Mixed Nanostructured Ti-W Oxides Films for Efficient Electrochromic Windows

Nguyen Nang Dinh, Dang Hai Ninh, Tran Thi Thao, and Truong Vo-Van

1 University of Engineering and Technology, Vietnam National University, Hanoi, 144 Xuan Thuy Street, Cau Giay, Hanoi 10000, Vietnam
2 Department of Physics, Concordia University, 7141 Sherbrooke Street West, Montreal, QC, Canada H4B 1R6

Correspondence should be addressed to Nguyen Nang Dinh, dinhnn@vnu.edu.vn

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1. Introduction

Electrochromism is a topic that has attracted a great deal of interest from researchers because of its potential application in various areas (photronics, optics, electronics, architecture, etc.). Electrochromic (EC) properties can be found in almost all the transition-metal oxides, and their properties have been investigated extensively in the last decades [1]. These oxide films can be coloured anodically (Ir, Ni) or cathodically (W, Mo); however, WO3 is clearly the preferred material for applications. This is principally due to the fact that WO3-based electrochromic devices (ECDs) have normally a faster response time to a change in voltage and a larger coloration efficiency (CE) as compared to devices based on other electrochromic materials. Recently, Granqvist et al. [2] have made a comprehensive review of nanomaterials for benign indoor environments. In this paper, the authors show the characteristic data for a 5 × 5 cm² flexible EC foil incorporating WO3, and NiO modified by the addition of a wide bandgap oxide such as MgO or Al2O3, PMMA-based electrolyte, and ITO films. Durability of the EC devices was demonstrated in performing several tens of thousands of coloration/bleaching cycles, and the device optical properties were found to be unchanged for many hours. To improve further the electrochromic properties, Ti-doped WO3 films were deposited by cosputtering metallic titanium and tungsten in an Ar/O2 atmosphere [3]. Another way to improve electrochromic properties of thin films is to use nanostructured crystalline films. For instance, nanocrystalline WO3 films were prepared by the organometallic chemical vapour deposition (OMCVD) method using tetra(allyl)tungsten. The size of grains found in these films was estimated by atomic force microscope (AFM) and scanning electron microscope (SEM) to be 20 ± 40 nm. The coloration of WO3 deposited on indium tin oxides (ITO) substrates (WO3/ITO) in 2 M HCl was less than 1 sec and the maximum coloration efficiency at 630 nm was 22 cm²×C⁻¹ [4]. However, the HCl electrolyte is not suitable for practical use. The Au-doped WO3 films were...
that porous and thick WO₃ films can produce a high CE. The open structure, fast response, and high normal state transmission made them good candidates for use in practical applications. The nanocrystalline TiO₂ anatase thin films on ITO, prepared by sol-gel dipping method, exhibited a good reversible coloration and bleaching process [7], but the response time was slow and the electrochromic efficiency was not large. Recently [8], we have shown that by using the so-called “doctor-blade” method, nanoporous TiO₂ anatase films on F-doped tin oxide (FTO) substrates (nc-TiO₂/FTO) were prepared for the ECDs with much improved electrochromic response time and coloration efficiency (CE). However, with such porous films, for a long exposed performance time, the durability of the devices was limited, making the resulting ECD less satisfying for smart windows applications. In this work, with the aim to enhance the stability of the EC devices on one hand by making more tightly knitted films, and on the other hand, to improve the CE of the ECD performance with the help of nanostructured heterojunctions of TiO₂/WO₃, we combined a doctor-blade technique for preparing large-area films with an electrochemical process for depositing WO₃ films into the nanoporous TiO₂ structures.

2. Experimental

To prepare nanostructured TiO₂ films for ECD, a doctor-blade technique was used following the process reported in [8]. A glass slide, overcoated with a 0.2μm thick FTO film having a sheet resistance of 15 Ω and a transmittance of 90%, was used as a substrate; the useful area that constitutes the sample studied was of 1 cm². A colloidal solution of 15 wt% nanoparticles (15 nm in size) of titanium oxide (Nyacol Products) in water was used. For producing thinner films, we added more distilled water to get ca. 5 wt% TiO₂ and a few drops of the liquid surfactant were added. Then the diluted solution was filled in the slot on the FTO electrode and spread along the tapes. The samples were left for drying during 15 min, then put to a furnace maintained at 450°C for 1 hour to recrystallize the nc-TiO₂ films.

