

## Research Article

# Mixed Nanostructured Ti-W Oxides Films for Efficient Electrochromic Windows

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With the aim to enhance the electrochromic (EC) efficiency and electrochemical stability of electrochromic devices (ECD), mixed nanostructured TiO<sub>2</sub>/WO<sub>3</sub> films were prepared by an electrochemical deposition method with the purpose of adding WO<sub>3</sub> nanoparticles to porous nanocrystalline doctor-blade TiO<sub>2</sub> (nc-TiO<sub>2</sub>) films. The results of the characterization of electrochromic properties in 1 M LiClO<sub>4</sub> + propylene carbonate (LiClO<sub>4</sub> + PC) of both the nc-TiO<sub>2</sub>/F-doped tin oxide (FTO) and WO<sub>3</sub>/TiO<sub>2</sub>/FTO configurations showed the reversible coloration and bleaching of the ECDs. The response time of the ECD coloration of WO<sub>3</sub>/TiO<sub>2</sub>/FTO was found to be as small as 2 sec, and its coloration efficiency (CE) as high as 35.7 cm<sup>2</sup> × C<sup>-1</sup>. By inserting WO<sub>3</sub> nanoparticles into the porous TiO<sub>2</sub> structures, WO<sub>3</sub>/TiO<sub>2</sub> heterojunctions were formed in the films, consequently enabling both the CE and electrochemical stability of the working electrodes to be considerably enhanced. Since a large-area WO<sub>3</sub>/TiO<sub>2</sub> can be prepared by the doctor-blade technique followed by the electrochemical deposition process, mixed nanostructured Ti-W oxides electrodes constitute a good candidate for smart window applications, taking advantage of the excellent coloration and stability properties as well as the simple and economical fabrication process involved.

## 1. Introduction

Electrochromism is a topic that has attracted a great deal of interest from researchers because of its potential application in various areas (photonics, 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, WO<sub>3</sub> is clearly the preferred material for applications. This is principally due to the fact that WO<sub>3</sub>-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 cm<sup>2</sup> flexible EC foil incorporating WO<sub>3</sub>, and NiO modified by the addition of a wide

bandgap oxide such as MgO or Al<sub>2</sub>O<sub>3</sub>, 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 WO<sub>3</sub> films were deposited by cosputtering metallic titanium and tungsten in an Ar/O<sub>2</sub> atmosphere [3]. Another way to improve electrochromic properties of thin films is to use nanostructured crystalline films. For instance, nanocrystalline WO<sub>3</sub> 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 WO<sub>3</sub> deposited on indium tin oxides (ITO) substrates (WO<sub>3</sub>/ITO) in 2 M HCl was less than 1 sec and the maximum coloration efficiency at 630 nm was 22 cm<sup>2</sup> × C<sup>-1</sup> [4]. However, the HCl electrolyte is not suitable for practical use. The Au-doped WO<sub>3</sub> films were

made by a dip-coating technique [5]. With fabrication of nanostructured  $\text{WO}_3$  films, Beydaghyan et al. [6] have shown that porous and thick  $\text{WO}_3$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  anatase films on F-doped tin oxide (FTO) substrates (nc- $\text{TiO}_2/\text{FTO}$ ) 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  $\text{TiO}_2/\text{WO}_3$ , we combined a doctor-blade technique for preparing large-area films with an electrochemical process for depositing  $\text{WO}_3$  films into the nanoporous  $\text{TiO}_2$  structures.

## 2. Experimental

To prepare nanostructured  $\text{TiO}_2$  films for ECD, a doctor-blade technique was used following the process reported in [8]. A glass slide, overcoated with a  $0.2\mu\text{m}$  thick FTO film having a sheet resistance of  $15\ \Omega$  and a transmittance of 90%, was used as a substrate; the useful area that constitutes the sample studied was of  $1\ \text{cm}^2$ . 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%  $\text{TiO}_2$  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  $450^\circ\text{C}$  for 1 hour to recrystallize the nc- $\text{TiO}_2$  films.

