Polymer Bulletin 59, 331–338 (2007)
DOI 10.1007/s00289-007-0777-6

Polymer Bulletin

Electrophoretic Display of surface modified TiO_2 driven by Poly (3,4-ethylenedioxythiophene) Electrode

Seung Hyun Cho[1], Young Rock Kwon[2], Seok Ki Kim[2], Chang Ho Noh[3] and Jun Young Lee[2] (✉)

[1]Polymer Technology Institute, Sungkyunkwan University, Suwon 440-746, Korea
[2]School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
[3]Samsung Advanced Institute of Technology, P. O. Box, 111, Suwon 440-600, Korea
E-mail: jylee7@skku.edu; Fax: 82-31-290-7330

Received: 13 February 2007 / Revised version: 3 April 2007 / Accepted: 22 April 2007

Summary

Electrophoretic display system was fabricated to investigate the effectiveness of transparent polymer electrode using Poly (3, 4-ethylenedioxythiophene) (PEDOT). The electrophoretic TiO_2 nanoparticles were coated to modify the surface. As a transparent polymer electrode, 3, 4-ethylenedioxythiophene (EDOT) was in-situ polymerized into PEDOT. When the reducing agent (N-dimethylacetamide, DMAc) was added, surface resistivity of PEDOT was dominantly reduced. With the DMAc addition of 40 wt% to the monomer content, surface resistivity was as low as 100Ω / □, and transmittance was almost 80% in visible ray region.

Introduction

In modern society where the information is one of the major properties and the accessibility to information plays an important role in everyday life, ubiquitous circumstances have become a reality. Therefore display technology for oncoming generation tends toward wearable, mobile systems which should be small and light weight. For these reasons in the field of display, research has been focused on flexible display technology since it can be applied to wearable computers, electronic papers, smart identity cards, etc.[1] Especially, electrophoretic display has drawn much attention due to its distinct properties such as low cost, flexible, light weight, good contrast ratio, wide angle view and low power consumption.[2,3]

Since conducting polymers in the electronics fields have unique advantages of low cost, low temperature fabrication on a flexible substrate, high stability and ease of processing, they can be one of the main targets of smart engineering. Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as promising conducting polymers because of high conductivity, low oxidation potential and high thermal and electrochemical stability.[4] Also the characteristics of almost transparency in doped state caused by low band gap of PEDOT allows this polymer to be a good candidate for transparent polymer electrode.[5]

In this study, conducting polymer solution was prepared with PEDOT to fabricate conducting polymer film to examine effectiveness as transparent polymer electrode material. Poly(vinylpyrrolidone) (PVP) was used as a matrix polymer and to lower the polymerization rate, N-dimethylacetamide (DMAc) was used as a reducing agent. Since transparency is essential for the use of electrode in flexible displays, the thickness of coated polymer was controlled to be less than 1 micrometer. TiO_2 nanoparticles coated with polystyrene (PS) for surface modification and dispersion stability by dispersion polymerization were used as the electrophoretic particles.

Experimental

Preparation of surface-modified TiO_2 nanoparticles

To modify titanium dioxide (TiO_2) particles with polystyrene (PS) to reduce density mismatch[6], the technique of miniemulsion polymerization was used as follows.[7,8] 1 g of TiO_2 (Aldrich, average diameter of 20~50nm) was fully dispersed in 20g of styrene (Aldrich) monomer by agitating for 5 min and ultrasonicating for 10 min using VCX 750 (Sonic & Materials, Inc.). 1.5g of Sodium Lauryl Sulfate (SLS, Aldrich) was dissolved in 200 mL of deionized water and then 1g of poly(ethylene glycol) methyl ether methacrylate (PEGMMA, Aldrich) was slowly added into the aqueous solution with stirring and N_2 purging. The two solutions were mixed and sonicated for 10 min. Miniemulsion polymerization was started by addition of 0.5g of potassium persulfate (KPS, Aldrich) dissolved in 10g of deionized water to the mixture of two solutions. Polymerization was carried out for 6 hrs at 60°C with stirring speed of 400~500 rpm then stopped by addition of 200mL of methanol at 0°C in cold bath. The encapsulated TiO_2 particles with different sizes were separated by centrifugation at 2000 rpm for 10 min. To investigate the mobility, 1.5g of encapsulated TiO_2 particles and 0.15g of blue dye (Oil Blue N; Aldrich) were dispersed in Halocarbon 0.8 Oil (Halocarbon).

