEDOT films with very smooth surface were successfully fabricated on glass substrates by *in-situ* polymerization. The prepared PEDOT films showed the conductivity ranging from 700 to 1,000 S/cm. In order to investigate the effect of doping level on the conductivity, PEDOT film with the conductivity of 700 S/cm was dedoped by treating it with 0.1 M NaOH solution for 60 seconds [15]. After NaOH treatment, the conductivity of the PEDOT film was decreased to 60 S/cm.

XPS analysis was conducted to measure doping level of the PEDOT film. XPS spectra of the PEDOT films with the conductivities of 700 S/cm and 60 S/cm are shown in Fig. 2(a) and (b), respectively. The S(2p) spectra for the PEDOT main chains appear at 163.9 eV and 164.4 eV. The S(2p) peak shown at 166.4 eV comes from the tosylate as the dopant neutralizing the positive charge in the PEDOT chains [16]. The S(2p) line appearing at

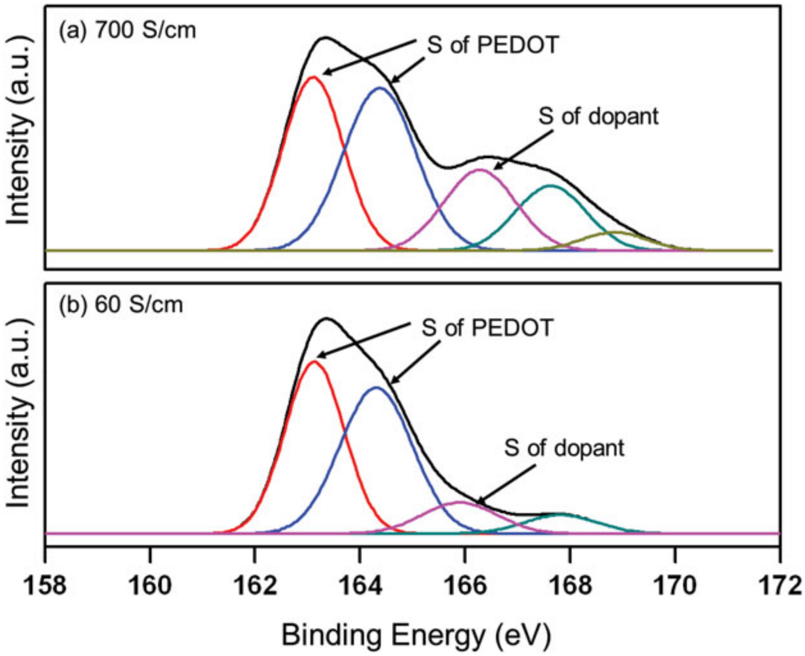

**Figure 2.** XPS spectra of (a) pristine PEDOT and (b) NaOH treated PEDOT thin films.

168 eV originates from the sulfonic acid group, $SO_3^-H^+$ as the free acid. The doping level can be estimated by the ratio of peak area of the PEDOT and the tosylate peaks. The calculated doping level was 0.26 and 0.11 for the PEDOT films with 700 S/cm and 60 S/cm, respectively, confirming that higher doping level produced more charge carriers and then higher conductivity.

### 3.2. *Effect of Co-dopant on Electrical Conductivity of PEDOT Thin Film*

To increase the electrical conductivity of PEDOT, various kinds of organic co-dopants such as MSA, NSA and PSA were used in the polymerization. We chose MSA as one of the co-dopants since the smaller molecular size may have possibility to penetrate more easily into the space between PEDOT chains and then may result in the high doping level or the close packing of PEDOT chains. NSA was chosen because it is anticipated that the planar structure of NSA may have the possibility to promote the formation of more expanded planar conformation and dense $\pi$-stacking of the PEDOT chains. Lastly, PSA was taken as the reference. The amount of co-dopants added in the polymerization solution was in the range of 0.1 to 1.0 molar ratio to EDOT monomer. Fig. 3(a) shows that the thickness of PEDOT film increased with the concentration of co-dopant. It is considered that the thicker PEDOT film was obtained with more co-dopant since higher concentration of the co-dopant made the PEDOT solution more acidic and then resulted in the faster polymerization [17].

Figure 3(b) displays electrical conductivity change of PEDOT thin film with the concentration of co-dopants. When MSA and PSA were used as the co-dopant, the electrical conductivity slightly increased with the concentration of co-dopant up to the molar ratio of 0.2. It is thought that the slight enhancement of conductivity resulted from more effective penetration into the space between the PEDOT chains due to their relatively smaller molecular sizes. However, the electrical conductivity steeply decreased to around 100 S/cm with the concentration of co-dopant over 0.2 molar ratio. The conductivity decrease must come from coil-like conformation of PEDOT chains formed during the fast polymerization since much excess use of dopant acids increased the acidity of the polymerization solution. On the other hand, the electrical conductivity of PEDOT film prepared with NSA co-dopant