To deposit WO₃ into nc-TiO₂/FTO, the peroxy-tungsten acid solution (H₂W₂O₁₁) was prepared. For this 4.6 g of high-purity metallic tungsten powder was dissolved in 25 ml H₂O₂ (30%). The excess H₂O₂ was decomposed by putting a large-area Pt sheet into the solution until gas evolution was stopped. After that, the solution was diluted to 50 mM by addition of water to form 500 mL of the solution and kept in cool air to avoid decomposition of peroxy tungstate to trioxide and polytungstate [9]. A standard three-electrode cell has been used: the working electrode was F-doped-SnO₂-coated glass (FTO) with a sheet resistance of 15 Ω the reference electrode was saturated calomel electrode (SCE); a Pt grille was used as counter electrode. By using potentiostat “Auto lab. PGS-30,” a potentiostatic method was chosen for film deposition. After their deposition, the films were dried in nitrogen gas. Electrochromic properties of the films were determined by cyclic voltametry in electrolytic solutions of 1 M LiClO₄ + Propylene carbonate (PC).

The film thickness was measured by an Alpha-step profiler and its surface morphology examined with the help of a field-emission scanning electron microscope (FE-SEM). X-ray diffraction analysis (XRD) was done on a Bruker “Advance-8D” X-ray diffractometer with X-ray Cu wavelength λ = 0.154 nm. Electrochemical processes were carried out on the same potentiostat. All measurements were executed at room temperature.

By using a JASCO “V-570” photospectrometer, in situ transmittance spectra of nc-TiO₂ in LiClO₄ + PC versus bias potential were recorded on the films of the working electrode mounted in a modified electrochemical cell which was placed under the pathway of the laser beam, and the three cell electrodes were connected to a potentiostat.

3. Results and Discussion

3.1. Electrochemical Deposition. Under an application of the potential of −1.5 V/SCE, the fact that the current density was increased with the increase in time would prove that W⁶⁺ was inserted into the working electrode with a compensation of negative charges (e⁻). Due to the bonding of W⁶⁺ with O²⁻ ions, WO₃ was formed. This further was confirmed by XRD analysis (see the next section). From all the deposition experiments, it was seen that the current density increased fast and reached a saturate value in 40 sec (Figure 1).

With this interval, the WO₃ volume almost filled up the pores in the porous TiO₂ film, and then stopped increasing at the saturate current density. However, the total time of 130 sec for the deposition was chosen. The thickness of as-deposited WO₃/TiO₂ films, checked on the Alpha-Step Pro-filer, was of ~570 nm. These films were slightly thicker than the initial doctor-blade nc-TiO₂ films (namely 550 nm).
3.2. Morphology and Crystalline Structure. In the doctor-blade deposition, the thickness of the films was found to be depending on preparation conditions such as the concentration of solutions and the speed of spread. The samples used for further investigation were taken from films chosen with a concentration of 5 wt% TiO₂ in water and a spread speed of 8 mm/s. A bright-field micrograph of the film surface is shown in Figure 2(a). The film is quite uniform, but some crystallized nanoparticles are a little larger than the initial TiO₂ particles dispersed in water (namely 20 nm in size). The thickness of the films was of ca. 550 nm. In comparison with the nanostructured films prepared by sol-gel method [7], these films are thicker and much more porous. Thus, between the nc-TiO₂ particles, there are numerous nanoscale pores which would favour the insertion of ions like Li⁺, Na⁺, and/or W⁶⁺ into the films, when a polarized potential is applied on the working electrode (nc-TiO₂/FTO). With the insertion of the Li⁺, one can obtain the ECD coloration, whereas the insertion of W⁶⁺ during the electrochemical deposition would result in the insertion of WO₃ nanoparticles into the nanostructured TiO₂ film. Figure 2(b) shows the FE-SEM of the surface of the TiO₂ electrode after the electrochemical process in the H₂W₂O₁₁ solution. During the deposition, we observed that the TiO₂/FTO electrode was coloured and became deep-blue with the increase in the deposition time. This coloration can be attributed to the insertion of W⁶⁺ (the ions from the H₂W₂O₁₁ electrolyte) into the TiO₂ films according to the following equation:

\[
\text{TiO}_2 \text{(transparent)} + x\text{W}^{3+} + xe^- \rightarrow \text{W}_x\text{TiO}_2 \text{(blue)},
\]

where W⁶⁺ plays the role of Li⁺ in the well-known equation [10]:

\[
\text{TiO}_2 \text{(transparent)} + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_x\text{TiO}_2 \text{(blue)}.
\]

From our previous work [11], it was shown that an electrochromic WO₃ film was deposited onto the FTO electrode by the electrochemical technique. Hereby, simultaneously with the EC coloration, one can deposit WO₃ particles into TiO₂/FTO to form a film with heterojunctions of WO₃/TiO₂ created from a mixture of WO₃ and TiO₂ nanoparticles. This would lead to the different features observed in the FE-SEM picture of the WO₃/TiO₂ film (Figure 2(b)) as compared to the FE-SEM picture for a nc-TiO₂ film (Figure 2(a)).

