



Original scientific paper

Electrochromism in tungsten oxide thin films prepared by chemical bath deposition

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Abstract

Tungsten oxide (WO_3) thin films were prepared by a simple, economical, chemical bath deposition method onto fluorine doped tin oxide (FTO) coated glass substrates. The electrochemical properties of the films were characterized by cyclic voltammetry. The obtained films exhibited electrochromism, changing color from initially colorless to deep blue, and back to colorless. Visible transmittance spectra of (WO_3) films were recorded in-situ in their both, bleached and colored states. From those spectra, absorption coefficient (α) and the optical energy gaps were evaluated. The dependence of the optical density on the charge density was examined and the coloration efficiency (η) was calculated to be $22.11\text{cm}^2\text{C}^{-1}$. The response times of the coloring and bleaching to an abrupt potential change from -2.5 V to $+2.5\text{ V}$ and reverse, were found to be 9.3 and 1.2 s respectively. The maximum light intensity modulation ability of the films, when the AM1.5 spectrum is taken as an input, was calculated to be about 50 %.

Keywords

Optical materials; cyclic voltammetry; response time; solar light modulation

Introduction

Electrochromism is a unique property of the material to change reversibly its optical properties when it is electrochemically reduced or oxidized [1]. Electrochromic materials exhibit color change between the clear transparent state and a darkened colored state, or between two colored states. At the same time, there are materials that exhibit multiple colored states and are described as

polyelectrochromic. The classification of the electrochromic materials is related to the potential at which the coloration process occurs. Materials with cathodic coloration exhibit coloration at negative potential, *i.e.* they darken upon reduction (charge insertion). Anodic materials, on the other hand, exhibit coloration at positive potential, *i.e.* they darken upon oxidation (charge extraction). When the electrochromic material is integrated in device, it could modulate the reflectance/transmittance of the incident illumination [2]. Electrochromic materials are currently attracting much interest in academia and industry for both their spectroelectrochemical and commercial applications [3]. Electrochromism is known to exist in many types of materials, both organic and inorganic. Common inorganic electrochromic materials are transition metal oxides and metal hexacyanometallates, while viologens, phthalocyanines, conducting polymers and metallopolymers are common organic and polymer electrochromic materials.

Transition metal oxides have attractive technological importance for electrochromic applications because they show considerable variation in stoichiometry, and can be quite easily deposited in a form of thin film which is appropriate for device manufacturing. Among them, tungsten oxide (WO_3) is of intense interest and has been extensively investigated due to its appreciable electrochromic properties in the visible and infrared region. It exhibits large optical modulation, good durability, low power consumption, less stress for the viewer's eyes, and relatively low price [4].

Electrochromic WO_3 thin films have been prepared by a large number of techniques, such as thermal evaporation, electrodeposition, spray pyrolysis, chemical vapor deposition, electron beam evaporation, magnetron sputtering, sol-gel methods [5 - 16] *etc.* Among these techniques, chemical bath deposition methods have many advantages: they do not require sophisticated expensive equipment, various substrates including metals, semiconductors or insulators can be used, the starting chemicals are commonly available and cheap, and the preparation parameters are easily controlled [17 - 21]. These methods have benefit of being easily realizable from the point of view of industrialization, especially on large area devices, with the required electrochromic properties [22, 23]. The electrochromic properties of WO_3 thin films, like the transmittance modulation (ΔT), coloration efficiency (η), switching time (τ), and cyclic durability, strongly depends on their structural, morphological and compositional characteristics [1, 2], which, in turn, depends directly on the deposition method and deposition conditions.

The target of this research is to investigate electrochromic properties of WO_3 thin films prepared by a simple chemical bath deposition method [24] and their possible application for solar light modulation.

Experimental

Tungsten oxide films were deposited onto fluorine doped tin oxide (FTO) coated glass substrates commercially available with transparency of about 80 % for visible light, and sheet resistance of about $10 - 20 \Omega \square^{-1}$. Before the deposition, the substrates were immersed in acetone and ethanol to be degreased in an ultrasonic bath, and then rinsed in deionized water and dried in air. WO_3 films were deposited from a chemical bath with optimized composition and process conditions.

