

CHARACTERIZATION OF STRUCTURAL AND ELECTROCHROMIC PROPERTIES OF NANOCOMPOSITE $\text{TiO}_2 - \text{WO}_3$ FILMS

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Abstract. *Using doctor-blade technique, followed by electrochemical deposition, nanocomposite $\text{WO}_3\text{-TiO}_2$ films were prepared. Structure, morphology and composition ratio of the nanocomposite films were characterized by a comprehensive analyzing the SEM, EDX, XRD and Raman scattering results. The reversible coloration and bleaching of TiO_2/ITO and $\text{WO}_3\text{-TiO}_2/\text{ITO}$ electrodes were demonstrated. The ECD coloration efficiency of $\text{WO}_3\text{-TiO}_2/\text{ITO}$ was found to be much larger ($55.1 \text{ cm}^2 \times \text{C}^{-1}$) than that of TiO_2/ITO ($34.3 \text{ cm}^2 \times \text{C}^{-1}$). The resulting nanostructured composites enables the coloration efficiency of the $\text{WO}_3\text{-TiO}_2$ film to be considerably improved. The results suggest a potential application of the nanocomposites of two electrochromic oxides in large-area energy-efficiency (or smart) windows.*

Keywords: electrochromic display (ECD), electrochemical deposition, SEM and EDX, XRD and Raman scattering, coloration efficiency.

I. INTRODUCTION

Electrochromic display (ECD) has been investigated extensively in the last decades because of its potential applications in light controlling, energy-efficient or smart windows [1]. ECD properties can be found in almost all the transition-metal oxides and they can be coloured anodically (Ir, Ni) or cathodically (W, Ti) [1–3]. Recently Granqvist *et al* [4] have made a comprehensive review of nanomaterials for benign indoor environments. In this report, the authors show the characteristic data for a $5 \times 5 \text{ cm}^2$ flexible ECD foil incorporating WO_3 , and NiO modified by the addition of a wide bandgap oxide such as MgO or Al_2O_3 , PMMA-based electrolyte, and ITO films. To improve further the electrochromic properties, Ti-doped WO_3 films were deposited by co-sputtering metallic titanium and tungsten in an Ar/O_2 atmosphere [5]. Another way to improve electrochromic properties of thin films is to use nanostructured crystalline films. For instance, nanocrystalline 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 time of WO_3 deposited on indium-tin-oxides (ITO) substrates (WO_3/ITO) in 2M HCl was less

than 1 sec and the maximum coloration efficiency at 630 nm was ca. $22 \text{ cm}^2 \times \text{C}^{-1}$ [6]. However, the HCl electrolyte is not suitable for practical use. The nanocrystalline TiO_2 anatase thin films on ITO prepared by sol-gel dipping method exhibited a good reversible coloration and bleaching process [7]. By using a so-called “doctor blade” method, nano-porous TiO_2 and mixed TiO_2/WO_3 films were prepared for the ECD with much improved electrochromic response time and coloration efficiency [8]. In present work, we combined the doctor-blade technique for preparing TiO_2 films with an electrochemical process for depositing WO_3 into the nano-porous TiO_2 films, with the aim to reveal structural and electrochromic properties of the mixed oxides films which contains numerous nanostructured heterojunctions of TiO_2/WO_3 .

II. EXPERIMENTAL

To deposit nanoporous TiO_2 films, a “doctor blade” technique was used following the process reported in [3]. A glass slide overcoated with a $0.2 \mu\text{m}$ thick ITO film having a sheet resistance of $10 \Omega/\square$ and a transmittance of 90% was used as a substrate; the useful area that constitutes the sample studied was of 1 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% TiO_2 and a few drops of the liquid surfactant were added. Then the diluted solution was filled in the slot on the ITO 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 re-crystallize the nc- TiO_2 films. To prepare WO_3 - TiO_2 on to ITO films (further shortly called WTO), 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 H_2O_2 (30%). The detailed process of the electrochemical deposition can be seen elsewhere [8]. By using potentiostat “Autolab. PGS - 30” a potentiostatic method was chosen for film deposition. After their deposition, the films were dried in nitrogen gas. Thickness of the WTO films is about 500 nm

The surface morphology and Energy Dispersive X-ray Spectroscopy (EDX) measurements were examined with the help of a field-emission scanning electron microscope (FE-SEM). X-ray diffraction analysis (XRD) and Raman scattering spectra (RSS) were done on a Bruker “Advance-8D” X-ray diffractometer and Lambram-1B, respectively. Electrochemical processes were carried-out on the same potentiostat Autolab. PGS - 30, using solutions of 1 M LiClO_4 + Propylene carbonate (PC)... All measurements were executed at room temperature.

