



# Electrocatalytic PProDOT–Me<sub>2</sub> counter electrode for a Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple in a WO<sub>3</sub>-based electrochromic device



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## ABSTRACT

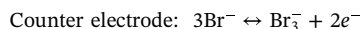
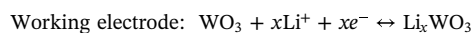
A new electrochromic device (ECD) was fabricated, consisting of poly(3,4-(2,2-dimethyl-propylenedioxy)thiophene) (PProDOT–Me<sub>2</sub>) and tungsten trioxide (WO<sub>3</sub>) films. The conventional cathodic EC material PProDOT–Me<sub>2</sub> acts as an electrocatalytic counter electrode here, working with an electrolyte which contains the Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple to accelerate the electrochromic process and lower the driving voltage of the ECD. The device can be fully colored at under −1.0 V and self-bleached at 0 V (in a short-circuited state) with high optical modulation of 72.4% at 680 nm. Compared with other self-bleaching devices, the response time of 5.6 s for coloring and 15.3 s for bleaching suggests an exceptional switching speed. Additionally, the coloration efficiency (CE) of the device reaches 88.9 cm<sup>2</sup>/C. When the long-term stability of the device was evaluated, no apparent deterioration was observed after 5000 cycles.

## 1. Introduction

Electrochromism refers to the phenomenon in which the optical properties (reflectivity, transmittance, absorptivity, etc.) of a material change steadily and reversibly under an external voltage, and is widely exploited in energy-efficient buildings, digital displays and anti-glare mirrors [1–3]. In 1969, Deb first proposed that WO<sub>3</sub> films could be switched between colorless and blue via an external voltage [4]. This discovery opened the door for researchers to explore electrochromic techniques and electrochromic devices based on WO<sub>3</sub> [5–7].

It has been found that PProDOT–Me<sub>2</sub>, one of the most frequently used cathodic EC materials in our previous studies, has an excellent matching effect with the Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple. Colored PProDOT–Me<sub>2</sub> (reduced state) can be easily oxidized by Br<sub>3</sub><sup>−</sup> without imposing any external conditions [8,9]. This phenomenon greatly aroused our interest as it could possibly be used to achieve fast self-bleaching of WO<sub>3</sub>-based ECDs. The key problem is whether electrons can transfer from colored WO<sub>3</sub> to PProDOT–Me<sub>2</sub> spontaneously. To check this, a special experiment was carried out in which a colored WO<sub>3</sub> film and a bleached PProDOT–Me<sub>2</sub> film were short-circuited, and then put into an electrolyte (0.1 M LiClO<sub>4</sub> in propylene carbonate). As a result, the PProDOT–Me<sub>2</sub> film immediately switched to the colored state, which implies that electrons are able to flow easily from colored WO<sub>3</sub> to PProDOT–Me<sub>2</sub>.

In this work, a non-complementary ECD involving two cathodic EC materials (WO<sub>3</sub> and PProDOT–Me<sub>2</sub>) and the Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple was designed. Notice that the WO<sub>3</sub> film is the working electrode for the electrochromic effect, while PProDOT–Me<sub>2</sub> is a counter electrode for transferring electrons rather than balancing charges like traditional counter electrodes [10,11]. The reactions at the two electrodes can be expressed as:



Moreover, in order not to affect the high transparency of the ECD in the bleached state, the coated PProDOT–Me<sub>2</sub> film was only a thin layer and can hardly change color during operation of the device. The Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple serves to balance charges and works with PProDOT–Me<sub>2</sub> to achieve self-bleaching and low-voltage driving of the ECD. Compared to an ECD with bare ITO glass as the counter electrode, the device developed here has a significantly faster bleaching process. The introduction of PProDOT–Me<sub>2</sub> also decreased the driving voltage of the coloring process from −1.5 V to −1.0 V. The ECD exhibits its largest optical contrast of 72.4% at 680 nm and has a high coloration efficiency of 88.9 cm<sup>2</sup>/C. Furthermore, the device shows robust stability over 5000 cycles without any obvious decline in performance. All of these results indicate that the introduction of the Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> redox couple and PProDOT–Me<sub>2</sub> not only speed up the EC process of the

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device, but also greatly reduce its driving voltage.