To deposit  $\text{WO}_3$  into nc- $\text{TiO}_2/\text{FTO}$ , the peroxy-tungsten acid solution ( $\text{H}_2\text{W}_2\text{O}_{11}$ ) was prepared. For this 4.6 g of high-purity metallic tungsten powder was dissolved in 25 ml  $\text{H}_2\text{O}_2$  (30%). The excess  $\text{H}_2\text{O}_2$  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-SnO<sub>2</sub> coated glass (FTO) with a sheet resistance of  $15\ \Omega$  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

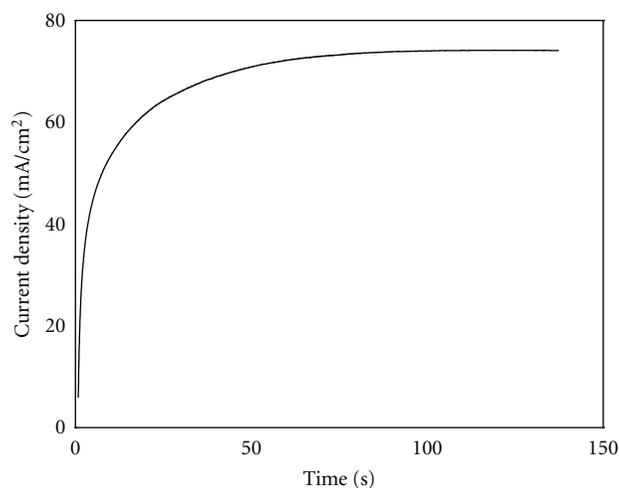


FIGURE 1: The time dependence of the current density during electrochemical deposition of  $\text{WO}_3$  under a negatively polarized potential of  $-1.5\ \text{V/SCE}$ .

determined by cyclic voltametry in electrolytic solutions of 1 M  $\text{LiClO}_4$  + 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  $\lambda = 0.154\ \text{nm}$ . 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- $\text{TiO}_2$  in  $\text{LiClO}_4$  + 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  $-1.5\ \text{V/SCE}$ , the fact that the current density was increased with the increase in time would prove that  $\text{W}^{6+}$  was inserted into the working electrode with a compensation of negative charges ( $e^-$ ). Due to the bonding of  $\text{W}^{6+}$  with  $\text{O}^{2-}$  ions,  $\text{WO}_3$  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  $\text{WO}_3$  volume almost filled up the pores in the porous  $\text{TiO}_2$  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  $\text{WO}_3/\text{TiO}_2$  films, checked on the Alpha-Step Pro-filer, was of  $\sim 570\ \text{nm}$ . These films were slightly thicker than the initial doctor-blade nc- $\text{TiO}_2$  films (namely  $550\ \text{nm}$ ).

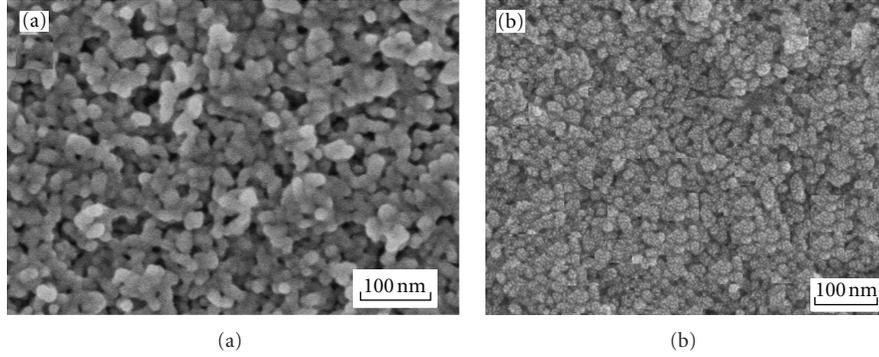
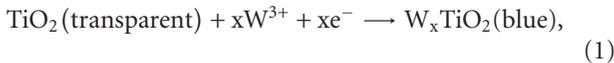
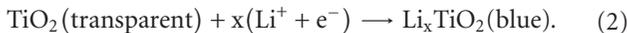


FIGURE 2: FE-SEM micrographs of as-prepared nc-TiO<sub>2</sub> films (a) and after the electrochemical deposition process in a H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> electrolyte (b).