By using a JASCO “V-570” photospectrometer, *in situ* transmittance spectra of both the nc- TiO_2/ITO and WTO/ ITO in LiClO_4 +PC vs. bias potential were recorded on 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.

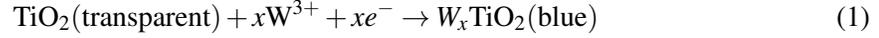
III. RESULTS AND DISCUSSION

III.1. SEM and EDX analysis

Fig. 1 shows a SEM micrograph of a WTO sample deposited onto porous- TiO_2/ITO for 600 s. Different places in the depth of the sample are marked by “Spectrum” for EDX measurements; the obtained EDX data are listed in Table 1.

It is known that with the insertion of the Li^+ one can obtain the ECD coloration [1], whereas the insertion of W^{6+} during the electrochemical deposition would result in the insertion of WO_3

into the nano-pores in the porous TiO_2 films. Fig. 1 shows the SEM of the surface of the TiO_2 electrode after the electrochemical process in the $\text{H}_2\text{W}_2\text{O}_{11}$ solution. During the deposition, we observed that the TiO_2/ITO electrode was coloured and became deep-blue with the increase of the deposition time. This coloration can be attributed to the insertion of W^{6+} (the ions from the $\text{H}_2\text{W}_2\text{O}_{11}$ electrolyte) into the TiO_2 films according to the following equation:



where W^{6+} plays the role of Li^+ in formation of the coloration state of Li_xTiO_2 [9].

Hereby, simultaneously with the ECD coloration, one can deposit WO_3 into nanoporous- TiO_2 to form a film with heterojunctions of WO_3/TiO_2 .

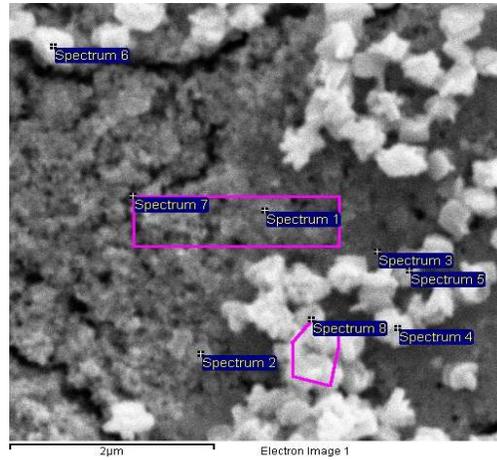


Fig. 1. SEM micrograph of $\text{WO}_3\text{-TiO}_2/\text{ITO}$ deposited in $\text{H}_2\text{W}_2\text{O}_{11}$ solution, at a potential of $-3.5\text{V}/\text{SCE}$ for 600 s.

Table 1. EDX data on the composition (at%) of chemical elements from the top to bottom in the WTO film (deposition time $t = 600$ s).

No.	Marked place	O	Ti	In	Sn	W	Total
1	Spectrum 4	30.89	7.82	2.46	1.25	57.58	100.00
2	Spectrum 6	35.13	10.36	0.74	0.16	53.61	100.00
3	Spectrum 8	32.56	12.19	1.40	1.07	52.78	100.00
4	Spectrum 5	32.77	12.48	2.47	1.16	51.12	100.00
5	Spectrum 2	33.88	13.58	2.66	1.29	48.59	100.00
6	Spectrum 7	33.82	17.38	2.13	1.47	45.20	100.00
7	Spectrum 3	31.95	19.49	2.58	1.67	44.31	100.00
8	Spectrum 1	33.98	22.12	2.04	1.37	40.49	100.00