## 2. Experimental section

### 2.1. Materials

The monomer 3,4-(2,2-dimethyl-propylenedioxy)thiophene (PProDOT-Me<sub>2</sub>) was synthesized by the method described in the literature [12]. Ethanol (99.8%), propylene carbonate (PC, 99.7%), acetonitrile (ACN, 99.8%), pure tungsten powder (99%), and hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Lithium perchlorate (LiClO<sub>4</sub>, 99%), bromine liquid (Br<sub>2</sub>, 99.5%) and lithium bromide (LiBr, 99.5%) were all purchased from Alfa Aesar.

### 2.2. Preparation of the working electrode (WO<sub>3</sub> film)

The WO<sub>3</sub> film was fabricated by the electrochemical deposition method [13]. 6 g of pure tungsten powder (99.99%) was mixed with 60 mL H<sub>2</sub>O<sub>2</sub> in a beaker. After filtering the reaction solution twice, the resulting white translucent solution was then refluxed in an oil bath at 51 °C, 65 °C and 85 °C for 12 h, 2 h and 30 min, respectively. An equal volume of ethanol was added at 85 °C and immediately cooled to 50 °C for 24 h. Finally, the solution was refrigerated for a week.

Electrodeposition was carried out using an electrochemical station in three-electrode mode, with a platinum sheet used as the counter electrode, a silver wire as a reference electrode and the ITO glass as the working electrode. The WO<sub>3</sub> film was deposited at a constant potential of -0.6 V for 250 s via a potentiostatic instrument and then immersed in ethanol for 60 s. Finally, the film was annealed at 300 °C for 30 min in a muffle furnace.

### 2.3. Preparation of the counter electrode (PProDOT-Me<sub>2</sub> film)

The electropolymerization of the PProDOT-Me<sub>2</sub> film was carried out in a solution of 0.01 M PProDOT-Me<sub>2</sub> and 0.1 M LiClO<sub>4</sub> in 50 mL acetonitrile. The film was prepared by applying a constant potential of 1.65 V to an ITO glass for 1 s. In addition, the film was rinsed in acetonitrile and then dried at room temperature to obtain the counter electrode [8,14].

### 2.4. Assembly of the electrochromic device

The ECD was assembled with the EC electrode and the counter electrode. The electrolyte, consisting of 2 mM Br<sub>2</sub> and 0.3 M LiBr in PC, was injected into the groove between the two layers of electrodes. To explore the effect of PProDOT-Me<sub>2</sub> on ECD, two kinds of devices were designed, as shown in Fig. 1. The difference between the two is that the one employed a thin PProDOT-Me<sub>2</sub> film, while the other used a bare ITO glass as the counter electrode.

## 3. Results and discussion

### 3.1. Morphology and structure analysis

The morphologies of two electrodeposited films were studied by scanning electron microscopy (SEM). The PProDOT-Me<sub>2</sub> film has a

fibrous network structure and is about 50–170 nm thick, according to Fig. 2a and b. Owing to the short deposition time, PProDOT-Me<sub>2</sub> did not form a continuous and uniform film, but adhered to the ITO surface in a disorderly fashion. The morphology of the WO<sub>3</sub> film is presented in Fig. 2c, displaying a uniform and smooth surface. The XRD pattern (Fig. 2d) shows that all the lattice diffraction peaks are associated with the ITO substrate, which demonstrates the amorphous structure of the WO<sub>3</sub> film.

