

# Electrochromic properties of multi-layer $\text{WO}_3 / \text{TiO}_2$ films made by electrochemical deposition

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**Abstract:** Multilayer thin films of  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  containing inorganic heterojunctions such as  $\text{TiO}_2/\text{FTO}$  and  $\text{WO}_3/\text{TiO}_2$  were prepared by electro-chemical deposition technique. From the cyclic voltammetry (CV) characteristics one can suggest that in the  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  multi-layer films there is also W-doped  $\text{TiO}_2$  structure, creating multi-heterojunctions of  $\text{WO}_3$ ,  $\text{TiO}_2:\text{W}$ ,  $\text{TiO}_2$  and F-doped  $\text{SnO}_2$ . Combining CV, time-current characteristic, *in-situ* transmittance spectra, the electrochromic performance of  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  was revealed. It is seen that the multi-layer electrochromic devices exhibited much larger electrochromic efficiency and faster response time than that of a standard single layer electrochromic device.

**Keywords:** Electrochromic device (ECD), Electrochemical deposition, *in-situ* transmittance spectra, ion insertion / extraction, heterojunction.

## 1. Introduction

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,  $\text{WO}_3$  is clearly the preferred material for applications. This is principally due to the fact that  $\text{WO}_3$ -based electrochromic devices (ECD) 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. To improve further the electrochromic properties, Ti-doped  $\text{WO}_3$  films were deposited by co-sputtering metallic titanium and tungsten in a  $\text{Ar}/\text{O}_2$  atmosphere [2]. The optical modulation was found to be around 70% and CE was  $66 \text{ cm}^2/\text{C}$ . Another way to improve electrochromic properties of thin films is to use nanostructured crystalline films. For instance, nanocrystalline  $\text{WO}_3$  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  $20 \div 40 \text{ nm}$ . The coloration of  $\text{WO}_3$  deposited on indium-tin-oxides (ITO) substrates ( $\text{WO}_3/\text{ITO}$ ) in 2M HCl

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was less than 1 sec and the maximum coloration efficiency at 630 nm was  $22 \text{ cm}^2 \times \text{mC}^{-1}$  [3]. However, the HCl electrolyte is not suitable for practical use. A slight improvement was achieved by using gold nanoparticles as dopants in  $\text{WO}_3$ . With fabrication of nanostructured  $\text{WO}_3$  films Beydaghyan *et al* [4] 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. We also have shown that nanocrystalline  $\text{TiO}_2$  anatase thin films on ITO prepared by sol-gel dipping method exhibited a good reversible coloration and bleaching process [5]. The lowest transmittance of 10% was obtained at the wavelength of 510 nm for full coloration (65% at the same wavelength in open circuitry). However the full coloration time was found to be large and CE was low .

Recently [6], nanostructured porous  $\text{TiO}_2$  anatase films with a grain size of 20 nm were deposited on transparent conducting F-doped  $\text{SnO}_2$  (FTO) electrodes by a doctor-blade method using a colloidal  $\text{TiO}_2$  solution (Nyacol Products). The response time of the ECD coloration was found to be as small as 2 s and the coloration efficiency could be as high as  $33.7 \text{ cm}^2 \times \text{C}^{-1}$ . *In situ* transmittance spectra and XRD analysis of the  $\text{TiO}_2$ /FTO working electrode demonstrated the insertion/extraction of  $\text{Li}^+$  ions into anatase  $\text{TiO}_2$ . Simultaneous use of chronoamperometry and XRD allowed the determination of the compound of the saturated coloration state of WE to be  $\text{Li}_{0.5}\text{TiO}_2$ . The results showed that nanostructured porous  $\text{TiO}_2$  films can be comparable in property to  $\text{WO}_3$  films.

In present work we combine two techniques, namely doctor-blade and electrochemical deposition for depositing multilayer thin films with nanostructured heterojunction of  $\text{WO}_3/\text{TiO}_2/\text{FTO}$ . Ion insertion (extraction) into (out from) the  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  electrode and electrochromic properties of the ECD devices were characterized by using both the electrochemical measurements and *in situ* transmittance spectra.