From Table 1 one can see that, besides W, Ti and O elements of WO_3 and TiO_2 , there were observed also In and Sn from ITO substrate. Although the presence of In, Sn and O of ITO affected

to the results of EDX, qualitatively one can estimate the composition distribution as follows. The total content of Ti and W is around 63 at%, Ti and W contents are compensated each by other in every places. Indeed, “Spectrum 4” is on the top of sample surface has the largest W-content, namely 57.58 at% and decreases to 40.49 at%, corresponding to “Spectrum 1”, the deepest place in the film. Whereas, Ti-content is the largest in “Spectrum 1” (22.12 at%) and decreases to 7.82 at% (the smallest value) in “Spectrum 4”. This proves that the volume of WO_3 decreased from the top to the bottom of the WTO film.

III.2. XRD and RSS analysis

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 TiO_2 , all XRD patterns of the ITO substrate do not appear (Fig. 2). In XRD patterns there are 10 intensive peaks: 4 peaks belong to anatase TiO_2 [10] and 6 peaks belong to WO_3 [11]. The fact that the peak width is rather large shows that the TiO_2 film was crystallized into small grains. To obtain the grain size τ we used the Scherrer formula:

$$\tau = \frac{0.9 \times \lambda}{\beta \times \cos \theta} \quad (2)$$

where λ is wavelength of the X-ray used ($\lambda = 0.154 \text{ nm}$), β the peak width of half height in radians and θ the Bragg angle of the considered diffraction peak [12]. From the XRD patterns the average half-height peak width of the grains was found to be $\beta = 0.0055$, consequently the size of grains was determined as $\tau \approx 30 \text{ nm}$. For 6 peaks of WO_3 , the average size estimated by formula (2) is the same as the size of pores in the nc- TiO_2 , namely about 20 – 25 nm. This result demonstrates that the nano-pores of the porous nc- TiO_2 film were filled-up with WO_3 .

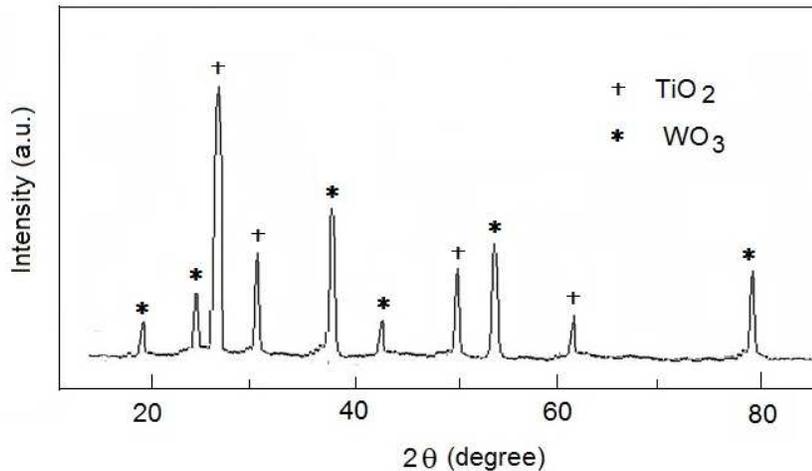


Fig. 2. XRD of a WO_3 - TiO_2 mixture (WTO) film made by electrochemical deposition of WO_3 onto “doctor-blade” nc- TiO_2 .

To reveal RSS of the WO_3 - TiO_2 /ITO film we recorded RSS of WO_3 /ITO with a thickness of WO_3 of 300 nm (Fig. 3). In this RSS there were also observed Raman bands of ITO at 196 cm^{-1}

and 377 cm^{-1} as reported in [7]. The other peaks correspond to Raman bands of crystalline (c-WO₃) and amorphous (a-WO₃) phases. Band at 986 cm^{-1} is of W=O bond (with W⁺⁴) [13]. The RSS shows the multi-valence of W ranging from 4 to 6. Both the crystalline and amorphous WO₃ possess good electrochromic properties, however c-WO₃ exhibits a better ECD in transmission regime, on contrary a-WO₃ - is better ECD in reflection regime [1]. In Fig. 4 there are two Raman spectra, one is of RSS of anatase TiO₂/ITO and the other is of WO₃/TiO₂/ITO.

