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# Electrochromic properties of organic-inorganic composite materials

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ABSTRACT

A new type of electroactive composite material based on tungsten trioxide ($WO_3$) and poly (tri(4-(2′-thienyl)) phenylamine) (P3TPA) was prepared. Using the $WO_3$/P3TPA as electroactive material, the electrochromic device was fabricated, and the electrochromic properties of $WO_3$/P3TPA were investigated. Compared with $WO_3$, the coloring switching time and the bleaching switching time of $WO_3$/P3TPA was decreased. The response speed became faster. The open-circuit memory of $WO_3$/P3TPA became better. The coloration efficiency of $WO_3$/P3TPA increased.

## 1. Introduction

Electrochromic materials have attracted attention because of their potential applications in energy conservation [1]. Electrochromic devices (ECDs) are used in smart windows, automotive rear-view mirrors, displays, sunglasses, etc. [2]. The most important prerequisites for ideal EC materials include high initial transparency, large optical contrast between colored and bleach states, short switching time, and long-term cyclic stability [3]. EC materials can be divided into two large kinds on the basis of the component, organic and inorganic materials. Traditional metal oxide semiconductors, such as $WO_3$ [4], $TiO_2$ [5], $MoO_3$ [6], $Nb_2O_5$ [7,8], NiO [9] are some of the inorganic EC materials. At present, some other researchers also investigate organic EC materials due to their variety of visual coloration and versatile structural morphologies [10–12].

Among all the materials studied thus far, $WO_3$ has emerged as the most extensively studied material, not only for electrochromism, but also for a variety of other device applications. Deb in 1963 first reported on the electrochromic properties of $WO_3$ [13]. Subsequently, many other researchers expanded on the subject [14]. ECDs based on $WO_3$ show outstanding electrochromic properties and have been used on smart windows [15], automotive rear-view mirrors [16], and electrochromic displays [17]. Nevertheless, despite the plentiful amount of work that has been done on the coloration phenomena in thin films of various morphological $WO_3$, many contradictions still exist. Further commercialization is limited by the long switching times and low coloration efficiency.

Among all the electrochromic materials, the conjugated polymers have attracted much attention because of their low cost for easy processing, multicolor adjustability and mechanical flexibility [18,19]. Organic conjugated polymers such as polythiophene, polyaniline (PANI), polypyrrole (PPy), Poly(3,4-ethylene-dioxythiophene) (PEDOT) and their derivatives, have been extensively investigated [20] and many of them exhibit good electrochromic properties. As a typical organic electrochromic material, PANI and its derivatives are important organic conjugated polymers to ECDs because of short coloring and bleaching switching times, high optical contrast, and high coloration efficiency [21]. PEDOT and its derivatives are also a class of outstanding EC conjugated polymers due to their high coloration efficiency and ability of diverse colors [22,23]. However, the low electrochemical and thermal stability of conjugated polymers results in a relatively short lifetime. These disadvantages have hindered the further development of organic

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ECDs applications [24].

Usually, three methods are used to improve the performance of organic ECDs [25]. Firstly, designing and synthesizing new organic conjugated compounds; Secondly, developing new inorganic and organic composite materials, or inorganic heterojunction; Thirdly, electrolytes play an important role in determining the long-term stability of the devices, so finding appropriate electroplates is another way to improve the performance of ECDs [26]. The main characteristics of inorganic–organic composite electrochromic materials are the advantages of each component and the improved ECD performance. Recently, electrochromic inorganic-organic complexes such as $TiO_2$/polythiophene, $IrO_2$/polyaniline and $WO_3$/polypyrrole have been studied [27–31].

In our previous work, we have investigated the electrochromic properties of the P3TPA denotes poly(tri(4-(2′-thienyl)) phenylamine) with triphenylamine and thiophene units (Scheme 1). It was found that the P3TPA exhibited reversible, clear color change from orange-yellow to blue on electrochemical doping and dedoping. However its electrochromic stability is poor. In this study, we prepared the inorganic-organic complex $WO_3$/P3TPA. Using the $WO_3$/P3TPA as electrochromic material, the electrochromic devices were prepared, and the electrochromic properties of $WO_3$/P3TPA were investigated.

