Research Article

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**In situ** polymerization of PEDOT:PSS films based on EMI-TFSI and the analysis of electrochromic performance

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**Abstract:** In this report, PEDOT composite films were prepared by **in situ** electrochemical polymerization. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) was used as an ionic liquid dopant for PEDOT:PSS films. Subsequently, these PEDOT:PSS/EMI-TFSI films were compared with PEDOT:PSS films based on their morphology, structure, electrochromic properties, and optical properties at different deposition voltages and deposition times. It was observed that the addition of EMI-TFSI enhanced all the aforementioned properties of the films. PEDOT:PSS/EMI-TFSI films were seen to have a larger ion diffusion coefficient \((1.38 \times 10^{-20}\text{ cm}^2\cdot\text{s}^{-1})\), a wider color change range \((43.48\%)\), a shorter response time \((\text{coloring} \text{ response time} = 1.2\text{ s}; \text{fading} \text{ response time} = 2\text{ s})\), and a higher coloring efficiency \((189.86\text{ cm}^2\cdot\text{C}^{-1})\) when compared with normal PEDOT:PSS films. The introduction of EMI-TFSI in the films ultimately resulted in superior electrochemical and optical properties along with higher stability.

**Keywords:** electrochromic, PEDOT:PSS, ionic liquids, polymerization

1 Introduction

Electrochromic (EC) materials are smart materials that can change their optical properties reversibly and continuously through an electrochemical reaction under the action of an applied voltage \((1)\). As a widely researched EC material, poly(3,4-ethylene dioxythiophene) (PEDOT) has the advantages of simple operation and easy control of the electrochemical polymerization process. PEDOT and its derivatives were synthesized on large scale and put into commercial use since its discovery by Bayer AG Laboratory \((2)\). Recently, the inceptions of sustainability, green chemistry, and engineering principles have been the pillars in both industry and academia. Green synthesis of PEDOT has become the desired goal pursued by related professionals. One bright idea is to find a breakthrough in synthetic solvents, using common solvents to replace organic solvents. However, it is difficult to dissolve the monomer EDOT(3,4-ethylene dioxythiophene) in common solvents such as water and the as-prepared film is relatively unstable.

To overcome this complication and facilitate processing and preparation, EDOT is usually doped with watersoluble electrolytes to prepare PEDOT composites like polystyrene sulfonic acid (PSS). PEDOT:PSS is a highly conductive water-soluble polymer composed of positively charged p-doped PEDOT and negatively charged PSS \((3–5)\). It has been extensively used in antistatic coating materials, capacitors, electrodes of photodiodes, transparent electrodes of solar cells, and hole transport layers of organic light-emitting diodes (LEDs) \((6–12)\). Water-soluble PSS, as a charge balance dopant, plays a dual role in charge balance and stable water dispersion \((13)\). Although PSS can effectively improve the solubility of EDOT and the processability of PEDOT conductive polymer, it does not significantly improve properties like conductivity and stability. Therefore, it is crucial to explore other dopants that can aid in enhancing these properties. Ethylene glycol, dimethyl sulfoxide, formamide \((14)\), and others are chosen to improve the properties of PEDOT:PSS composite films \((15)\). Despite these efforts, the electrochemical performance and optical contrast of PEDOT:PSS require further improvements \((16–20)\).
In recent years, ionic liquids (ILs) have become the primary choice for secondary doping due to their superior electrical conductivity, low volatility, large electrochemical window, thermal stability, and nonflammability (21,22).

