

Tricolor Electrochromism of PEDOT Film Electrodeposited in Mixed Solution of Boron Trifluoride Diethyl Etherate and Tetrahydrofuran: Hypsochromic Effect

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ABSTRACT: PEDOT [poly (3,4-ethyldioxythiophene)] films have been electrochemically prepared in mixed solution of boron trifluoride diethyl etherate and tetrahydrofuran (BFEE-THF). The film shows tricolor electrochromism which is claret red at -0.8 V, light grey at 0.2 V, and sea blue at 1.0 V. The film retains 74% of the original electroactivity and unperturbed electrochromic behaviors after 3000 cycles indicating potential applications on EC devices. Spectroelectrochemistry indicates that the π - π^* transition absorption peak (λ_{max}) in the neutral state is located at 512 nm and the calculated energy gap (E_g) is 1.76 eV by the onset wavelength. Compared to the electropolymerization of PEDOT films in conventional solvent, tricolor electrochromism can be ascribed both to the low onset oxidation potential and polymerization rate in BFEE-THF, which may result in a low conjugation length of PEDOT. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3764–3771, 2013

KEYWORDS: conducting polymers; tetrahydrofuran; optical properties; electrochemistry

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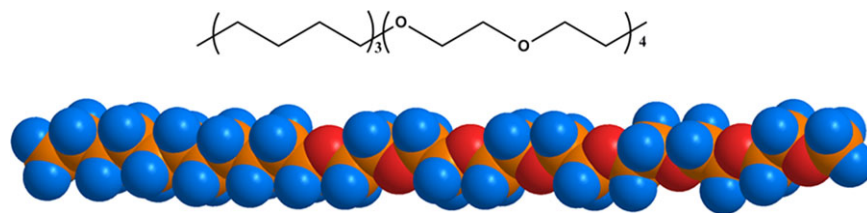
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INTRODUCTION

An electrochromic material can change its color in a persistent and reversible manner by an electrochemical reaction and the phenomenon is called electrochromism.¹ Among various conducting polymers for electrochromics, poly (3,4-ethylenedioxythiophene) (PEDOT) gains special interest due to its low oxidation potential, excellent stability and high conductivity.^{2–4} Furthermore, PEDOT films synthesized in conventional organic solvents or aqueous solutions show color changing from dark blue to highly transmissive light blue upon oxidation.^{5–7} Recently, one desired goal of electrochromics is that single electrochromic electrode can exhibit colors as much as possible. Some redox-active dopants have been used to add new colored states in the electrochromic films.⁸ Fei et al. used poly (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (PABTS) as dopants in PEDOT showing three color changes (blue, grey, and green).⁹ However, it is actually a polymer composite, while the redox-active dopants show color change under redox potential and add new colored states to the polymer. Apart from a few conducting polymers, other single electrochromic material can rarely achieve more than two colors.²

During the past decades, boron trifluoride diethyl etherate (BFEE) has been found to be an excellent electrolyte for electropolymerization of conducting polymers to exhibit exciting properties.^{10,11} Its main characteristic is the considerable lowering of the oxidation potential that is necessary for preparing high quality electrochromic films. Shi et al. synthesized polythiophene using BFEE as solvent-electrolyte system that solved the problem of "thiophene paradox," and the resultant polythiophene film exhibited fascinating properties.¹² Reynolds et al. prepared polythiophene and its derivatives in BFEE presenting high quality and various electrochromic properties which are different to these films prepared in acetonitrile (ACN).¹³ However, few have been reported about the electropolymerization of 3,4-ethylenedioxythiophene (EDOT) in BFEE for the reasons of low solubility and strong interaction between BFEE and the oxygen of EDOT.¹⁴ Tetrahydrofuran (THF) is a good solvent for monomers which shows high nucleophilicity and can be used to solve the aforementioned contradictions.¹⁵

In this work, we prepared PEDOT films in the mixed solution of BFEE and THF. The resultant films present high quality and



Scheme 1. The chemical structure and three dimensional structure of MOA-K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good electrochemical properties. Compared to the PEDOT films prepared in conventional solvent such as ACN and aqueous solution, the film exhibits hypsochromic effect in the neutral state and presents tricolor electrochromism which shows claret red at -0.8 V, light grey at 0.2 V, and sea blue at 1.0 V.

EXPERIMENTAL

Materials

EDOT (Aldrich) is used as received. Supporting electrolytes (lithium perchlorate, LiClO_4 , analytical grade), surfactant (MOA-K), acetonitrile (ACN, high performance liquid chromatography (HPLC)), BFEE (analytical grade), tetrahydrofuran (THF, HPLC), and propylene carbonate (PC, HPLC) are purchased from Tianjin Chemical Reagent Institute. MOA-K is a mixture of α -dodecyl polyoxyethylene (8) ether and α -tetradecyl polyoxyethylene (8) ether, and the chief structure is shown in Scheme 1.¹⁶ Deionized water (resistivity ~ 18.2 M Ω) obtained through Milli-Q system is used as a solvent. Indium tin oxide (ITO, 1.5×2 cm, $8\text{--}9\Omega/\square$) is a product of Zhuhai kaivo Electronic Components Co., Ltd.

