

Enhanced electrochromic properties of TiO₂ nanoporous film prepared based on an assistance of polyethylene glycol

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Abstract. Polyethylene glycol (PEG) was employed as pore-forming agent to prepare TiO₂ nanoporous film based on spin-coating a TiO₂ nanoparticle mixed paste on fluorine doped tin oxide (FTO) glass. The electrochromic and optical properties of the obtained TiO₂ film were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and UV-Vis spectrophotometer. The results show that the PEG in the mixed paste endows the TiO₂ film with well-developed porous structure and improves the uniformity of the TiO₂ film, which are helpful for the rapid intercalation and extraction of lithium ions within the TiO₂ film and the strengthening of the diffuse reflection of visible light in the TiO₂ film. As a result, the TiO₂ film derived from the mixed paste with PEG displays higher electrochemical activity and more excellent electrochromic performances compared with the TiO₂ film derived from the mixed paste without PEG. The switching times of coloration/bleaching are respectively 10.16/5.65 and 12.77/6.13 s for the TiO₂ films with PEG and without PEG. The maximum value of the optical contrast of the TiO₂ film with PEG is 21.2% while that of the optical contrast of the TiO₂ film without PEG is 14.9%. Furthermore, the TiO₂ film with PEG has better stability of the colored state than the TiO₂ film without PEG.

1. Introduction

Electrochromic materials, showing a reversible color and transparency change during electrochemical oxidation and reduction, have displayed a great potential for applications, such as smart windows, low-power displays, auto-mobile anti-glare rearview mirror and e-papers [1-3]. In general, electrochromic materials can be divided into organic and inorganic ones according to the material components. In 1961, the pioneered work performed by Piatt [4] marks the investigation start of the inorganic electrochromic materials. Recently, motivated by the practical requirements of electrochromic devices, much effort has been dedicated to improve the electrochromic properties of the inorganic electrochromic materials, such as the optical contrast, coloration efficiency and response time.

As an important type of the inorganic electrochromic materials, many transition-metal oxides with variable oxidation state, including nickel oxide (NiO), niobium pentoxide (Nb₂O₅), molybdenum trioxide (MoO₃) and titanium oxide (TiO₂), were reported due to their high refractive indexes, good chemical and thermal stabilities and wide bandgaps [5-7]. Among them, the TiO₂ has exhibited particular potential as an electro-active material, because of its high activity, strong oxidation capability and superior chemical stability. However, there still exist many shortcomings for the TiO₂ electrochromic film, such as slow switching speed and poor optical contrast. Recently, it is recognized that the fabrication of the TiO₂ electrochromic film with ordered structure or nanoporous structure



provides a useful technique for enhancing the electrochromic properties [8, 9]. In this work TiO₂ nanoporous film was synthesized via an assistance of polyethylene glycol (PEG) as pore-forming agent based on spin-coating a TiO₂ nanoparticle mixed paste on fluorine doped tin oxide (FTO) glass. The PEG in the mixed paste not only endowed the TiO₂ film with well-developed nanoporous structure, but also improved the uniformity of the TiO₂ film. Therefore, the electrochromic performances of the obtained TiO₂ film were enhanced.

2. Experimental

2.1. Preparation of TiO₂ nanoporous film

The TiO₂ nanoparticles (particle size: ~30 nm) were obtained from Alfa Aesar chemical Co. LTD, and used without further purification. First, 2 g of TiO₂ nanoparticles was ground in a mortar with 0.8 g of PEG (MW: 20000), 15 mL of deionized water, 0.2 mL of acetylacetone, 1 mL of alcohol and 1 mL of 10% Triton X-100 aqueous solution to obtain a TiO₂ mixed paste with PEG. For comparison, a TiO₂ mixed paste without PEG was achieved by the same process. Then, both of the mixed pastes were coated on FTO glass by spin-coating. After being sintered at 450 °C for 30 min, the film was treated with 40 mM TiCl₄ aqueous solution followed by heat treatment at 450 °C for 30 min. The TiO₂ films derived from the mixed pastes with PEG and without PEG are labeled as NTF-1 and NTF-2, respectively.

2.2. Characterizations and measurements

The morphology of the TiO₂ film was characterized by an optical microscope (OM) and a field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Japan). The transmittance of the TiO₂ film on FTO at different wavelengths was obtained by using a UV-Vis spectrophotometer (TU-1901, China). A three-electrode cell was used for both of the cyclic voltammetry (CV) and chronoamperometry (CA) measurements. The cell included a platinum counter electrode, an Ag/AgCl reference electrode and a 1 M LiClO₄ dissolved in propylene carbonate as electrolyte. The TiO₂ film under study was employed as a working electrode. The CV measurement was realized at 50 mV/s scan rate between -2 and 2 V potential range. A coloration potential of -2 V and a bleaching potential of +2.0 V were applied for 30 s one after another in CA measurement.