The crystalline structure of the films was confirmed by using an accessory for films with a small angle of the X-ray incident beam. For such a thick film of nc-TiO₂, all XRD patterns of the FTO substrate do not appear (Figure 3(a)). XRD patterns show all the diffraction peaks corresponding to titanium oxide. Indeed, for the doctor-blade film, in the XRD patterns, there are the most intense peak of the (101) direction corresponding to \(d = 0.352 \text{ nm}\) and three smaller peaks corresponding to 0.238, 0.190, and 0.149 nm. These diffraction peaks are quite consistent with the peaks for a single crystal of TiO₂ anatase.

The fact that the peak width is rather small shows that the TiO₂ anatase film was crystallized into large grains. To obtain the grain size \(r\), we used the Scherrer formula:

\[
\tau = \frac{0.9 \lambda}{\beta \cdot \cos \theta},
\]

where \(\lambda\) is wavelength of the X-ray used (\(\lambda = 0.154 \text{ nm}\)), \(\beta\) the peak width of half height in radians and \(\theta\) the Bragg angle of the considered diffraction peak [12]. From the XRD patterns, the half-height peak width of the (101) direction was found to be \(\beta = 0.005\), consequently, the size of (101) grain was determined as \(\tau \approx 20 \text{ nm}\). Similarly, the size for the other grains was found to be from 25 to 30 nm. This is in good agreement with data obtained by FE-SEM for the average size of particles where the crystalline grains were not identified by the Miller indexes (see Figure 2(a)).

The XRD patterns of the WO₃/TiO₂ (Figure 3(b)) possess both the peaks of TiO₂ and WO₃, where one peak of (004) direction of TiO₂ was not revealed and relative intensity of the peaks changed a little bit. This is due to the presence of WO₃ particles, whose average size, estimated by formula (1), is the same as the size of pores. This result, together with the observation of the FE-SEM pictures (Figure 1), demonstrates that WO₃ particles were indeed filling-up the nanopores of the porous nc-TiO₂ film.
3.3. Electrochemical Property. Figure 4 presents a chronoamperometric plot obtained by setting up five lapses of 5 sec for the coloration and bleaching, corresponding to $-1.50 \text{ V/SCE}$ and to $+1.50 \text{ V/SCE}$, respectively. To calculate the inserted charge ($Q$) for the coloration state, we use the formula for integrating between the starting and ending times of each lapse of time as follows:

$$Q = \int_{t_1}^{t_2} J(t) \, dt. \quad (4)$$

The insertion charge was found to be $Q_{in} = 21 \text{ mC/} \text{cm}^2$, whereas for the extraction process the charge was $Q_{ex} = 19 \text{ mC/} \text{cm}^2$, that is slightly different from the insertion charge. The fact that the insertion and extraction charges are similar proves the reversibility of the electrochromic coloration/bleaching process—a desired characteristic for the electrochromic performance of the WO$_3$/TiO$_2$-based electrochromic devices.

Figure 5 shows the cyclic voltammetry (CV) spectra of a WO$_3$/TiO$_2$/FTO electrode cycled in 1 M LiClO$_4$ + PC. In the positive scanning direction (PSD) there are two peaks of the current density at potentials of $-1.0 \text{ V/SCE}$ and at $-0.32 \text{ V/SCE}$. In the negative scanning direction (NSD) there are also two similar peaks. This proves the reversibility of the insertion/extraction of Li$^+$ into/out of the WO$_3$/TiO$_2$/FTO electrode. Moreover, the CV spectra of the WO$_3$/TiO$_2$/FTO electrode possess a different characteristic from the one of each compound for either WO$_3$/FTO or TiO$_2$/FTO. These CV spectra can be seen as just the CV of a mixture of WO$_3$ and TiO$_2$ electrodes cycled simultaneously in LiClO$_4$ + PC electrolyte.

Therefore the electrochromic performance of the WO$_3$/TiO$_2$/FTO electrode in LiClO$_3$ + PC can be described by two cathodic reactions; one is [13, 14]:

$$\text{WO}_3 + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_x\text{WO}_3 \quad (5)$$

and the other one is reaction (2).

3.4. Electrochromic Performance. For a sample with a 570 nm thick WO$_3$/TiO$_2$ film, the in situ transmission spectra, obtained during coloration at a polarized potential of $-1.2 \text{ V/SCE}$ are given in Figure 6.