Equipments

Electrochemical polymerization and characterizations are performed on a CHI660D working station. Scanning electron microscope (SEM) measurements are taken by using a Hitachi S4800 Scanning electron microscopy. X-ray photoelectron spectroscopy (XPS) spectra are recorded on a Thermo Fisher Scientific K-Alpha1063. The images of the electrochromic films are taken by a canon EOS 500D digital camera. The ASD Field Spec® Fland Held Device is used as a Vis-NIR spectrum test tool with wavelength range from 380 to 1050 nm.

Electrochemical Polymerization and Measurements

The PEDOT films (as marked by P1, P2, and P3) are prepared by potentiostatic 1.2 , 1.05 , and 1.3 V with polymerization charge of 100 mC/cm^2 in 0.2 M $\text{LiClO}_4/\text{ACN}$ solution, mixed solution of BFEE-THF with the feed ratio of BFEE/THF at 2: 3, and 0.05 M MOA-K and 0.2 M LiClO_4 aqueous micellar solution, respectively, and the concentrations of EDOT in these solutions are 20 mM. ITO/glass electrode, stainless foil and Ag/AgCl are used as working electrode, counter electrode and reference electrode, respectively. The working and counter electrodes are sequential rinsed 20 min in ethanol, acetone, and deioned water under ultrasonic before use. Electrochemical and optical properties are measured in 0.2 M LiClO_4/PC solution. All of the electrochemical experiments are taken at 27°C under nitrogen atmosphere unless specified.

RESULTS AND DISCUSSION

Electrochemical Polymerization

The polarization curves of EDOT in ACN, aqueous micellar solution and BFEE-THF are shown in Figure 1. The onset potential for anodic current ($E_{\text{pa onset}}$) of EDOT in BFEE-THF, ACN, and aqueous solution are 0.82 V, 1.07 V, and 0.92 V, respectively. The relatively lower $E_{\text{pa onset}}$ in BFEE-THF could be related with the weak interaction between the Lewis acid (BFEE) and EDOT monomer system. The interaction can reduce the aromaticity of the latter and promotes the abstraction of an electron from the α -position of the heterocyclic ring, which facilitates the oxidation of EDOT and decrease the $E_{\text{pa onset}}$.^{13,15} Besides, the low $E_{\text{pa onset}}$ in BFEE-THF and aqueous solution also implies that more EDOT radical cations can be easily formed in these solutions.

Cyclic voltammograms (CVs) of the three solutions without EDOT, and EDOT in these solutions at a scan rate of 100 mV/s are presented in Figure 2. As seen in Figure 2 (inset), the three solutions are stable during the polymerization process of EDOT. While EDOT added into the solutions, the oxidation current density increases with the increasing cycles, and the observable films are formed on the working electrodes for the three systems.¹⁷ The redox behaviors and increments of EDOT in ACN, BFEE-THF, and aqueous solution are completely different, which is an indication of different electrochemical properties between PEDOT films deposited in these solutions. A low current density [Figure 2(a)] implies low polymerization rate in BFEE-THF and more regular films then can be formed.¹⁸

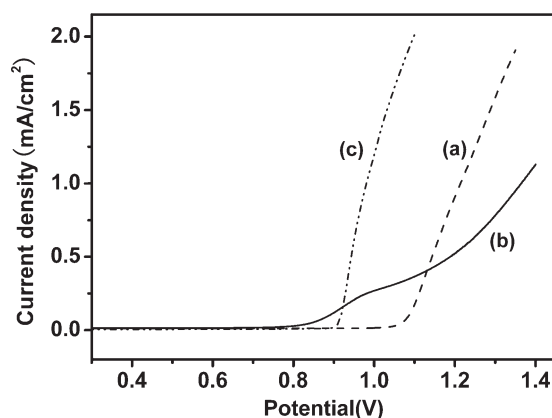


Figure 1. Polarization curves of EDOT in (a) 0.2 M $\text{LiClO}_4/\text{ACN}$, (b) BFEE-THF, (c) 0.05 M MOA-K and 0.2 M LiClO_4 aqueous micellar solution. Scanning rate: 10 mV/s .