**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 spread speed. The samples used for further investigation were taken from films chosen with a concentration of 5 wt% TiO<sub>2</sub> 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 TiO<sub>2</sub> 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-TiO<sub>2</sub> particles, there are numerous nanoscale pores which would favour the insertion of ions like Li<sup>+</sup>, Na<sup>+</sup>, and/or W<sup>6+</sup> into the films, when a polarized potential is applied on the working electrode (nc-TiO<sub>2</sub>/FTO). With the insertion of the Li<sup>+</sup>, one can obtain the ECD coloration, whereas the insertion of W<sup>6+</sup> during the electrochemical deposition would result in the insertion of WO<sub>3</sub> nanoparticles into the pores of the nanostructured TiO<sub>2</sub> film. Figure 2(b) shows the FE-SEM of the surface of the TiO<sub>2</sub> electrode after the electrochemical process in the H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> solution. During the deposition, we observed that the TiO<sub>2</sub>/FTO electrode was coloured and became deep-blue with the increase in the deposition time. This coloration can be attributed to the insertion of W<sup>6+</sup> (the ions from the H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> electrolyte) into the TiO<sub>2</sub> films according to the following equation:



where W<sup>6+</sup> plays the role of Li<sup>+</sup> in the well-known equation [10]:



From our previous work [11], it was shown that an electrochromic WO<sub>3</sub> film was deposited onto the FTO electrode by the electrochemical technique. Hereby, simultaneously with the EC coloration, one can deposit WO<sub>3</sub> particles into

TiO<sub>2</sub>/FTO to form a film with heterojunctions of WO<sub>3</sub>/TiO<sub>2</sub> created from a mixture of WO<sub>3</sub> and TiO<sub>2</sub> nanoparticles. This would lead to the different features observed in the FE-SEM picture of the WO<sub>3</sub>/TiO<sub>2</sub> film (Figure 2(b)) as compared to the FE-SEM picture for a nc-TiO<sub>2</sub> 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-TiO<sub>2</sub>, 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  $d = 0.352$  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 TiO<sub>2</sub> anatase.

The fact that the peak width is rather small shows that the TiO<sub>2</sub> anatase film was crystallized into large grains. To obtain the grain size  $\tau$ , we used the Scherrer formula:

$$\tau = \frac{0.9 \lambda}{\beta \cdot \cos \theta}, \quad (3)$$

where  $\lambda$  is wavelength of the X-ray used ( $\lambda = 0.154$  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  $\tau \approx 20$  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 WO<sub>3</sub>/TiO<sub>2</sub> (Figure 3(b)) possess both the peaks of TiO<sub>2</sub> and WO<sub>3</sub>, where one peak of (004) direction of TiO<sub>2</sub> was not revealed and relative intensity of the peaks changed a little bit. This is due to the presence of WO<sub>3</sub> 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 WO<sub>3</sub> particles were indeed filling-up the nanopores of the porous nc-TiO<sub>2</sub> film.