Preparation of conducting polymer electrode

Conducting polymer solution

For the in-situ chemical polymerization of PEDOT thin film as a transparent electrode, 3, 4-ethylenedioxythiophene (EDOT, Bayer) as a monomer, poly (vinylpyrrolidone) (PVP, Aldrich, average molecular weight of 360,000) as a binder and n-dimethylacetamide (DMAc, Aldrich) as a reducing agent were mixed with the weight ratio of 51:15:34, respectively and dissolved in n-butanol (Junsei Chemical Co., Ltd., Japan) with stirring and sonicated. To investigate the effect of reducing agent, the solution without DMAc was also prepared. Also to decide the optimum amount of DMAc, 30 wt % of PVP to EDOT monomer and 20~90 wt % of DMAc to EDOT monomer was mixed. 50 wt. % of oxidant solution was prepared by dissolving ferric p-toluenesulfonate (FTS, Bayer) in n-butanol.

Conducting polymer electrode

The conducting solution, prepared by mixing the monomer containing solution and oxidant solution, was spin coated on the glass using K-359SD-1 spinner (Kyowa Riken Co., Ltd., Japan). After the glass coated with conducting solution was kept in a convection oven at 70°C for 20 min, it was washed with methanol to dissolve out the un-reacted materials and dried at 70°C for 5 min.

Characterization

The sizes and shapes of TiO_2 nanoparticles coated with PS were determined by high resolution transmission electron microscope (HRTEM, JEOL 300kV, Japan). The miniemulsion polymerization was confirmed by Fourier Transform Infrared (FT-IR) spectrometer (SPECTRUM2000, Perkin Elmer, USA) and thermal characterization was performed using thermogravimetric analyzer (TGA, Shin Do Scientific Co., Korea) at the heating rate of 20°C/min. The electrical conductivity of transparent PEDOT thin film was measured by a four-probe method and expressed as specific surface resistivity (Ω / □) which was obtained by measuring the resistance between the two Platinum (Pt) wire electrodes pressed on the surface of the PEDOT thin film where the distance between the electrodes and the length of the electrodes were 1 cm. To optimize the condition to obtain PEDOT thin film with highly transparent and low surface resistivity, UV-visible (UV-Vis) Spectroscopy (Lambda 19, Perkin Elmer, USA) was performed.

Preparation of Cell

For the fabrication of polymer electrode cell to investigate the movement of electrophoretic particles, PEDOT was coated on two polypropylene films. The imide tape spacer gave a gap between two confronting PEDOT coated films. Electrophoretic particles with blue dye dispersed in halocarbon oil were injected into the gap, and then the cell was sealed with epoxy.

Results and Discussion

Figure 1 shows the FT-IR spectra of PS, pristine TiO_2 and PS coated TiO_2 nanoparticles. The spectrum of PS coated TiO_2 confirms the successful coating by exhibiting all characteristic peaks of both PS and TiO_2, including the peaks at 2950 cm^{-1} (C-H stretching, PS), at 1440 cm^{-1} (C-H bending, PS) and at 700 cm^{-1} (Ti-O stretching, TiO_2). TEM images in Figure 2 also confirm the encapsulation. The size increase of TiO_2 in Figure 2(b) indicates that PS was coated on the surface of TiO_2 nanoparticles by miniemulsion polymerization. Also it is confirmed that the shape of PS coated TiO_2 nanoparticles is sphere. The size and shape of nanoparticles influence the electrophoretic behavior. The size increase of particles lowers the density and thus mobility can be improved and the shape of sphere can reduce the drop of reflexibility due to the bistability.