## 2. Experimental

### 2.1. Materials

Tungsten trioxide ($WO_3$) and $Pdcl_2(PPh_3)_2$ were purchased from Beijing HWRK Chem Co., Ltd. 2-Thienylboronic acid, tetrabutylammonium perchlorate (TBAP) and tris(4-bromophenyl) amine were purchased from Alfa Aesar. Potassium carbonate ($K_2CO_3$), tetrahydrofuran (THF), acetonitrile (ACN), dichlormethane (DCM), and sodium chloride (NaCl) were purchased from Tianjin Hongyan Chem Co., Ltd. Lithium perchlorate ($LiClO_4$) was purchased from Aladdin Industrial Corporation. Sodium sulfate ($Na_2SO_4$) was purchased from Beijing Liudian Chem Co., Ltd. Petroleum ether was purchased from Guangdong JHD Co., Ltd.

### 2.2. Instruments

NMR spectra were obtained on a Bruker AVANCE-500 FT-NMR using tetramethylsilane as internal standard. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. Mass spectra were recorded on a GCMS-QP 2010 mass spectrometer. The cyclic voltammogram (CV) and electropolymerization were carried out by the CHI750A electrochemical workstation. AFM images were obtained on a DI/MultiMode from Veeco.

The parameters of the ECD including optical contrast and open-circuit memory were measured on a Helios-γ UV–vis spectrophotometer. The coloration efficiency and switching time were measured on the CHI750A electrochemical workstation.

### 2.3. Synthesis of tri (4-(2′-thienyl)) phenylamine (3TPA)

The synthesis of 3TPA is described in Scheme 1. 3TPA was prepared by Suzuki coupling reactions according to the procedure as followed: 1.45 g tris(4-bromophenyl)amine, 1.92 g 2-thienylboronic acid, 90 mg $Pdcl_2(PPh_3)_2$, 150 ml THF and 100 ml $K_2CO_3$ (2 M) were added into a dry and clean 500 ml three-neck flask. The mixture was heated to reflux for 48 h, and then poured into a saturated solution of ammonium chloride and extracted with dichloromethane for three times. The organic phase was washed with brine and then dried over anhydrous sodium sulfate, filtered and removed the solvent. The solid residue was purified by silica-gel column chromatography to give a pale yellow crystalline solid. Yield: 59%.

### 2.4. Preparation of the $WO_3$/P3TPA composite film

A 100–150 nm thick $WO_3$ film was deposited on a ITO-coated glass substrate by vacuum deposition (vacuum pressure $4 \times 10^{-3}$ Pa).

At room temperature, the electropolymerization of 3TPA was carried out in an ACN solution of $5.0 \times 10^{-2}$ M 3TPA and 0.1 M TBAP by repetitive cycling at scan rate of 100 mV $s^{-1}$. The reference electrode was the Hg/$Hg^{2+}$ electrode; the counter electrode was the platinum wire, and the ITO-coated $WO_3$ was the working electrode. The P3TPA was directly coated onto $WO_3$. Fig. 1 shows the cyclic voltammogram of the electropolymerization of 3TPA on the ITO-coated $WO_3$ electrode. The current density increased during the repeated potential scanning. The results suggest that the electropolymerization of 3TPA was achieved and P3TPA finally formed.

