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Electrochemical preparation of PMeT/TiO₂ nanocomposite electrochromic electrodes with enhanced long-term stability

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Abstract In this work, 3-methylthiophene (MeT) was electrochemically incorporated with nano- and mesoporous TiO₂ films to form poly(3-methylthiophene) (PMeT)/TiO₂ nanocomposite electrochromic electrodes. TiO₂ films, which were previously coated on the ITO glass sheets through a well-established technique, were introduced to enhance the adhesion of the polymers to the substrates and thus increase the long-term stability of the devices. With this effort, the nanocomposite electrodes were found to retain up to 60% of their optical response after 3,500 deep and double potential steps and retain up to 50% of their electroactivity after 10^4 same steps, exhibiting enhanced long-term stability. Switching time and the maximum optical contrast ($\Delta T\%$) of the nanocomposite electrodes were found to be 0.6 s and 45%, respectively. Moreover, our work showed that electrochemically incorporating conductive polymers (CPs) with TiO₂ mesoporous films was an effective method to form high-quality CP/TiO₂ nanocomposite electrodes, which can be used widely in battery cathodes, photovoltaic cells, photocatalytic reaction, and photoelectrochromic cells and were supposed to enhance their performances.

Keywords TiO₂ · 3-Methylthiophene ·
Electropolymerization · Nanocomposite · Electrochromic

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Introduction

Over the past two decades, various electrochromic devices (ECDs) based on conducting polymers (CPs; polyaniline, polypyrrole, polythiophene, etc.), which are used in rear-view mirrors, smart windows, and displays [1–7] because of their striking electrochemical and optical properties, have received significant attention. However, the realization of practical, long-lasting CP electrochemical devices remains an elusive goal because of performance limitations that include slow switching speeds, poor long-term stability, and short lifetimes [8–10]. Among them, poor long-term stability is one of the most important reasons why few commercial applications have been brought to the markets [11, 12].

CP-based ECDs also have a multilayered structure, where the electrochromic electrode is separated by an electrolyte from the charge-balancing counter electrode. The electrochromic electrodes are usually based on a CP film supported on a conducting substrate (CS; indium tin oxide (ITO) glass, stainless steel, platinum (Pt) sheet, etc.), and play an important role in performances of ECDs [13]. Electropolymerization is a commonly used technique for the synthesis of CPs on CSs. Among other advantages, a film is directly deposited on the surface of CSs and the film thickness can be easily controlled. The poor interfacial adhesion of the CPs to the CSs is, however, a major pending problem, which leads to the poor stability and

short lifetime of the electrodes [14, 15]. Till now, few efforts have focused on increasing adhesion of polymers to substrates to enhance the long-term stability of the electrodes. Jerome et al. [16] developed a full electrochemical two-step procedure to anchor polymers on the substrates firmly, which enhanced interfacial adhesion of polymers to substrates and increased long-term stability of the electrodes. Therefore, enhancing interfacial adhesion of the CPs to the substrates is an effective way to increase the long-term stability of the electrodes [17].

Transparent nano- and mesoporous TiO_2 films can be prepared on conducting substrates through well-established synthetic processes [18]. A characteristic feature of these films is that they typically have a high porosity, since the films are actually composed of numerous coadjacent nano-size TiO_2 grains. The rest of the interstices of the films were filled with poly(3-methylthiophene) (PMeT) to obtain PMeT/TiO_2 nanocomposites.

This work is our most recent exploration in the development of enhanced long-term stability of ECDs by increasing the adhesion of polymers to the substrates. 3-Methylthiophene (MeT) was electropolymerized to incorporate with nano- and mesoporous TiO_2 films which were previously coated on the ITO glass sheets with good adhesion to form poly(3-methylthiophene) (PMeT)/TiO_2 nanocomposite electrochromic electrodes. Through introducing TiO_2, the stability and the durability of the nanocomposite electrodes were found to be enhanced evidently. They also exhibited rapid switching speed and high optical contrast between a transmissive light-blue-doped state and red natural state. To the best of our knowledge, TiO_2 mesoporous films were for the first time employed to increase the adhesion of the polymers to the substrates and enhance the long-term stability of the electrodes. Considering the wide utilization of CPs and TiO_2, this method can be employed to prepare CP/TiO_2 nanocomposites which can be applied in battery cathodes, photovoltaic cells, and photocatalytic reactions and are supposed to improve their performances.

