Transparent Electrode based on Poly(3,4-ethylenedioxythiophene)

Keuk Ryoul Song , Hye Kyong Min, Eung Ju Oh and Yong Bae Kim*
Dept. of Chemistry, Myongji University, Yong In, Kyonggi Do 449-728, Korea
Phone : +82-31-330-6180 , E-mail : ejoh@mju.ac.kr
***Dept. of Chemistry, Konkuk University, Seoul 143-701, Korea**

Abstract

PEDOT [poly(3,4-ethylenedioxythiophene)] powder soluble in common organic solvent were synthesized by oxidative polymerization of EDOT (3,4-ethylene dioxythiophene) monomer using functional dopant, DEHSNa [sodium di(2-ethylhexyl)sulfosuccinate]. Transparent electrodes were made by spin casting of PEDOT/organic solvents on substrates. The electrode showed the transmittance < 90% in visible region and the surface resistance of > ~ 10^3 ohm/□, respectively.

1. Introduction

Transparent electrode is an essential component in optoelectronic device and display application. Transparent electrode requires several performances: optical transparency, low surface resistance etc. The most widely used material for this purpose is ITO (indium-tin oxide). However, ITO should be deposited on the substrates by vacuum technology such as thermal evaporation, high frequency sputtering etc, which needs high cost.

Over the years, many attentions have been focused on conducting polymers which have advantages in processibility, mechanical property etc. for this purpose. In 1992, Cao reported that transparent electrodes which were prepared on PET substrate by spin coating of polyaniline solution [1]. They showed the transmittance of less than 90 % in visible region and low surface resistance up to 80 ohm/□. Flexible light emitting diode was fabricated with this electrode [2].

Recently Bayer Co. reported the semitransparent conducting polymer, PEDOT [poly(3,4-ethylenedioxy thiophene)] which has a band gap of 1.6 eV [3-4]. However Bayer's PEDOT has a aqueous dispersion form so there are some problems such as thin film processing, film uniformity etc.

In this study, soluble PEDOT was synthesized using functional dopant, DEHSNa and transparent electrode was fabricated with PEDOT /organic solvent solutions by spin casting.

2. Experimental

Soluble PEDOT powder (PEDOT-DEHS) was prepared by following procedure. Dopant DEHSNa (0.01 mol) was added to 400 ml distilled water in 1 L beaker and was mechanically stirred for 2 hrs. Then monomer EDOT (0.021 mol) was added and was stirred for 30 mins. Oxidant, iron(III) chloride anhydrous (0.05 mol) was dissolved in 100 ml distilled water in 250 ml beaker. Oxidant solution was poured to the solution which contains dopant and monomer to polymerize EDOT. Reaction was kept to proceed for 24 hrs under the magnetic stirring. The solution was filtered and filter cake was dried under the dynamic vacuum for 48 hrs to make PEDOT powder.

Homogeneous solutions (concentration 2~ 3 wt.%) were prepared by dissolving PEDOT powder in organic solvents (chloroform, IPA, ethanol etc.).

Transparent electrodes were fabricated by spin casting of PEDOT solution on glass (5 x 5 cm^2). Rotating speed was controlled 150 ~ 1000 rpm.

Transmittance of the electrode was measured in the range of 150 ~ 1200 nm (Shimadzu Co., UV-3100). Thickness of the film was measured with α–step (Tenco, α–step 500).

3. Results and discussion

Figure 1 shows the structure of the dopant used in the synthesis, DEHSNa. DEHSNa has two alkyl (ethylhexyl) groups with moderate chain length which has an affinity to non polar solvents and polar oxygen atoms in two ester groups and sulfonate group which is expected to render the affinity to polar solvents. It was reported that DEHSNa increase the solubility of polypyrrole in various organic solvents up to 10 wt.% [5].