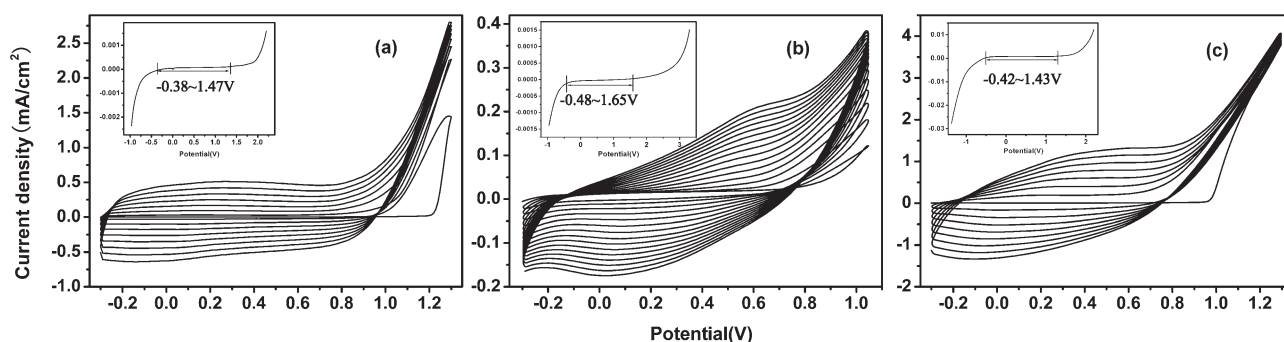


Figure 2. CVs of 0.02 M EDOT and these three solution without EDOT (inset) in (a) ACN, (b) BFEE-THF, (c) aqueous solution at a scan rate of 100 mV/s.

XPS, Thermal Stability and Morphology

To analyze the composition and doping level of P2, the film is fully oxidized under an applied potential at 1.0 V before XPS test. Figure 3 presents the XPS spectra of the polymer. There is no large difference between P2 and PEDOT films deposited in ACN and aqueous solutions, indicating that PEDOT film formed on the ITO electrode.⁶ As the film gets oxidized, the doped counter ions enter into the polymer chain. The doping level can be calculated as the ratio of doped ions and the polymer units.⁷ ClO_4^- ions are used as doped ions here. As expected, the at % of Cl is 2.58 while the at % of S is 6.43. So the atomic ratio of Cl/S is about 0.40, which is higher than others doped by polystyrene sulfonate (PSS) or CF_3SO_3^- PEDOT.^{6,19} A high doping level can be attributed to the high quality film deposited in the mixture solution of BFEE and THF and the small molecular size of the ClO_4^- which favors their injection into the film.

The thermal stability of conducting polymers is very important for their potential applications.²⁰ Figure 4 presents the thermogravimetry (TG) curves of P1, P2, and P3 films at a heating rate of $10^\circ\text{C min}^{-1}$ from 80 to 450°C . An initial weight loss for all polymer films between 80 and 125°C can be assigned to the evaporation of residual solvent and water. The loss percentage in the range is 2 to 4%. P1 losses 82% of weight in the range of $125\text{--}190^\circ\text{C}$. P3 shows two obvious weight losses: one is located between 125 and 220°C with a weight loss of 43%, and the other is located in the range of $280\text{--}355^\circ\text{C}$ with a weight loss of 24%. However, P2 shows much more stable than P1 and P3, the residue of P1, P2, and P3 at 450°C is 11, 46, and 28%,

respectively. These results indicate a high quality film formed, which can be attributed to the regular polymerization of EDOT in BFEE-THF.

The properties of conducting polymers are strongly dependent on their morphology and structure.²¹ The morphology and thickness of P1, P2, and P3 are presented in Figure 5. As seen from Figure 5(b), P2 film shows an accumulation state of weenie globules (almost 50–80 nm), P1 and P3 exhibit a globule structure with diameters ranging from 300 to 500 nm and 150 to 200 nm, respectively [Figure 5 (a,c)]. The weenie globules and compact structure of P2 can be ascribed to both of the low polymerization rate and onset oxidation potential. Furthermore, P1, P2, and P3 films presents almost same thickness under same polymerization charge, which are 246, 283, and 265 nm, respectively.

Cyclic Voltammograms

Cyclic voltammogram is the most widely used technique for acquiring qualitative information about electrochemical redox reaction of conducting polymers.²² Figure 6 presents the typical CVs of P1, P2, and P3 films. As seen in Figure 6, the redox couples of A1/C1, A2/C2, and A3/C3 can be attributed to the conversion between doped and dedoped states of PEDOT films which is represented by the following simplified reaction²:



From CVs, a higher anodic peak potential of P2 indicates the higher highest occupied molecular orbital (HOMO) orbit existing

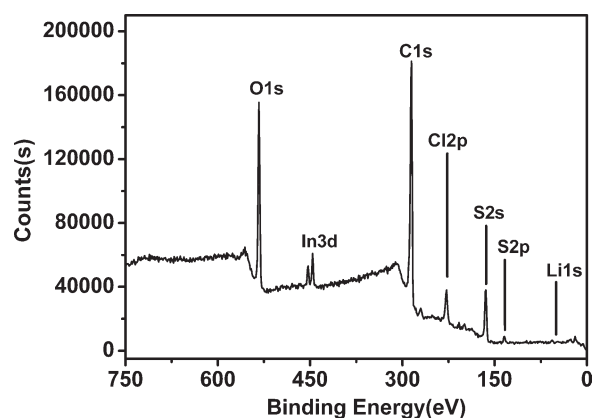


Figure 3. XPS spectra of P2 film in the oxidized state.