## 2. Experimental

To prepare nanostructured  $\text{TiO}_2$  films for ECD, a doctor-blade technique was used following the process reported in [6]. A glass slide overcoated with a  $0.2 \mu\text{m}$  thick FTO film having a sheet resistance of  $15 \Omega$  per square and a transmittance of 90% was used as a substrate; the useful area that constitutes the sample studied was of  $1 \text{ cm}^2$ . For depositing  $\text{WO}_3$  films onto  $\text{TiO}_2/\text{FTO}$ , peroxotungstic acid solution was used. This  $\text{H}_2\text{W}_2\text{O}_{11}$  solution was prepared by dissolving 4.6 g of pure W metallic powder in 25 ml of peoxithydro ( $\text{H}_2\text{O}_2$ ) wt. 30%. After getting complete dissolution, distilled water was added to reach a total  $\text{H}_2\text{W}_2\text{O}_{11}$  solution volume of 500 ml. The film deposition was carried-out on an Auto.Lab-Potentiostat-PGS-30 by using the "Potentiostatic" regime with a standard three-electrode cell: the working electrode (WE) was  $\text{TiO}_2/\text{FTO}$ , the counter electrode (CE) is Pt grid and the reference electrode is saturate calomel (SCE). The potential applied onto the WE for depositing was  $-500 \text{ mV/CSE}$ . The thickness and surface morphology of the films were checked field-emission scanning electron microscope (FE-SEM). Electrochemical processes were carried-out by above mentioned potentiostat. 1M  $\text{LiClO}_4$  + propylene carbonate ( $\text{LiClO}_4$  + PC) solution was used for electrolyte. All measurements were performed at room temperature.

By using a JASCO “V-570” photospectrometer, *in situ* transmittance spectra of nc-TiO<sub>2</sub> in LiClO<sub>4</sub>+PC vs. time were recorded on the films of the WE mounted into 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

FE-SEM micrographs revealed the morphology of the surface of TiO<sub>2</sub>/FTO electrode made by doctor-blade technique (Fig. 1a) and the surface of this electrode after being electrochemically coated in the H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> solution (Fig. 1b). During the depositing we observed that the TiO<sub>2</sub>/FTO electrode was colouring and became deeper blue with the increase of deposition time. This coloration can be attributed to the insertion of W<sup>3+</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:



which is quite similar to well-known equation [7]:



From our previous work, it is known that the electrochromic WO<sub>3</sub> film could also be deposited onto the FTO electrode by the electrochemical technique [8]. Thus, parallel with the coloration process one can obtain a WO<sub>3</sub> layer that was deposited onto TiO<sub>2</sub>/FTO to form a multilayer film with a structure of WO<sub>3</sub>/TiO<sub>2</sub>/FTO. By this way one can make heterojunctions of WO<sub>3</sub> and TiO<sub>2</sub> nanoparticles. This is the reason why the second micrograph (Fig. 1b) have different features in comparison with the first one (Fig. 1a).

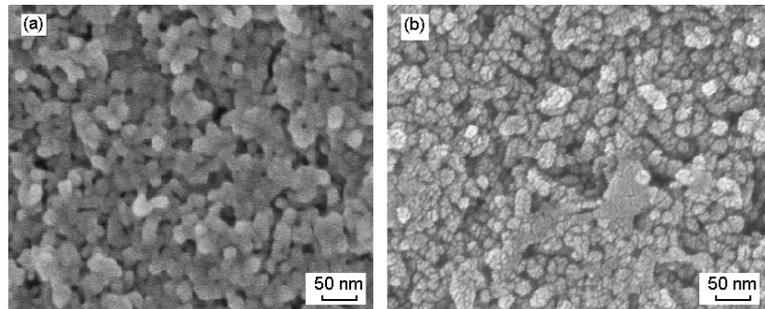


Fig. 1. FE-SEM micrographs of as-prepared nc-TiO<sub>2</sub> films (a) and after being electrochemically deposited in H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> electrolyte (b).