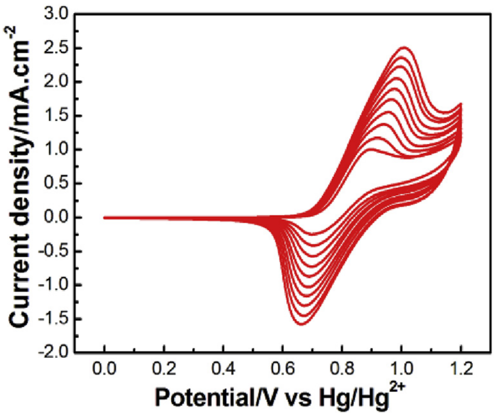
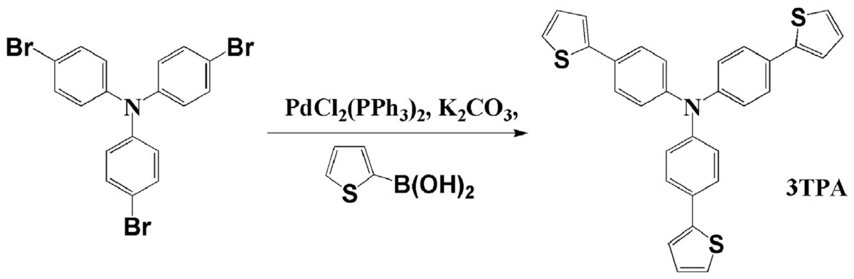


**Fig. 1.** The electropolymerization of 3TPA ($5.0 \times 10^{-2}$ M) at 100 mV/s for ten times in the ACN solution with 0.1 M TBAP.



**Scheme 1.** The Synthesis route of 3TPA.

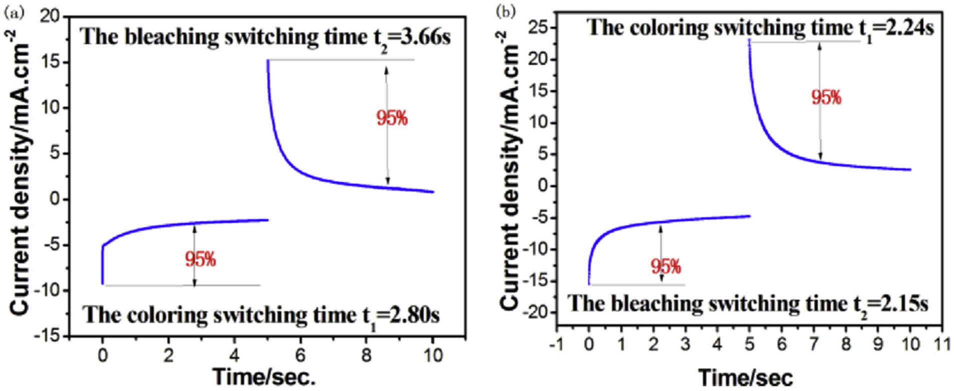


**Fig. 2.** The coloring time and bleaching time of the electroactive film in the ACN solution with 0.05 M TBAP and 0.05 M $LiClO_4$. a: $WO_3$ film and b: $WO_3$/P3TPA film.

### 2.5. *Preparation of the electrochromic device*

Using the ITO and Pt wire as electrodes, the $WO_3$ film or $WO_3$/P3TPA composite film as active material, and the ACN solution containing 0.05 M TBAP and 0.05 M $LiClO_4$ as electrolyte, the ECD was prepared. The device structure is ITO glass/active materials/electrolyte solution/Pt.

## 3. Results and discussion

### Electrochromic properties of the $WO_3$/P3TPA composite film

The $WO_3$ film exhibited a reversible, clear color change between colorless and deep blue for applied voltages of +2.5 V and −2.5 V between the ITO and the platinum wire electrodes in the electrolyte solution. The $WO_3$/P3TPA composite film switched from yellow to blue for applied voltage of +2.5 V and from blue to yellow for applied voltage of −2.5 V. The results suggest that the $WO_3$/P3TPA composite film possess reversible electrochromic properties.