Homopolymerized polystyrene which are impurities affecting the resolution might be formed during polymerization process, and they can be eliminated by centrifugation. The encapsulated nanoparticles were separated in terms of size and specific gravity by centrifugation as shown in Figure 3 confirming a linear relationship between residual TiO_2 content after thermal degradation and centrifugation speed. Figure 4 shows the effect of DMAc as reducing agent on the surface resistivity of PEDOT. When monomer (EDOT), matrix polymer (PVP) and oxidant (FTS) were dissolved in n-butanol and polymerized without the reducing agent in the oven at 70°C, the surface resistivity was higher than polymerized with the reducing agent.

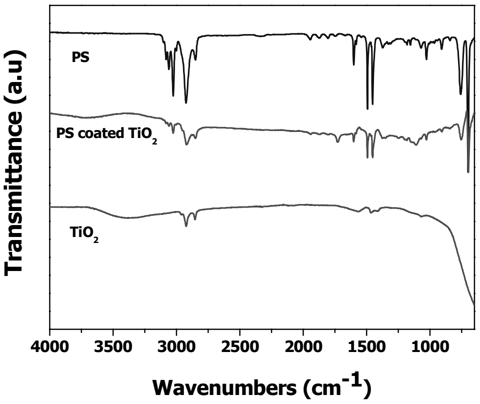
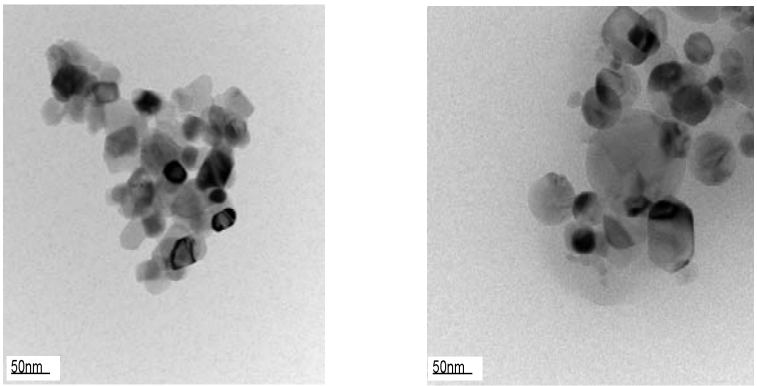


Figure 1. FT-IR spectra of PS, TiO_2, PS-coated TiO_2 nanoparticles



(a) (b)

Figure 2. TEM images of (a) pristine TiO_2 nanoparticles and (b) PS-coated TiO_2 nanoparticles

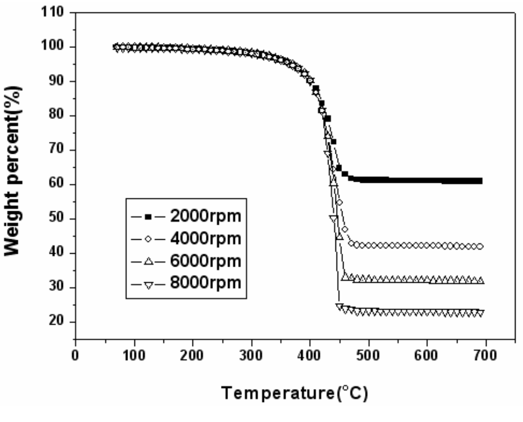


Figure 3. TGA thermogram of PS-coated TiO_2 nanoparticles collected under various centrifugation speeds