3. Results and discussion

The electrochromic performances of the TiO₂ films of NTF-1 and NTF-2 were measured using a three-electrode electrochemical cell in 1 M LiClO₄ in PC electrolyte solution. Figure 1(a) shows the transmittance of both the TiO₂ films on FTO glasses in the bleached and colored states with applying potentials of +2 and -2 V, respectively. In the bleached state, the transmittance of NTF-1 is lower than that of NTF-2 in a wavelength range between 400 and 700 nm, indicating the existence of more well-developed porous structure in the former TiO₂ film owing to its stronger diffuse reflection of visible light. The transmittance of NTF-1 and NTF-2 in the bleached state at a wavelength of 550 nm is 69.3% and 73.5%. When the potential is switched to -2 V, the color of both the TiO₂ films quickly changes from colorless to blue. The transmittance of NTF-1 and NTF-2 in the colored state at a wavelength of 550 nm is 56.5% and 61.4%. The optical contrast (i.e. the transmittance difference between the film in the bleached state and in the colored state) of the TiO₂ films of NTF-1 and NTF-2 is displayed in Figure 1 (b). As a whole, NTF-1 derived from the mixed paste with PEG shows a larger transmittance modulation than NTF-2 derived from the mixed paste without PEG. The maximum value of optical contrast is 21.2% (at 400 nm) and 14.9% (at 700 nm) for NTF-1 and NTF-2, respectively.

Figure 2 exhibits the stability of the colored TiO₂ films of NTF-1 and NTF-2 under a condition without applying any potential. With the prolonged time, the color of both the TiO₂ films gradually changes from blue to colorless, as shown in the inserts in Figure 2. When the time is 25 min, the relative transmittance (T_t/T_0) (1.018) of NTF-1 is slightly lower than that (1.027) of NTF-2. It

indicates that the TiO₂ film prepared via an assistance of PEG possesses stronger storage capacity of lithium (Li⁺) ions and better stability.

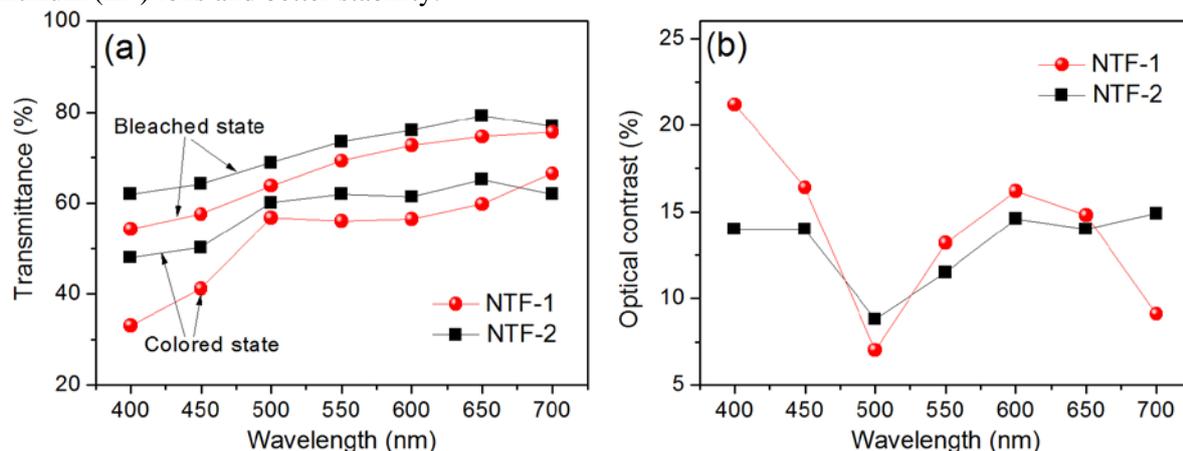


Figure 1. Transmittance (a) and optical contrast (b) of TiO₂ films derived from mixed pastes with PEG (NTF-1) and without PEG (NFT-2).

