

Optimized ion diffusion depth for maximizing optical contrast of environmentally friendly PEDOT:PSS electrochromic devices

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Abstract: Because the electrochromic (EC) performance significantly affects the diffusion of ions into the EC layer, EC layer thicknesses vary, ranging from approximately 100 nm to 400 nm. Their optimized and maximized EC performance in both optical contrast and color-switching behaviors are investigated as a function of EC layer thicknesses and applied bias voltages. Commercially available poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS) is selected as the EC layer due to its environmentally friendly condition and expected reproducible uniformity. Among the four different thicknesses of the PEDOT:PSS layer fabricated, the ~200 nm thick PEDOT:PSS layer exhibits the highest optical contrast ratio at an applied bias voltage of + 3.0 V for the bleached state and - 3.0 V for the colored state. Moreover, through increasing the applied bias voltage slightly to + 3.5 V/- 3.5 V, the color-switching speed is also significantly improved from 10 s to 5 s for switching from the bleached state to the colored state.

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1. Introduction

Electrochromism is generally defined as the reversible color and/or optical changes in materials that respond to an applied voltage [1]. Due to its reversible change in optical properties, electrochromic devices (ECDs) have garnered significant interest for potential applications in display for reflective modes [2], in mirrors and smart windows for shielding light [3], and in military camouflage architecture for protection [4]. Typically, ECDs consist of face-to-faced two-electrode (or more) electrolytic cells that include an electrolyte and electrochromic materials (one or more).

Electrochromic materials can be organic or inorganic, and they can reversibly change visible color when oxidized or reduced in response to an applied electrical potential. As electrochromic (EC) materials, organic and/or polymer materials are more promising due to their easily tunable color transition and simple processability compared with inorganic materials. Recently, conducting polymers (ECP) such as polyaniline [5], polythiophene [6], and polypyrrole [7] have been widely investigated as potential materials in terms of easy processability and effective cost. However, these basic structured materials typically have a low contrast ratio and slow response time. Therefore, there have been numerous efforts to improve the EC performance through modifying the EC materials by adding additives or synthesizing derivatives that exhibit approximately ten-second response ranges with irregular coloration drawbacks, and these methods are sophisticated to obtain uniform EC performance [8–12]. Of these EC materials, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) is very attractive due to its environmentally friendly conditions formulated in an aqueous solution and relatively stable electrochemical reaction in atmosphere condition. Furthermore, PEDOT:PSS is a commercially available product that enables qualified results with reproducibility. There are several trade names for PEDOT:PSS such as the Clevious series that has different grades according to the weight ratio changes between PEDOT and PSS that represent various viscosities and conductivities. Because PEDOT:PSS is a well-known material for EC polymers, one type of PEDOT:PSS series, i.e. Clevious P, is used in this work. However, to date, there have been very important, but easily overlooked points. As is well known, the electrochromic performance primarily relies on the diffusion of ions into the electrochromic material and this affects the contrast ratio and response time. Therefore, the appropriate thickness of the PEDOT:PSS layer would optimize the diffusion path of the ions into the layers and result in a higher contrast ratio and faster color-switching speed. In this work, improvements in the EC performance with reproducibility and uniformity using commercial PEDOT:PSS are demonstrated for potential application in contemporary ECDs.

2. Experimental sections

2.1. Materials

PEDOT:PSS was purchased from Heraeus Precious Metals GmbH & Co. (Germany) and used as received. Also, 1,2-dichlorobenzene (DCB, 99.0%), propylene carbonate (PC, 99.7%, anhydrous), tetrabutylammonium hexafluorophosphate (TBAPF₆, 99.0%), and lithium trifluoromethane-sulfonate (LiCF₃SO₃, 99.9%) were supplied by Sigma-Aldrich (USA) and used without further purification. Indium tin oxide (ITO) glass substrates with a sheet resistance (R_s) of 25 Ω /sq were used.

