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Synthesis, characterization and electrochromic properties of hybrid triphenylamine-dithiafulvene polymer films

Yi Wang, Zhongquan Wan*, Junlong Niu, Shengwei Tang, Xianghan Liu, Yuyu Yang and Chunyang Jia

School of Electronic Science and Engineering, Shenzhen Institute for Advanced Study, University of Electronic Science and Technology of China, Chengdu, China

*Corresponding author: zqwan@uestc.edu.cn

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Abstract: A dithiafulvenyl-substituted triphenylamine derivative (TPA-DTF) has been synthesized and employed to deposit an electrochromic polymeric film by convenient electrochemical oxidative coupling reactions. Furthermore, the electrochemical and optical properties of the polymer film were tested using UV-visible spectroscopic, cyclic voltammetry and film morphology analysis. The results showed that the polymeric film shows broad absorption around 650 nm in the visible region, with color changes from light-yellow to blue corresponding potential difference varying from -0.2 to 0.8 V. The polymer film exhibited fast switching time (1.3 and 1.4 s), high optical contrast (over 40%) and high coloration efficiency (CE) of 303.16 $cm^2\ C^{-1}$.

1. Introduction

Electrochromism refers to a phenomenon where materials undergo electrochemical reactions accompanied by the change of their optical characteristics from a bleaching to a coloration state corresponding variation in potential biases. Due to the energy efficient properties of electrochromic (EC) materials, various EC materials have been developed since past decades, including transition metaloxides, metal complexes, conducting polymers (CPs), organic small molecules with redox activity and metallosupramolecular polymers. Electrochromic devices (ECDs) making use of EC materials have been employed for various application such as building glass and information displays, *etc*. ECDs exhibits better color-tuning response and user friendly features than thermochromic or photochromic devices, which makes them a hot topic for research and development efforts. [1]

Triphenylamine-based derivatives (TPA) and polymers have been widely investigated as solar cells, filed effect transistors and ECDs because of their well-known electrochemical activity and photoactive properties. [2] TPA-based compounds are easy to oxidize to form cationic radicals with a distinct color change. Hence, TPA-based organic polymer materials can be suitable candidates for the applications in ECDs. The preparation methods of TPA-based polymer films usually include dip-coating, spin-coating, electro polymerization, *etc.* The electro polymerization of TPA derivatives provides outstanding advantages by combining a simple one-step synthesis method. At the same time, the polymer films can be directly grow on the electrode surface by electro polymerization.[2] The method also solves the solubility problems associated with the conventional methods. Hsiao *et al.* reported a variety of TPA-based EC film materials by the conveniently electro polymerization.[3] Lu *et al.* reported an efficient and low-cost electrodeposition method for the construction of EC films based on metal-organic frameworks with redox TPA groups.[4] Leriche *et al.* synthesized a variety of hybrid conjugated systems combining a TPA core and one to three dithiafulvenyl branches, and analyzed their polymerization mechanisms in depth.[5] In conclusion, it is an effective method to prepare novel TPA-based electrochromic materials by electro polymerization approach.

In this work, the triphenylamine-dithiafulvenyl (TPA-DTF) organic molecule has been synthesized. Dithiafulvenyl group is a well-known electron-donating group and has been used in various photoelectric materials and devices. The P (TPA-DTF) polymer was electrochemically successfully polymerized on a conductive substrate (ITO) by one-step oxidation polymerization. The resultant

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polymer film of P (TPA-DTF) showed excellent electrochromic properties. Therefore, this polymer film has good application prospect for ECDs.

2. Experimental section

2.1 Materials

Triphenylamine (TPA) was purchased from Astatech. Tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$), 4, 5-Bis (methylthio)-1, 3-dithiole-2-thione and 4, 4’-Diformyltriphenylamine were purchased from Sigma-Aladdin. 0.1 M $TBAPF_6$ in acetonitrile (CH_3CN) solution was used as electrolyte in the electrochemical performance tests.

2.2 Synthesis of TPA-DTF

The synthesis route of *TPA-DTF* is given in Figure 1. The *TPA-DTF* was synthesized according to previous report. [5] 500 mg 4, 4’-Diformyltriphenylamine and 1.5 g 4, 5-Bis (methylthio)-1, 3-dithiole-2-thione were added to boiling solution of toluene (5ml) with stirring. Then, 3.5 ml triethylphosphite were continued to be added to the flask. The mixture was continuously stirred at reflux for four hours and injected with nitrogen. After the reaction finished, the dichloromethane was added while the mixture was cooled. Next, the mixture was washed with brine. After evaporation of the excess solvent in the beaker, the residue was dissolved in little smallest CH_2Cl_2. Then, the petroleum ether was added to afford the formation of a pure orange solid. NMR ^1H ($CDCl_3$): 7.24 (m, 1H), 7.08 (m, 12H), 6.42 (s, 2H), 2.42 (m, 12H).