### 3.2. Working mechanism of the ECD

Fig. 3 shows the coloring and bleaching process of the ECD. When a negative voltage is applied to the working electrode, electrons flow into the WO<sub>3</sub> film. Simultaneously, Li<sup>+</sup> is inserted into the WO<sub>3</sub> film to balance the charge and Br<sup>-</sup> is oxidized to Br<sub>3</sub><sup>-</sup> at the counter electrode, turning the WO<sub>3</sub> film to a colored state. When the device was switched to the short-circuited state without an applied voltage, electrons easily transfer from the working electrode to the counter electrode through the external circuit. They then flow into the electrolyte, which makes Br<sub>3</sub><sup>-</sup> turn into Br<sup>-</sup>, accompanied by the migration of Li<sup>+</sup> out of the WO<sub>3</sub> film. Therefore, the WO<sub>3</sub> film transforms into the bleached state.

### 3.3. Optical performance of the ECD

The transmittance of the two devices (Fig. 1) at different voltages was measured and the results are shown in Fig. 4. As seen from the figure, the device with PProDOT-Me<sub>2</sub> shows lower transmittance than that without PProDOT-Me<sub>2</sub> at the same voltage, which means that it can be more easily colored at a lower voltage. When the voltage was applied at -1.0 V, the device with PProDOT-Me<sub>2</sub> was almost completely colored. In contrast, the device without PProDOT-Me<sub>2</sub> was still not completely colored at -1.5 V. Therefore, when a thin PProDOT-Me<sub>2</sub> film is introduced, the driving voltage of the ECD can be reduced to -1.0 V, and the ΔT<sub>max</sub> (maximum transmittance contrast) becomes 72.4% at 680 nm.

ECDs generally require the application of an opposite voltage to switch their state from colored to bleached. However, our improved device, can easily transform from colored to bleached using only the short-circuited state. By recording the transmittance change of the ECDs (Fig. 5a), we can calculate their response time. The device with PProDOT-Me<sub>2</sub> has a coloring response time of 5.6 s, while the bleaching time is 15.3 s. In contrast, the response time of the device without PProDOT-Me<sub>2</sub> could not be calculated due to its poor switching performance over the same time period.

In order to better compare the two devices, their bleaching behavior was investigated in detail (Fig. 5b). The ECD with PProDOT-Me<sub>2</sub> in a short-circuited state bleaches much faster than in the open-circuit state. From Fig. 5b one can also see that in the open-circuit state the device bleaches slowly even if not short-circuited. This is most likely due to the diffusion of Br<sub>3</sub><sup>-</sup> ions in the electrolyte from the PProDOT-Me<sub>2</sub> electrode to the WO<sub>3</sub> electrode.

### 3.4. Electrochemical properties analysis

To understand how the counter electrodes affect the reactions, the electrochemical properties of the PProDOT-Me<sub>2</sub> film and bare ITO glass in Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox electrolyte were investigated.

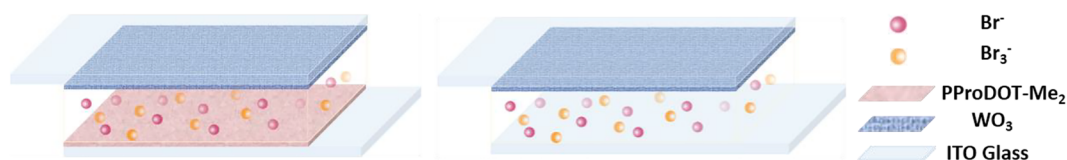


Fig. 1. Structure of the two devices under study.