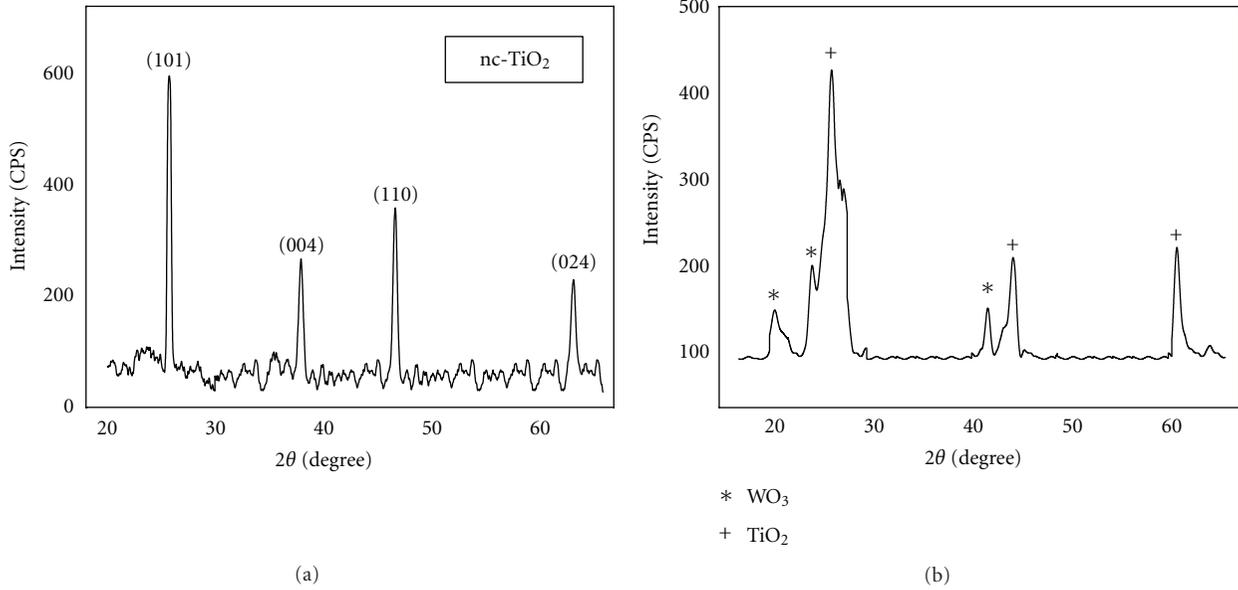


FIGURE 3: XRD of a nc-TiO<sub>2</sub> doctor-blade film (a) and of a WO<sub>3</sub>/TiO<sub>2</sub> film coated by electrochemical deposition.

**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  $-1.50$  V/SCE and to  $+1.50$  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  $Q_{in} = 21 \text{ mC} \times \text{cm}^{-2}$ , whereas for the extraction process the charge was  $Q_{ex} = 19 \text{ mC} \times \text{cm}^{-2}$ , 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<sub>3</sub>/TiO<sub>2</sub>-based electrochromic devices.

Figure 5 shows the cyclic voltammetry (CV) spectra of a WO<sub>3</sub>/TiO<sub>2</sub>/FTO electrode cycled in 1 M LiClO<sub>4</sub> + PC. In the positive scanning direction (PSD) there are two peaks of the current density at potentials of  $-1.0$  V/SCE and at  $-0.32$  V/SCE. In the negative scanning direction (NSD) there are also two similar peaks. This proves the reversibility of the insertion/extraction of Li<sup>+</sup> into/out of the WO<sub>3</sub>/TiO<sub>2</sub>/FTO electrode. Moreover, the CV spectra of the WO<sub>3</sub>/TiO<sub>2</sub>/FTO electrode possess a different characteristic from the one of each compound for either WO<sub>3</sub>/FTO or TiO<sub>2</sub>/FTO. These CV spectra can be seen as just the CV of a mixture of WO<sub>3</sub> and TiO<sub>2</sub> electrodes cycled simultaneously in LiClO<sub>4</sub> + PC electrolyte.

Therefore the electrochromic performance of the WO<sub>3</sub>/TiO<sub>2</sub>/FTO electrode in LiClO<sub>4</sub> + PC can be described by two

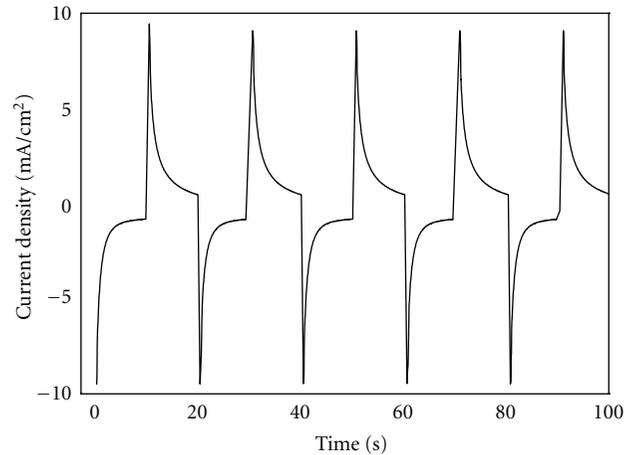
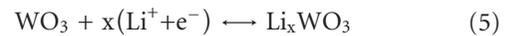