Fig. 2 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 time of each lapse of time as follows:

$$Q = \int_{t_1}^{t_2} J(t) dt \quad (3)$$

The insertion charge was found to be  $Q_{in} = 75 \text{ mC}\times\text{cm}^{-2}$ , whereas for the extraction process the charge was  $Q_{ex} = 71 \text{ mC}\times\text{cm}^{-2}$ , that is slightly different from the insertion charge. The fact that the insertion and extraction charges are similar proves that the electrochromic process was a good reversible one - a desired characteristic for the electrochromic performance of the  $\text{TiO}_2$ -based electrochromic display.

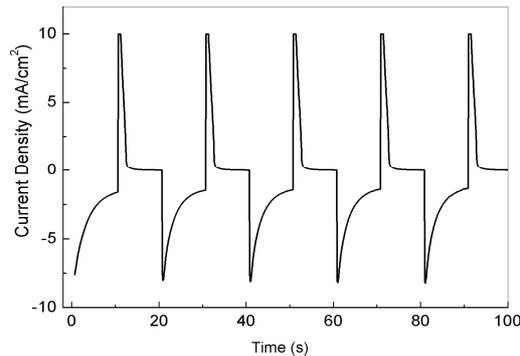


Fig. 2. Insertion and extraction of  $\text{Li}^+$  ions into/out of the  $\text{WO}_2/\text{TiO}_2/\text{FTO}$  electrode. The inserted charge (a bottom half cycle) of the saturated coloration state and the completely bleaching state (a top half cycle), respectively are  $Q_{in} = 75 \text{ mC}\times\text{cm}^{-2}$  and  $Q_{ex} = 71 \text{ mC}\times\text{cm}^{-2}$ .

Fig. 3 presents CV spectra of the multilayer WE (namely  $\text{WO}_3/\text{TiO}_2/\text{FTO}$ ) cycled in 1M  $\text{LiClO}_4$  in propylene carbonate ( $\text{LiClO}_4/\text{PC}$ ). In the positive scanning direction (PSD) there are 2 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 2 similar peaks. This proves the reversibility of the insertion / extraction of  $\text{Li}^+$  into / out of the  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  electrode. Moreover, the CV spectra of the multilayer electrode of  $\text{WO}_3/\text{TiO}_2/\text{SnO}_2$  cycled in  $\text{LiClO}_4/\text{PC}$  solution possess quite different characteristic than the one of the each single layer electrode of either  $\text{WO}_3/\text{FTO}$  or  $\text{TiO}_2/\text{FTO}$ . This may be explained by the fact that during depositing a part of numerous  $\text{W}^{3+}$  ions replaced  $\text{Ti}^{2+}$  of  $\text{TiO}_2$  lattice, creating so called a W-doped  $\text{TiO}_2$ , namely  $\text{Ti}_{(1-y)}\text{W}_y\text{O}_2$ .

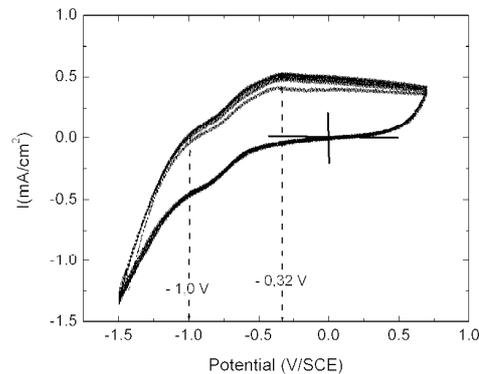
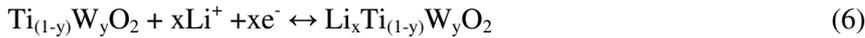


Fig. 3. Cyclic voltammetry spectra of  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  cycled in  $\text{LiClO}_4/\text{PC}$  (scanning rate  $v = 100 \text{ mV/s}$ ).

Therefore electrochromic performance of the multilayer electrode in  $\text{LiClO}_4+\text{PC}$  for  $\text{WO}_3/\text{FTO}$  and  $\text{TiO}_2/\text{FTO}$  can be described, respectively by two well known following reactions [1]:



For  $\text{Ti}_{(1-y)}\text{W}_y\text{O}_2$  can be suggested by a similar reaction, as follows:



where “y” is the atomic concentration of W that substitutionally replaced Ti in  $\text{TiO}_2$  lattice.