The bath solution was prepared by dissolving 1.65 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 90 ml deionized water. The substrates were immersed in the beaker filled with deposition solution, and vertically supported against its walls. Then, the whole system was heated slowly, up to 95°C with continuous stirring. The preparation of the bath solution and the deposition of the thin films have been explained in details in Ref. [24]. The thickness of the films depends on the deposition time. In this work the deposition time was 20 min, and the thickness of the films was 150 nm.

The electrochemical properties of WO₃ films were characterized by cyclic voltammetry measurements performed using Micro AUTOLAB II equipment (Eco-Chemie, Utrecht, Netherlands) in one compartment three electrodes electrochemical cell with WO₃ film as working, platinum wire as counter, and saturated calomel electrode (SCE) as a reference electrode. The cycling was carried out in 1 mol dm⁻³ KCl aqueous solution as an electrolyte. The voltage scan rate was 10 mV s⁻¹, and the film working area was 1 cm².

Electrochromic investigations were performed *in situ* in an electrochromic device (ECD) consisted of: home-built glass cell (4 × 2.5 × 4 cm), WO₃ film deposited on FTO substrate as working electrode (WE), blank FTO substrate as counter electrode (CE), and 1 mol dm⁻³ KCl aqueous solution as an electrolyte. The distance between the electrodes was about 1.5 cm, the volume of the electrolyte was about 20 ml, and the active surface area of the electrodes was approximately 6 cm².

The optical transmittance spectra were recorded by using Varian CARY 50 Scan UV-Visible spectrophotometer in the wavelength range from 300 to 900 nm, in both, the completely colored and bleached states of the film. An electrochromic cell with two clean FTO substrates filled with electrolyte was measured as 100 % background. Coloration and bleaching of the film were performed with -2.5 V and +2.5 V respectively. Spectra were recorded 3 min after the voltage was applied. In order to obtain intermediate states of coloration, the film was also colored with coloration potentials of -1.5 V and -2 V.

The visible transmission spectra were used for evaluation of the optical band gaps E_g of the WO₃. For that purpose, the absorption coefficient (α) was evaluated from the transmittance data (T) and the film thickness (t), using the equation [25]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (1)$$

The optical band gaps of the film were evaluated from the absorption coefficient by fitting the data to the relation [26 - 28]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where, A is a constant, $h\nu$ is the energy of the incident photon, E_g is the optical energy gap, and n is a number which determines the type of electron transition causing the absorption. The value of n is 1/2 for direct allowed, 3/2 for direct forbidden, 2 for indirect allowed, and 3 for indirect forbidden transitions.

The coloration efficiency (η) of the WO₃ was calculated from the optical density change (ΔOD) at a wavelength of 700 nm, and the charge density ($\Delta Q/S$) during coloration after the films were fully bleached:

$$\eta = \frac{S \log(T_b/T_c)}{\Delta Q} \quad (3)$$

where T_b and T_c are the transmittance of the fully bleached and colored states respectively, ΔQ is the injected charge, determined by the applied current and the time of its application, and S is the active area of the electrochromic film.

The time needed for the electrochromic film to reach some fraction (usually above 70 %) of its maximum colored or bleached state (response time, τ) was examined as a change in the transmittance at 700 nm due to abrupt voltage change between +2.5 V and -2.5 V.

For an electrochromic material to be practically successful, it must have the ability to switch between its bleached and colored states frequently, whilst maintaining other important features

consistently. Cycle life is defined as the number of cycles completed before the material fails, and measures material stability. The cycling behavior of chemically deposited WO_3 films during electrochromic switching was directly observed spectroscopically by the *in situ* measurements of the transmittance at 700 nm of the fully bleached and colored states of the film after some number of cycles. The cycling was performed by alternatively applying potential of ± 2.5 V.