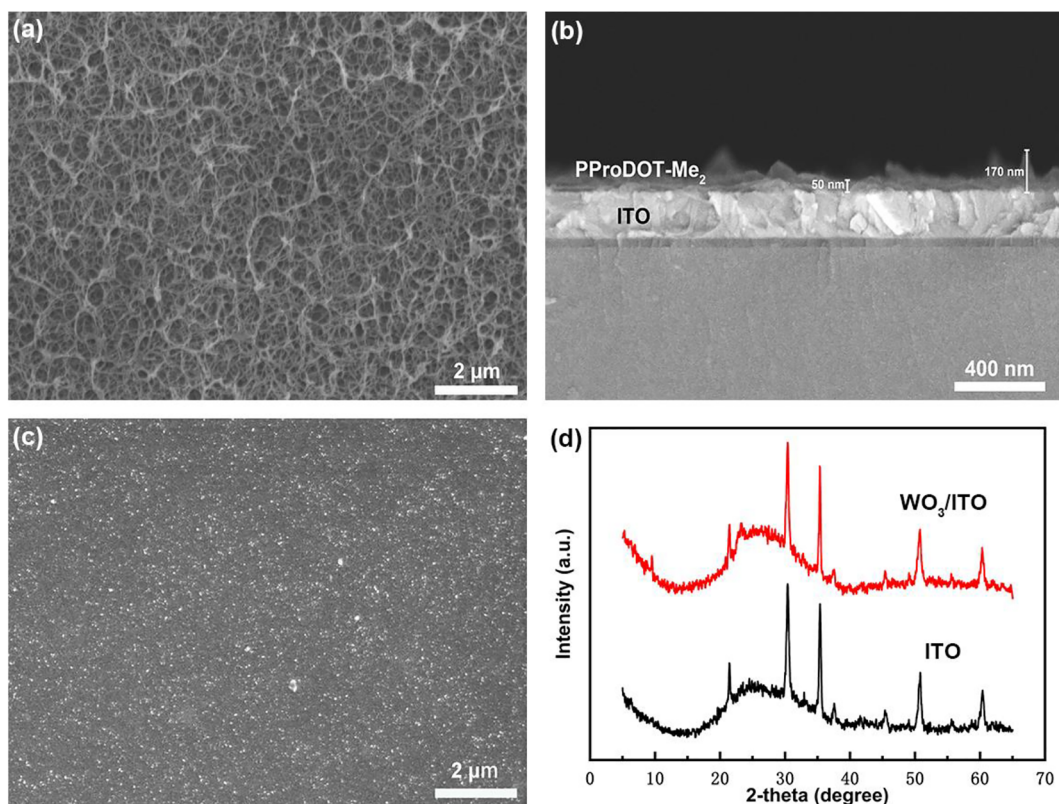


Fig. 2. (a) Surface and (b) cross-sectional SEM images of the PProDOT-Me<sub>2</sub> film; (c) Surface SEM diagram and (d) XRD patterns of the WO<sub>3</sub> film.

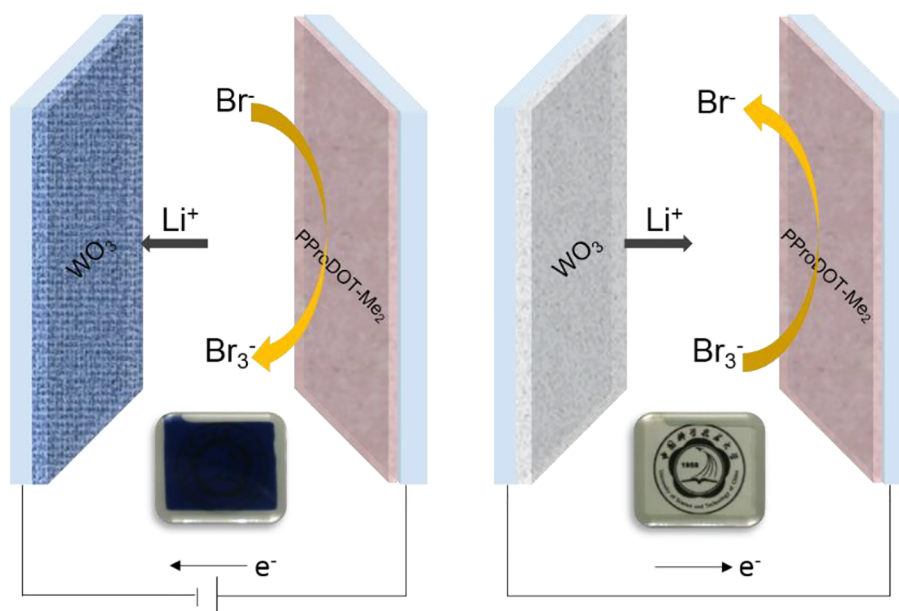


Fig. 3. Working mechanism of the ECD at an external voltage of (a)  $-1.5$  V for coloring, and (b)  $0$  V (in short-circuited state) for bleaching.