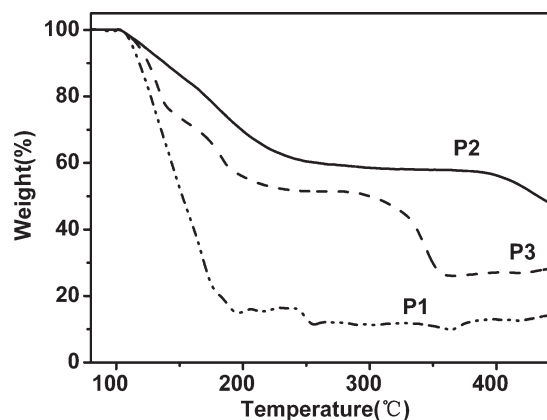


Figure 4. Thermal stability of P1, P2, and P3 film.

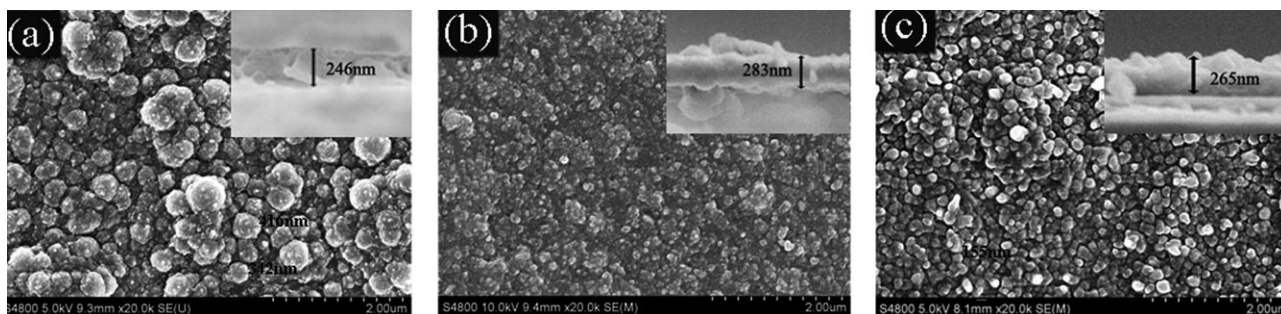


Figure 5. SEM images and thickness of (a) P1, (b) P2, and (c) P3 films.

which implies the difference of band gap in the three polymers. During the CVs, the films show rich color change which will be specified in the following text.

Investigation of peak current intensity of CVs with respect to scanning rates will indicate the nature of electrochemical process.²³ The CV curves of P2 film are shown in Figure 7 in monomer free electrolyte at different scanning rates. The polymer shows a single, well-defined redox process, the current density is proportional to the scanning rate, indicating that the film is electroactive and well adhesive to the electrode (Figure 7). With the increase of scanning rate, the potentials of anodic and cathodic peak current densities show positive and negative shift, which implies quasireversible redox processes in high scanning rates. Furthermore, the anodic and cathodic peak current densities show a linear proportion to scan rate as expected (Figure 7, inset), demonstrating that the electrochemical processes are not diffusion limited.²⁴

The stability of electrochromic conducting polymers toward long-term switching between the neutral and oxidized states is one of the most important factors for the application of electrochromic materials in device utilities.²⁵ The electrochemical stability of P2 film is characterized by 3000 times of CV test in the potential range of -0.8 V to 1.0 V at a scanning rate of 100 mV/s [Figure 8(a)]. After 3000 cycles, the film retains 74% of its original electroactivity and the changes of anodic peak current density (j_{pa}) and (j_{pc}) are 27 and 28%, respectively. After 1000 cycles, P3 film retains 70% of its original electroactivity,

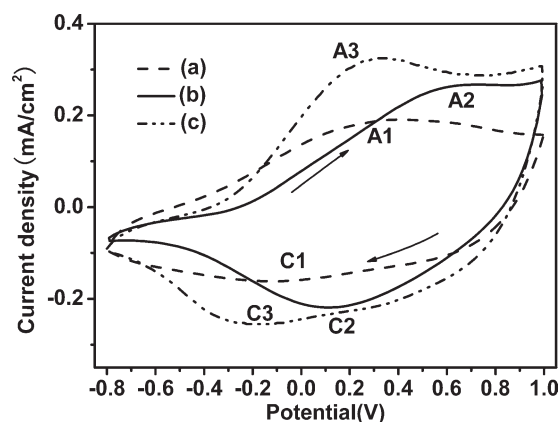


Figure 6. Cyclic voltammograms of (a) P1, (b) P2, and (c) P3 films at a scanning rate of 100 mV/s.

and there is no obvious change of electroactivity between 1000 and 2000 cycles [Figure 8(b)], the higher stability of P2 film than P3 can be attributed to regular polymerization of EDOT in BFEE-THF. These results indicate that the P2 film has a reasonable environmental and redox stability and could be used as a promising candidate material for electrochromic devices.