Materials and methods

Materials

3-Methylthiophene (MeT, Aldrich) was purchased and used as received. Boron trifluoride ethyl ether (BFEE) was purchased from Sinopharm Chemical Reagent Co., Ltd. The room temperature ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM]PF_6) was purchased from Chemer Chemical Co. Ltd (Hangzhou, China). Nanocrystalline TiO_2 powder (P25) was purchased from Degussa. All chemicals were of analytical grade.

Procedures

Preparation of the nanocomposite electrodes included two main steps. The first step was to prepare the nanoporous TiO_2 film on the indium tin oxide (ITO) glass sheet (<10 Ω/□, 1×2 cm^2), which is described in detail elsewhere [19]. Briefly, 1 wt.% nanocrystalline TiO_2 powder (P25 Degussa) was ultrasonically dispersed in a 0.5 M Ti(OC$_4$H$_9$)$_4$ ethanol solution for about 20 min. This solution was spin coated (2,500 rpm, 30 s) three times to deposit TiO_2 thin film on the ITO glass substrates. The samples were dried in ambient conditions at 100 °C and followed by a fast heat treatment at 450 °C for 60 s. After that, transparent and even TiO_2 films can be obtained from the ITO glass sheets. The following step was preparing the nanocomposite electrodes through electropolymerizing MeT onto the TiO_2-coated substrates made before. The potentiostatic (1.5 V) electropolymerization of MeT (0.01 M) in 100 ml BFEE was carried out in a three-compartment electrolysis cell with TiO_2-coated sheet as working electrode, platinum (Pt) sheet (1×2 cm^2) and a 1.0-mm diameter Ag wire (convenient for operations) served as the counter electrode and the pseudo-reference electrode, respectively. The distance between the working electrode and counter electrode was 10 mm. Before electropolymerization, the working electrode was immersed in the electrolyte for 10 min leaving the mesoporous TiO_2 film soaked fully. The charge passed during the process was recorded and denoted as the polymerization charge [20]. The thickness of the film was controlled by monitoring the amount of the charge (about 50 mC cm^{-2}).

The fabricated electrochromic devices contained two electrodes with electrolyte between them. The nanocomposite electrode was employed as the electrochromic electrode, and another piece of ITO glass sheet with the same size was employed as the counter electrode. The two electrodes were then sealed with a UV-hardening epoxy resin, keeping the internal space at approximately 10 μm using an insulating polymer spacer. [BMIM]PF_6 was infused between the two electrodes and served as the electrolyte.

Measurements

The morphologies of the TiO_2 film and PMeT/TiO_2 nanocomposite were investigated using a field emission scanning electron microscope (SEM; JSM-6700F, JEOL Inc.). The UV–visible absorption spectra of the nanocomposite electrodes were obtained using a Shimadzu-23101PC spectrophotometer. The cyclic voltammograms of the nanocomposite electrodes were obtained using CHI660c electrochemical station (CHI, Chenhua, Shanghai, China) on a three-electrode system in [BMIM]PF_6. A square-wave