Two symmetrical CE-CE cells were designed to measure the charge transfer impedance at the counter electrode (CE) [15]. The structures and Nyquist plots of the symmetrical cells are shown in Fig. 6. It can be seen that the plot of PProDOT-Me<sub>2</sub> is divided into three parts (black curve in Fig. 6b), while the bare ITO is roughly a straight line, which illustrates that PProDOT-Me<sub>2</sub> has a smaller current transfer impedance. In order to compare the impedance of the two more intuitively, the corresponding analog circuits were designed (insets of Fig. 6) according to the structure of the symmetrical cells. Here  $R_s$  is the series resistance

of the cells,  $R_{ct}$  and  $C$  are the transfer impedance and capacitance at the interface between the electrode material and the electrolyte, respectively, while  $W_b$  represents the diffusion impedance of the material in the electrolyte. Apart from the first small semi-circle in the case of the PProDOT-Me<sub>2</sub>-based cell, the curves of the simulated data and the experimental data agree well within the test range, supporting the choice of analog circuit. The values of the circuit elements for two symmetrical cells were obtained by fitting with ZSimpWin software and results are shown in Table 1. The  $R_{ct}$  of the ITO and PProDOT-Me<sub>2</sub>

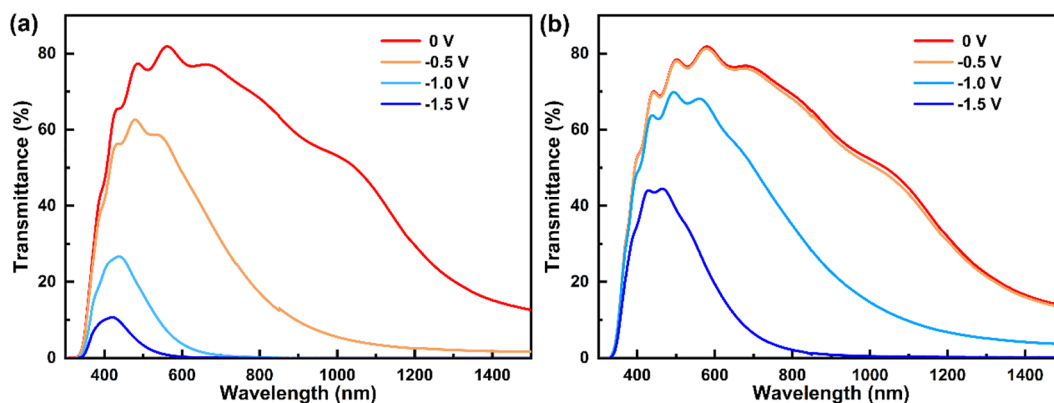


Fig. 4. Transmittance spectra of (a) the ECD with PProDOT-Me<sub>2</sub> and (b) the ECD without PProDOT-Me<sub>2</sub> at different voltages.