2.2. Thickness-varied EC layer preparation using PEDOT:PSS

ITO glass substrates with a size of 2×3 cm were first wet-cleaned in an ultrasonic bath using deionized (DI) water and MeOH, followed by drying with N_2 gas and then surface activation for 8 min in a UV/ozone-chamber. Next, approximately 1 ml of PEDOT:PSS was dispensed onto the substrate using a plastic pipette in order to cover the entire substrate's surface prior to the spin-coating. After spin-coating (@ 2000 rpm for 15 s), the PEDOT:PSS films were baked on a hotplate at 120°C for 10 min in air. This step was repeated in order to obtain the desired thickness of PEDOT:PSS.

2.3. Liquid electrolyte (L-EI) and electrochromic device (ECD) preparation

The thickness-controlled PEDOT:PSS spin-coated cleaned ITO glass substrates were placed with the ITO sides face-to-face and sealed with a $100\ \mu\text{m}$ -thick thermal adhesive tape in order to keep the gap constant and to prevent attacks from oxygen and moisture. The final form of the prepared ECD structure was ITO/PEDOT:PSS/L-EI/ITO. Then, the prepared liquid electrolyte, which was a mixture of 10 mM of LiCF_3SO_3 and 100 mM of TBAPF_6 dissolved in DCB and PC (v:v = 3:1), was injected and filled by capillary force. For the ECDs, the active area was 1.5×1.5 cm.

2.4. Characterization

The film thickness of the spin-coated PEDOT:PSS were measured using an Alpha-step 500 profilometer. The optical transmittance spectra of the thickness-varied PEDOT:PSS were obtained using a UV-visible-NIR spectroscopy (Perkin Elmer Lambda 750 Spectrometer, USA). The optical contrast ratio and response time were measured via the converted luminous transmittance (resulting in absorption changes) after applying the reverse bias voltage ranging from -3.5 V to $+3.5$ V for both bleached and colored states, respectively, using an LCD electro-optical measurement system (LCD 5200, Otsuka Electronics Co., Ltd., Japan) in transmission mode using the standard illuminant D65 (halogen lamp) as a light source.

3. Results and discussion

The schematic of the overall process flow for the ECD preparation is illustrated in Fig. 1. In the first step, the ITO glass substrate was cleaned and its surface was treated in order to obtain a hydrophilic state using a UV/ozone treatment in order to improve the film uniformity of PEDOT:PSS that is dispersed in water (Fig. 1(a)). After spin-coating the PEDOT:PSS to the desirable thickness, double-side adhesive tape was placed on the ITO glass substrate (Figs. 1(b) and 1(c)). Then, an upper ITO glass substrate with an in/out hole punched was placed with the ITO face-to-face and it was bonded to the PEDOT:PSS-coated ITO glass substrate (Fig. 1(d)). Once the liquid electrolyte was injected, the EC device was prepared (Fig. 1(e)).

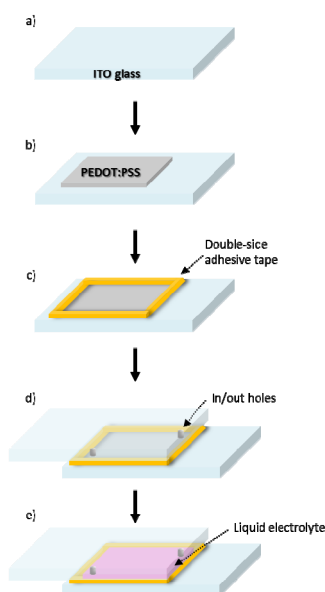


Fig. 1. Schematic of the overall process flow for the ECD preparation. (a) The ITO glass substrate is surface cleaned and then treated in order to obtain a hydrophilic state surface using a UV/ozone chamber. (b) PEDOT:PSS is spin-coated onto the ITO glass, and the thickness of the PEDOT:PSS layers was varied; the final thicknesses are 100 nm, 200 nm, 300 nm, and 400 nm under repeated spin-coating at a fixed spin rpm. (c) Then, double-side adhesive tape is placed on PEDOT:PSS coated ITO glass substrate, and (d) it was covered with another cleaned ITO glass substrate that was placed with the ITO face-to-face. (e) Finally, the ECD is prepared after injecting the liquid electrolyte through the in/out holes.