Electrochromic Properties

The electrochromic properties of P1, P2, and P3 are investigated under various applied potentials. The optical images are shown in Figure 9. P2 exhibits tricolor electrochromism. At an applied potential of -0.8 V, the film in the dedoped state shows a claret red color, and passes to light grey at 0.2 V for the reason of ClO_4^- insertion. When the applied potential increases to 1.0 V, the film turns into sea blue color. Whereas P1 film presents dark blue at -0.8 V, blue at 0.2 V, and light blue at 1.0 V which is consistent with reference.^{1,15,26} P3 exhibits blue violet at -0.8 V, blue at 0.2 V, and light blue at 1.0 V.^{27,28} It is interesting that PEDOT film electrodeposited in BFEE-THF shows tricolor electrochromism, which is quite different to those films prepared in ACN and aqueous solution.

The Commission Internationale de l'Eclairage (CIE) system is used as a quantitative scale to present and define the colors of PEDOT film.¹⁶ The values of L (Luminance), a (Hue), and b (Saturation) are calculated by the reflectivity spectra and relative

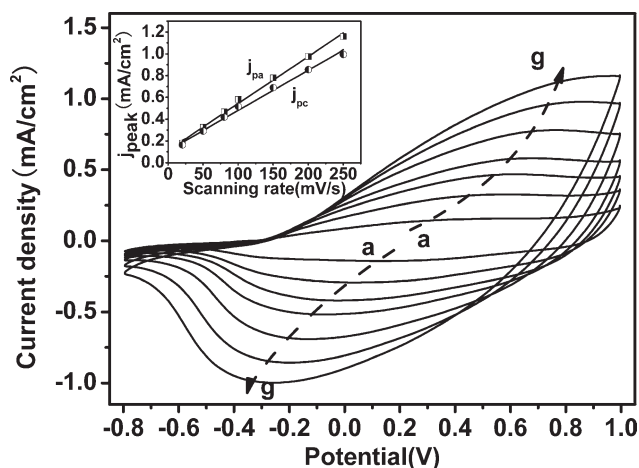


Figure 7. Scan rate dependence of P2 film at a scan rate of (a) 20, (b) 50, (c) 80, (d) 100, (e) 150, (f) 200, (g) 250 mV/s, inset: anodic and cathodic peak currents as a function of the scanning rate.

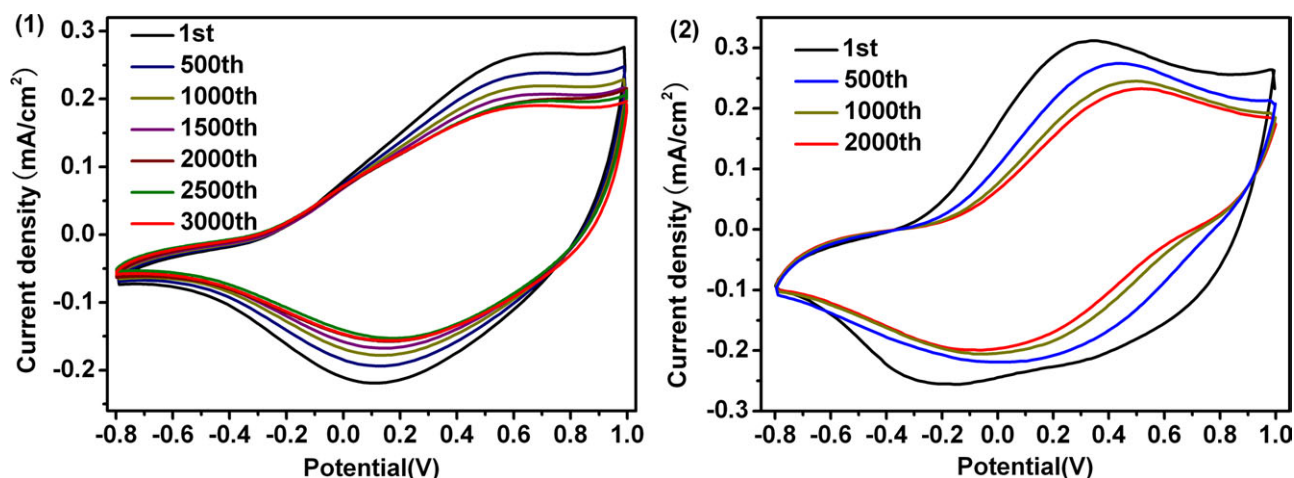


Figure 8. Electrochemical stability of (a) P2 and (b) P3 with a scan rate of 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