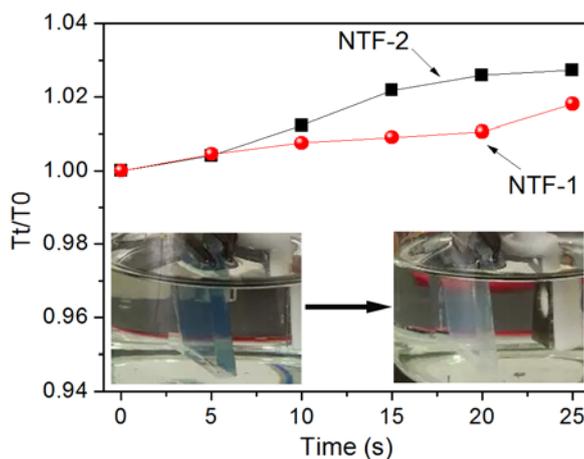


Figure 2. Stability of the colored TiO₂ films derived from mixed pastes with PEG (NTF-1) and without PEG (NFT-2) in the released state of potential. The inserts show the photos of NTF-1 at time of 0 and 25 min.

Response time is an important parameter to measure the speed that electrochromic film varies between colored and bleach states by applying different potentials. The switching kinetics is investigated by evaluating the times defined as the requirement for 90% of the total current density change. Figure 3(a) demonstrates the CA curves of the TiO₂ films of NTF-1 and NTF-2. From Figure 3(a), the switching times are 10.16 s for coloration and 5.65 s for bleaching for NTF-1, significantly quicker than those measured for NTF-2. The switching times of the coloration and bleaching of the latter are 12.77 and 6.13 s, respectively. These results indicate that a fast switching speed is achieved within the TiO₂ film prepared via an assistance of PEG (NTF-1) because of the rapid Li⁺ ion intercalation and extraction, a thesis that could be supported by the results of the CV measurements. The CV curves of the TiO₂ films of NTF-1 and NTF-2 are revealed in Figure 3(b). The cathodic and anodic peaks of the TiO₂ film appear at around -1.5 and -0.5 V, respectively, which are assigned to Li⁺ ion insertion into and extraction out of the TiO₂ framework. The electrochemical reaction can be expressed as $\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$ [10]. It is well known that the insertion and extraction of

Li^+ ions and electrons from a film result in coloration and bleaching, respectively. It is obvious from Figure 3(b) that the peak current density of NTF-1 is higher than that of NTF-2, suggesting that the TiO_2 film based on an assistance of PEG shows a higher electrochemical activity, which is associated with its superior electrochromic performances.

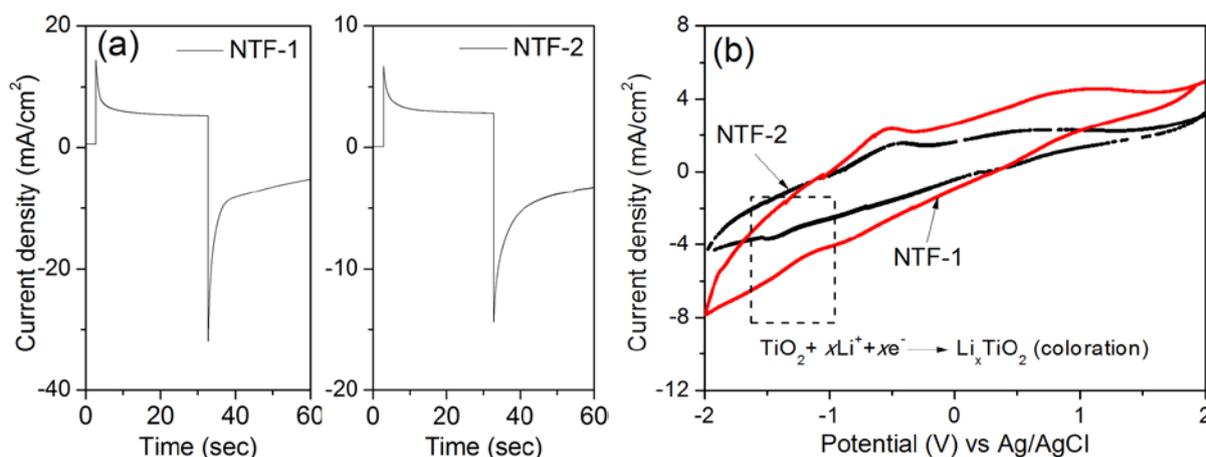


Figure 3. CA (a) and CV (b) curves of TiO_2 films derived from mixed pastes with PEG (NTF-1) and without PEG (NFT-2).