### 3.1. *Switching time*

The switching or response time is one of the most important parameters for ECDs. The switching time includes the coloring time and bleaching time. To evaluate the switching time of the ECD based on the $WO_3$ and the $WO_3$/P3TPA films, the chronoamperometry was used in typical three-electrode configuration. Fig. 2 shows that the coloring time and bleaching time of $WO_3$ film is 2.80 s and 3.66 s, respectively, and the coloring time and bleaching time of $WO_3$/P3TPA film is 2.24 s and 2.15 s, respectively. Compared with the $WO_3$ film, the coloring time and bleaching time of the $WO_3$/P3TPA film are decreased by 20% and 41.3%, respectively.

Fig. 3 shows AFM images of the $WO_3$ and $WO_3$/P3TPA films. The surface roughness (Rms) of $WO_3$ and $WO_3$/P3TPA film is 5.164 nm and 31.817 nm, respectively. The rough surface morphology facilitates the injection and extraction of ions and reduces the switching time of electrochromic materials [32,33]. Therefore, the coloring and bleaching times of the $WO_3$/P3TPA film are shorter than that of the $WO_3$ film.

### 3.2. *Open-circuit memory*

The open-circuit memory of an electrochromic material is defined as the time that the material retains its color without voltage application [34]. The open-circuit memory is an important parameter of electrochromic materials. To evaluate the open-circuit memory of electrochromic materials, the transmittance of the $WO_3$