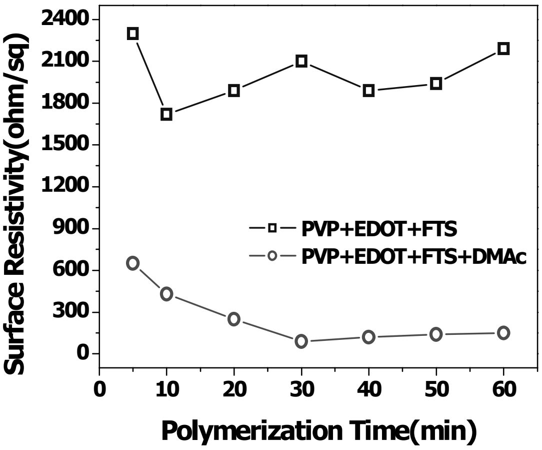
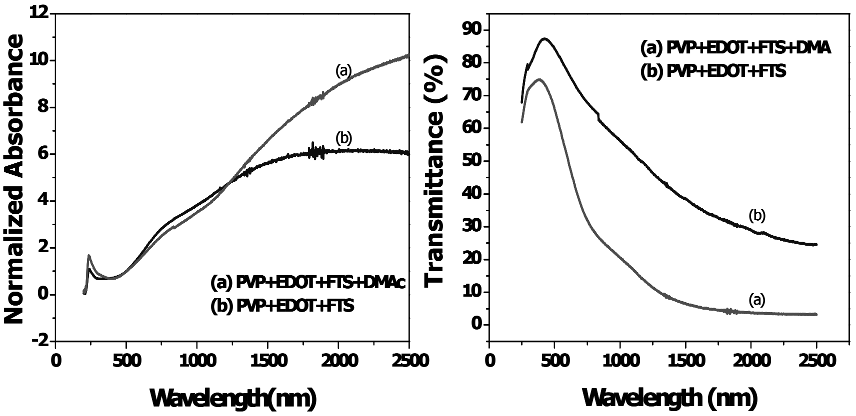


Figure 4. Effect of the reducing agent on the surface resistivity

Also when DMAc was added, the polymerization took about 30 min and the surface resistivity was as low as 90 Ω / □, whereas the polymerization time without DMAc was about 10 min and the surface resistivity was about 1720 Ω / □.

This indicates that the reducing agent controls and lowers the polymerization rate and gives enough time for PEDOT to be polymerized with more stabilized structure. We also compared absorbance and transmittance of the polymerized PEDOT with or without DMAc via UV-Visible spectroscopy. As can be seen in Figure 5 (a), the absorbance is higher with DMAc due to the drop of surface resistivity. We assume that this is because PEDOT film polymerized with DMAc could have high conductivity caused by existence of more electrons in the excited states.

Also the transmittance was measured to study the characteristics as transparent electrodes as shown in Figure 5 (b). When DMAc was not added in the polymerization process, the transmittance was above 70 % with the highest value of 89 % in the visible ray region. However with DMAc, the transmittance was above 60 % with the highest value of 73 % in the narrower region.



(a) (b)

Figure 5. Effect of the reducing agent on the absorbance and transmittance

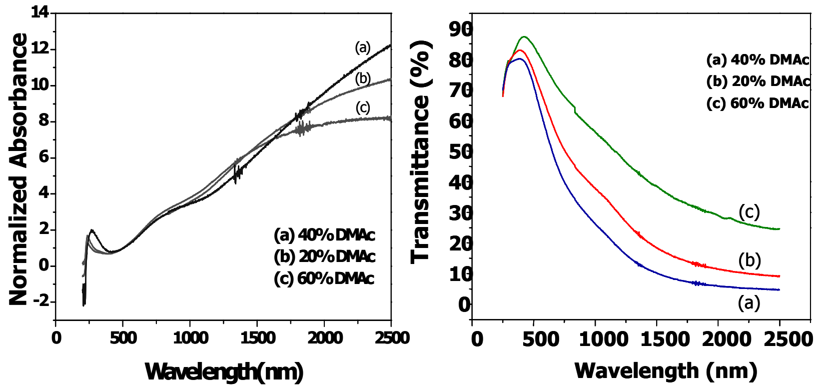


Figure 6. Effect of the amount of reducing agent on the absorbance and transmittance

Figure 6 shows the change in surface resistivity with DMAc content. The surface resistivity was reduced to 100 Ω/□ until 40 wt% addition of DMAc, and then started to increase again. This might be because too much reducing agent over 40wt% of monomer content inhibits the proper polymerization due to the too slow polymerization rate.