FIGURE 4: Insertion and extraction of Li<sup>+</sup> ions into/out of the WO<sub>3</sub>/TiO<sub>2</sub>/FTO electrode. The inserted charge (a bottom half cycle) of the saturated coloration state and the completely bleaching state (a top half cycle), respectively, are  $Q_{in} = 21 \text{ mC} \times \text{cm}^{-2}$  and  $Q_{ex} = 19 \text{ mC} \times \text{cm}^{-2}$ .

cathodic reactions; one is [13, 14]:



and the other one is reaction (2).

**3.4. Electrochromic Performance.** For a sample with a 570 nm thick WO<sub>3</sub>/TiO<sub>2</sub> film, the *in situ* transmission spectra, obtained during coloration at a polarized potential of  $-1.2$  V/SCE are given in Figure 6.

Figure 6 shows the transmittance of a 570 nm thick WO<sub>3</sub>/TiO<sub>2</sub> film in 1 M LiClO<sub>4</sub> + PC at different polarizing bias potentials (from  $-0.5$  V/SCE to  $+0.3$  V/SCE). From this

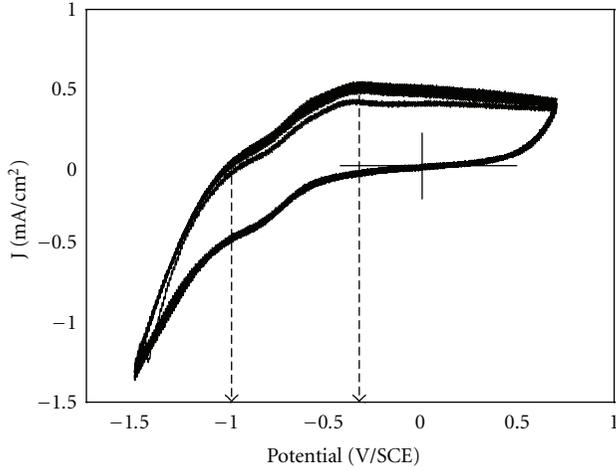


FIGURE 5: Cyclic voltammograms spectra of  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  cycled in  $\text{LiClO}_4 + \text{PC}$  (scanning rate  $\nu = 100 \text{ mV/s}$ ).

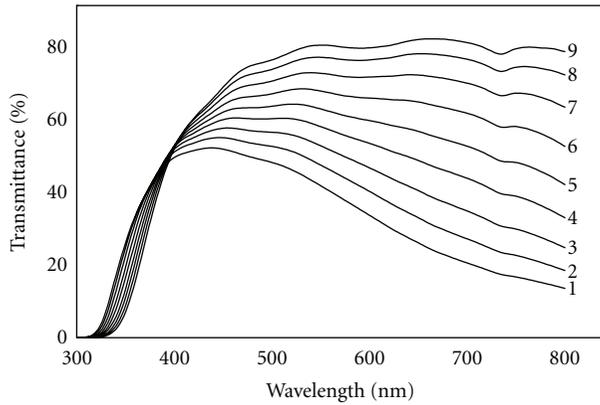


FIGURE 6: Transmittance spectra of the  $\text{WO}_3$  film filled in  $1 \text{ M LiClO}_4 + \text{PC}$  solution with polarized potential ranging from  $-0.5 \text{ V/SCE}$  to  $+0.3 \text{ V}$ . Curves 1, 2, 3, 4, 5, 6, 7, 8, and 9 correspond, respectively, to  $-0.5, -0.4, -0.3, -0.2, -0.1, 0, +0.1, +0.2,$  and  $+0.3 \text{ V/SCE}$ .

