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## Time-resolved electrochromic properties of MoO<sub>3</sub> thin films electrodeposited on a flexible substrate

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**Abstract** In this paper, a MoO<sub>3</sub> thin film was firstly electrodeposited on flexible ITO/PET substrates. Its electrochromic properties were examined using an electrochemical workstation coupled in situ with a charge-coupled device (CCD) spectrophotometer. The film was characterized by XRD and AFM. The electrodeposited MoO<sub>3</sub> thin film on the ITO/PET substrate showed a large transmittance contrast between the colored and bleached states, a quick response, and good durability and reversibility. The low working potential range, -0.5 to 1.6 V (vs. Ag/AgCl), for the MoO<sub>3</sub>/ITO/PET film prepared in this work makes it a good candidate for flexible smart windows, as well as other plastic electrochromic devices.

**Keywords** Molybdenum oxide · Electrodeposition · Electrochromism

### Introduction

Among the transition metal trioxide thin films, MoO<sub>3</sub> has been widely studied in recent decades, owing to its photochromic and electrochromic properties, its electrocatalytic activities to ClO<sub>3</sub><sup>-</sup> [1] and NO<sub>2</sub><sup>-</sup> [2], and as a cathodic material in lithium batteries [3]. It is one of the best candidates for fabricating electrochromism devices because of its quick response, high coloration efficiency, low start-up potential and mild color change, i.e. from gray-blue to transparent. Recently, it was also employed to make electrochromic paper [4].

MoO<sub>3</sub> thin films can be deposited by a variety of techniques such as sputtering [5, 6], vacuum evaporation

[7], chemical deposition [8], the sol-gel method [9] and recently by electrodeposition [2, 10, 11]. Among these methods, the electrodeposition technique is probably the most economic and capable of producing large uniform thin oxide films with good electrochromic properties [10]. In most reported cases, MoO<sub>3</sub> was deposited on a solid substrate so that the films could be heated at different temperatures to adjust its electrochromic properties. However, in some cases, it is of great interest to choose a flexible substrate for MoO<sub>3</sub> deposition, considering the advantages of a foldable substrate. To our knowledge, little work has been done in this area. This is probably due to two main problems in flexible substrates: (1) the MoO<sub>3</sub> film deposited on a plastic substrate cannot be well crystallized; (2) the conductivity of ITO on the flexible substrate, which greatly influences the transmittance change of electrochromism devices, is not as good as that of solid substrates. In this paper, we chose a low-resistance, transparent ITO/PET flexible substrate for MoO<sub>3</sub> electrodeposition. The optically transparent substrate made it easy to monitor the transmittance change caused by the electron/ion insertion and extraction. With the ion/electron insertion or extraction, ideal reversible electrochromic properties were observed on the electrodeposited MoO<sub>3</sub>/ITO/PET film. During the electrochromic process, a CCD spectrophotometer enabled us to obtain various kinetic parameters and record time-resolved full-wavelength spectra of the MoO<sub>3</sub> film, which reflected its response time and transmittance change. An electrochromic performance test showed that the thin MoO<sub>3</sub> layer on ITO/PET had a large transmittance contrast and its colored state could be kept in air for more than 12 h. XRD and AFM were employed to detect the nature of the MoO<sub>3</sub> films on the ITO/PET.

### Experimental

MoO<sub>3</sub> thin films were electrodeposited on the surface of ITO/PET flexible films (type III, square resistance ~100 Ω cm<sup>-2</sup>; Shenzhen Beiqing Thin-Films Technology, China) in 0.037 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> aqueous solution. H<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) was used to