Figure 7(a) represents the electrophoretic behavior of electrophoretic particles. When there is no electric field applied, the particles are freely dispersed and when the electric field is applied, the white electrophoretic particles (TiO_2) move according to the attractive-repulsive force under the electric field. Figure 7(b) compares the

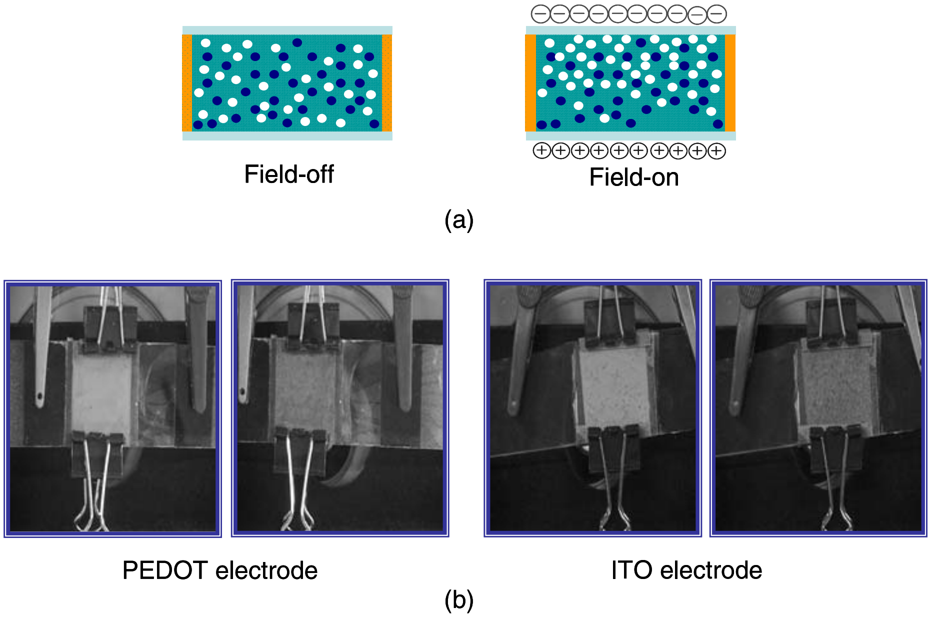


Figure 7. (a) Schematic representation of electrophoretic behavior
(b) Preliminary trial to compare electrophoretic behavior on PEDOT electrode and ITO electrode

movement of electrophoretic particles in the cell prepared with PEDOT electrode and ITO electrode, respectively. The particles showed movement in both cells. However the time for display was longer for the PEDOT electrode.

Conclusions

In order to reduce density mismatch of TiO_2 nanoparticles and dielectric medium and to increase dispersion stability, TiO_2 nanoparticles were coated with PS via miniemulsion polymerization. As a transparent polymer electrode, EDOT, that is transparent because polymer absorption band lies in infrared region, was in-situ polymerized. When the reducing agent (DMAc) was added, surface resistivity of PEDOT was dominantly reduced. With the DMAc addition of 40 wt% to the monomer content, surface resistivity was as low as 100Ω / □, and transmittance was almost 80% in visible ray region. We confirmed that PEDOT electrode could be used as transparent polymer electrode material in electrophoretic displays by comparing the movement of electrophoretic particles in the cell fabricated with PEDOT electrode and ITO electrode. Intensive studies to improve drive speed and electrophoretic properties are in progress.

Acknowledgements. This work was supported by the Sungkyunkwan University Advanced Institute of Nano Technology and by the Samsung Advanced Institute of Technology Consignment of Research and Development.

References

1. Chen Y, Au J, Kazlas P, Ritenour A, Gates H, McCreary M (2003) Nature 136:423
2. Chomskey B, Albert JD, Yoshizawa H, Jacobson J (1998) Nature 394:253
3. Kim C, Joung M, Ahn S, Kim G, Kang S, You I, Oh J, Myoung H, Baek K, Suh K (2005) Synthetic Metals, 151:181
4. Groenendaal L, Jonas F, Freitag D, Pielartzik H, Reynolds J (2000) Adv. Mater. 12:481
5. Grunathan K, Murugan A, Marimuthu R, Mulik U, Amenekar D (1999) Mater. Chem. Phys. 61:173
6. Landfester, K (2001) Adv. Mater. 13:765
7. Tang P, Sudol E, Silebi C, El-aasser M (1991) J. Appl. Polym. Sci. 43:1059
8. Sun Q, Deng Y, Wang Z (2004) Macromol. Mater. Eng. 289:288