In Table 1, the solubility of PEDOT powder is listed. PEDOT doped with DEHSNa (PEDOT-DEHS) showed the solubility of ~5 wt.% in weakly polar solvents such as chloroform 1,2-dichloroethane and ~3 wt% in various alcohols. However, PEDOT-DEHS

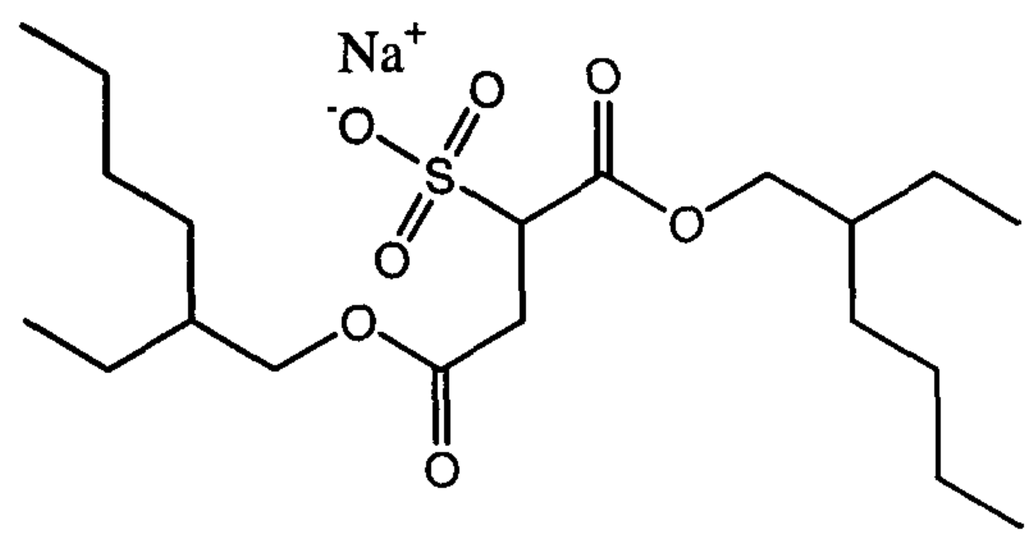

Figure 1. Structure of dopant, sodium di(2-ethylhexyl)sulfosuccinate..

	chloroform	IPA	methanol	ethanol
solubility (wt.%)	~ 5	~ 3	~ 3	~ 3
surface resistance (Ω/□)	> 10^3	> 10^4	> 10^6	> 10^6

Table 1. Solubility of PEDOT-DEHS in organic solvents and surface resistance of spin cast film.

was not soluble in polar solvents such as NMP, DMSO, DMF and dimethyl acetamide. The particle size of PEDOT-DEHS/alcohol solution appeared to be less than 1 μm.

Spin cast films prepared from PEDOT-DEHS /organic solvents solution showed excellent film uniformity and adhesion property with substrate. Also flexible, free standing film could be cast from PEDOT -DEHS/chloroform solution. Electrical conductivity of PEDOT-DEHS/chloroform free standing film was 15 S/cm.

In Table 1, surface resistances of spin cast film on glass substrate from various organic solvents are also listed. Minimum surface resistance of spin cast film from PEDOT-DEHS/chloroform solution was ~10^3 Ω/□. However, spin cast film from PEDOT-DEHS/alcohol solutions showed higher surface resistance than ~10^4 Ω/□. Surface resistance of the spin cast films varied with the rotating speed, film thickness, concentration of the solution etc.