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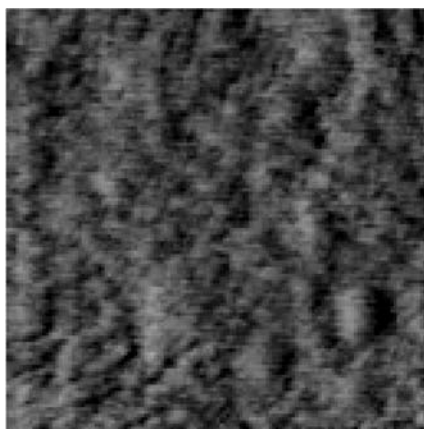
adjust the pH of the solution to 0.8. The anode was a Pt wire and the cathode was a ITO/PET film (area  $1 \times 2 \text{ cm}^2$ ). The cathodic electrodeposition was performed at a constant current of  $5 \times 10^{-4} \text{ A}$  for 300 s by a CHI660 electrochemical workstation (CH Instruments, Tenn., USA). The kinetic deposition process was monitored by a SM240 CCD spectrophotometer (CVI Spectral Instruments, Putnam, Conn., USA) while the electrodeposition was performed.

The electrochromic experiments were performed in a home-made electrochemical cell with two quartz windows.  $\text{LiClO}_4$  ( $1.0 \text{ mol L}^{-1}$ ) in propylene carbonate solution was used for all experiments. All electrochemical processes were performed by the CHI660 electrochemical workstation and the potential was referenced to the home-made solid Ag/AgCl electrode with a reference potential of 0.2065 V vs. NHE at 298 K, and the counter electrode was a Pt wire. All transmittance spectra were monitored by the SM240 CCD spectrophotometer while the electrochromic redox process was carried out. XRD [Rigata/max-C diffractometer (Cu K $\alpha$ )] and AFM (AFM-2, Zhejiang University) were employed to give insight into the nature of the  $\text{MoO}_3$  coatings. All AFM measurements were made in air at room temperature.

## Results and discussion

### Film morphology

The  $\text{MoO}_3$  film electrodeposited in  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution was gray-blue, which has been reported to be one of the best electrochromic films of all electrodeposited  $\text{MoO}_3$  films [11].  $\text{H}^+$  doped into the film during the process of electrodeposition reduced the  $\text{Mo}^{6+}$  to  $\text{Mo}^{5+}$  and caused the initial blue. The  $\text{MoO}_3$  coatings on the ITO/PET looked uniform. In Fig. 1, AFM shows the morphology features of the  $\text{MoO}_3$ /ITO/PET thin film in a  $500 \times 500 \text{ nm}$  area. It is obvious that the  $\text{MoO}_3$  prepared in this work was amorphous. The XRD measurements for the as-deposited  $\text{MoO}_3$ /ITO/PET thin film showed a very broad band at a  $2^\circ$  range from  $10^\circ$  to  $50^\circ$ , which also indicated an amorphous  $\text{MoO}_3$  phase was formed thereon. Many investigations have demonstrated that the existence of structural  $\text{H}^+$  and the amorphous material combined with a porous micro-structure were favorable for a quick electrochromic response [10, 12, 13]. We also observed that the