ILs are organic salts composed of cations and anions that are liquid at or near room temperature (usually below 100°C). They are often called “green solvents” because of their environmentally friendly properties. Based on the differences between cations and anions, ILs can be divided into subcategories like alkyl imidazole, alkyl quaternary phosphorous cations, alkyl quaternary ammonium cations, alkyl pyridine cations, halogen anions, etc. A variety of ILs with different properties can be formulated from the aforementioned cations and anions. Badre combined 1-ethyl-3-methylimidazolium tetracyanoborate (EMIM-TCB) with PEDOT:PSS in a solution to prepare a composite with excellent transparency. Its conductivity was as high as 2.084 S·cm⁻¹ (23). It is expected to be used as a transparent polymer electrode. Dobbin and Mecerreyes reported that PEDOT:PSS composite films were prepared by doping different ILs as conductivity enhancers to improve the electrochemical performance of the films (24,25). Kee reported that the mechanical and electrical properties of PEDOT:PSS can be manipulated simultaneously via the modification of IL additives. The cation/anion modification of ILs distinctly improves the electrical conductivity of PEDOT:PSS up to ≈1.075 S·cm⁻¹ (26).

As for thermodynamics, according to Yemata, binary treatment with HNO₃ and IL substantially improved the σ and S values of the PEDOT films, which shows potential in real applications such as thin-film TE generators (27). It has been proven that conductive polymers composed of ILs and PEDOT:PSS have high affinities and supramolecular ordering abilities. Because of their unique characteristics, ILs have a wide range of applications in many fields, such as the synthesis, catalysis, and separation of organic and inorganic solvents, electrolytes in electrochemical devices, storage of enzymes, and reaction media (28). ILs are majorly used as dopants added into PEDOT:PSS by mechanical stirring to obtain a PEDOT:PSS/IL composite. This study does not reference any reports about preparing PEDOT:PSS/IL or PEDOT/IL in “one step” by EDOT or its derivatives, as the preparation of PEDOT:PSS/IL composite films by in situ electrochemical polymerization greatly shortens the preparation time without a second process. Herein, green synthesis of PEDOT has been successfully conducted by IL dropping, which has not been covered by former research.

In this paper, the in situ electrochemical polymerization of polythiophene-based composites is carried out along with relevant research on their properties. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) was particularly chosen owing to its hydrophilic anion alkyl side chains and hydrophilic cation functional groups. The hydrophobic group well clads the EDOT, and the hydrophilic group contacts the external aqueous solution to increase the solubility of EDOT. Thus, EDOT can be readily transported to the electrode surface and polymerized under the action of an external voltage signal. During the experiment, PEDOT:PSS and PEDOT:PSS/EMI-TFSI composite films were prepared by in situ electrochemical polymerization using EDOT, poly(sodium 4-styrenesulfonate), and EMI-TFSI. The morphology and structure of the PEDOT:PSS/EMI-TFSI composite films were characterized using a scanning electron microscope (SEM) and a Fourier infrared spectrometer. The electrochemical and optical properties of the composite films were tested by an electrochemical workstation coupled with a UV-visible spectrophotometer. The effects of EMI-TFSI on the composite films were explored by observing their parameters like morphology, structure, EC performance, electrochemical performance, and optical performance. The results are important for the basic research of electrochromism and open a new direction for achieving the long-desired green synthesis, durable, and large optical-modulation EC devices.

2 Experimental

EDOT and EMI-TFSI were acquired from Macklin, while PSS with M̅c.a = 50,000–100,000 and propylene carbonate (PC) were obtained from the Guangdong Wengjiang Chemical Reagent Factory, China. Lithium perchlorate (LiClO₄) was from Aldrich and the deionized water was from Watsons. All these compounds were used directly. Before the in situ electrochemical polymerization, the doped indium tin oxide (ITO) glass sheets were ultrasonically cleaned with acetone, ethanol, and deionized water in sequence, for which, each glass sheet was placed in a separate test tube to ensure maximum cleanliness. Then, the treated sheets were dried in an oven, put in a Petri dish, and sealed (29).

Equal volumes of 0.32 g of LiClO₄ aqueous solution and 17.85 g of PSS aqueous solution were ultrasonically mixed to obtain an electrolyte solution A. About 8.93 g of EDOT was slowly dropped into solution A and mixed ultrasonically to obtain solution B. Finally, 5 g of EMI-TFSI was added to solution B after standing for some time and mixed ultrasonically to obtain solution C. An equivalent
solution B without the addition of EMI-TFSI was also prepared for comparison.