Figure 2 shows the transmittance of the electrode fabricated with PEDOT-DEHS/chloroform solution in the range of 360 nm ~ 1200 nm. The electrodes showed the transmittance higher than 80 % at visible region (Inset). Transmittance decreased with the increase in film thickness. For example, transmittance

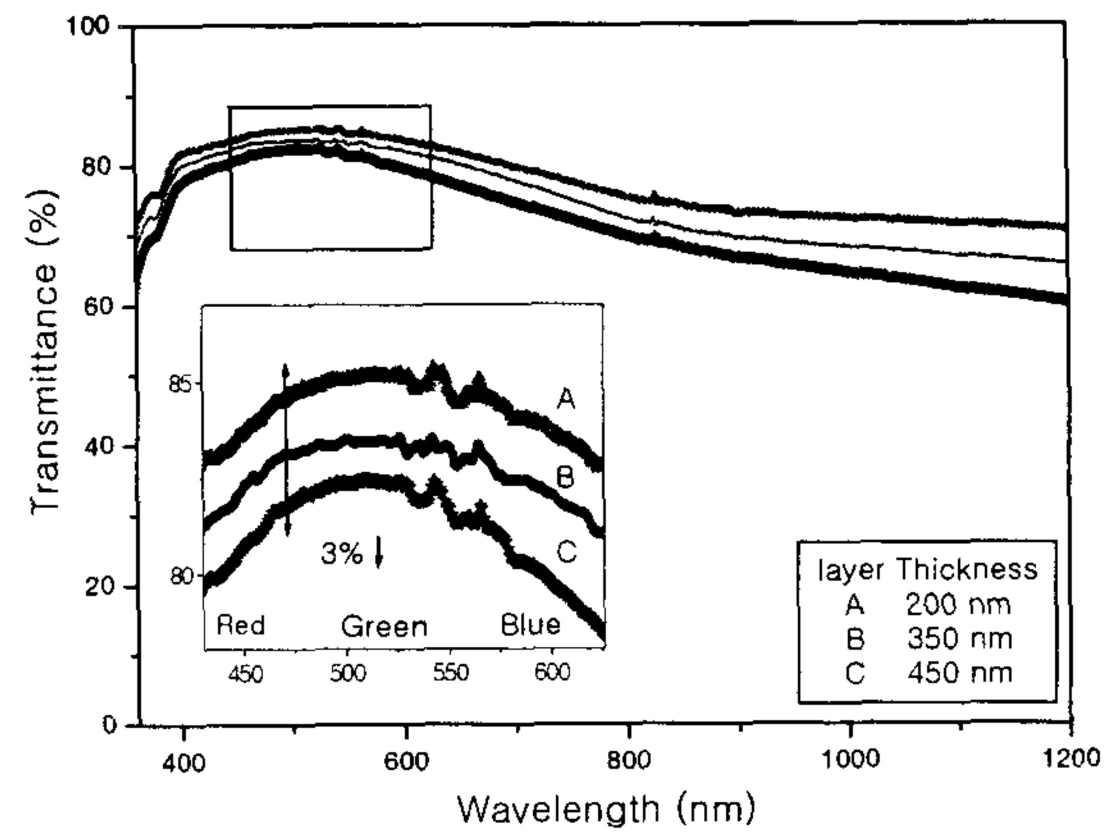

Figure 2. Transmittance of electrode prepared from PEDOT/chloroform solution.