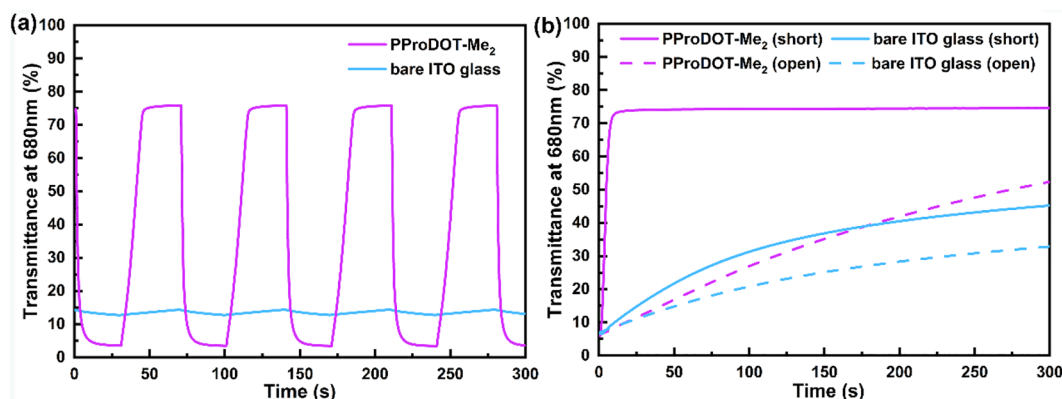


Fig. 5. (a) Recycle curves of the two ECDs. (b) Bleaching process of the two ECDs in short-circuited and open-circuit states.

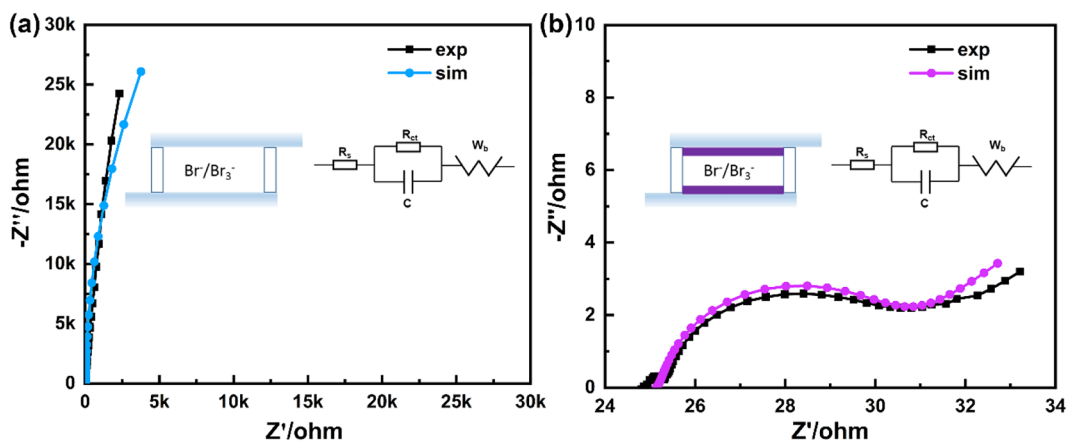


Fig. 6. Nyquist plots of (a) bare ITO and (b) PProDOT-Me<sub>2</sub>-based symmetrical CE-CE cells with the corresponding analog circuits (inset).

Table 1

The circuit elements' values of two symmetrical CE-CE cells.

Symmetrical cells	Circuit elements' values			
	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$C$ (mF)	$W_b$ ( $mS \cdot sec^{-0.5}$ )
ITO	27.270	$1.892 \cdot 10^5$	$6.00 \cdot 10^{-3}$	3.183
PProDOT-Me <sub>2</sub>	25.130	4.321	1.355	86.260

based symmetrical cells are  $1.892 \cdot 10^5 \Omega$  and  $4.321 \Omega$ , respectively. The result shows that electrons are more likely to recombine on the PProDOT-Me<sub>2</sub> surface than on the ITO surface, which means electrons can

easily flow from PProDOT-Me<sub>2</sub> to the Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox electrolyte.