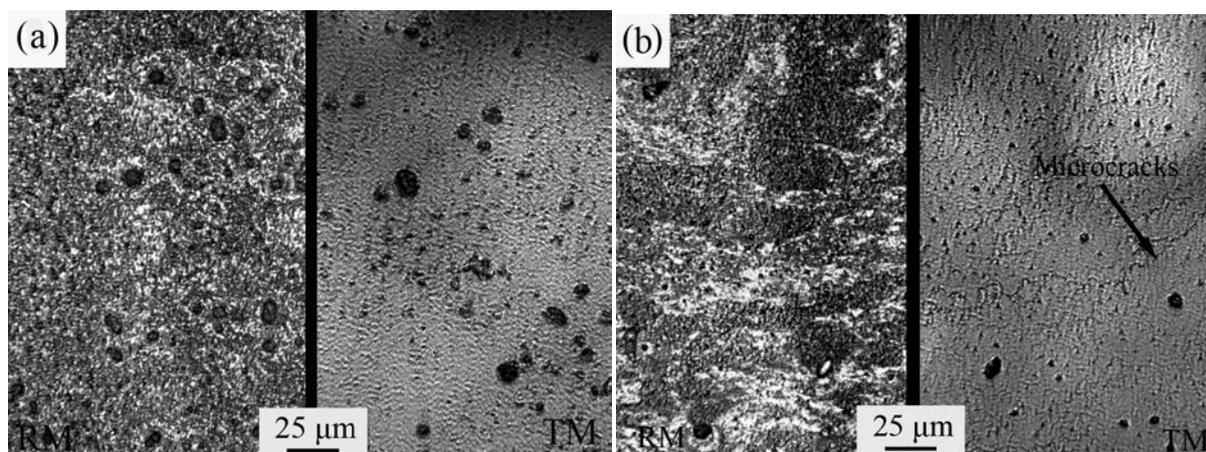


Figure 4. OM morphologies of TiO_2 films derived from mixed pastes with PEG (a) and without PEG (b) in reflection mode (RM) and in transmittance mode (TM).

Figure 4 exhibits the OM morphologies of the TiO_2 films of NTF-1 and NTF-2 in reflection mode (RM) and in transmittance mode (TM). It is obvious from Figure 4 that the morphological difference of two TiO_2 films could be observed. NTF-1 based on an assistance of PEG is more uniform compared to NTF-2 in spite of the existence of slightly more macropores with a size of 1~10 μm (the black phases) in the former TiO_2 film. Moreover, the microcracks appeared on NTF-2 are not observed on NTF-1. These results suggest that the PEG with high viscosity in the mixed paste is beneficial for the uniformity of the TiO_2 film. The SEM image in Figure 5 further proves that the TiO_2 film of NTF-1 based on an assistance of PEG possesses well-developed nanoporous structure, which provides effective channels for Li^+ ion diffusion to further participate in the electrochemical reaction. From above analyses, we could carefully conclude that the excellent performances of the TiO_2 film based on an assistance of PEG are attributed to the well-developed nanoporous structure and high uniformity of the TiO_2 film induced by PEG to a great extent.

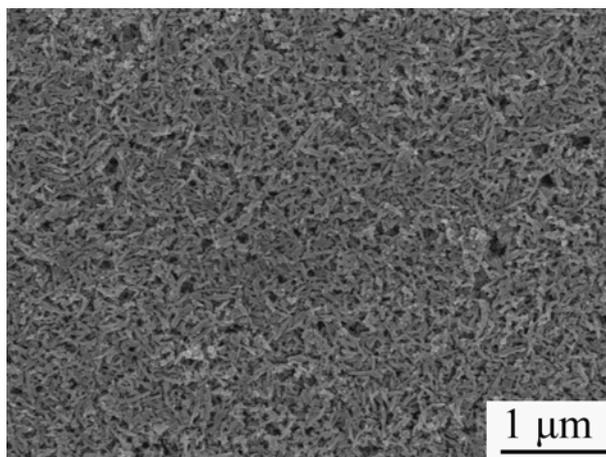


Figure 5. SEM image of TiO₂ film prepared via an assistance of PEG (NTF-1).

4. Conclusion

TiO₂ nanoporous film is synthesized using PEG as pore-forming agent based on spin-coating a TiO₂ nanoparticle mixed paste on FTO glass. The TiO₂ film derived from the mixed paste with PEG displays higher electrochemical activity and more excellent electrochromic performances compared with the TiO₂ film derived from the mixed paste without PEG. The switching times of the coloration/bleaching are respectively 10.16/5.65 and 12.77/6.13 s for the TiO₂ films with PEG and without PEG. The maximum value of the optical contrast of the TiO₂ film with PEG is 21.2% while that of the optical contrast of the TiO₂ film without PEG is 14.9%. Furthermore, the TiO₂ film with PEG possesses stronger storage capacity of lithium (Li⁺) ions and better stability. The outstanding performances could be attributed to the well-developed nanoporous structure and the high uniformity of the TiO₂ film induced by PEG to a great extent.

Acknowledgements

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