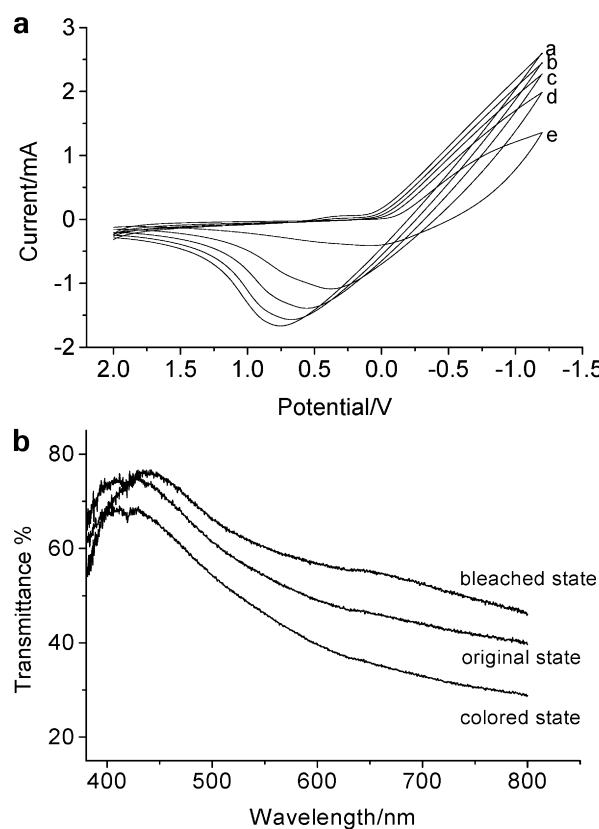


**Fig. 1** AFM image of a  $500 \times 500 \text{ nm}$  part of a  $\text{MoO}_3$  film electrodeposited on a flexible PET/ITO substrate

as-deposited  $\text{MoO}_3$  film dissolved in aqueous solution with a cathodic polarization, which was similarly reported in previous work [14, 15]. According to the theory founded by Arnoldussen [16], the dissolving behavior can be explained by the triangular structure of polymolybdenum acid. However, when the  $\text{MoO}_3$ /ITO/PET was dried in air for several hours, it was much more stable in aqueous solution and in  $\text{LiClO}_4$  + propylene carbonate solution, and there was strong affinity between the PET/ITO surface and the  $\text{MoO}_3$  film. This stability is of great importance for  $\text{MoO}_3$  film utility in smart window fabrication.

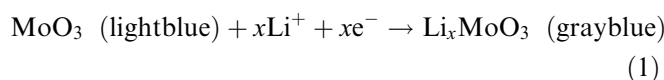
### Electrochromic performance

Figure 2a showed cyclic voltammograms of  $\text{MoO}_3$  electrodeposited on ITO/PET at scan rates of 20– $100 \text{ mV s}^{-1}$ . Two redox current peaks for reduction (intercalation) or oxidation (de-intercalation) processes were observed. The oxidation curve featured an irreversible process since the amorphous films had a broad distribution of energetically different intercalation sites.



**Fig. 2** **a** Cyclic voltammograms of a PET/ITO/ $\text{MoO}_3$  thin film in  $1.0 \text{ mol L}^{-1}$   $\text{LiClO}_4$ /propylene carbonate solution with scan rates of (a)  $100 \text{ mV s}^{-1}$ , (b)  $80 \text{ mV s}^{-1}$ , (c)  $60 \text{ mV s}^{-1}$ , (d)  $40 \text{ mV s}^{-1}$  and (e)  $20 \text{ mV s}^{-1}$ . **b** The transmittance change obtained during the process of cyclic voltammetry (scan rate  $60 \text{ mV s}^{-1}$ ). The bleached state and colored states correspond to 1.6 V and  $-0.5 \text{ V}$ , respectively

A CCD spectrophotometer was employed to detect the in situ spectra while the electrochromic reaction was taking place. Figure 2b was recorded while the cyclic voltammetry was in progress. The bleached and colored states corresponded to 1.6 V and  $-0.5$  V, respectively. The transmittance of the colored state was smaller than that of the freshly prepared  $\text{MoO}_3$  thin film on the ITO/PET substrate, which implied that a negative potential inserted  $\text{Li}^+/\text{e}^-$  in  $\text{LiClO}_4/\text{propylene carbonate}$  electrolyte into the film and  $\text{Mo}^{6+}$  was reduced to  $\text{Mo}^{5+}$ . When the potential moved to a positive range,  $\text{Li}^+/\text{e}^-$  were driven out by the electric field and the transmittance became larger. The integration of the total charge between  $-0.5$  and  $1.6$  V was  $1.975 \text{ C cm}^{-2}$  for the cathodic charge and  $1.823 \text{ C cm}^{-2}$  for the anodic charge for the as-deposited  $\text{MoO}_3$  film electrode at a scan rate of  $20 \text{ mV s}^{-1}$ . This electrochemical process can be described by Eq. 1:



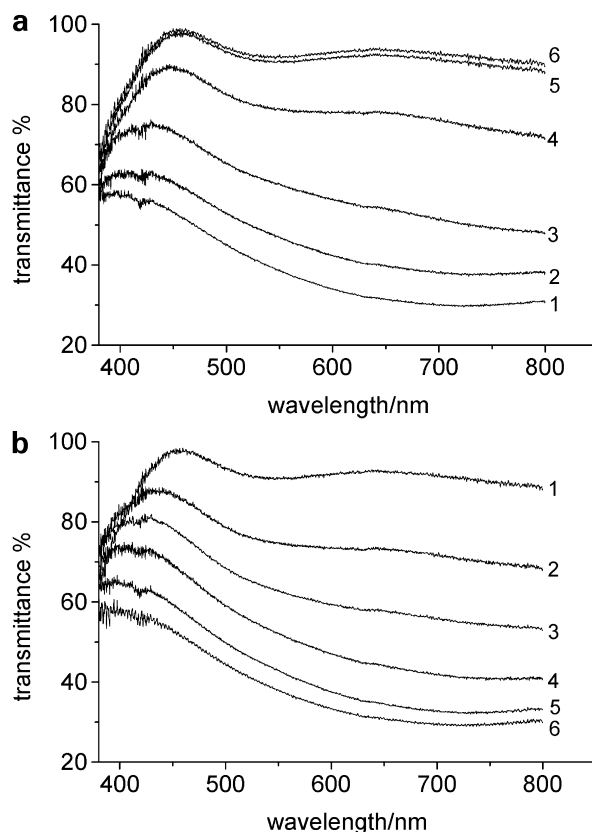
It was reported previously that the insertion coefficient  $x = QM/\rho dFS$  [17], where  $Q$  is the charge,  $M$  is the molar weight of  $\text{MoO}_3$ ,  $\rho$  is the density of  $\text{MoO}_3$  ( $\sim 5 \text{ g cm}^{-3}$ ),  $d$  is the thickness of the thin film ( $\sim 100 \mu\text{m}$ ),  $F$  is the Faraday constant, and  $S$  is the area of the electrode ( $\sim 2 \text{ cm}^2$ ). Thus, as shown in Table 1, the insertion coefficient of the as-deposited  $\text{MoO}_3$  thin film was calculated to be quite close for the cathodic and anodic processes. For example,  $x$  at  $20 \text{ mV s}^{-1}$  for the cathodic and anodic processes was 0.132 and 0.122, respectively. The charge reversibility was about 92.4%, which indicated that intercalation and de-intercalation for the prepared  $\text{MoO}_3$  thin film were relatively comparable. Similar phenomena were also observed for other scan rates, as shown in Table 1, which displays a comparison of charges and insertion coefficients for the intercalation and de-intercalation processes at various scan rates.

In order to investigate the response of  $\text{MoO}_3$  films on ITO/PET more clearly, an in situ spectroelectrochemical experiment was performed to monitor the electrochromic process while  $1.6 \text{ V}$  and  $-0.5 \text{ V}$  were applied separately to the working electrode. Figure 3a shows the bleaching process with  $1.6 \text{ V}$  applied and Fig. 3b is the coloration process with  $-0.5 \text{ V}$ . Considering the time span between the two adjacent spectra, it is obvious that

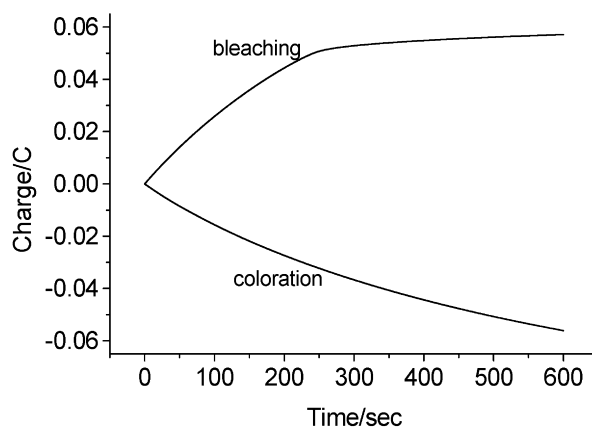
**Table 1** Comparison of charges and insertion coefficients for the intercalation and de-intercalation processes at various scan rates