For characterization of the electrochromic device, in-situ transmittance spectra was done on a device having structure of “FTO |  $\text{LiClO}_4+\text{PC}$  |  $\text{WO}_3/\text{TiO}_2/\text{FTO}$ ”. The transmittance spectra of the device vs. coloration time were plotted in Fig. 4.

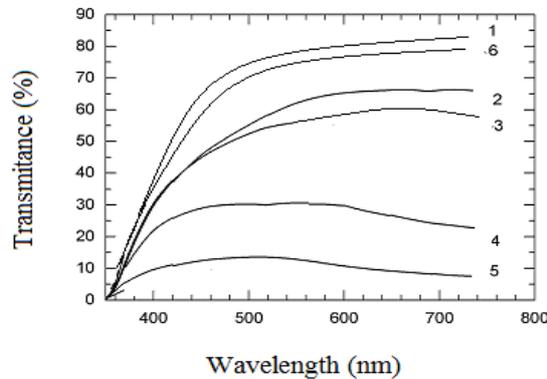


Fig. 4. *In-situ* transmittance spectra vs. time of the device with a structure FTO |  $\text{LiClO}_4+\text{PC}$  |  $\text{WO}_3/\text{TiO}_2/\text{FTO}$  at potential of -2.5 V/SCE. Curve “1” – without voltage one the WE. Curves “2, 3, 4 and 5” – coloured with 5, 10 and 15 sec respectively; curve “6” – bleaching state.

At  $\lambda = 550$  nm (for the best human-eye sensitivity) the transmittance of the open circuit state is as high as 78%, whereas the transmittance of the saturated coloration state is as low as 10% (see curves 1 and 5 in Fig. 4). For all the visible range, the complete bleaching of the device occurred much faster than the saturation coloration, as seen in Fig. 2. The bleaching and coloration processes were measured under the application of negatively and positively polarized voltage to the WE, respectively. These processes were clearly associated to the  $\text{Li}^+$  insertion /extraction from the  $\text{LiClO}_4+\text{PC}$  electrolyte into /out of the nc- $\text{WO}_3/\text{TiO}_2/\text{FTO}$  electrode. Similarly to the results reported previously [9], we attained a transmittance at  $\lambda = 550$  nm ( $T_{550}$ ) equal to 75% upon bleaching and to 25% after a coloration period of 40s. The largest optical modulation was observed for red light ( $T_{700}$ ): the gap between the transmittances of bleaching and coloration states was of 60%. For blue light ( $T_{400}$ ) the optical modulation at wavelength 400 nm was much smaller, i.e. about 20%. This would result from the strong absorption by both FTO and  $\text{TiO}_2$  at shorter wavelengths. From the above mentioned results, it is seen that the efficient coloration can be attributed to both the high porosity of the nc- $\text{TiO}_2$  and multilayer nanostructured electrochromic films.

#### 4. Conclusion

Multilayer electrochromic films with nanostructured porous TiO<sub>2</sub>/WO<sub>3</sub> heterojunctions were prepared on transparent conducting FTO electrodes by a doctor-blade method followed by electrochemical deposition. Electrochromic performance of WO<sub>3</sub>/TiO<sub>2</sub>/FTO was carried out in 1M LiClO<sub>4</sub> + propylene carbonate and a good reversible coloration and bleaching process was obtained. Combining CV, time-current characteristic, *in-situ* transmittance spectra, the electrochromic performance of WO<sub>3</sub>/TiO<sub>2</sub>/FTO was revealed. The response time of the ECD coloration was found to be as small as 5 s. Multi-layer electrochromic devices exhibited larger electrochromic efficiency and faster response time than that of a standard single layer electrochromic device. The results showed that nanostructured porous TiO<sub>2</sub> combined with WO<sub>3</sub> particles embedded in the films can be comparable in property to the best electrochromic films.

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