In order to understand the linear relationship between the thickness and transmittance changes, the optical properties of the PEDOT:PSS film were investigated using UV-Vis-NIR spectroscopy. The PEDOT:PSS layer thicknesses were varied in order to obtain four different sets via spin-coating repeated times at a fixed spin speed of 2000 rpm, and their thickness were measured using an Alpha-step 500 profilometer. As depicted in Fig. 2(a), the measured layer thickness of the PEDOT:PSS increased from approximately 100 nm to 400 nm (referred to as P1 to P4) with increased numbers of spin-coating, and their optical transmittances were clearly affected by the increasing layer thickness (see Figs. 2(b) and 2(c)).

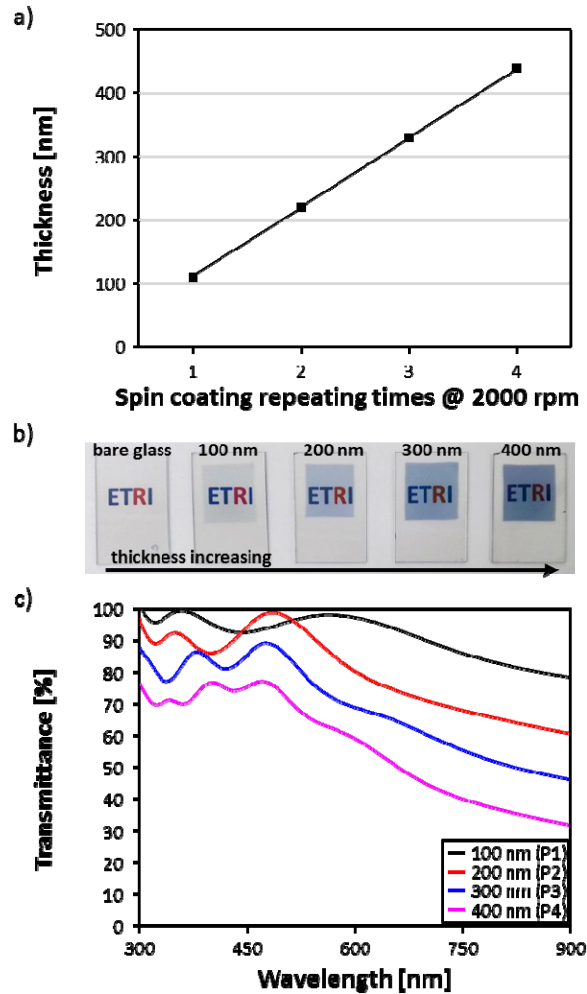


Fig. 2. (a) The measured PEDOT:PSS layer thickness as a function of repeated spin-coating at a fixed spin speed of 2000 rpm. (b) Photos of the thickness-varied PEDOT:PSS films. The film thickness is increased from right to left via repeated spin-coating. (c) UV-Vis-NIR spectra of the PEDOT:PSS film thickness with various thicknesses of 100 nm (referred to as P1), 200 nm (referred to as P2), 300 nm (referred to as P3), and 400 nm (referred to as P4) under repeated spin-coating at a fixed spin rpm.