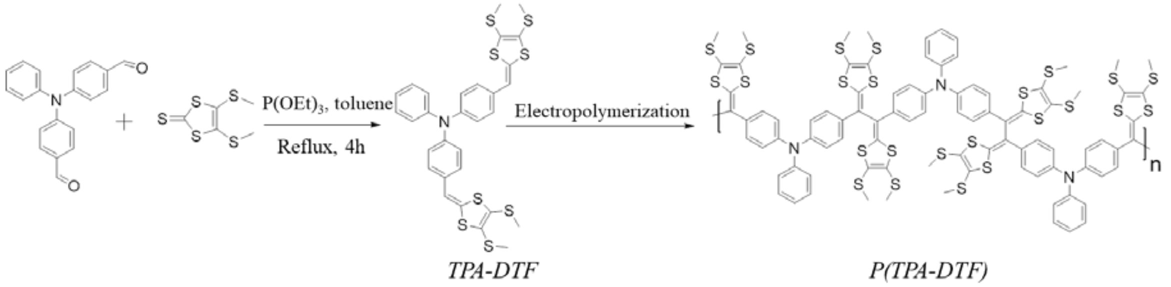

Figure 1. Synthesis of compounds *TPA* and the structure of P (TPA-DTF).

2.3 Fabrication of P (TPA-DTF) films

The P (TPA-DTF) film was electrodeposited by cyclic voltammetry (CV) in a three-electrode cell. The 0.65 × 2.2 cm^2 ITO glass was used as the working electrode. The platinum foil (Pt) was used as the counter electrodes. The Ag/AgCl electrode was used as reference electrodes. The electrodeposition solution was obtained by mixing 2 mg *TPA*-DTF monomer, 0.1 mol $TBAPF_6$ in the 10 ml dichloromethane solution. The potential cycle was carried out from -0.2 V to 1.4 V for the circular of 400 segments at 100 mV s^{-1}. The *P* (TPA-DTF) film-modified ITO substrates were rinsed gently with CH_2Cl_2/ethanol (v/v, 1:1) and set to dry in air.

2.4 Characterization

The morphologies of *P (TPA-DTF)* films were characterized by SEM (JEOL JSM-7600F). The electrochemistry performances analysis of the polymer film was carried out using electrochemical workstation (CHI660C). The optical properties of the *P (TPA-DTF)* film was detected using UV-visible spectrophotometer (MAPADA UV6100).

3. Results and Discussion

3.1 Electropolymerization and morphology characterization

Figure 2a shows the electro polymerization process of *TPA-DTF* monomer on ITO glass. The film morphology of P (TPA-DTF) was evaluated by SEM. Figure 2b shows the *P (TPA-DTF)* film morphology on the surface of ITO substrate undergoing the electro polymerization process. The uniform accumulation of small nanoparticles is found on surface of the film. In the voids of the nanoparticle stack, part of the pore structure remains. The special porous morphology of the polymer film is conducive in improving electrochromic properties which can shorten ion diffusion paths. Figure 2c displayed the cross-section morphology of the polymer film by the SEM. Besides, from Figure 2c we can see that the polymer film with a thickness of roughly 55 nm and adheres closely to the ITO surface.