As shown in Figure 1, the electrochemical polymerization was completed with a three-electrode system using an electrochemical workstation (AUT86732, AUTO LAB, Switzerland). A 9 mm × 50 mm ITO conductive glass sheet was used as the working electrode (WE) while the platinum sheet served as the counter electrode (CE) and the Ag/AgCl (in saturated 3.0 M NaCl solution) glass tube served as a reference electrode (RE). In the *in situ* electrochemical polymerization process, different voltages (1.2, 1.3, 1.4, and 1.5 V) and different deposition times (20, 30, and 40 s) were compared to determine the optimum preparation process parameters.

The as-prepared PEDOT:PSS composite films and PEDOT:PSS/EMI-TFSI composite films were treated with absolute ethanol and distilled water several times before the tests (30). The morphological characteristics of the composite films were investigated through the SEM test. It can be seen from Figure 3a that the films exhibit many raised fold-like structures. Similar structures, but with a bigger scale, can also be found in the PEDOT:PSS composite film (Figure 3b). Therefore, it can be concluded that the addition of EMI-TFSI promotes the formation of finer structures.

### 3.1 Morphological structure characteristics

To determine the structure of the PEDOT:PSS/EMI-TFSI composite film, an FTIR test was performed both on PEDOT:PSS and PEDOT:PSS/EMI-TFSI. As shown in Figure 2, the strong infrared absorption peaks of thiophene characteristic groups can be seen at 1,644 and 1,641 cm⁻¹. In the infrared curve ((b) in Figure 2), the absorption peak at 1,361 cm⁻¹ is attributed to the anionic functional group O=S=O, and the absorption peak at 1,187 cm⁻¹ is attributed to C=F, which comes from EMI-TFSI (31). According to the above analysis, it can be inferred that the IL EMI-TFSI is successfully doped into the PEDOT:PSS composite film.

The morphological characteristics of the PEDOT:PSS/EMI-TFSI composite film were investigated through the SEM test. It can be seen from Figure 3a that the films exhibit many raised fold-like structures. Similar structures, but with a bigger scale, can also be found in the PEDOT:PSS composite film (Figure 3b). Therefore, it can be concluded that the addition of EMI-TFSI promotes the formation of finer structures.

### 3.2 Electrochemical performance

In order to illustrate the influence of EMI-TFSI on the composite film, its electrochemical performance was analyzed with cyclic voltammetry (CV). The background CV of the electrode substrate (ITO) in a 0.2 M LiClO₄/PC solution is also presented for comparison. As shown in Figure A1 (in the Appendix), 1.6 V is the reaction potential of the electrolyte. When the applied voltage is lower than 1.6 V, the water present in PC and dissolved oxygen will not give additional peaks.
The corresponding results of the PEDOT:PSS/EMI-TFSI composite film are demonstrated in Figure 4. The CV curves of the composite films were obtained at a scan rate of 0.05 V·s\(^{-1}\) in a 0.2 M LiClO\(_4\)/PC solution and a voltage range from \(-1.5\) to \(+1.5\) V. Figure 4 clearly illustrates that when the potential is negative, the composite films are in a reduced state, showing a dark blue appearance. However, when the potential becomes positive, the composite films take an oxidized state, presenting a light blue color. This is a reversible redox process.

It is also evident that the effects of deposition time and deposition voltage on PEDOT:PSS/EMI-TFSI and PEDOT:PSS are similar. The peak current and the embedded area of the CV curve gradually increase with an increase in the deposition time. In addition, the peak in the reduced state shifts to a lower potential with increasing deposition time and deposition voltage. This manifests that relatively low energy would be required to trigger the redox reaction when the films are deposited for a relatively long time and at high voltage. Moreover, the maximum peak current (oxidation

Figure 3: SEM micrographs of (a) PEDOT:PSS/EMI-TFSI and (b) PEDOT:PSS deposited at 1.4 V for 40 s.