Furthermore, as is well-known, there is an optimal point to have the maximum optical contrast of EC behavior versus the optimum thickness of the EC layers. Because the EC performance is primarily affected by reduction and oxidation reactions that react with the ions in the electrolyte, the diffusion path of the ion into the EC layer is affected by its thickness. Therefore, in order to obtain significantly improved EC performance in terms of higher bleaching/coloring ratios and faster color-switching speeds, the optical transmittance changes that depend on the PEDOT:PSS thickness variations were monitored and compared under different applied voltages. The transmittance (T) is defined as follows [13]:

$$T = \frac{P}{P_0}, \quad (1)$$

where P_0 is the light of the radiant power incident on the device and P is the radiant power of the transmitted light. In our system, the transmittance changes under an applied bias voltages

is converted to the luminous transmittance (T_{lum}) using the CIE 1931 photopic reference for the human eye, which is defined as follows [14]:

$$T_{lum} = \frac{\int T(\lambda)f(\lambda)d\lambda}{\int f(\lambda)d\lambda}, \quad (2)$$

where $T(\lambda)$ is the measured film transmittance, $f(\lambda)$ is the eye-sensitive luminous spectral efficiency, and $d\lambda$ is the each wavelength that is integrated wavelength (λ) ranging from 380 nm to 780 nm. Therefore, the luminous transmittance is weighted average of the transmittance in the whole wavelength range. However, the transmittance changes for ECDs is often affected by the thickness of EC layers, which have transmittance differences that are described in Eqs. (3) and (4) as follows [15]:

$$T_b = \exp(-\alpha_b d), \quad (3)$$

$$T_c = \exp(-\alpha_c d), \quad (4)$$

where α is the linear absorption coefficient and d is the thickness of the EC layer. The subscripts b and c indicate the optical changes of the bleaching and coloring states of the EC layers, respectively, when the bias potential is applied. In order to determine the attainable contrast of the ECD, the measured T_b and T_c can be used as written in Eq. (5):

$$CR = \frac{\exp(-\alpha_b d)}{\exp(-\alpha_c d)} = \frac{T_b}{T_c} \quad (5)$$

The CR is the calculated ratio of the transmittance changes between T_b and T_c , which is called the contrast ratio. As Eq. (4) demonstrates, the CR is affected by the thickness of the EC layers. Moreover, the CR is highly dependent on the applied voltage. Therefore, in order to observe the optical changes, the ECD cells were prepared with four different thicknesses of EC layer, and the Li^+ ion-based liquid electrolyte was injected into the ECD cells.

Figure 3 presents the luminous transmittance changes of T_b and T_c with the thickness variation of P1 (referred to as 100 nm thick-layer), P2 (referred to as 200 nm thick-layer), P3 (referred to as 300 nm thick-layer), and P4 (referred to as 400 nm thick-layer) that were measured as a function of the applied voltages ranging from + 0.5 V to + 3.5 V for the bleached state and -0.5 V to -3.5 V for the colored state. As seen in Figs. 3(a) and 3(b), when the PEDOT:PSS thickness was thin (i.e. P1), there was no distinguishable changes in the T_b and T_c even with increases in the voltage; this indicates that the thickness of P1 is not sufficient to enable ion numbers to move into layers causing insufficient colored state. In contrast, when the thickness was very thick, e.g. P3 and P4, the colored state exhibited fully absorbed light through increases in the applied negative voltage, which was similar to the bleached state causing decreases in the transparency. This results from the long diffusion path of the ions causing difficulties for ions to emerge from the EC layers. Therefore, there should be an optimized thickness for the EC layer in order to obtain sufficient T_b and T_c ; the optimized thickness was found to be P2. Although the colored state remained lower than P3 and P4 through increases in the negative voltage, the transmittance of the bleached state increased slightly. The contrast ratios among P1, P2, P3, and P4 were calculated and are plotted in Fig. 3(c). P2 exhibited a remarkable CR improvement at + 3.0 V and -3.0 V, which is likely to preserve the high transparency in higher applied voltages.