potential (vs counter electrode) step method coupled with optical spectroscopy was used to probe switching time and color contrast in these ECDs. Transmittance dynamic response to fixed wavelength (500 nm) was also tested using the Shimadzu-23101PC spectrophotometer. The stability test was carried out by applying repeated square-wave potential (vs counter electrode) on the devices and recording the current.
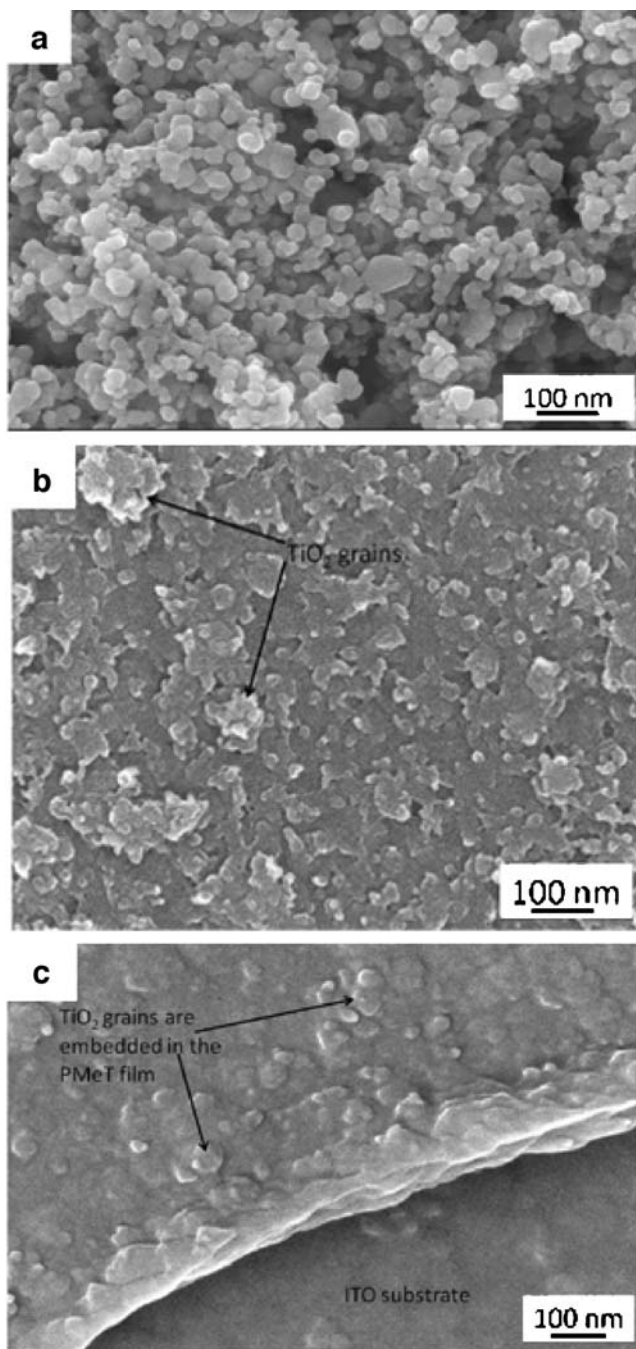

Fig. 1 **a** SEM image of mesoporous TiO_2 film on ITO substrate. SEM images of PMeT/TiO_2 nanocomposite when **b** PMeT just partly filled the interstice of the TiO_2 film (charge density about 20 mC cm^{-2}) and **c** PMeT fully covered the TiO_2 film

Results and discussion

Preparation of nanocomposite electrodes

Nano- and mesoporous TiO_2 thin films could be prepared on ITO sheets through well-established method [18, 21]. The average size of the TiO_2 grains which connected with each other to form the whole mesoporous film was about 30 nm (Fig. 1a shows SEM photo of mesoporous TiO_2 films). The prepared TiO_2 films were thin films with high porosity [22], which enables the electrolyte to soak into the films more efficiently.

MeT monomers were potentiostatically electropolymerized on TiO_2-coated ITO sheets to form the nanocomposite electrodes. The anodic oxidation of the monomers first took place within the interstices of the mesoporous network, directly on the exposed ITO surface which was not covered by the TiO_2 grains, and PMeT growth would occur principally within the interstices at the beginning. As more and more PMeT were electrochemically deposited, interstices of the TiO_2 film were filled by PMeT (Fig. 1b, SEM image of PMeT/TiO_2 nanocomposite with charge density of 20 mC cm^{-2}, the interstices were partly filled by PMeT) and finally, the TiO_2 film would be covered by the PMeT (Fig. 1c). Figure 2 is a schematic diagram which shows the forming process of the PMeT/TiO_2 nanocomposite electrodes. Within the nanocomposite, PMeT filled all the rest of the spaces of the film. In other words, TiO_2 grains were embedded in the PMeT and anchored PMeT firmly on the substrate.