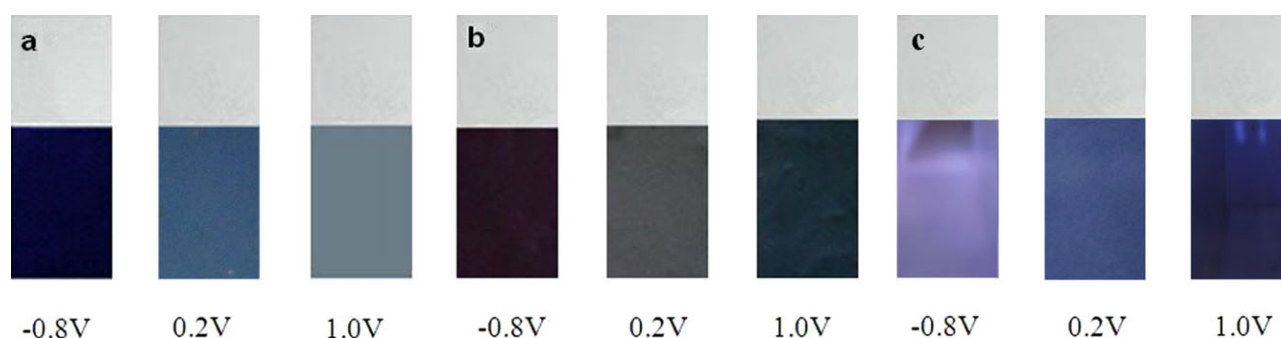


Figure 9. Images of (a) P1, (b) P2, and (c) P3 films under various applied potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrochromic behaviors of PEDOT films under various applied potentials are listed in Table I. With CIE $L^*a^*b^*$, the color contrast (ΔE) of electrochromic process can be defined as the following equation²⁹:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

The values of ΔL , Δa , and Δb are the difference of L , a , b between the dedoped and doped film. The color contrast of P1,

Table I. Colorimetric Properties of P1, P2, and P3 films

Material	Color	L	a	b	ΔE
P1	Dark blue(-0.8 V)	7.2	15.1	-32.2	
	Blue(0.2 V)	42.3	-4.5	-21.2	
	Light blue(1.0 V)	55.3	-5.4	-6.6	58.2
P2	Claret red(-0.8 V)	17.3	13.4	-8.3	
	Light grey(0.2 V)	39.8	-1.2	-2.6	
	Sea blue(1.0 V)	24	-5.3	-10.2	20
P3	Blue violet(-0.8 V)	49.8	10.2	-19.4	
	Blue(0.2 V)	39.5	3.7	-26.6	
	light blue(1.0 V)	69.8	2.7	-10.8	23.1

P2, and P3 is 58.2, 23.1, and 20, respectively. The low color contrast of P2 can be mainly attributed to the low luminance difference between the neutral and oxidized state.

Spectroelectrochemistry is a powerful way to investigate the optical properties of an electrochromic conducting polymer upon potential change, which also provides information on the electronic structure of the conducting polymer.^{17,25} The P2 is swept between -0.8 V and 1.0 V. As seen in Figure 10 (a), the π - π^* transition absorption peak (λ_{\max}) in the neutral state is located at 512 nm and the band gap (E_g) is calculated as 1.76 eV by the onset wavelength. As the film gets oxidized, the charge carrier bands at longer wavelengths increase in intensity, polaron bands (0.2 V) around 483 and 805 nm are observed. As the applied potential increases to 1.0 V, the film shows electronic absorption at long wavelength of 924 nm due to bipolaron band.

The PEDOT films present various color change, especially, P1, P3, and P2 exhibit dark blue, blue violet, and claret red in the neutral state, respectively. The absorption spectra of P1, P2, and P3 in the neutral state are shown in Figure 10(b). The λ_{\max} for these three samples are 607, 554, and 512 nm, respectively, revealing an obvious hypsochromic effect from P1, P3, to P2. The difference of λ_{\max} contributes to the different