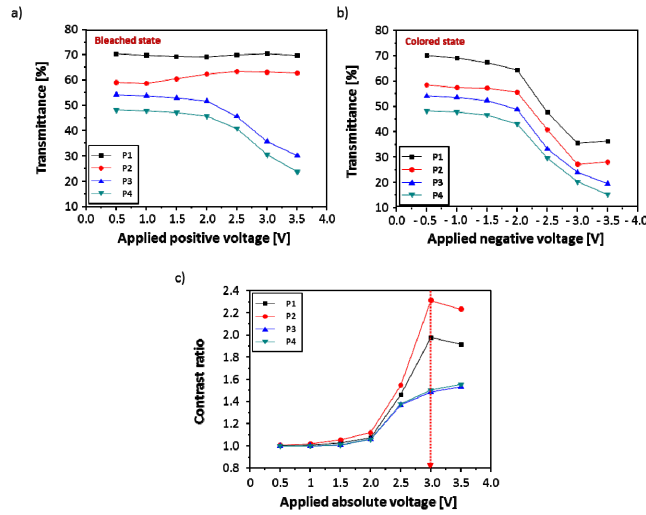


Fig. 3. The measured luminous transmittance changes of (a) bleached and (b) colored states of the thickness-varied P1, P2, P3, and P4 under different applied voltages ranging from -3.5 V to $+3.5$ V. (c) The calculated contrast ratio demonstrates that the EC layer thickness required to obtain higher T_b and lower T_c must be optimized, and it is found that P2 with ~ 200 nm-thick layer is optimal.

In order to investigate the color-switching speed of P2-ECD, the optical response time was measured at the applied reverse bias voltages of $+3.0$ V and -3.0 V, which have been proven to have the highest contrast ratio (see Fig. 3(c)). As depicted in Fig. 4(a), the optical transmittance changed and caused the appearance of a bleached state from the colored state when the positive voltage was applied, and it required approximately 1.7 s. However, as marked in the figure, when the optical transmittance changed to the colored state from the bleached state, the color-switching speed was very slow and required up to 10 s (see Fig. 4(a), circle). Therefore, in order to strongly push the ion diffusion in and out for the PEDOT:PSS EC layer, the applying reverse bias voltage was increased slightly to $+3.5$ V and -3.5 V. Even though the bleaching time exhibited a similar response behavior, the coloring time was significantly improved to be 5 s. Photographs of the prepared ECD cells are presented in Fig. 4(b). The upper photo is the initial state of ECD cells as prepared, and the below photos are the bleached and colored states maintaining transparency and darkness when the bias voltages of $+3.5$ V and -3.5 V, respectively, are applied alternatively.

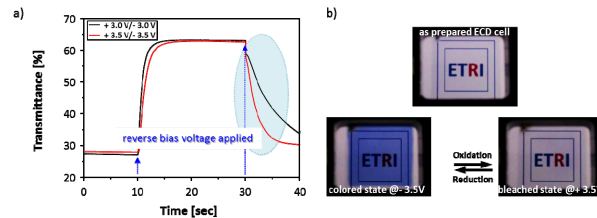


Fig. 4. Optical transmittance changes of (a) P2-ECD under an applied reverse bias voltage of $+3.0$ V/ -3.0 V and $+3.5$ V/ -3.5 V at a time of 40 s, and (b) photographs of the ECD cells in the initial state as prepared (up), colored state (right), and bleached state (middle) at the voltage indicated.

4. Conclusion

In order to optimize the electrochromic (EC) performance in both the optical contrast ratio and color-switching speed, an easy and efficient method is proposed through varying the

thickness of the EC layers, with using commercially available PEDOT:PSS as the EC material. Moreover, through using PEDOT:PSS thicknesses ranging from 100 nm to 400 nm, the results demonstrated that the effective and optimal improvement of the optical contrast ratio was achieved with an EC layer thickness of ~ 200 nm (referred to as P2). This indicates how the EC layer thickness affects the diffusion path of the ion in a liquid electrolyte. In addition, the color-switching speed was also significantly improved and exhibited a faster response reduced from 10 s to 5 s for switching from the bleached state to the colored state when the bias voltage was applied up to + 3.5 V/-3.5 V from + 3.0 V/-3.0 V.

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