The ability to switch between two states (bleached and colored) in a relatively short response time makes the tungsten oxide films a possible candidate for transmittance modulation device. Taking the solar irradiance spectrum AM1.5 for a normal incident illumination on tungsten oxide based electrochromic device (ECD = glass/FTO/ WO_3 /electrolyte/FTO/glass) and the absorption coefficient spectra of the WO_3 film in its bleached and colored states, the output integral of the spectral intensity and the integral of the spectral modulation could be calculated [29].

Results and discussion

The WO_3 films investigated in this work exhibited good electrochromic behavior. They could be repeatedly colored and bleached by alternative application of a negative and positive potential respectively, versus a counter electrode. WO_3 is cathodically coloring material which means that it possesses a reduced colored state. It is transparent in oxidized state (positive potential), and has a deep blue color in reduced state (negative potential). The X-ray diffraction (XRD) analysis showed that the films were crystalline [24].

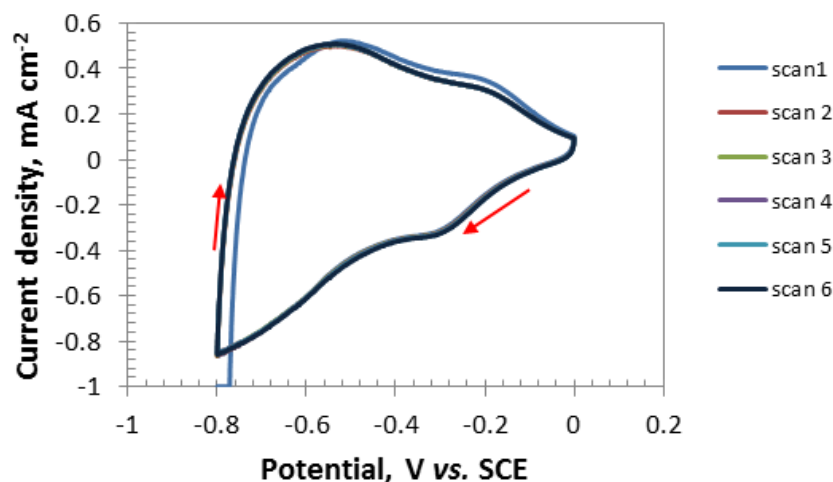


Figure 1. Cyclic voltammetric curves (six cycles) of chemically deposited WO_3 thin film. Arrows indicate direction of the potential scan.

The electrochromic behavior of the films was examined by cycling voltammetry. The cyclic voltammetric (CV) curves were obtained by sweeping the potential in the range of -0.8 V to 0 V vs. SCE at scanning rate of a 10 mV s^{-1} . In Fig. 1 are presented six CV curves of the WO_3 thin film. As can be seen all CV curves (except the first one) have a same shape, which means that the films exhibited good stability. The CV curves also showed an increase of the cathodic current density to -0.86 mA cm^{-2} at -0.8 V, due to the reduction process occurring in the film and its switching to the blue color, whereas the anodic peak is observed at around -0.541 V due to the oxidation process and bleaching of the film. The coloring process is followed by reduction of W^{VI} ions and double injection of potassium ions and electrons, and the bleaching process is followed by oxidation of W^{V} ions and double extraction of potassium ions and electrons. The following equation can express the coloring/bleaching process:



It was observed [30] that during the coloration process, the XRD peaks change in the position and in the intensities indicating a structural transition associated with intercalation of ions. When the ions were deintercalated by applying reverse potential, the crystalline structure reverts to the initial lattice. However, this phenomenon remains to be studied in our future research.

The optical transmittance of the films was recorded to understand the type of electron transition and it was used to evaluate optical energy gap. By analyzing the optical transmission spectra, it is also possible to determine whether the optically induced transition is direct or indirect, and allowed or forbidden.

The optical transmission spectra of the WO_3 film in the wavelength range from 350 to 900 nm in both, bleached and colored states, taken *in situ*, are presented in Fig. 2. One can see significant transmittance difference (more than 60%) that occurs in the red region of the visible spectrum with tendency to continue in the near infrared (NIR) region.