Figure 4: Cyclic voltammetry curve of (a) PEDOT:PSS deposited at 1.4 V for different times, (b) PEDOT:PSS deposited at different voltages for 40 s, (c) PEDOT:PSS/EMI-TFSI deposited at 1.4 V for different times, and (d) PEDOT:PSS/EMI-TFSI deposited at different voltages for 40 s.
peak current, $i_{pc}$) and the maximum embedding area of the PEDOT:PSS/EMI-TFSI film are 0.001587 and 0.00396 V·A, respectively, while those of the PEDOT:PSS film are 0.000779 and 0.00190 V·A, respectively. Therefore, the addition of EMI-TFSI increases the maximum peak current and the maximum embedding area about two times at the same deposition voltage and deposition time. Therefore, it can be concluded that PEDOT:PSS/EMI-TFSI composite films have a higher electrochemical activity and charge storage capacity when compared with PEDOT:PSS films.

It is important to note that not only the peak current of the PEDOT:PSS/EMI-TFSI composite films is higher but also their ratios of the oxidation peak current ($i_{pc}$) and the reduction peak current ($i_{pa}$) are also different. As shown in Figure 4a and c, the $i_{pc}$ and $i_{pa}$ of the former are 0.001587 and 0.001603 A, respectively, and $i_{pc}/i_{pa}$ is 0.99, which is very close to 1.00. On the other hand, the $i_{pc}$ and $i_{pa}$ of the latter are 0.000779 and 0.000701 A, respectively, while their corresponding $i_{pc}/i_{pa}$ is 1.11. It is important to point out that the closer to 1 the $i_{pc}/i_{pa}$ ratio is, the better the reversibility of the film. Obviously, the PEDOT:PSS/EMI-TFSI composite films have higher circular reversibility.

In fact, the redox reaction involves charge transfer across the electrolyte–electrode interface, thus resulting in the change of film porosity (32). The electron–ion coupling in conductive polymers is experimentally studied using cyclic voltammetry by calculating the ion diffusion coefficient (33). The ion diffusion coefficient can be calculated by the Randles–Sevcik equation (34):

$$I_{p0} = 0.4463ZF^2A(VFRT)^{1/2}C_D^{1/2}V^{1/2}$$

where $F$ (= 9.65 × 10^4 C·mol⁻¹) is the Faraday constant, $Z$ is the number of electrons transferred (here, $Z$ = 1), $R$ (= 8.314 J·K⁻¹·mol⁻¹) is the molar gas constant, $T$ (= 298.15 K) is the temperature, $A$ (1 cm²) is the effective surface area of the working electrode, and $V$ (0.05 V·s⁻¹) is the scan rate. The electrolyte concentration was 0.2 mol·L⁻¹, and the surface concentration of the active ions was 200 mol·mL⁻¹. The effective diffusion coefficient $D$ of the ion was calculated based on Eq. 2 and the results are shown in Figure 5.

Clearly, the ion diffusion coefficient of PEDOT:PSS/EMI-TFSI and PEDOT:PSS demonstrates an upward trend with an increase in the deposition time. However, the ion diffusion coefficient of both the films first show an upward trend with an increase in the deposition voltage, followed by a downward trend when the voltage is increased more than 1.4 V. Nonetheless, the ion diffusion coefficient of the PEDOT:PSS/EMI-TFSI film is much higher than that of the PEDOT:PSS film deposited under the same conditions. Deposited at 1.4 V for 40 s, the ion diffusion coefficient of PEDOT:PSS/EMI-TFSI is $1.38 \times 10^{-20}$ cm²·s⁻¹, while that of PEDOT:PSS is $0.34 \times 10^{-20}$ cm²·s⁻¹, which makes the former about 4 times higher. This observation can explain why the introduction of EMI-TFSI promotes the redox reaction of the PEDOT:PSS composite film.

### 3.3 Optical performance

The effects of EMI-TFSI on the EC properties of the PEDOT:PSS films, such as optical contrast, the response time, and the coloring efficiency, were investigated. Subsequently, the optical transmittance and dynamics of both films were analyzed and compared.