The cyclic voltammetry (CV) characteristics of the PProDOT-Me<sub>2</sub> film and the bare ITO glass were measured in the Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox electrolyte (Fig. 7). It can be seen that the CV for the bare ITO glass has no obvious peaks, which means that no redox reaction occurs on its surface, i.e., it can neither gain nor lose electrons, nor transfer them into the electrolyte. On the other hand, the CV for PProDOT-Me<sub>2</sub> has three pairs of distinct peaks. The oxidation peak at 0.36 V and the reduction peak at 0.10 V represent the redox potential of PProDOT-Me<sub>2</sub> itself. Furthermore, the oxidation peaks (0.95 V and 1.28 V) and the corresponding reduction peaks (0.64 V and 1.03 V) correspond to the redox potential of the Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> couple and can be expressed by the following equation:

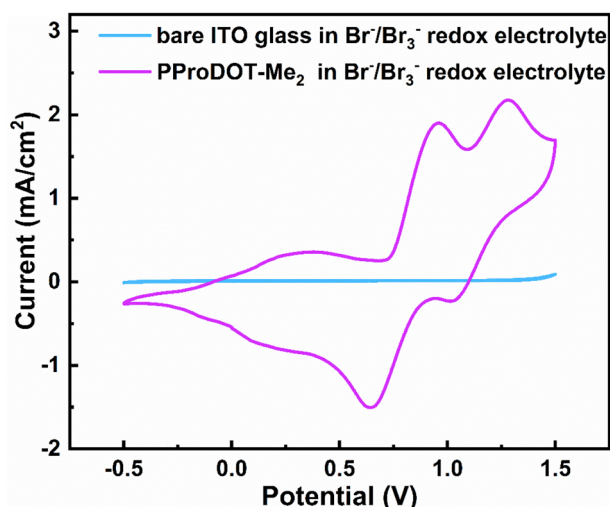


Fig. 7. The cyclic voltammograms (CV) of PProDOT-Me<sub>2</sub> film (red line) and bare ITO glass (blue line) in Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox electrolyte. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

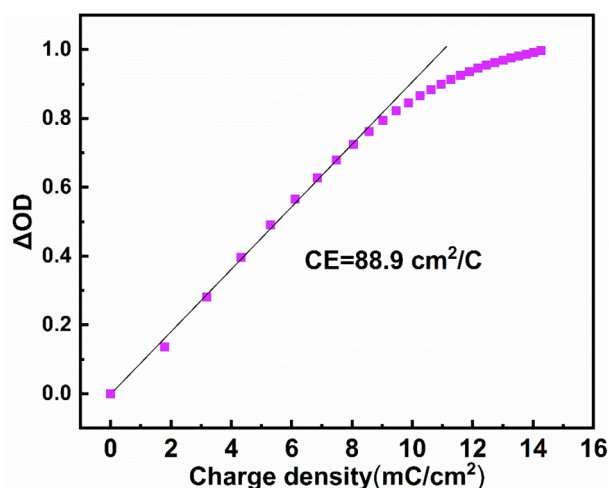
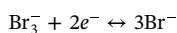
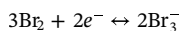


Fig. 8. The plot of  $\Delta OD$  at 680 nm as a function of charge density.



It can be observed that the minimum reduction potential of Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> (0.64 V) is higher than the oxidation potential of PProDOT-Me<sub>2</sub>,

which indicates that PProDOT-Me<sub>2</sub> can be easily oxidized by the Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox electrolyte. Furthermore, the surrounding area and peak current densities of PProDOT-Me<sub>2</sub> curve are larger than those of bare ITO glass, indicating its greater charge capacity.

### 3.5. Coloration efficiency and cyclic stability of the ECD

The coloration efficiency (CE) represents the change in the optical properties of electrochromic devices caused by the amount of the charge injected per unit area. This can be calculated by:

$$CE = \frac{\Delta OD}{Q} = \frac{\log\left(\frac{T_b}{T_c}\right)}{Q}$$

where  $Q$  is the amount of charge injected per unit area;  $\Delta OD$  means the variation of optical density; and  $T_b$  and  $T_c$  are the transmittances of ECDs in the bleached and colored state at a certain wavelength, respectively. By recording the current change curve of the ECD, the CE of the ECD under  $-1.0$  V can be calculated using the above equation, and is found to be  $88.9 \text{ cm}^2/\text{C}$  as shown in Fig. 8. The color efficiency is superior to that of similar devices [16].