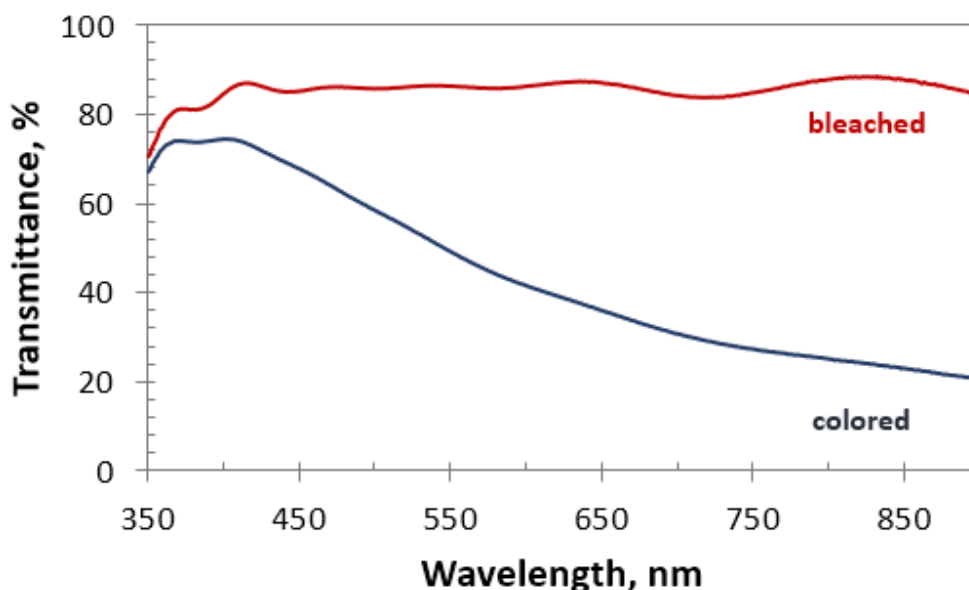


Figure 2. In-situ visible transmittance spectra of chemically deposited WO_3 thin film in the bleached and colored states.

Fig. 3 shows the optical transmittance of the ECD constructed by using chemically deposited WO_3 film in its bleached and colored states for an applied bleaching potential of +2.5 V and coloring potentials of -1.5 V, -2 V, and -2.5 V. The recorded transmission spectra for the device in the bleached state for positive potentials lower than +2.5 V are indistinguishable from the spectrum of the device bleached at +2.5 V, and hence are not shown. Also, no difference was observed when negative potentials higher than -1.5 V were applied. The film started to change its color at -1.5 V, and one can see that the spectra recorded at -1.5 V, -2 V and -2.5 V are distinguishable from each other, and from the spectrum of the bleached state of the film. No significant difference was observed between the spectra recorded at coloration potentials of -2.5 and -3 V, which means that the film is wholly reduced at -2.5 V. Actual photographs of the device in the bleached (+2.5 V) and colored (-1.5 V, -2 V, and -2.5 V) states are presented in Fig. 4. From these photographs one could clearly notice the different shades of blue obtained by different coloring potentials.

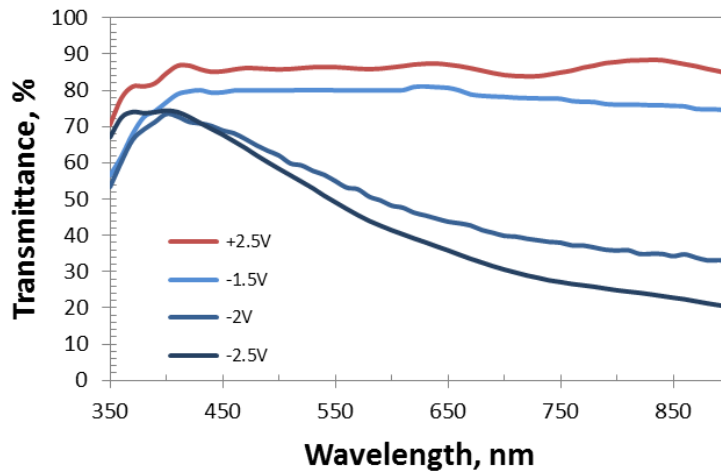


Figure 3. In-situ visible transmittance spectra of chemically deposited WO_3 thin film bleached at +2.5 V and colored -1.5 V, -2 V, and -2.5V.