Figure 6 shows the transmittance of a 570 nm thick WO$_3$/TiO$_2$ film in 1 M LiClO$_4$ + PC at different polarizing bias potentials (from $-0.5 \text{ V/SCE}$ to $+0.3 \text{ V/SCE}$). From this
reported previously [8], the optical modulation at the visible range for WO3/TiO2/FTO at longer wavelengths is improved. Herein, we attained a transmittance at $\lambda = 550 \text{ nm (}T_{550}\text{)}$ equal to 84% upon bleaching and to 42% after a coloration period of 30 s. The largest optical modulation in the visible range was observed for red light ($T_{700}$) as seen in Figure 7: the gap between the transmittances of bleaching and coloration states was of 70%. For blue light ($T_{400}$), the optical modulation at wavelength 400 nm was negligible, that is about 5%. This would result from the strong absorption by both WO3 and TiO2 at shorter wavelengths.

From the above-mentioned results for the ECDs with heterojunctions of WO3/nc-TiO2, it is seen that the efficient coloration can be achieved due to a double-coloration process, such as shown in (2) and (5). To evaluate the electrochromic coloration efficiency ($\eta$) we used a well-known expression relating the efficiency with the optical density ($\Delta OD$), consequently the transmittances of coloration ($T_c$) and bleaching states ($T_b$), and the insertion charge ($Q$), as follows [15]:

$$\eta = \frac{\Delta OD}{Q} = \frac{1}{Q} \ln \left( \frac{T_b}{T_c} \right).$$

At a wavelength of 550 nm, $Q_{in} = 21 \text{ mC cm}^{-2}$, $T_b = 85\%$ and $T_c = 40\%$, the coloration efficiency was determined to be $35.7 \text{ cm}^2 \text{ C}^{-1}$. The larger the wave length is, the higher the coloration efficiency is. In the visible range of wavelengths, all the found values of $\eta$ are comparable to those for WO3 films [16] and much higher than those for TiO2 films [7] prepared by sol-gel techniques and titanium-lanthanide oxides deposited by magnetron sputtering and coloured in a LiClO4 + PC solution [17].

To investigate the ageing process of two types of electrochromic devices, the first one is made from nc-TiO2 and the second one from WO3/nc-TiO2 electrode, we measured the optical density versus bias potential after cycling these electrodes in 1 M LiClO4 + PC for 103 cycles. At a fixed wavelength, the larger is the difference between $T_c(\lambda)$ of the colored state and $T_b(\lambda)$ of the bleached state, the higher is
the value of ΔOD. The potential dependence of ΔOD at λ = 550 nm for two above-mentioned electrodes is shown in Figure 8. From this figure, we can see that for both the mentioned electrodes, the best optical density has been found for the bias potential of +0.5 V/SCE. At this potential, the largest number of Li+ cations would be inserted into the electrodes making the TiO2 and WO3 structures change to Li4TiO2 to Li4WO3, respectively. The number of colour centers (namely Li4TiO2 and Li4WO3) is dependent on the number of Li+ cations and electrons injected into the electrodes. In general, this number increases proportionally to the bias potential applied on the working electrode. The reason why the ΔOD of the nc-TiO2 based ECD decreased faster than that of WO3/TiO2 is revealed by the monitoring of the film thickness of the electrodes during the electrochromic performance. After 10^5 cycles of the ECD performance, the thickness of both electrodes was checked with the Alpha step profiler, and it was found that a part of the nc-TiO2 film was removed while the WO3/nc-TiO2 was maintained almost unchanged. This demonstrates that WO3 attached to TiO2 particles enables the structure of WO3/nc-TiO2 film to be much more strengthened. Thus the devices with WO3/TiO2 nano-heterojunctions would possess a larger ECD lifetime.

4. Conclusion

Mixed nanostructured Ti-W oxides films were prepared by electrochemical deposition of WO3 onto doctor-blade nc-TiO2/FTO films. Electrochromic performance studies of both the nc-TiO2/FTO and WO3/TiO2/FTO configurations were carried out in 1 M LiClO4 + PC for as-prepared (a; c) and after cycling for 10^3 cycles (b; d).

By incorporating WO3 inserted between TiO2 nanoparticles, WO3/TiO2 heterojunctions were formed in the films. The resulting nanostructured film enables both the coloration efficiency and electrochemical stability of the working electrodes to be considerably improved. Since a large-area WO3/TiO2 electrode can be prepared by the doctor-blade method, followed by an electrochemical deposition, this type of electrode constitutes a good candidate for smart window applications, taking advantage of its excellent properties in terms of EC efficiency and electrochemical stability, as well as the simplicity of the fabrication process.

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References