The transmittance of the films was tested using a UV spectrophotometer coupled with the electrochemical workstation in the voltage range from −1.5 to +1.5 V and the wavelength range of 400–800 nm, and then the maximum transmittance difference, i.e., the maximum optical contrast ($\Delta T$) was calculated. The corresponding results are shown in Figure 6. It was observed that the $\Delta T$ of the PEDOT:PSS/EMI-TFSI film is much higher than that of the PEDOT:PSS film deposited under the same conditions.

![Figure 5: The ion diffusion coefficient at (a) different deposition times and (b) different voltages.](image_url)
With the dropping of EMI-TFSI, the polaron energy level with smaller band gap forms. At the optimal conditions of 1.4 V and 40 s, PEDOT:PSS/EMI-TFSI exhibited a large transmittance contrast ($\Delta T = 43.48\%$). Compared with PEDOT:PSS, there is a 5% increase in optical modulation. The variation in $\Delta T$ of the films with increasing deposition voltage and deposition time followed a similar trend. $\Delta T$ first increases till a voltage of 1.4 V and then decreases when the voltage is further increased. As far as the deposition time is concerned, $\Delta T$ shows a monotonically increasing trend. Evidently, the $\Delta T$ of the PEDOT:PSS/EMI-TFSI film is always higher than that of the PEDOT:PSS film. This result further verifies that the introduction of EMI-TFSI can promote the discoloration range of the PEDOT:PSS composite film.

Figure 7 shows the results of the kinetics analysis conducted on the films. The response time and coloring efficiency are calculated as follows:

$$t = t_b - t_c$$

$$\Delta OD = \log(T_b/T_c)$$

where $t_b$ is the bleach time of the EC material, $t_c$ is the coloring time of the EC material, $T_b$ is the transmittance of the EC material in the oxidized state (fading state), $T_c$ is the transmittance of the EC material in the reduced state (colored state), and $Q$ is the amount of charge injected per unit area of the EC material during the oxidation-reduction process.

The response time curves of PEDOT:PSS/EMI-TFSI film and PEDOT:PSS films were obtained based on Figure 7 and Eq. 2, and are shown in Figure 8. The variation in the response time of both films shows similar trends as before. Both the composite films have the shortest response time and the fastest discoloration speed when prepared at 1.4 V for 40 s. However, the response time of the PEDOT:PSS/EMI-TFSI film is much shorter than that of the PEDOT:PSS film deposited under the same conditions. The $t_b$ and the $t_c$ of the former are just 2 and 1.2 s, respectively, while for the latter they are 3.1 and 2 s, respectively. Hence, it proves that the addition of EMI-TFSI can

$$CE = \frac{\Delta OD}{Q}$$

Figure 6: Optical transmittance of (a) PEDOT:PSS films deposited at different voltages for a definite time, (b) PEDOT:PSS films deposited at a definite voltage for different times, (c) PEDOT:PSS/EMI-TFSI films deposited at different voltages for a definite time, and (d) PEDOT:PSS/EMI-TFSI films deposited at a definite voltage for different times.

Figure 7: Kinetics of (a) PEDOT:PSS films deposited at 1.4 V for 40 s and (b) PEDOT:PSS/EMI-TFSI films deposited at 1.4 V for 40 s.
shorten the response time by 40% and accelerate the speed of discoloration by 35%.

Eqs. 3 and 4 were used to obtain the coloring efficiency curves of PEDOT:PSS/EMI-TFSI and PEDOT:PSS films (Figure 9). Clearly, both the films possessed the highest coloring efficiency (CE) and the fastest discoloration rate when prepared at 1.4 V for 40 s. The CE of the PEDOT:PSS/EMI-TFSI film (189.86 cm²·C⁻¹) is much higher than that of the PEDOT:PSS film (122.65 cm²·C⁻¹) deposited under the same conditions. This result further solidifies that the EMI-TFSI can promote the discoloration rate and the EC performance of the PEDOT:PSS composite film.