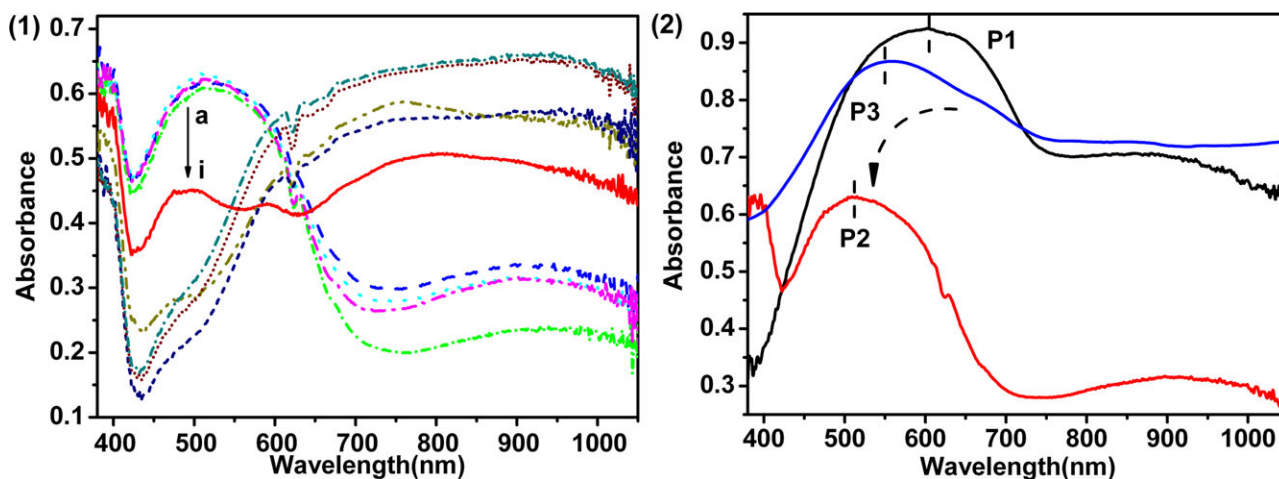


Figure 10. Spectroelectrochemical spectrum of (a) P1 with applied potentials (V) between -0.8 and 1.0 : (a) -0.8 , (b) -0.6 , (c) -0.4 , (d) -0.2 , (e) 0.2 , (f) 0.4 , (g) 0.6 , (h) 0.8 , (i) 1.0 , and (b) Absorption spectrum of P1, P2, and P3 in the neutral state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrochromic properties, especially the color of films in the neutral state. To further investigate the hypsochromic effect, the band gaps of P1, P2, and P3 are calculated through the onset wavelength. The corresponding values are 1.63 eV, 1.76 eV, and 1.66 eV, respectively. As the composition of three films is same, the various band gaps could be mainly ascribed to different

conjugation lengths. And it is well known that short conjugation length can induce high band gap. Therefore, the hypsochromic effect from P1, P3, to P2 could be attributed to the shorter conjugation length of P2 and P3 than P1.

Based on the comparison of the electropolymerization of these three polymers, two reasons are used to explain the short

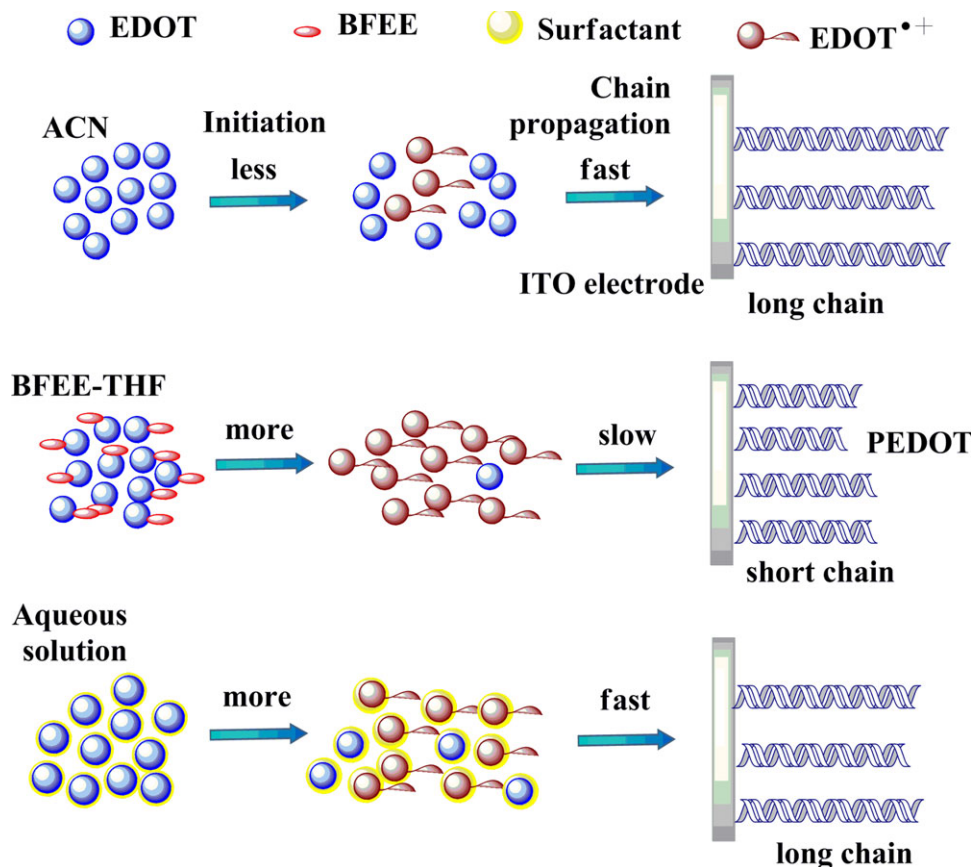


Figure 11. Schematic polymerization of EDOT in ACN, BFEE-THF and aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