Cyclic stability is an important index of electrochromic devices. Fig. 9 illustrates the transmittance and response time curves of the ECD at 680 nm before and after 5000 cycles. The transmittance of the ECD changes less than 5% after 5000 cycles, for both colored and bleached states. The bleaching transmittance at 680 nm is 76.2% after 5000 cycles, compared to 75.9% for the initial cycle with nearly no changes. However, the transmittance of the colored state at 680 nm declines slightly from 3.5% to 4.1%. Moreover, the coloring and bleaching times after 5000 cycles are nearly 5.7 s and 15.6 s respectively, i.e., close to the initial values. From these results it can be concluded that there was no distinct degradation of optical performance, indicating that the device has robust cyclic stability.

## 4. Conclusion

In this work, an ECD based on the widely used electrochromic material WO<sub>3</sub> was investigated. The conventional cathodic EC material PProDOT-Me<sub>2</sub> was introduced as a counter electrode to catalyze the anodic species Br<sup>-</sup>/Br<sub>3</sub><sup>-</sup> redox couple in the electrolyte. The device was a simple sandwich structure and could be straightforwardly assembled. The ECD showed a high optical modulation of 72.4% at 680 nm (75.9% for the bleached state and 3.5% for the colored state), and the coloration efficiency (CE) was up to  $88.9 \text{ cm}^2/\text{C}$ . When compared with a corresponding device without PProDOT-Me<sub>2</sub> (the counter electrode was bare ITO glass), we found that the introduction of PProDOT-Me<sub>2</sub> obviously reduced the coloring voltage from  $-1.5$  V from  $-1.0$  V, and the response time of the ECD was also shortened (5.6 s for the coloring process and 15.3 s for the bleaching process).

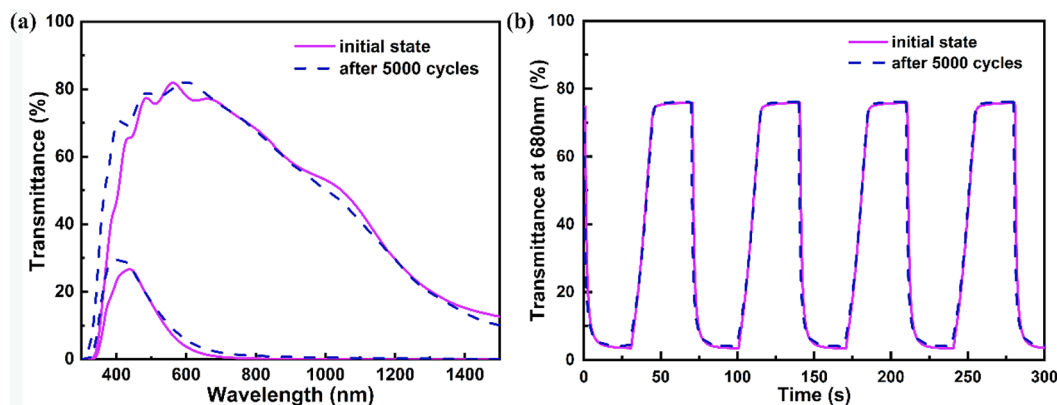


Fig. 9. (a) Transmittance and (b) response curves of the ECD at 680 nm in the initial state and after 5000 cycles.

Furthermore, when the ECD worked over 5000 cycles, no major changes could be observed, indicating that the improved device has satisfactory cyclic stability. Since the ECD can be easily driven by a low voltage and self-bleaches in a rapid and stable fashion, it has broad, long-term application potential in specific electrochromic fields like auto-dimming rear mirrors and anti-glare glasses that require self-bleaching.

#### Authors' contributions

Kai Sheng and Fang Xu conceived and designed the study. Kai Sheng, Kui Shen performed the experiments. Kai Sheng wrote the paper. Fang Xu, Kui Shen, Jianming Zheng and Chunye Xu reviewed and edited the manuscript. All authors read and approved the manuscript.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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