3.4 Stability

In order to illustrate the influence of EMI-TFSI on the stability of PEDOT:PSS composite films, the SEM test was conducted and the morphological characteristics of the films were investigated after 250 cycles (Figure 10). Figure 10a shows that the structure of the PEDOT:PSS/EMI-TFSI film has almost no change. However, the surface of the PEDOT:PSS film becomes smooth and fold-like structures, similar to those shown in Figure 3a, were observed here.

In order to illustrate the influence of EMI-TFSI on the stability of PEDOT:PSS composite films, coloring kinetics and chronograph coulomb (CC) with 100 circles are performed. The optical switching stability of the PEDOT:PSS/EMI-TFSI film was observed between the application of a square wave potential of −0.5 and +0.5 V using a pulse width of 10 s. It has been clearly shown that the transmittance contrast of PEDOT:PSS/EMI-TFSI films was always maintained at about 30%. However, for the blank group, the transmittance difference dropped drastically after 30 cycles of scanning. The EC stability of the PEDOT:PSS electrodeposited...
in an aqueous solution is relatively poor. The main reason is the low solubility of EDOT and insufficient adhesion to the substrate (ITO glass). With the addition of EMI-TFSI, EDOT can be evenly distributed in an aqueous solution and transported to the electrode surface. Therefore, it can be summarized that the addition of EMI-TFSI helps to promote the stability of the PEDOT:PSS electrochemical performance and color change performance (Figure 11).

Figure 12 shows the CC curves of both films. After a few circles of descent, the film doped with EMI-TFSI maintains the stability of charge injection and extraction. The movement of the electric charge is the most direct factor that causes the polymer doping state to change,

Figure 10: SEM micrographs of 250 cycles for (a) PEDOT:PSS/EMI-TFSI and (b) PEDOT:PSS.

Figure 11: The coloring kinetics of films (a) PEDOT:PSS/EMI-TFSI for 250 circles and (b) PEDOT:PSS for 30 circles.
and thus, the color change occurs (35). Large amounts of cation/anion present in the aqueous solution promote the charge transfer and reaction balance. The result further proves that EMI-TFSI can promote the cycle stability of EC.

4 Conclusions

In this article, PEDOT:PSS/EMI-TFSI films were successfully polymerized by in situ electrochemical polymerization. They were then compared with the PEDOT:PSS films based on their morphology, structure, EC properties, and optical properties at different deposition voltages and deposition times. The main conclusions obtained are as follows:

(1) The addition of EMI-TFSI can increase the maximum peak current and the maximum embedding area about two times at the same deposition voltage and deposition time. It helps to promote the electrochemical activity, circular reversibility, and charge storage capacity of the films. The optimal condition for film deposition is 1.4 V for 40 s.

(2) EMI-TFSI can improve the electrochemical and optical properties of PEDOT:PSS films. The PEDOT:PSS/EMI-TFSI film has a larger ion diffusion coefficient of $1.38 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1}$, which is about 4 times higher than that of the PEDOT:PSS film. EMI-TFSI brings the maximum optical contrast ($\Delta T$) of the film to 43.48% (5% more than PEDOT:PSS). At the same time, a shorter response time (coloring response time = $1.2 \text{ s}$; fade response time = $2 \text{ s}$) and a higher coloring efficiency ($189.86 \text{ cm}^2 \text{ C}^{-1}$) can be obtained.

(3) EMI-TFSI can also improve the stability of the PEDOT:PSS composite film.

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References


(31) Fan J, Wan S, Xu G, Cui XT, Luo XJ. Preparation and electrochemical catalytic application of nanocrystalline cellulose doped poly(3,4-ethylenedioxythiophene) conducting polymer


Appendix

The background CV of the electrode substrate (ITO) in 0.2 M LiClO₄/PC solution is also presented for comparison. As shown in Figure A1, 1.6 V is the reaction potential of the electrolyte.

Figure A1: Cyclic voltammetry curve of ITO in an electrolyte.