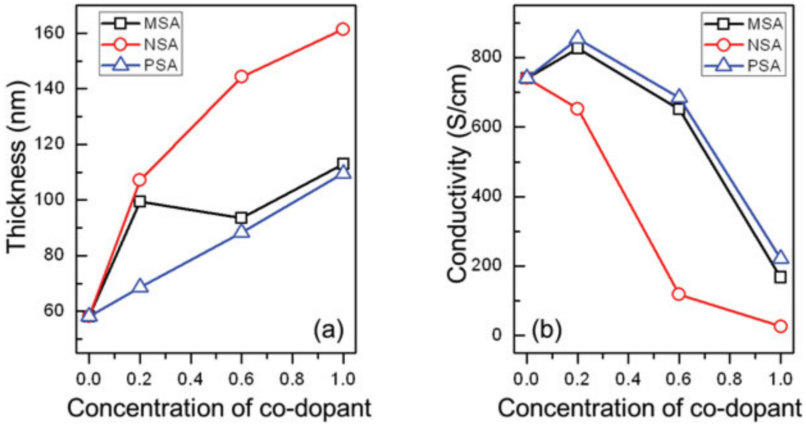

**Figure 3.** Changes of (a) thickness and (b) conductivity of PEDOT thin film with concentration of co-dopant.

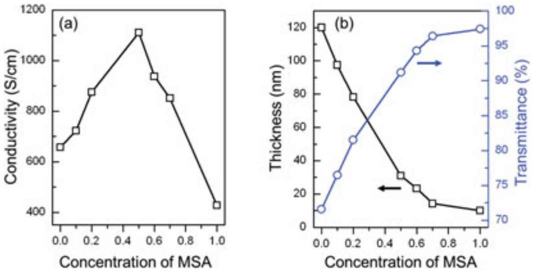

**Figure 4.** Changes of (a) electrical conductivity and (b) thickness and transmittance at 550 nm of the PEDOT thin film with the concentration of MSA and additional pyridine.

monotonically decreased with the concentration of NSA, possibly because the molecular size of NSA seems to be too large to penetrate into the PEDOT chains.

When PEDOT was polymerized with MSA co-dopant, we tried to control polymerization rate by adding the additional same molar concentration of pyridine as the concentration of MSA in the polymerization solution. Pyridine made the polymerization solution less acidic and thus slowed down the polymerization rate [18]. Figure 4(a) shows the electrical conductivity change of the PEDOT with the concentration of MSA and additional pyridine. When additional pyridine was added, the electrical conductivity increased with the content of co-dopants up to 0.5 molar ratio, possibly because of formation of more expanded conformation due to the controlled polymerization rate. However, it was observed that electrical conductivity decreased with concentration of MSA over 0.5 as shown in Fig. 4(a) since much excess use of pyridine made polymerization take place too slowly. Figure 4(b) shows the changes of thickness and transmittance at 550 nm of PEDOT film with the concentration of MSA. Thickness of PEDOT film decreased with increasing concentration of MSA due to the reduced polymerization rate with the additional pyridine, while transmittance increased with increasing concentration of MSA.

When 0.5 molar ratio of MSA was used as co-dopant with the same amount of additional pyridine, the electrical conductivity was highest as 1,110 S/cm. It is considered that the increased conductivity resulted from the increased doping level. Figure 5 shows

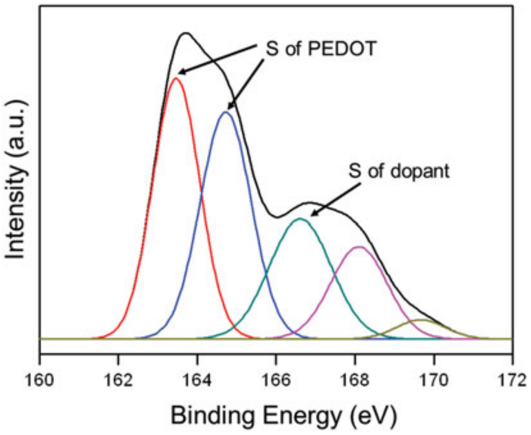

**Figure 5.** XPS spectrum of MSA co-doped PEDOT thin film.

S(2p) spectrum of the MSA co-doped PEDOT thin film. The calculated doping level of MSA co-doped PEDOT thin film was 0.31 which is higher than 0.26 of only tosylate-doped PEDOT, confirming more doping of PEDOT with MSA co-dopant.

It was confirmed that MSA as a co-dopant produced the higher electrical conductivity. We tried to find out optimum condition to produce the highest electrical conductivity with MSA co-dopant. The highest electrical conductivity of PEDOT was achieved by following condition. Monomer solution was prepared by dissolving 1.4 mmol of EDOT and 2.1 mmol of pyridine in 1 ml of 1-butanol without PVP. Oxidant solution was prepared by dissolving 5.6 mmol of FTS and 0.7 mmol of MSA in 2 ml of 1-butanol. The electrical conductivity of PEDOT thin film fabricated using the above condition reached the highest value of about 1,500 S/cm.

## 4. Conclusions

PEDOT thin film was fabricated by *in-situ* polymerization of 3,4-ethylenedioxythiophene (EDOT) as a monomer and iron(III) p-toluenesulfonate (FTS) as the oxidant and the dopant source. We investigated the effect of doping level on the conductivity by X-ray photoelectron spectroscopy (XPS) and found that the higher doping level led to higher electrical conductivity. We used several kinds of co-dopants such as methanesulfunic acid, naphthalenesulfonic acid and p-toluenesulfonic acid to increase the conductivity of PEDOT. When methanesulfonic acid was used as co-dopant with additional pyridine, electrical conductivity of PEDOT thin film increased up to 1,500 S/cm.

## Acknowledgment

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