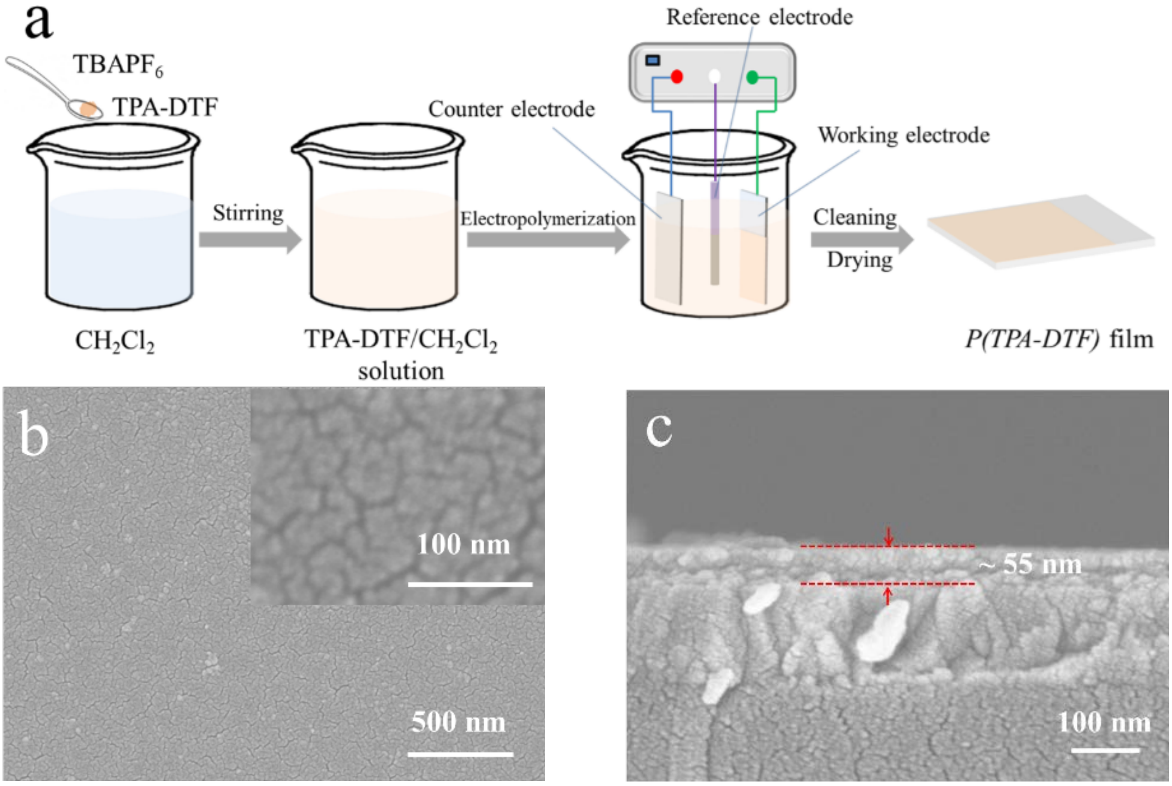

Figure 2. (a) Schematic illustration of preparation process of polymers. (b) Surface morphology of as-prepared film and (c) film cross-sectional morphology.

3.2 Cyclic voltammetry

To investigate the electrochromic properties of *P* (TPA-DTF*)* film, cyclic voltammogram (CV) of the *P (*TPA-DTF*)* film were measured in 0.1 M TBAPF$_6$/CH$_3$CN. Figure 3a shows the CV curves for *P (*TPA-DTF*)* film from 10 mV s^{-1} to 100 mV s^{-1}. The CV curves of polymer film at 100 mV s^{-1} displays two reversible oxidation redox couples which can be attributed to the redox activity of *TPA* group at half-wave potentials ($E_{1/2}$) of 0.51 V and 1.26 V. The cathodic and anodic peaks have shifted when the scanning rate increased from 10 mV s^{-1} to 100 mV s^{-1}. However, the shape of these redox peaks was highly symmetrical indicating that the *P (TPA-DTF)* film have outstanding electrochemistry kinetic performance.

3.3 UV- visible spectra

The UV-visible spectra of the *P (TPA-DTF)* film are shown in Figure 3b (from -0.2 to 1.2 V). The absorption curve of the film changes obviously with the continuous increase of the applied voltage. The original *P (TPA-DTF)* film displayed strong absorption at about 390 nm. The film absorption peak was significantly enhanced at 650 nm, when the applied voltage was increased to 0.8 V. The color of *P (TPA-DTF)* film changes from light-yellow to blue as the applied voltage changes.