figure, one can see a large difference in transmittance spectra in the visible range of the film between the colored (curve 1) and bleached (curve 9) states. The transmittance at  $\lambda = 550 \text{ nm}$  (the sensitivity peak of human eye) from  $\sim 85\%$  with the bleached state decreased to  $40\%$  with the colored state, corresponding respectively to bias potential from  $+0.3 \text{ V/SCE}$  to  $-0.5 \text{ V/SCE}$ . This result indicates that the electrochemically deposited  $\text{WO}_3/\text{TiO}_2$  films exhibited an excellent EC performance that can be comparable to the one of the cosputtered Ti-doped  $\text{WO}_3$  films, as reported in [3]. The transmittance decreases with the increasing of the bias potential in NSD interval.

The bleaching and coloration processes were measured under the application of negatively and positively polarized voltage to the working electrode, respectively. These processes were clearly associated with the  $\text{Li}^+$  insertion (extraction) from the  $\text{LiClO}_4 + \text{PC}$  electrolyte into (out of) the  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  electrode. In comparison with results

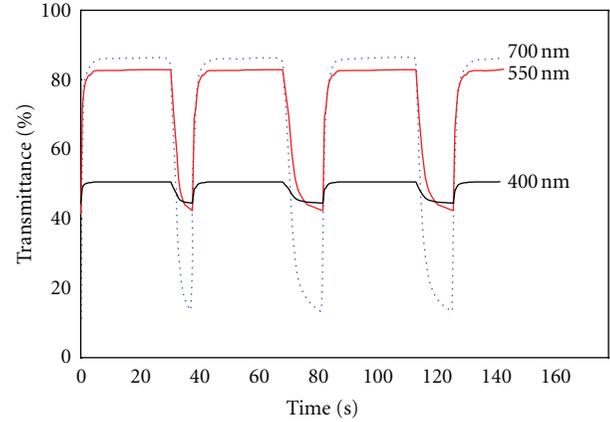


FIGURE 7: Time-dependence transmittance of the  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  during electrochromic performance for three different wavelengths: 400, 550, and 700 nm.

reported previously [8], the optical modulation at the visible range for  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  at longer wavelengths is improved. Herein, we attained a transmittance at  $\lambda = 550 \text{ nm}$  ( $T_{550}$ ) 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  $400 \text{ nm}$  was negligible, that is about  $5\%$ . This would result from the strong absorption by both  $\text{WO}_3$  and  $\text{TiO}_2$  at shorter wavelengths.

From the above-mentioned results for the ECDs with heterojunctions of  $\text{WO}_3/\text{nc-TiO}_2$ , 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 ( $\Delta\text{OD}$ ), consequently the transmittances of coloration ( $T_c$ ) and bleaching states ( $T_b$ ), and the insertion charge ( $Q$ ), as follows [15]:

$$\eta = \frac{\Delta\text{OD}}{Q} = \frac{1}{Q} \ln\left(\frac{T_b}{T_c}\right). \quad (6)$$

At a wavelength of  $550 \text{ nm}$ ,  $Q_{\text{in}} = 21 \text{ mC} \times \text{cm}^{-2}$ ,  $T_b = 85\%$  and  $T_c = 40\%$ , the coloration efficiency was determined to be  $35.7 \text{ cm}^2 \times \text{C}^{-1}$ . The larger the wavelength is, the higher the coloration efficiency is. In the visible range of wavelengths, all the found values of  $\eta$  are comparable to those for  $\text{WO}_3$  films [16] and much higher than those for  $\text{TiO}_2$  films [7] prepared by sol-gel techniques and titanium-lanthanide oxides deposited by magnetron sputtering and coloured in a  $\text{LiClO}_4 + \text{PC}$  solution [17].