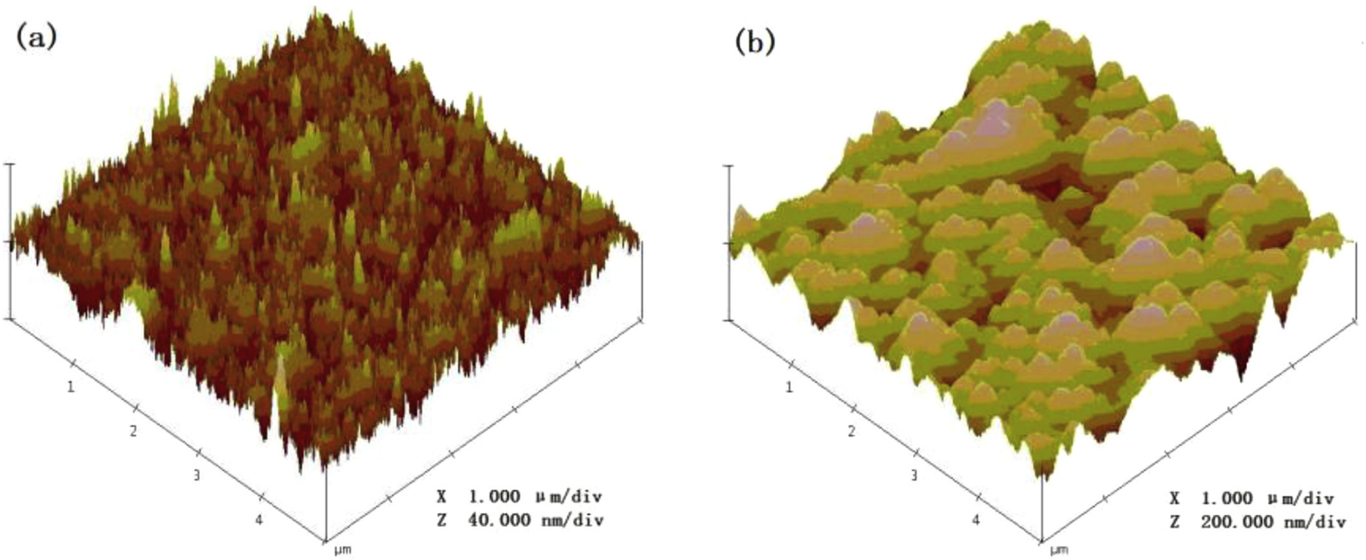


**Fig. 3.** The AFM images of the (a) $WO_3$ film and (b) $WO_3$/P3TPA film.

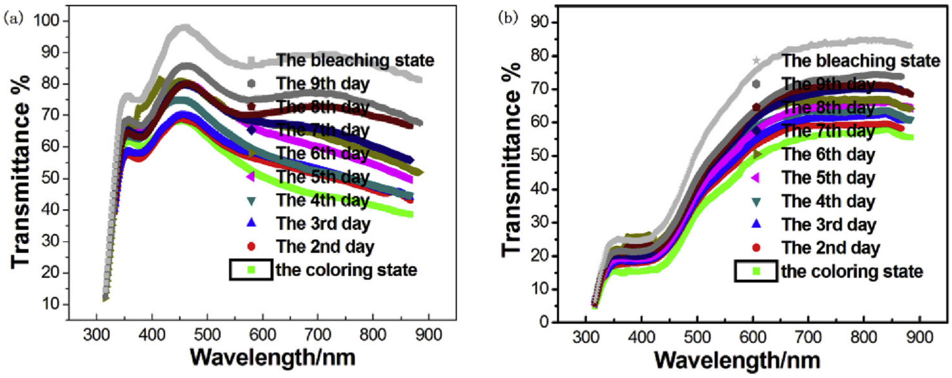


**Fig. 4.** The open-circuit memory of electroactive materials in the ACN solution containing 0.05 M TBAP and 0.05 M $LiClO_4$. a: $WO_3$ film and b: $WO_3$/P3TPA film.

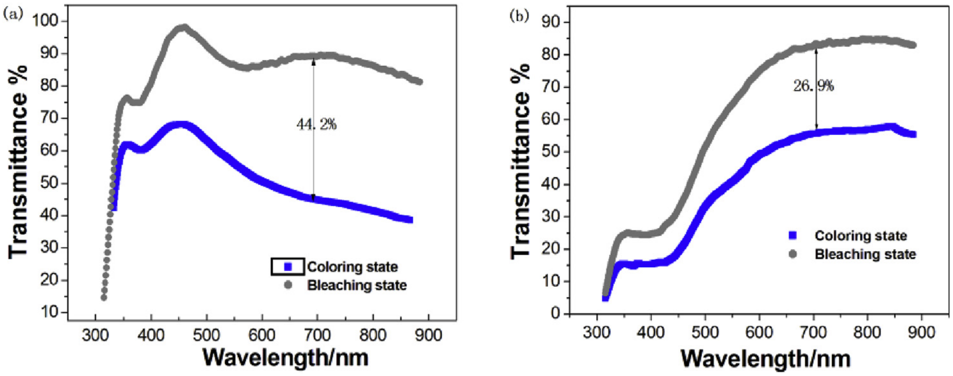


**Fig. 5.** The optical contrast of the electroactive materials at the coloring and bleaching state in ACN solution containing 0.05 M TBAP and 0.05 M $LiClO_4$. a: $WO_3$ film and b: $WO_3$/P3TPA film.

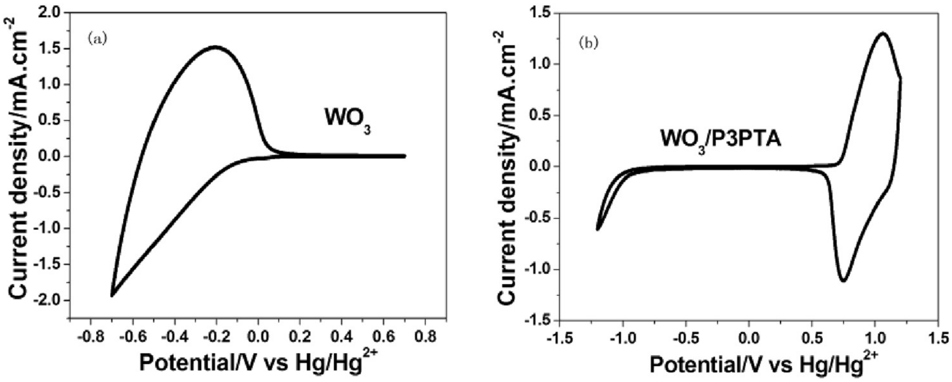


**Fig. 6.** The CV of the electroactive materials in the CAN solution containing 0.05 M TBAP–0.05 M $LiClO_4$. Scan rate = 100 mV/s. a: $WO_3$ film; b: $WO_3$/P3TPA film.