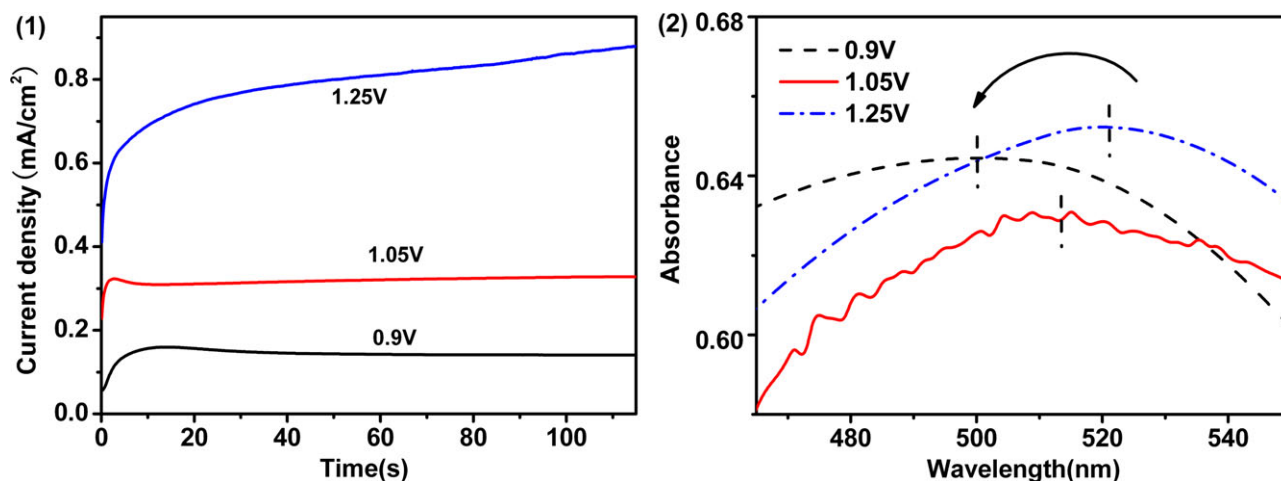


Figure 12. (a) Chronoamperometric response of EDOT electropolymerization in BFEE-THF under potentiostatic 0.9, 1.05, and 1.25 V; (b) Absorption spectrum of PEDOT films deposited under potentiostatic 0.9, 1.05, and 1.25 V in the neutral state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conjugation length of P2: (1) low onset oxidation potential, (2) sluggish polymerization. Figure 11 shows the schematic polymerization of EDOT in ACN, BFEE-THF, and aqueous micellar solutions. As been well known, the electropolymerization mechanism of EDOT is believed to involve either radical-cation/radical-cation coupling or reaction of a radical-cation with a neutral monomer.³⁰ EDOT molecules loss electrons to form radical-cations at the beginning of polymerization, and low onset oxidation potential indicates that more EDOT radical-cations can be easily formed in the BFEE-THF and aqueous micellar solutions during the initiation process, then there are more oligomers to propagate. As the chains begin to propagate, high polymerization rate of EDOT in ACN and aqueous solution induces the oligomers to grow instantaneously, which become much larger than the solubility and form long chains of PEDOT to deposit on the electrode. However, sluggish polymerization of EDOT in BFEE-THF induces the oligomers to grow regularly, which will deposit on the electrode with short chain once the oligomers just no longer dissolve in the electrolyte solution.

To show the relation between the polymerization rate and absorption spectrum of neutral films, PEDOT films are electro-deposited at different potentials and dedoped at -0.8 V. Figure 12 shows the chronoamperometric response of EDOT electropolymerization in BFEE-THF and absorption spectrum of the resultant PEDOT films in the neutral state. The plateau current increases with the increase of the applied potential, indicating the increase of polymerization rate.³¹ High polymerization rate could induce long conjugation length, and then lead to red-shift, and vice versa.^{32,33} It is obvious that λ_{\max} is blue-shift in the neutral state as the polymerization potential decreases.

CONCLUSIONS

PEDOT films have been successfully electrodeposited on ITO electrode in mixed solution of BFEE-THF. The film exhibits tri-color electrochromism with reversible color changing from claret red (-0.8 V), light grey (0.2 V) to sea blue (1.0 V). And the neutral PEDOT prepared in BFEE-THF exhibits the hypso-

chromic effect of absorption spectrum, which is speculated on attributing to the short conjugation length. Based on the comparison of the electropolymerization of these three polymers, low onset oxidation potential and sluggish polymerization are used to explain the short conjugation length.

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