To investigate the ageing process of two types of electrochromic devices, the first one is made from  $\text{nc-TiO}_2$  and the second one from  $\text{WO}_3/\text{nc-TiO}_2$  electrode, we measured the optical density versus bias potential after cycling these electrodes in  $1 \text{ M LiClO}_4 + \text{PC}$  for  $10^3$  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

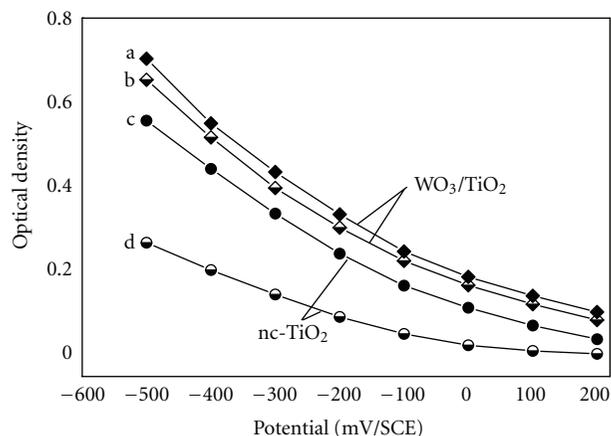


FIGURE 8: The potential dependence of the optical density of nc-TiO<sub>2</sub>/FTO (two bottom curves) and WO<sub>3</sub>/TiO<sub>2</sub>/FTO (two top curves) electrodes during electrochromic performance in 1 M LiClO<sub>4</sub> + PC for as-prepared (a; c) and after cycling for 10<sup>3</sup> cycles (b; d).

the value of  $\Delta OD$ . The potential dependence of  $\Delta OD$  at  $\lambda = 550$  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<sup>+</sup> cations would be inserted into the electrodes making the TiO<sub>2</sub> and WO<sub>3</sub> structures change to Li<sub>x</sub>TiO<sub>2</sub> to Li<sub>x</sub>WO<sub>3</sub>, respectively. The number of colour centers (namely Li<sub>x</sub>TiO<sub>2</sub> and Li<sub>x</sub>WO<sub>3</sub>) is dependent on the number of Li<sup>+</sup> 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  $\Delta OD$  of the nc-TiO<sub>2</sub> based ECD decreased faster than that of WO<sub>3</sub>/TiO<sub>2</sub> is revealed by the monitoring of the film thickness of the electrodes during the electrochromic performance. After 10<sup>3</sup> 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-TiO<sub>2</sub> film was removed while the WO<sub>3</sub>/nc-TiO<sub>2</sub> was maintained almost unchanged. This demonstrates that WO<sub>3</sub> attached to TiO<sub>2</sub> particles enables the structure of WO<sub>3</sub>/nc-TiO<sub>2</sub> film to be much more strengthened. Thus the devices with WO<sub>3</sub>/TiO<sub>2</sub> nano-heterojunctions would possess a larger ECD lifetime.

#### 4. Conclusion

Mixed nanostructured Ti-W oxides films were prepared by electrochemical deposition of WO<sub>3</sub> onto doctor-blade nc-TiO<sub>2</sub>/FTO films. Electrochromic performance studies of both the nc-TiO<sub>2</sub>/FTO and WO<sub>3</sub>/TiO<sub>2</sub>/FTO configurations were carried out in 1 M LiClO<sub>4</sub> + propylene carbonate. The reversible coloration and bleaching process of WO<sub>3</sub>/TiO<sub>2</sub>-based electrochromic devices was demonstrated. The response time of the ECD coloration of WO<sub>3</sub>/TiO<sub>2</sub>/FTO was found to be as small as 2 s and the coloration efficiency could be as high as 35.7 cm<sup>2</sup> × C<sup>-1</sup>. *In situ* transmittance spectra of the WO<sub>3</sub>/TiO<sub>2</sub>/FTO working electrode showed the

insertion/extraction of Li<sup>+</sup> ions into/out of the electrode. By incorporating WO<sub>3</sub> inserted between TiO<sub>2</sub> nanoparticles, WO<sub>3</sub>/TiO<sub>2</sub> 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 WO<sub>3</sub>/TiO<sub>2</sub> 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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