and $WO_3$/P3TPA films were measured using a UV–vis spectrophotometer, respectively. Fig. 4a shows that when the applied voltages is −2.5 V, the transmittance at 700 nm of the $WO_3$ film at the blue coloring state is 44.8%, whereas it is 89.1% at the bleaching state. When the applied voltage of −2.5 V is removed, the transmittance at 700 nm changes from 44.8% to 77.1% after nine days, which represents a change of 72.9%. The open-circuit memory of the $WO_3$/P3TPA composite film is shown in Fig. 4b. When the applied voltage is +2.5 V, the transmittance at 700 nm of the $WO_3$/P3TPA film at the blue coloring state is 55.7%. The transmittance at 700 nm of the $WO_3$/P3TPA film at the yellow state (the bleaching state) is 82.8%. When the applied voltage of +2.5 V is removed, the transmittance is 72.4% after nine days and the transmittance change is 30.0%. The results suggest that the open-circuit memory of the $WO_3$/P3TPA film is better than that of the $WO_3$ film.

### 3.3. *Optical contrast*

The optical contrast (ΔT) is a parameter of the color change of the electrochromic material. It is defined as the transmittance gap between two coloring states with different applied potentials [35]. Fig. 5 shows the transmittance spectra of the $WO_3$ and $WO_3$/P3TPA films at the coloring and bleaching states. In Fig. 5a, the ΔT at 700 nm of the $WO_3$ film is 44.2% between the deep blue state and the colorless transparent state, whereas the ΔT at 700 nm of the $WO_3$/P3TPA film is 26.9% between the blue and yellow state.

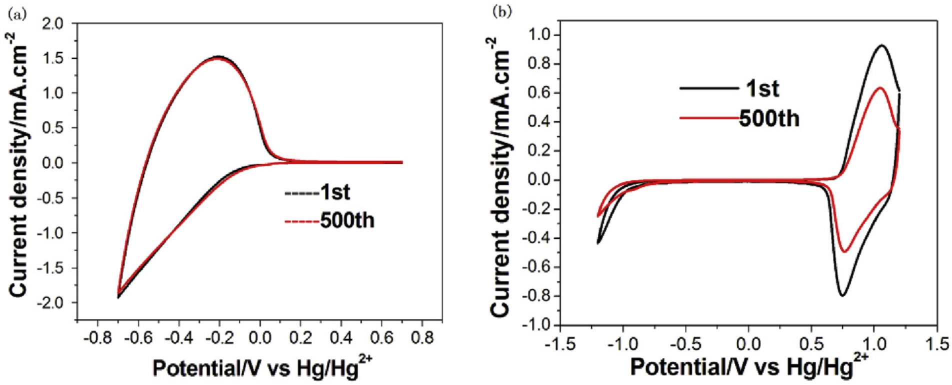


**Fig. 7.** The CV of active materials for the 1st and 500th cycle in the ACN solution containing 0.05 M TBAP-0.0 5 M $LiClO_4$, Scan rate = 100 mV/s. a: $WO_3$ film and b: $WO_3$/P3TPA film.

Compared with $WO_3$ film, the optical contrast of $WO_3$/P3TPA film has about 17.3% decrease. This is because the P3TPA film is yellow when it is in the bleaching state but $WO_3$ film presents colorless.