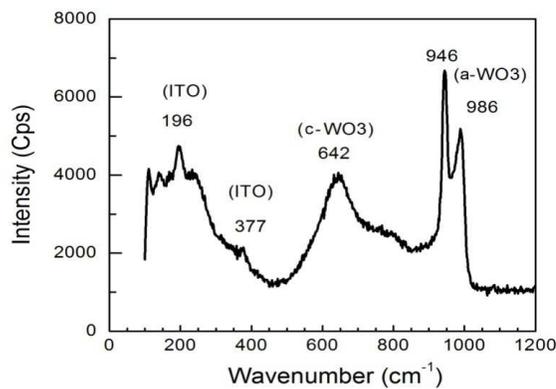


Fig. 3. Raman spectrum of WO₃/ITO film deposited for 600 s.

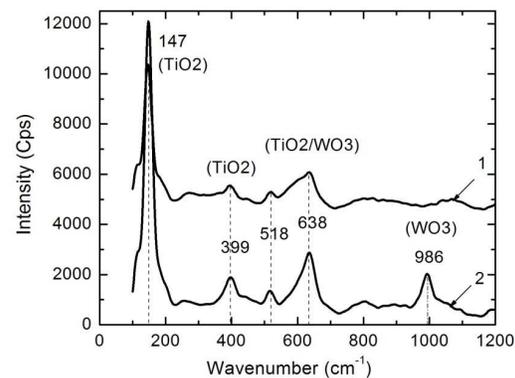


Fig. 4. Raman spectra of the TiO₂/ITO (curve “1”) and WO₃/TiO₂/ITO film (curve “2”)

Besides a large volume of WO₃ that is filled-up in nc-TiO₂, the WO₃ layer deposited on the TiO₂ surface is very thin ($\sim 50\text{ nm}$). Thus RSS bands of TiO₂ appeared intensively, while in the RSS of WO₃ only two bands appeared (namely at 638 and 986 cm^{-1}). For TiO₂, the strongest band (147 cm^{-1}) corresponds to the bandgap (E_g) mode. Note that bulk anatase TiO₂ has the E_g peak of 143 cm^{-1} . The fact that E_g peak shifted to a larger wavenumber range again proves that TiO₂ was crystallized in nanoparticles form [14]. The results of XRD, EDX and RSS showed that by electrochemically depositing WO₃ onto nanoporous TiO₂, one can prepare nanocomposites of WO₃ and TiO₂ with numerous heterojunctions of two wide bandgap semiconductors. Both the TiO₂ and WO₃ are the anodic electrochromic materials. Thus it may be expected that ECD devices made from the WTO films would have an enhanced electrochromic performance.

III.3. Electrochromic performance

To compare electrochromic performance two working electrodes (WE) such as TiO₂/ITO and WTO/ITO, we measured *in-situ* transmittance of the WE at polarized potentials. Fig. 5 shows the transmittance of these electrodes filled in 1 M LiClO₄ + PC at polarizing bias potentials (from -2.5 V/SCE to $+1.5\text{ V/SCE}$). The bleaching and coloration processes were measured under the application of negatively (i.e. -2.5 V/SCE) and positively polarized (i.e. $+1.5\text{ V/SCE}$) potential to the WE, respectively. These processes were clearly associated with the Li⁺ insertion (extraction) from the LiClO₄+PC electrolyte into (out of) the TiO₂/ITO and WO₃/TiO₂/ITO electrodes.

