CHARACTERIZATION OF STRUCTURAL AND ELECTROCHROMIC PROPERTIES OF NANOCOMPOSITE TiO$_2$ – WO$_3$ FILMS

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Abstract. Using doctor-blade technique, followed by electrochemical deposition, nanocomposite WO$_3$-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 WO$_3$-TiO$_2$/ITO electrodes were demonstrated. The ECD coloration efficiency of WO$_3$-TiO$_2$/ITO was found to be much larger (55.1 cm$^2$ × C$^{-1}$) than that of TiO$_2$/ITO (34.3 cm$^2$ × C$^{-1}$). The resulting nanostructured composites enables the coloration efficiency of the WO$_3$-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 × 5 cm$^2$ flexible ECD foil incorporating WO$_3$, and NiO modified by the addition of a wide bandgap oxide such as MgO or Al$_2$O$_3$, 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)itungsten. 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 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 cm² × C⁻¹ [6]. However, the HCl electrolyte is not suitable for practical use. The nanocrystalline TiO₂ 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 TiO₂ and mixed TiO₂/WO₃ 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 TiO₂ films with an electrochemical process for depositing WO₃ into the nano-porous TiO₂ films, with the aim to reveal structural and electrochromic properties of the mixed oxides films which contains numerous nanostructured heterojunctions of TiO₂/WO₃.

II. EXPERIMENTAL

To deposit nanoporous TiO₂ films, a “doctor blade” technique was used following the process reported in [3]. A glass slide overcoated with a 0.2 μm thick ITO film having a sheet resistance of 10 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 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-TiO₂ films. To prepare WO₃-TiO₂ on to ITO films (further shortly called WTO), 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 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 Brucker “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 LiClO₄ + 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-TiO₂/ITO and WTO/ITO in LiClO₄+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-TiO₂/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 W⁵⁺ during the electrochemical deposition would result in the insertion of WO₃
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 H$_2$W$_2$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 H$_2$W$_2$O$_{11}$ electrolyte) into the TiO$_2$ films according to the following equation:

\[
\text{TiO}_2\text{(transparent)} + xW^{3+} + xe^- \rightarrow W_x\text{TiO}_2\text{(blue)}
\]  

where W$^{6+}$ plays the role of Li$^+$ in formation of the coloration state of Li$_x$TiO$_2$ [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$_2$.

![SEM micrograph of WO$_3$-TiO$_2$/ITO deposited in H$_2$W$_2$O$_{11}$ solution, at a potential of - 3.5V/SCE for 600 s.](image)

**Fig. 1.** SEM micrograph of WO$_3$-TiO$_2$/ITO deposited in H$_2$W$_2$O$_{11}$ solution, at a potential of - 3.5V/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).

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

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 $\tau$ we used the Scherrer formula:

$$\tau = \frac{0.9 \times \lambda}{\beta \times \cos \theta}$$  \hspace{1cm} (2)

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 average half-height peak width of the grains was found to be $\beta = 0.0055$, consequently the size of grains was determined as $\tau \approx 30$ 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$_2$.](image)

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-WO$_3$) and amorphous (a-WO$_3$) 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 WO$_3$ possess good electrochromic properties, however c-WO$_3$ exhibits a better ECD in transmission regime, on contrary a-WO$_3$ - is better ECD in reflection regime [1]. In Fig. 4 there are two Raman spectra, one is of RSS of anatase TiO$_2$/ITO and the other is of WO$_3$/TiO$_2$/ITO.

![Fig. 3. Raman spectrum of WO$_3$/ITO film deposited for 600 s.](image)

![Fig. 4. Raman spectra of the TiO$_2$/ITO (curve “1”) and WO$_3$/TiO$_2$/ITO film (curve “2”).](image)

Besides a large volume of WO$_3$ that is filled-up in nc-TiO$_2$, the WO$_3$ layer deposited on the TiO$_2$ surface is very thin (~ 50 nm). Thus RSS bands of TiO$_2$ appeared intensively, while in the RSS of WO$_3$ only two bands appeared (namely at 638 and 986 cm$^{-1}$). For TiO$_2$, the strongest band (147 cm$^{-1}$) corresponds to the bandgap ($E_g$) mode. Note that bulk anatase TiO$_2$ has the $E_g$ peak of 143 cm$^{-1}$. The fact that $E_g$ peak shifted to a larger wavenumber range again proves that TiO$_2$ was crystallized in nanoparticles form [14]. The results of XRD, EDX and RSS showed that by electrochemically depositing WO$_3$ onto nanoporous TiO$_2$, one can prepare nanocomposites of WO$_3$ and TiO$_2$ with numerous heterojunctions of two wide bandgap semiconductors. Both the TiO$_2$ and WO$_3$ 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 TiO$_2$/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 LiClO$_4$ + PC at polarizing bias potentials (from −2.5 V/SCE to +1.5 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 V/SCE) potential to the WE, respectively. These processes were clearly associated with the Li$^+$ insertion (extraction) from the LiClO$_4$+PC electrolyte into (out of) the TiO$_2$/ITO and WO$_3$/TiO$_2$/ITO electrodes.

Above-mentioned results for the ECD properties of WTO films that contain nano-heterojunctions of WO$_3$/TiO$_2$ demonstrate that the efficient coloration were achieved due to a double
coloration process according to following reactions in the WE:

\[ \text{TiO}_2 (\text{transparent}) + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_x\text{TiO}_2 \text{ (blue),} \]
\[ \text{WO}_3 (\text{transparent}) + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_x\text{WO}_3 \text{ (blue).} \]

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 - 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, \(\eta_1\) is almost the same value as reported in [3] for TiO\(_2\)/FTO, whereas \(\eta_2\) obtained in this work is larger than that of WO\(_3\)/TiO\(_2\)/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 \(\eta\) 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 TiO$_2$ were filled-up with WO$_3$, consequently creating numerous heterojunctions of two anodic electrochromic materials of nc-TiO$_2$ and nc-WO$_3$. The reversible coloration and bleaching process of WO$_3$/TiO$_2$ and WTO/ITO based electrochromic devices was demonstrated. The ECD coloration efficiency of TiO$_2$/ITO and WTO/ITO was found to be as large as 34.3 cm$^2$ × C$^{-1}$ and 55.1 cm$^2$ × C$^{-1}$, respectively. The resulting nanostructured film enables the coloration efficiency of the working electrodes to be considerably improved. Since a large-area WO$_3$/TiO$_2$ 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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