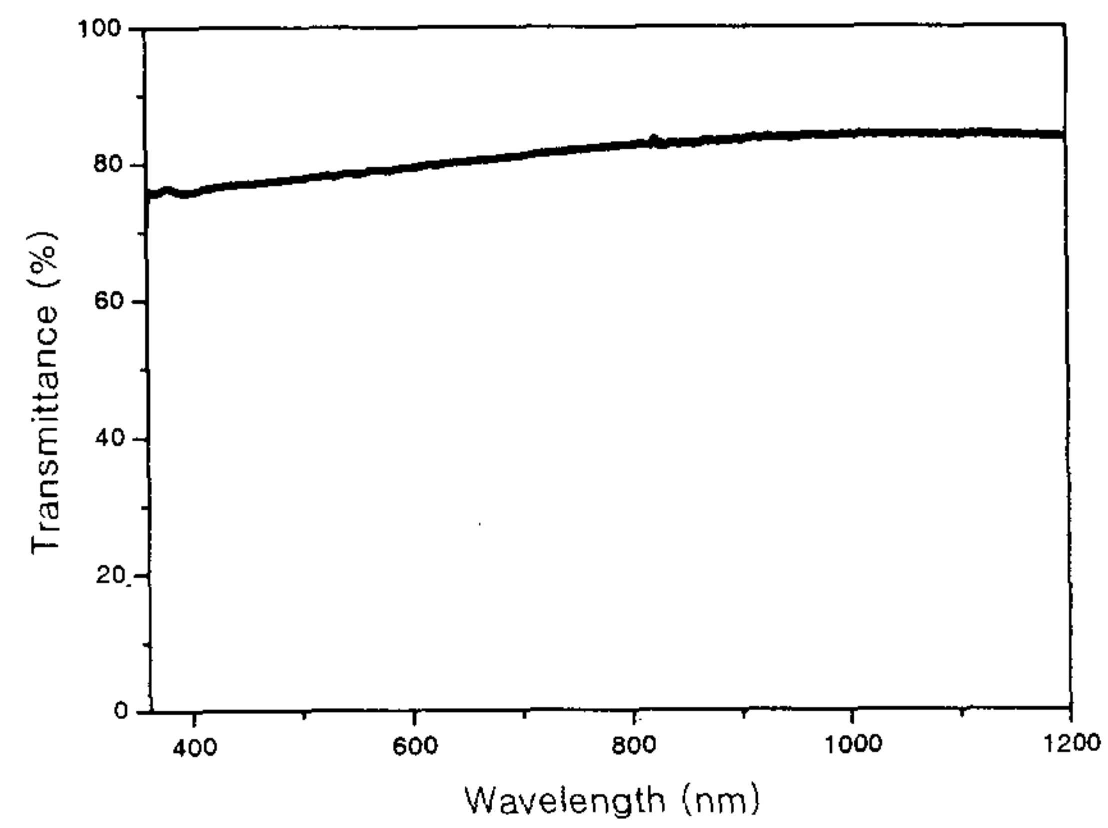

Figure 3. Transmittance of electrode prepared from PEDOT/IPA solution.

of the electrode was ~ 82 % for the film thickness of ~450 nm but was ~ 85 % for the film thickness of ~200 nm at 500 nm region. The difference in transmittances in the range of 420 ~ 620 nm region was less than 3 % which suggest that PEDOT-DEHS is a good candidate material for display application in industry.

Figure 3 showed the transmittance of electrode prepared from PEDOT/IPA solution. Transmittance of the electrode was lower than 80 % which is lower than that of the electrode prepared from PEDOT/ chloroform. It is apparent that the transmittance and surface resistance are affected by solvents.