$Q_a$ (C)	$Q_c$ (C)	$V$ (mV $\text{s}^{-1}$ )	$x$ (a)	$x$ (c)
$1.823 \times 10^{-3}$	$1.975 \times 10^{-3}$	20	0.122	0.132
$4.441 \times 10^{-3}$	$4.876 \times 10^{-3}$	40	0.298	0.334
$6.753 \times 10^{-3}$	$7.461 \times 10^{-3}$	60	0.453	0.500
$7.954 \times 10^{-3}$	$8.971 \times 10^{-3}$	80	0.533	0.601
$8.844 \times 10^{-3}$	$9.908 \times 10^{-3}$	100	0.593	0.664

the transmittance changed quickly and greatly at the beginning; with the lapse of time, the change rate slowed down. The transmittance reached a relatively stable value after 600 s. Comparing this phenomenon with Fig. 4, which describes the relationship between time and the number of charges inserted (coloration process)/



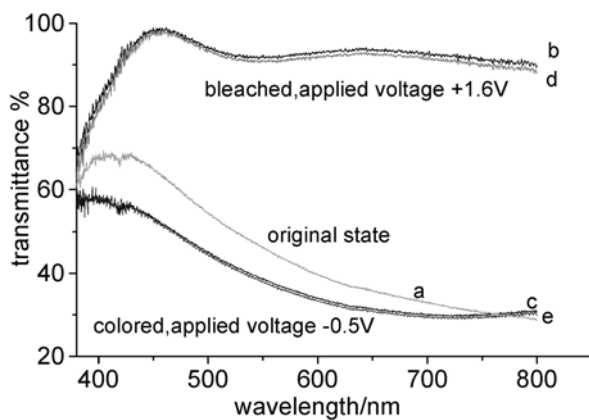
**Fig. 3a, b** In situ CCD transmission spectra for a PET/ITO/ $\text{MoO}_3$  thin film in  $1.0 \text{ mol L}^{-1} \text{ LiClO}_4/\text{PC}$  solution (curve 1, 0 s; 2, 40 s; 3, 100 s; 4, 200 s; 5, 360 s; 6, 600 s). **a**  $1.6 \text{ V}$  was applied; **b**  $-0.5 \text{ V}$  was applied



**Fig. 4** Charge transfer diagram for the bleaching and coloring processes. The PET/ITO/ $\text{MoO}_3$  thin film was immersed in  $1.0 \text{ mol L}^{-1} \text{ LiClO}_4/\text{PC}$  solution and  $1.6 \text{ V}$  (bleaching) or  $-0.5 \text{ V}$  (coloration) was applied

extracted (bleaching process), we may regard the diffusion of  $e^-$ , instead of the voltage applied, as the control factor for transmittance change. In the bleaching process of Fig. 4, the extracted  $e^-$  was almost in a logarithmic dependence with time in the first 260 s, which caused the quick transmittance increase from curve 1 to 5 in Fig. 3a. After 300 s,  $e^-$  extracted from the  $\text{MoO}_3$  film almost reached a stable value and curve 6 in Fig. 3a changed little from curve 5 without more  $e^-$  extracted. This phenomenon also implied that only a certain number of  $e^-/\text{Li}^+$  can be extracted/inserted under a certain voltage and  $e^-$  was a proper parameter to describe the electrochromic phenomena of the  $\text{MoO}_3$  film to some extent. Although we cannot observe the obvious stable state of the coloration process in Fig. 4, the inserting speed of  $e^-$  slowed down with the lapse of time. The charge versus time plot in Fig. 4 also showed that the reduction (coloration process) may be fully diffusion controlled due to a larger resistance of the oxidized film; however, a transition from thin film behavior to diffusion control was observed in the case of oxidation.