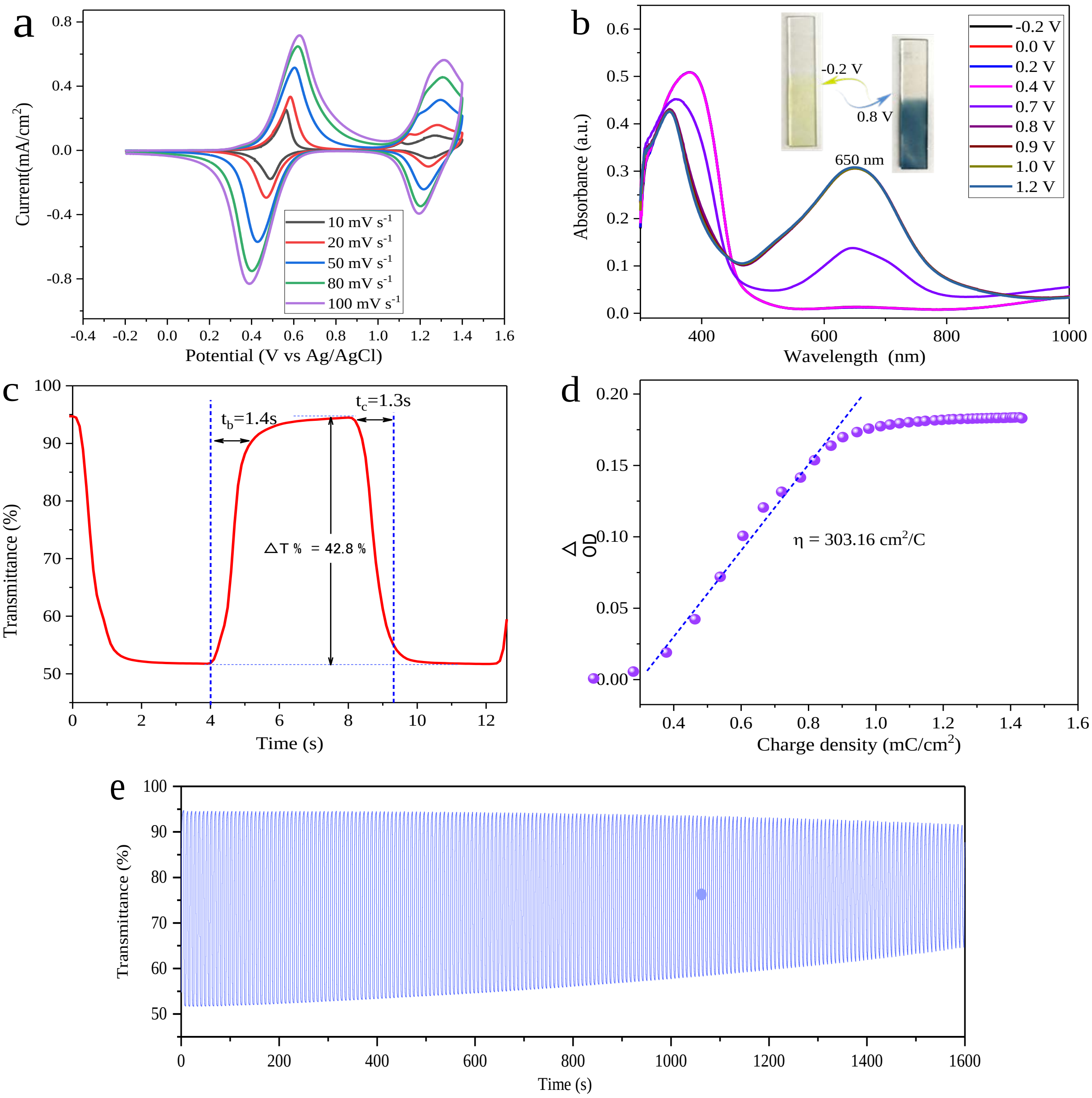

Figure 3. (a) CV curves of the P (TPA-DTF) film; (b) UV-visible spectra of the polymer films at various potentials, (c) Switching speed of the P (TPA-DTF) film. (d) Coloration efficiency of the P (TPA-DTF) film at 650 nm; (e) cycle performance of the P (TPA-DTF) film at 650 nm.

3.4 Response time

The *P (TPA-DTF)* film electrochromic response time was further determined. Herein, response time was measured the time of 90% max transmittance modulation change at the wavelength of 650 nm. The response time of the polymer film was 1.3 s for coloring and 1.4 s for bleaching, respectively (Figure 3c). Here, the switching time between two states is relatively faster than previously reported results available in literature. [1, 4]

3.5 Coloration efficiency

Coloration efficiency (*CE*) is a fundamental parameters for electrochromic film which defined as the change in optical density (△OD) per unit of inserted or extracted charge, mathematically defined as: [3]

$$\triangle OD = \log (T_b/T_c) \qquad (1)$$

$$\square\,\square = \triangle OD/Q \qquad (2)$$

Where □ is *CE* and Q is the inserted or extracted charge per unit area. T_b and T_c represent the transmittance of the film in the bleached and colored state The CE of the *P (TPA-DTF)* film is calculated by the curve slope in the Figure 3d. The CE of the film is 303.16 cm^2 C^{-1} at 650 nm.

3.6 Cyclic stability

Cyclic stability is an importance parameter for practical applications of ECDs. Figure 3e displays the time dependence of the polymer film transmittance at 650 nm via chronoamperometry at 0.8 V for 8 s and -0.2 V for 8 s. As shown in Figure 3e, the highest optical contrast (ΔT %) based on *P (TPA-DTF)* films is 42.8% in the visible region. Averagely, the polymer film shows over 40 % variation in transmittance ($\triangle T_{ave}$). However, transmittance variation of the polymer film was only limited to 12.5 % after 200 cycle, indicating good stability.

4. Conclusion

In summary, we achieve the preparation of P (TPA-DTF) electrochromic film by conveniently electro polymerization method. As a result, the P (TPA-DTF) film presents fast response time of 1.3 s for coloring and 1.4 s for bleaching, high optical contrast of above 40 % at 650 nm, excellent CE of 303.16 cm^2 C^{-1}. The P (TPA-DTF) film materials can be applied for various innovative applications like energy efficient smart windows, optical displays, etc.

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