Above-mentioned results for the ECD properties of WTO films that contain nano-heterojunctions of WO₃/TiO₂ demonstrate that the efficient coloration were achieved due to a double

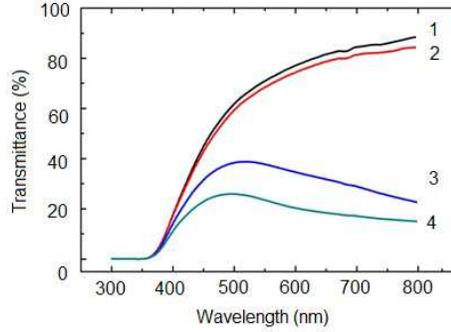
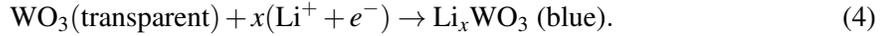
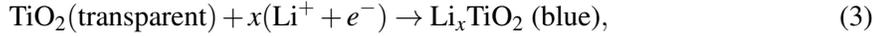


Fig. 5. Transmittance spectra of TiO_2/ITO and WTO/ITO ($\text{WO}_3/\text{TiO}_2/\text{ITO}$) electrodes filled in 1M LiClO_4 + PC solution with polarized potential ranging from -2.5 V/SCE to + 1.5 V/SCE: Curves 1 and 2 correspond to bleaching state of TiO_2/ITO and WTO/ITO ; curves 3 and 4 correspond to coloration state of TiO_2/ITO and WTO/ITO , respectively.

coloration process according to following reactions in the WE:



To evaluate the electrochromic coloration efficiency (η) we used a well-known expression relating the efficiency with the optical density (ΔOD), consequently the transmittances of coloration (T_c) and bleaching states (T_b), and the insertion charge (Q), as follows [15]:

$$\eta = \frac{\Delta OD}{Q} = \frac{1}{Q} \ln \left(\frac{T_b}{T_c} \right), \quad (5)$$

At a wavelength of 550 nm - the largest sensitivity of human eyes, $Q_{in} = 21 \text{ mC} \times \text{cm}^{-2}$ (taken from the electrochemical measurements), for TiO_2/ITO : $T_b = 72\%$ and $T_c = 35\%$; for WTO/ITO : $T_b = 70\%$ and $T_c = 22\%$. Using formula (5), the coloration efficiency was determined to be $\eta_1 = 34.3 \text{ cm}^2 \times \text{C}^{-1}$ and $\eta_2 = 55.1 \text{ cm}^2 \times \text{C}^{-1}$ for TiO_2/ITO and WTO/ITO , respectively. Herein, η_1 is almost the same value as reported in [3] for TiO_2/FTO , whereas η_2 obtained in this work is larger than that of $\text{WO}_3/\text{TiO}_2/\text{ITO}$ electrode, as reported in [8] ($35.7 \text{ cm}^2 \times \text{C}^{-1}$). This is because the WTO film (500 nm) is thinner than the WO_3/TiO_2 film (570 nm). It is clearly seen that WTO/ITO electrode possesses much larger electrochromic efficiency than the one of TiO_2/ITO . For both electrodes, the larger is the wavelength, the higher is the coloration efficiency. In the visible range of wavelengths all the values of η of WTO/ITO are found to be comparable to those for WO_3 films [16] and much higher than those for TiO_2 films prepared by sol-gel technique [7] and titanium-lanthanide oxides deposited by magnetron sputtering and coloured in a LiClO_4 + PC solution [17].

IV. CONCLUSION

Composite films from nano TiO_2 and WO_3 were prepared by electrochemical deposition of WO_3 onto “doctor-blade” nc- TiO_2/ITO films. Combining characterization methods such as

SEM, EDX, XRD and Raman scattering, the structure and compound of the nanocomposite films were revealed. In these composite films, the pores in nano-porous TiO₂ were filled-up with WO₃, consequently creating numerous heterojunctions of two anodic electrochromic materials of nc-TiO₂ and nc-WO₃. The reversible coloration and bleaching process of WO₃/TiO₂ and WTO/ITO based electrochromic devices was demonstrated. The ECD coloration efficiency of TiO₂/ITO and WTO/ITO was found to be as large as 34.3 cm² × C⁻¹ and 55.1 cm² × C⁻¹, respectively. The resulting nanostructured film enables the coloration efficiency 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 electrodes constitutes a good candidate for smart window applications, taking advantage of its excellent properties in terms of ECD efficiency and electrochemical stability as well as the simplicity of the fabrication process.

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