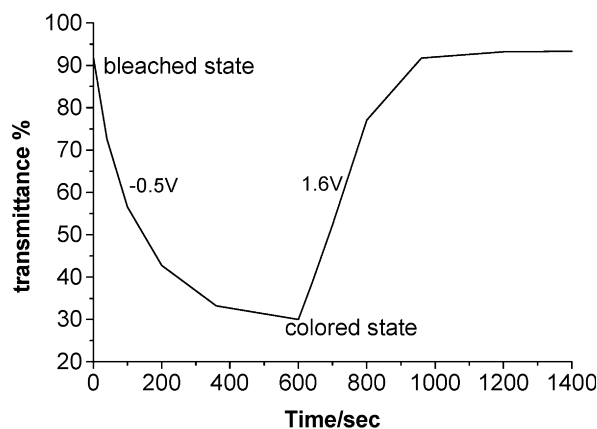
We studied the reversibility of the electrodeposited  $\text{MoO}_3$  thin film on the ITO/PET substrate by cyclic voltammetry. The  $\text{MoO}_3$  film was subjected to a CV scan from  $-1.2$  to  $2.0$  V with a scan rate of  $50 \text{ mV s}^{-1}$  and the amount of  $e^-$  inserted was used to represent the electrochromic property of the  $\text{MoO}_3$  film. We observed that, in the first 10 cycles, the  $e^-$  charge inserted reduced from  $1.867 \times 10^{-2} \text{ C}$  (cycle 1) to  $5.117 \times 10^{-3} \text{ C}$  (cycle 10); after 12 cycles, the  $e^-$  charge inserted reached a stable value of  $\sim 3.67 \times 10^{-3} \text{ C}$  and did not change further. This demonstrated that the electrodeposited  $\text{MoO}_3$  thin film on the ITO/PET flexible substrate had a good reversibility after 12 cycles. The good reversibility is observed directly in Fig. 5, where  $+1.6$  V and  $-0.5$  V were applied in turn. Curve a shows the initial transmittance spectra of the freshly prepared  $\text{MoO}_3$  film (spectra of the



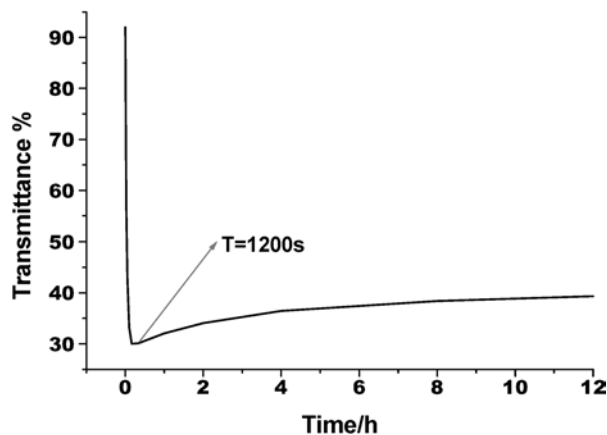
**Fig. 5** Spectral transmittance of the PET/ITO/ $\text{MoO}_3$  thin film in  $1.0 \text{ mol L}^{-1} \text{ LiClO}_4/\text{PC}$  solution. (a) Original state (freshly prepared  $\text{MoO}_3$  thin film on PET/ITO). (b) Bleached state ( $1.6$  V applied for 600 s). (c) Colored state ( $-0.5$  V applied for 600 s after step b). (d) Bleached state ( $1.6$  V applied for 600 s after step c). (e) Colored state ( $-0.5$  V applied for 600 s after step d)