The electropolymerization of the monomers can be implemented potentiostatically, galvanostatically, or potentiodynamically. The potentiodynamic growth of the polymer films is time consuming vis-à-vis the other methods and thus not generally adopted to synthesize significant quantities of film, but it is a technique that the redox characteristics of the polymers can be monitored for
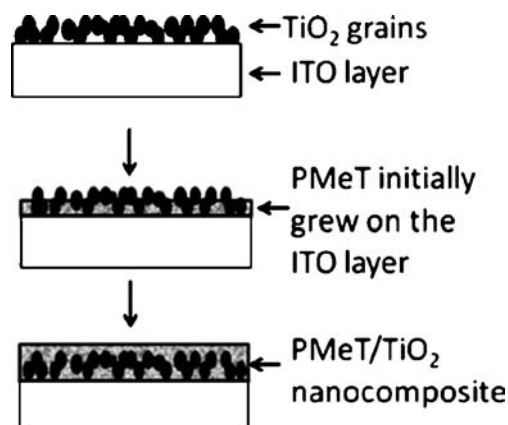

Fig. 2 Schematic illustration of the electrochemical incorporation procedure used for the preparation of PMeT/TiO_2 nanocomposite electrodes

electrochemical analysis. Thus, cyclic voltammetry (CV), one of the potentiodynamic techniques, was employed in this work to obtain more details during the electropolymerization processes [23]. Figure 3a shows the cyclic voltammogram of the electropolymerization of MeT on TiO$_2$-coated ITO substrates. The oxidation of MeT began at +1.1 V with the formation of polymer on exposed ITO surface. The cyclic voltammogram also exhibits broad anodic and cathodic peaks corresponding to the oxidation and the reduction of the preformed polymer. The peak current increased proportionally with the number of scans. This was characteristic of the formation of a conductive and electroactive polymer on a conductive substrate surface. With the consecutive scans, the voltammetric wave associated with the oxidation of the polymer became slightly
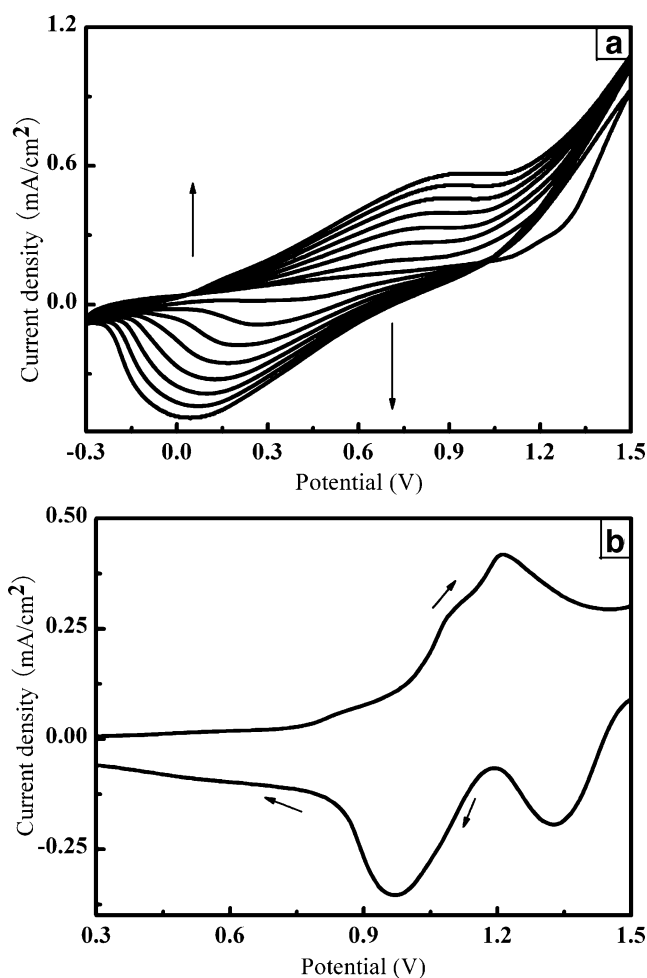
more anodic and reduction became more cathodic, which were more clearly displayed by the position move of the redox peaks. It can be explained by heterogeneous electron-transfer kinetics and a decrease in conductive, counter-ion mobility and possibly conjugation length [23].