**Table 1**
Coloration efficiency of $WO_3$ and $WO_3$/P3TPA.

| Parameters | $WO_3$ | $WO_3$/P3TPA |
|---|---|---|
| Optical density variation (ΔOD) | 0.298 | 0.173 |
| Injected charge ($Q_A$, mC cm$^{-2}$) | 7.06<br>(coloring charge) | 3.93 |
| Extracted charge ($Q_R$, mC cm$^{-2}$) | 7.86 | 3.10<br>(coloring charge) |
| Charge loss ratio (%) | 11.4% | 21.1% |
| Coloration efficiency (η, cm$^2$/C) | 42.2 | 55.8 |
| Improvement of η (%) | – | 24.4% |

### 3.4. Coloration efficiency

The coloration efficiency (η) characterizes the charge utilization ratio of electrochromic materials. The high coloration efficiency indicates that the ECD exhibits large optical modulation for small inserted or extracted charge. The coloration efficiency η is calculated with the following equation [36].

$$\eta = \Delta OD/Q = \log[T_b/T_c]/Q_A \quad (1)$$

where the η (cm$^2$/C) is the coloration efficiency at a given wavelength, ΔOD is the variable optical density, $Q_A$ (mC/cm$^2$) is the injected charge, and $T_b$ and $T_c$ represent the bleaching and coloring transmittance, respectively.

Fig. 6 shows the CV curves of the electroactive materials. Fig. 7 shows the CV curves of the $WO_3$ and $WO_3$/P3TPA films in the first and 500th cycle. Compared with the $WO_3$ film, there is no