Figure 4. Photographs of ECD **A:** bleached at +2.5 V, **B:** colored at -1.5 V, **C:** -2 V and **D:** -2.5 V.

The optical energy gaps of the films were evaluated utilizing the transmittance data and the equations (1) and (2). The plots of $(\alpha h\nu)^2$ versus $h\nu$ for the chemically deposited WO_3 thin film in both, bleached and colored states, are shown in Fig. 5. The film showed a better fit for $n = 0.5$ which shows the direct electron transition mechanism in both states (bleached and colored) of chemically deposited WO_3 films. The energy gaps were calculated from the linear parts in Fig. 3 as intercepts with the photon energy axis. The evaluated band gaps for the film in its bleached and colored states were 3.38 eV and 3.32 eV respectively. These values are in good agreement with the reported values on tungsten oxide thin films [31].

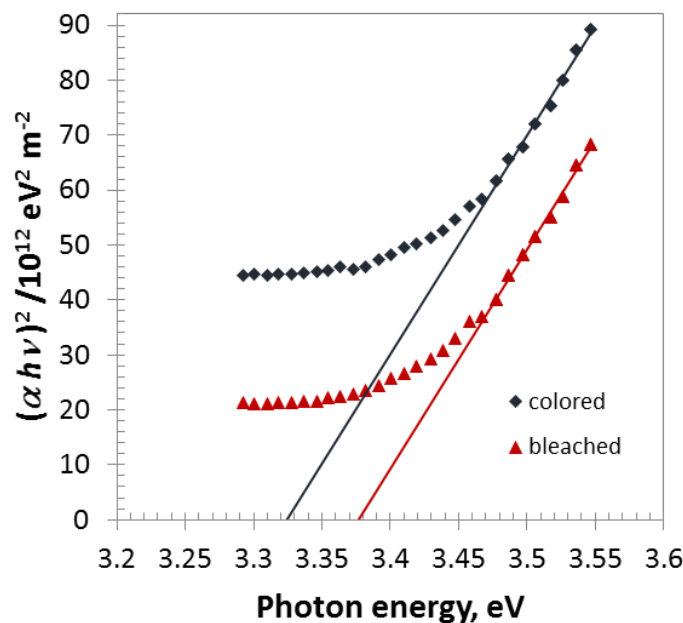


Figure 5. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ for WO_3 thin films prepared by chemical bath deposition.

To investigate in more detail the optoelectrochemical properties of the chemically deposited WO_3 thin films, the optical density change (ΔOD) was plotted against the charge density change ($\Delta Q/S$), and displayed in Fig. 6. The coloration efficiency η at 700 nm was extracted as the slope of the line fitted to the linear region of the curve. The calculated η value was found to be $22.11 \text{ cm}^2 \text{ C}^{-1}$. The η value obtained in this work is higher when compared to the values obtained for electrodeposited and sol-gel coated WO_3 thin films [32-35], but lower compared to the values obtained for the sputtered WO_3 [36].