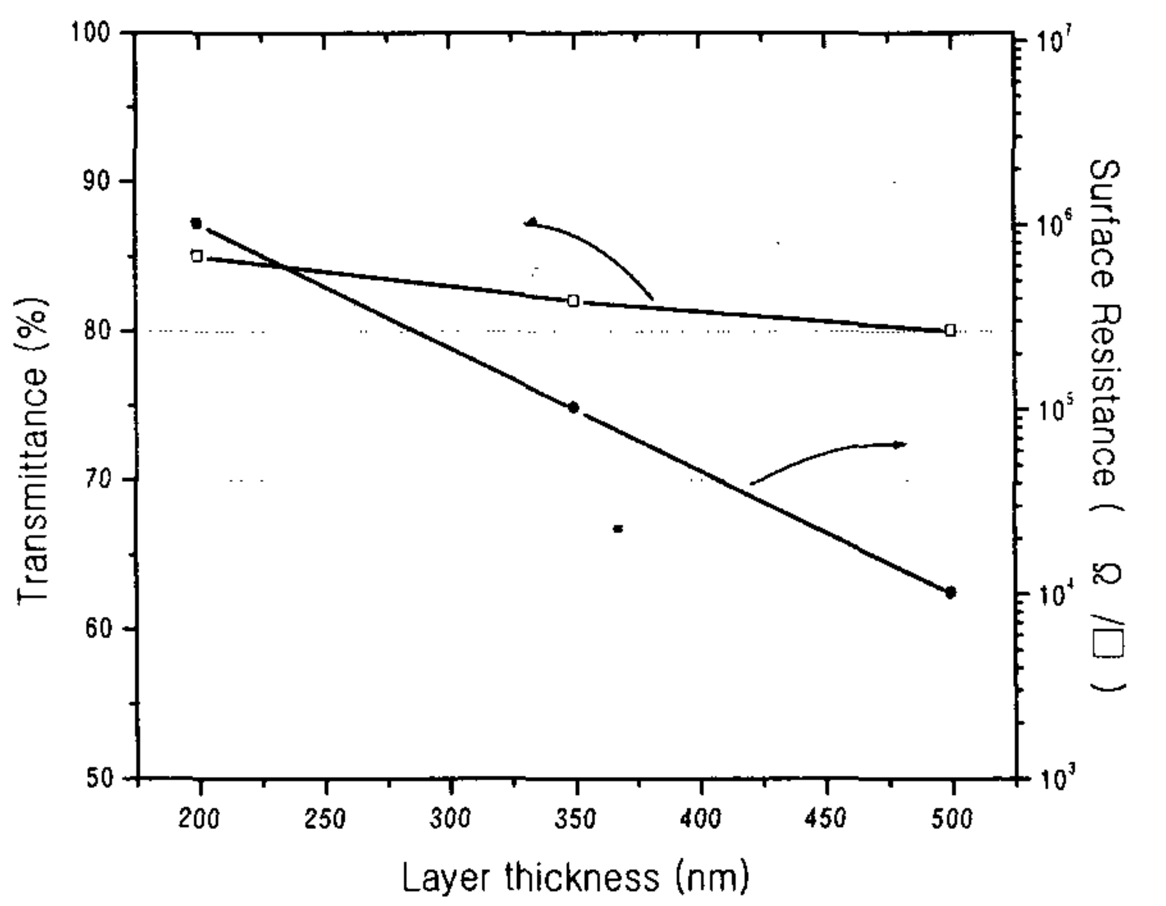

Figure 4. Transmittance and surface resistance of the electrode prepared from PEDOT/chloroform solution as a function of layer thickness.

Figure 4 shows the transmittance and surface resistance of the electrode prepared from PEDOT/chloroform solution. As the thickness of layer increases from 200 nm to 500 nm, the transmittance of the electrode decreases from 85 % to 80 % and surface resistance decreases from ~ 10^6 Ω/□ to ~ 10^4 Ω/□.

Surface resistance of the electrodes based on PEDOT-DEHS solution was lowered up to 1 order by using additives such as tertiary amines. The electrodes made in this study show lower performance than that of ITO electrode. To achieve better performance of the electrode based on conducting polymers such as PEDOT, the electrical conductivity of the polymer should be improved.

4. Conclusion

Transparent electrodes were fabricated with PEDOT [poly(3,4-ethylenedioxythiophene) which is soluble in organic solvents. Transmittances of the electrode were lower than 85 % and surface resistances were higher than 10^3 Ω/□.

5. Acknowledgements

This work was supported by the Advanced Backbone IT technology development project of the Ministry of Information & Communication in republic of Korea.

6. References

[1] Y. Cao, G.M. Treacy, P. Smith, A.J. Heeger, Appl. Phys. Lett., 60(22) 2711 (1992).

[2] G. Gustaffson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, Nature, 357, 477 (1992).

[3] G. Heywang, F. Jonas, Adv. Mater., 4, 116 (1992).

[4] Q. Pei, G. Zuccarello, M. Ashlskog, O. Inganas, Polymer 25, 1347 (1994).

[5] E.J. Oh, K.S. Jang, A.G. MacDiarmid, Synthetic Metals, 125(3) 267(2001).