Cyclic voltammetry

A typical CV curve of PMeT/TiO$_2$ nanocomposite electrodes in pure BMIMPF$_6$ is shown in Fig. 3b. The characteristic peak because of oxidation of PMeT is observed at +1.21 V and two reduction peaks can be observed at 0.97 and 1.33 V in reduction half-cycle. Instead of a pair of redox peak, multiple redox peaks appeared in the CV curve. At the different scan rates, the number of peaks was unaltered and peak current varied linearly with scan rate.

For the multiple redox peaks, different possibilities to explain the multiple redox peaks have been supposed to be: different oxidation levels, different conjugation lengths, structural effects, structural relaxation and conformational changes, two different types of doping sites, swelling effects, chemical modification of the polymer, and resistivity changes [24, 25]. Normally, different oxidation levels, regarded as polaron, bipolaron, and metallic states, are found in conjugated heterocyclic polymers which were supposed to be responsible for redox peaks [26].

Electrochromic performances

The color change of the nanocomposite electrodes was evaluated using spectroelectrochemistry, a tool based on the in situ collection of a UV–vis absorbance spectrum exhibited by the electrode at various equilibrium potentials. The spectroelectrochemistry of the nanocomposite elec-
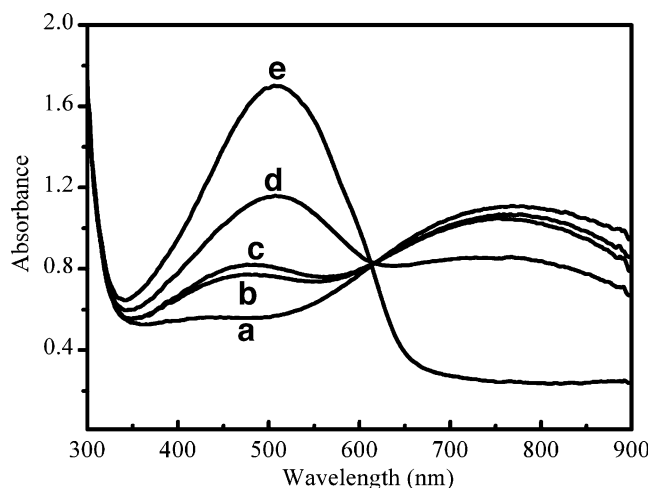

Fig. 3 a Cyclic voltammograms during electropolymerization of MeT (0.01 M) on TiO$_2$-coated ITO sheet in BFEE. The potential scan rate was 50 mV s^{-1} (arrows indicate the peak development with successive scans). The potentials were relative to the pseudo-reference electrode. b Cyclic voltammogram of the nanocomposite electrodes recorded in pure [BMIM]PF$_6$ ionic liquid at a scan rate of 100 mV s^{-1} (arrows indicate the scan direction). The potentials were relative to the pseudo-reference electrode

Fig. 4 In situ UV–vis absorption spectra of the nanocomposite recorded at different negative going potentials (V): 1 (a), 0.5 (b), 0 (c), −0.5 (d), and −1 (e)

trode is shown in Fig. 4. Like most other PMeT-based electrodes, the electrode at different potentials overlapped at 610 nm [27]. These indicated the intrinsic spectral properties of PMeT/TiO$_2$ nanocomposite electrodes which had no colorless state. Beginning at 1 V, the nanocomposite was in doped state, exhibiting the absorbance relatively low level peak at 770 nm and coloring light blue. As the potential became more cathodic, absorbance increased. Red nanocomposite could be attained at −1 V and had a well-defined charge transfer band with an absorbance peak at 500 nm, which was consistent with that previously observed in PMeT electrodes [28].