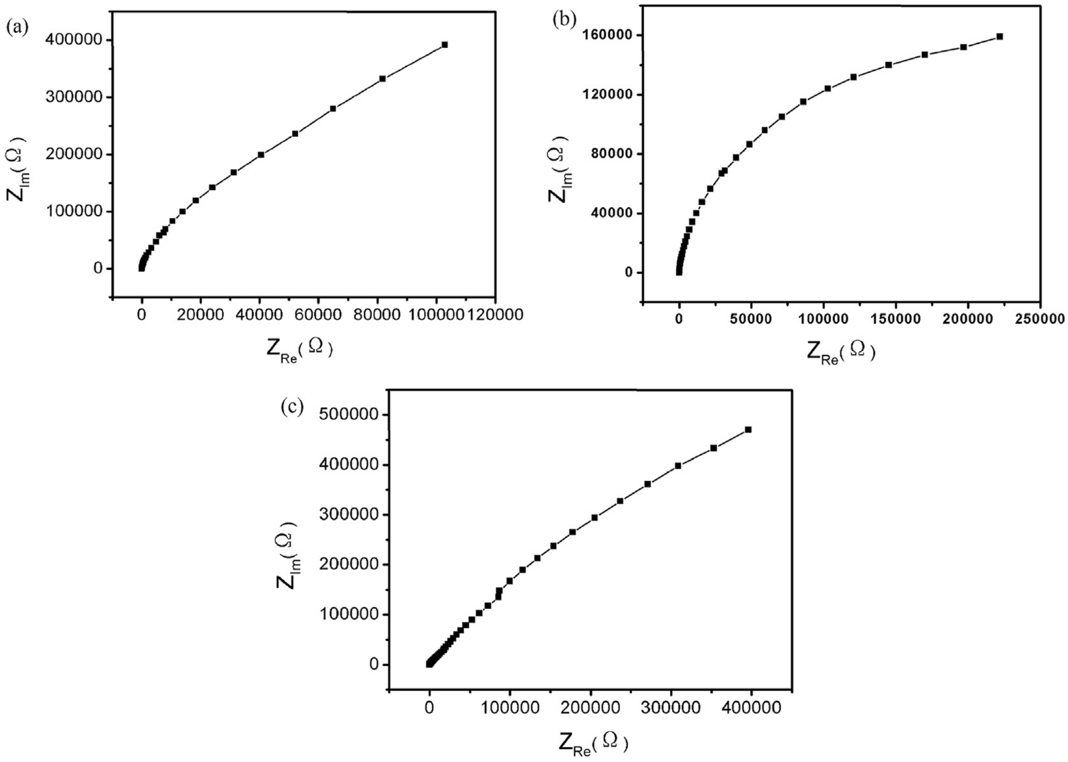


**Fig. 8.** The AC impedance diagrams of (a)$WO_3$ film, (b) P3TPA film, (c) $WO_3$/P3TPA film.

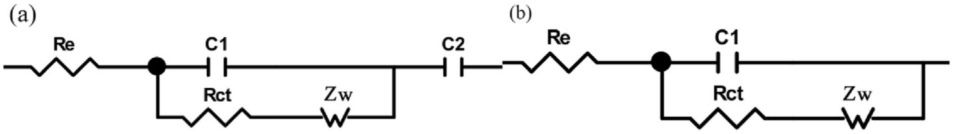


**Fig. 9.** The equivalent circuit used for fitting the experimental impedance data (a) $WO_3$ film, (b) P3TPA film and $WO_3$/P3TPA film.

**Table 2**
Parameters of EIS plots.

| | $R_e/\Omega$ | $C_1$/F | Rct/Ω | $C_2$/F |
|---|---|---|---|---|
| $WO_3$ film | 27.75 | $6.19 \times 10^{-5}$ | $1.906 \times 10^5$ | $4.726 \times 10^{-5}$ |
| P3TPA film | 82.78 | $2.11 \times 10^{-6}$ | $2.254 \times 10^5$ | – |
| $WO_3$/P3TPA film | 53.24 | $3.82 \times 10^{-6}$ | $1.281 \times 10^4$ | – |

remarkable negative signal on the CV curve of the $WO_3$/P3TPA film. According to Figs. 5 and 6 and equation (1), the calculated results can be seen in Table 1. Compared with the $WO_3$ film, the $WO_3$/P3TPA film has lower ΔOD, lower injected ($Q_A$) and extracted charge ($Q_R$), and higher charge loss ratio. However, the coloration efficiency of the $WO_3$/P3TPA film is better than that of the $WO_3$ film. The coloration efficiency of the $WO_3$/P3TPA film is 55.8 $cm^2$/C.

### 3.5. Alternating current (AC) impedance

To further understand the electrochemical behavior of the films, electrochemical impedance spectroscopy (EIS) measurements were measured by applying an AC voltage of 5 mV between a frequency range of 10 mHz and 10 kHz [37]. Fig. 8 shows the impedance diagrams of $WO_3$ film, P3TPA film and $WO_3$/P3TPA film, respectively. Fig. 9 presents the equivalent circuit models for these films. $R_e$ is the electronic resistance of the solution; $R_{ct}$ and $C_1$ represent the charge-transfer resistance and the capacity of the layer; $C_2$ is the limiting capacitance; $Z_w$ is the Warberg impedance [38]. The detailed parameters can be calculated using ZSim software. The results lists in Table 2. It is found that the P3TPA film shows larger resistance than $WO_3$ and $WO_3$/P3TPA films. Usually, the conductivity of organic material is a bit poor than metal oxide. The $WO_3$/P3TPA film shows lower resistance than the $WO_3$ film which indicates the charge transfer of the composite film is faster than that of $WO_3$. It is mean that the response time of $WO_3$/P3TPA film is faster than that of $WO_3$ which fits with the resistances.

## 4. Conclusion

In this study, using the organic-inorganic composite material ($WO_3$/P3TPA) as electroactive material, the electrochromic device was fabricated, and the electrochromic properties of $WO_3$/P3TPA were investigated. Compared with $WO_3$, the coloring switching time of $WO_3$/P3TPA was decreased by 20.0%, the bleaching switching time was decreased by 41.3%, and the open-circuit memory was improved. The coloration efficiency of $WO_3$/P3TPA for $WO_3$ increased from 42.2 $cm^2$/C to 55.8 $cm^2$/C.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2017.05.222.

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