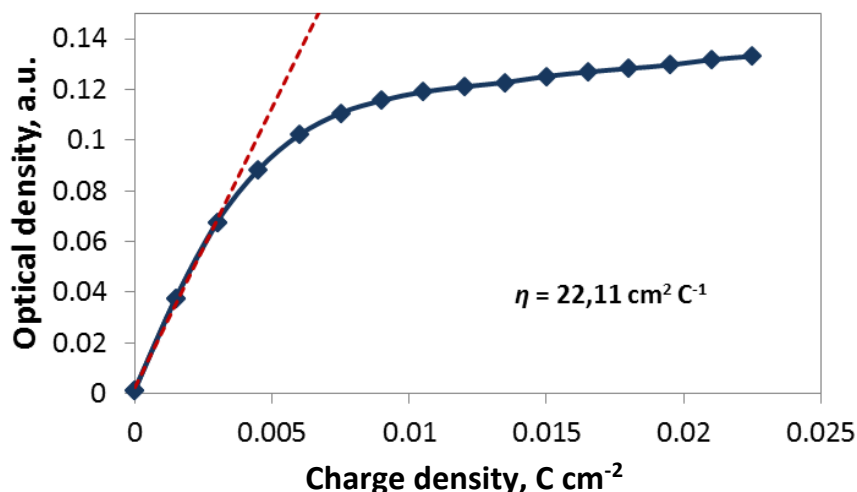


Figure 6. Optical density variation with respect to the charge density measured at 700 nm

In order to investigate the transition response time between coloration and bleaching, the transmittance was measured *in-situ* through the ECD. The applied potential was switched between 2.5 V (transparent state) and -2.5 V (blue state). Fig. 7 shows the dynamic coloration/bleaching characteristics of the ECD, recorded at the wavelength of 700 nm. The coloration and bleaching times (τ_c and τ_b), defined as time required for achieving 70 % of the total transmission change [37, 38] was found to be 9.3 s and 1.2 s respectively, which means that the coloring kinetics is slower than the bleaching one. The faster bleaching time is due to the good conductivity of the tungsten bronze (K_xWO_3) and the conductor (K_xWO_3) to semiconductor (WO_3) transition. On the other hand, the slower coloration time is due to the higher resistance during WO_3 to K_xWO_3 transition [39].

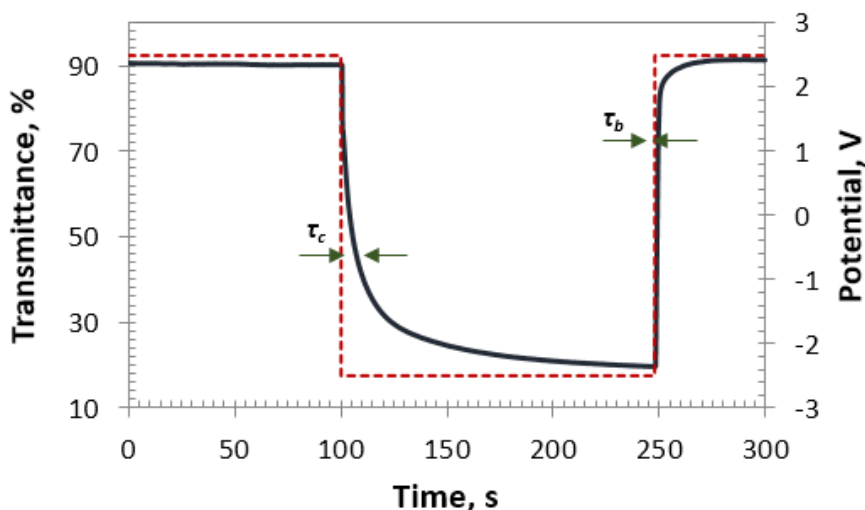


Figure 7. Switching time characteristics (at 700 nm) between the colored and bleached states for ECD, measured at ± 2.5 V.

Fig. 8 shows the transmittance at 700 nm of the ECD in the bleached and colored states up to 10000 color-bleach cycles. As can be seen from Fig. 8, the transmittance shows insignificant variations which means that the electrochemically deposited WO₃ films are stable and could be electrochemically switched for 10⁴ cycles without serious deterioration. Unfortunately, after the 10⁴ cycles the optical transmittance change rapidly decreased, so we could say that the device durability is up to 10⁴ cycles of bleaching and coloring.