Figure 5a shows the potential type which was applied on the devices between +1.2 and −1.5 V with a 5-s delay at each potential to measure the optical transmission changes of the nanocomposite electrodes. The data were obtained by monitoring the transmission of monochromatic light at 500 nm. It can be observed from Fig. 5b that the optical
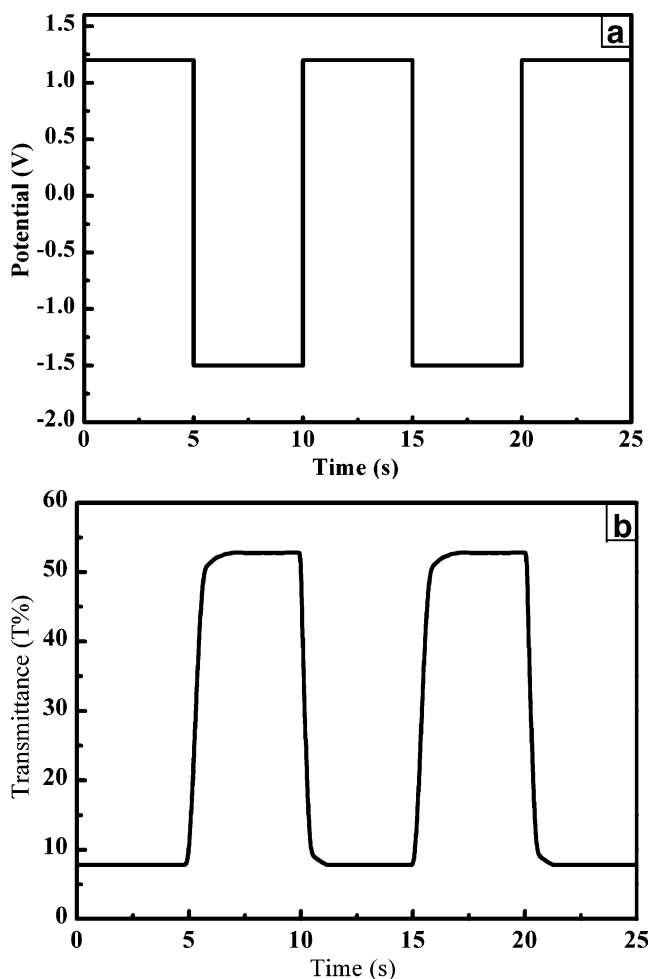

Fig. 5 a Potential applied on the devices which switched between +1.2 and −1.5 V with a 5-s delay. **b** Switching of an electrochromic device based on PMeT/TiO$_2$ nanocomposite electrode under the potential showed in **a**; change of transmittance ΔT% (about 45%) monitored at λ$_{max}$=500 nm

contrast of the nanocomposite electrodes is about 45%, and the nanocomposite electrodes switched rapidly (about 0.6 s) between the undoped state and doped state (the switching time was calculated at 90% of the full switching time because it is difficult to perceive any further color change with the naked eye beyond this point). Under the same optical contrast (45%), this switching speed (0.6 s) was as fast as that of ordinary PMeT electrodes [27]. Contrary to our expectations, the switching speed did not slow down after introducing TiO$_2$. TiO$_2$ is in fact a semiconductive material. Small surface concentration of holes (in the dark) and relative poor electron conductivity should, therefore, cause the potential drop and hinder the electron transport between substrates and polymers, which would slow down the switching speeds of the devices. However, individual nanoparticles in the nano- and mesoporous TiO$_2$ are too small to sustain the junction potential drop. In other words, when the TiO$_2$ film is thin enough (about 50 nm), electron transport between substrates and polymers could not be evidently hindered [29]. The thickness of the TiO$_2$ films fabricated by us was about 50 nm, which could be measured from the profile image (SEM) of the films. Therefore, after introducing TiO$_2$, the electron transport between the polymer and substrate was not hindered, and the switching speeds of the nanocomposite electrodes did not slow down. However, if the TiO$_2$ film was thick, it was true that the switching speeds of the nanocomposite electrode would slow down evidently because of the poor electron conductive of the TiO$_2$. When the ITO glass sheets were spin coated six times with the gel to prepare the nanocomposite electrodes, the switching time of the ECDs was found to be 1.2 s.