original state) and curve b represents the bleached transmittance after  $1.6$  V was applied for 600 s. Then  $-0.5$  V was applied for another 600 s and curve c was obtained. The transmittance change between curves b and c gave a contrast of 63% at 680 nm between the bleached state at  $1.6$  V and the colored state at  $-0.5$  V. The contrast ratio is given by  $\text{CR} = T_b/T_c = 3.1$ , where  $T_b$  and  $T_c$  are the transmittance of the bleached and the colored forms, respectively. The contrast ratio was much greater than the  $\text{WO}_3$  film on PET/ITO reported previously [12]. When the colored film (curve c) was subjected to another 600 s of  $+1.6$  V, the transmittance spectrum (curve d) of the bleached film was obtained and it almost overlapped with curve b. This process proved the good reversibility of the electrodeposited  $\text{MoO}_3$  coating on ITO/PET plastic. Curve e was observed after the bleached  $\text{MoO}_3$  film was subjected to another  $-0.5$  V again; the little difference between curve c and e also demonstrated the good reversibility.

Dynamic measurements on electrodeposited  $\text{MoO}_3$  showed an acceptable switching rate. As visible in Fig. 6, the transmittance at 680 nm was recorded while  $-0.5$  V and  $+1.6$  V were applied. From the slope of the bleaching/coloration process it could be concluded that the bleaching speed was much faster than coloration. After 300 s of  $+1.6$  V on  $\text{MoO}_3$  film, the transmittance was almost at a stable value that was in good agreement with Fig. 4. This could be explained by a “saturate effect” [13]. When a positive potential was applied to the  $\text{MoO}_3$  film, electrons and  $\text{Li}^+$  were driven out of the surface under the force of the electric field. The number of extracted  $\text{Li}^+$  under a fixed voltage could be represented by the number of extracted  $e^-$  in Fig. 4, because one extracted/inserted  $\text{Li}^+$  always corresponded to one extracted/inserted  $e^-$  in Eq. 1.  $\text{Li}^+$  must overcome the surface barrier potential, which was much higher for inner  $\text{Li}^+$  than for  $\text{Li}^+$  occupying the surface “color center”. With a fixed potential exerted on the  $\text{MoO}_3$  film, the energy provided by the electric field could only drive a certain number of  $\text{Li}^+$  out of the film (i.e., in



**Fig. 6** In situ transmittance change at 680 nm when  $-0.5$  V and  $1.6$  V were applied in turn



**Fig. 7** Behavior of PET/ITO/MoO<sub>3</sub> thin film transmittance in accordance with time:  $-0.5$  V was applied for 1200 s for coloration and the transmittance was obtained in a  $1.0 \text{ mol L}^{-1}$  LiClO<sub>4</sub>/PC solution. The transmittance increased less than 10% after 12 h

Fig. 4, only a fixed number of  $e^-$  could be extracted under 1.6 V), which led to the stable transmittance of the MoO<sub>3</sub> film after 300 s. To demonstrate the memory property of the electrodeposited MoO<sub>3</sub> film on ITO/PET, the freshly prepared MoO<sub>3</sub> film was subjected to  $-0.5$  V for 1200 s, then was stored in air for 12 h in the colored state. The transmittance was recorded over 12 h, as shown in Fig. 7. In the first 4 h the transmittance increased about 7% and then reached a relatively stable state with little transmittance change, so that the transmittance increased less than 3% during 4–12 h. The small transmittance change gives a potential application for smart windows.

## Conclusions

Gray-blue MoO<sub>3</sub> thin film was electrodeposited on a flexible ITO/PET substrate and looked uniform. The AFM and XRD measurements showed its amorphous structure. Such a structure was good for electrochromic properties. The transmittance change scale was from

30% to 93%, which was much better than previous results for WO<sub>3</sub> films on a flexible substrate. The kinetic bleaching/coloration process measured by a CCD spectrophotometer proved that the switching time was less than 5 min. The colored state could be maintained for more than 12 h, with the transmittance increasing less than 10%. This memory effect is suitable for normally used smart windows.

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