Electrochromic efficiency, η, was calculated according to Eq. 1 [5] using the data obtained from spectrochronocoulometric experiments at λ$_{max}$ value:

$$\eta(\lambda) = \frac{\log T_b - \log T_c}{Q} \tag{1}$$

where T_b is the transmittance of the bleached form at a certain wavelength, T_c the transmittance of the colored form at the same wavelength, and Q is the charge density (in C cm^{-2}) necessary to produce the chromatic change. The η values were about 180 cm^2 C^{-1} at 500 nm for PMeT, which are in accordance with the values cited in the other literatures (between 100 and 250 cm^2 C^{-1}) [27, 28].

Long-term stability

Quite often, the stability limits the utility of the electrodes in electrochromic device applications [30]. Through monitoring peak current and transmittance of the devices, we can establish their electroactive and electrochromic degra-

dation. Long-term redox switching stability studies were performed by continuously stepping the voltages of the devices between +1.2 and −1.5 V with a 5-s delay at each potential (Fig. 5a shows the type, but the time is not limited by 25 s). Figure 6 shows the transmittance results for a long-term redox stepping experiment performed on the device at $\lambda = 500$ nm. It can be seen that this device was relatively stable to attain its colored state, yet began to lose its transmissive state during the high number of switches. Generally, it was found that the devices based on the nanocomposite electrodes were able to retain approximately 60% of their optical response after 3,500 deep, double potential steps. The long-term stability of the nanocomposite electrodes was enhanced compared with that of PMeT-based electrodes reported in the other literatures (1,000 steps [31], 1,380 steps [32], and 2,300 steps [33]). Also, the data in Fig. 6 show that a 5-s potential step provided adequate time for an optical steady state to be achieved, thus confirming that the long-term stability studies were conducted for a "full" cycle. Figure 7 shows the peak current variations of devices as a function of switching number while continuously stepping the voltages of the devices up to 10^4 times between +1.2 and −1.5 V with a 5-s delay at each potential. The data were recorded at interval of 1,000 switches. The nanocomposite electrodes could switch up to up to 10^4 times for 50% retention of electroactivity, indicating the good long-term stability of electroactivity.

For all CP-based electrochemical electrodes, degradation of performances is inevitable during the repeated doping/undoping processes. The poor adhesion of CP to substrate is an important reason for the poor stability of the CP-based electrodes. Delamination of CP from substrate, which
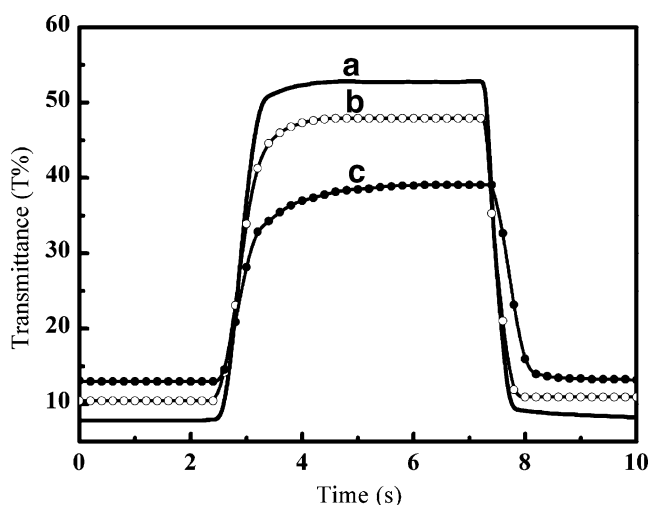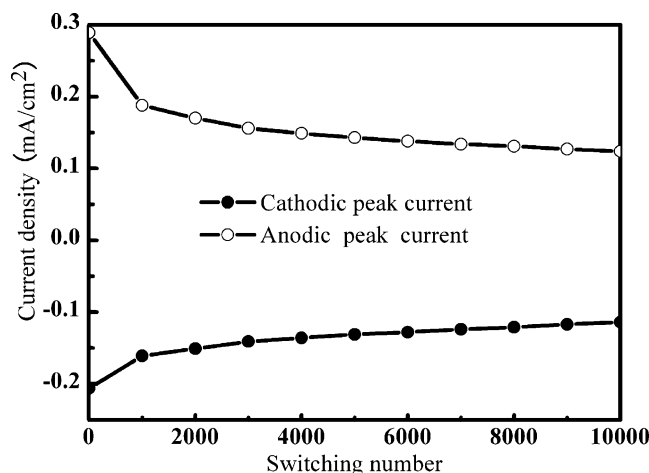

Fig. 7 Variation of anodic and cathodic current peaks as a function of switching numbers. Sample the peak current date at an interval of 1,000 switches during 10^4 double potential stepping (Fig. 5a shows the style) on ECDs

resulted from poor adhesion, always led to breakdown of electrodes [30]. Normally, conducting substrates are inorganic materials and smooth, while CP films are organic. There are a lot of differences between them in terms of properties. Thus, polymers adhered to substrates just through the physical sorption. The adhesion from it is poor compared with that from chemical bond and Van der Waals forces [16]. Moreover, it is well known that upon electrochemical doping (undoping), CPs undergo oxidation (reduction) of the polymer backbone resulting in dimensional changes of the backbone [8]. However, the dimensions of conducting substrate do not change at all as that of CP altered. The difference of dimension change between the CP and substrate leads to stress in the interface. Under repeated stress (repeated doping and undoping), the substrate–polymer connection is corroded easily and the CP-based electrodes delaminate, which leads to the breakdown of the electrodes.

The introduced TiO_2 can connect two different components firmly just like ligament connecting bone and muscle. On the one hand, the technique of preparing TiO_2 films on the substrates is well established, and the good adhesion of the film to the substrate has been confirmed by the other researches [18, 22]. In our experiments, we found that the TiO_2 film on the electrode even can go through ultrasonic washing for several hours. On the other hand, the polymer (PMeT) filled all interstices of the TiO_2 film to form PMeT/TiO_2 nanocomposite, in which the nanosize TiO_2 grains anchored the polymer firmly on the substrate. Therefore, this special structure allowed the excellent adhesion of the polymer to the substrate and prevented electrode from delaminating under repeated stress. Enhanced adhesion led to the increased long-term stability of the nanocomposite electrodes.

Fig. 6 Long-term redox stepping results showing transmittance changes during double potential stepping at *a* 1, *b* 1,500, and *c* 3,500 double potential steps (Fig. 5a shows the style). Transmittance monitored at $\lambda_{max} = 500$ nm

Conclusions

MeT monomers can be successfully electropolymerized to incorporate with mesoporous TiO_2 films to form PMeT/TiO_2 nanocomposite electrodes. Within the nanocomposite electrodes, the TiO_2 grains anchored the polymers on the CSs and thus increased the adhesion of the polymers to the substrates. Enhanced adhesion led to improved long-term stability of the electrochromic electrodes. The PMeT/TiO_2nanocomposite electrodes were found to retain up to 60% of their optical response after 3,500 deep, double potential steps and 50% of their electroactivity after 10^4 same steps, exhibiting improved long-term switching stability. They also exhibited as fast as 0.6 s switching time between a transmissive light-blue-doped state and red natural state. Moreover, our work showed that electrochemically incorporating PMeT with TiO_2 mesoporous film was an effective method to form high-quality PMeT/TiO_2 nanocomposite electrodes. Considering the wide applications of CPs and TiO_2, this method can be used to prepare the nanocomposites used in battery cathodes, photovoltaic cells, photocatalytic composites, photoelectrochromic cells and are supposed to enhance their performances.

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