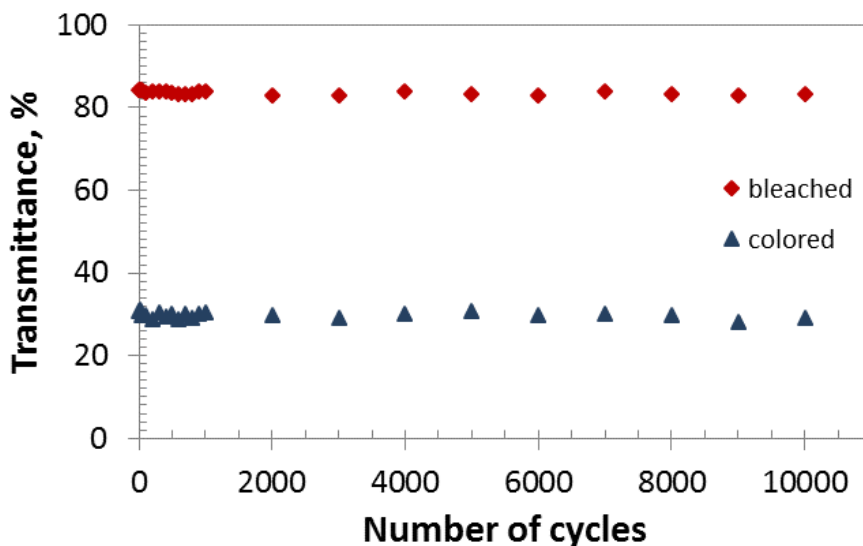


Figure 8. In-situ transmittance (at 700 nm) of chemically deposited WO₃ thin film in the bleached and colored states vs. number of cycles.

Finally, the irradiance of the solar spectrum AM 1.5 [40] and the absorption coefficient spectra (calculated from the transmittance spectra) of the chemically deposited WO₃ films in their bleached and colored states (Fig. 9), were taken as input parameters. The output spectral intensities transmitted across the WO₃ films were calculated and presented in Fig. 10. The results of the numerical integration for the spectral intensity within the visible region (350 – 900 nm) are presented in Table 1.

Table 1. Integral transmitted intensity from 350 to 900 nm (*I_t*) through the WO₃ films in their bleached and colored states.

| State | <i>I_t</i> / W m ⁻² |
|----------|--|
| Bleached | 506 |
| Colored | 253 |

The relative change of the integrated intensity (the visible transmitted intensity and the light modulation) could be calculated by the equation:

$$\text{Modulation} \approx \frac{I_t(\text{bleached}) - I_t(\text{colored})}{I_t(\text{bleached})} \tag{5}$$

Using the results from the Table 1 and the equation (5), the integrated intensity modulation of about 50 % was achieved, which is considerable value that gives the opportunity for implementation of the chemically deposited WO₃ films in electrochromic devices such as electrochromic windows.

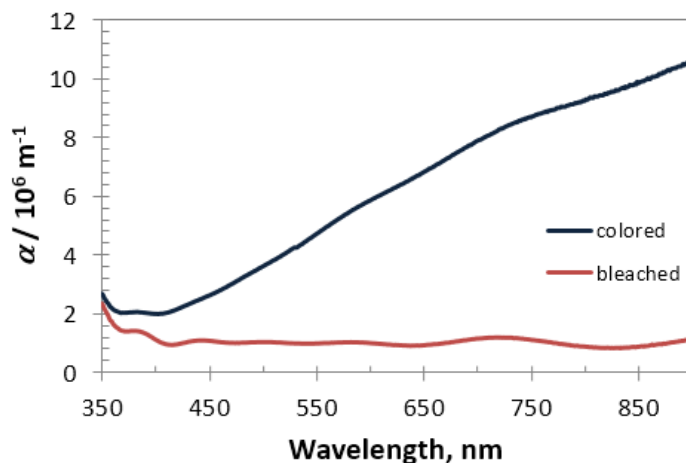


Figure 9. Absorption coefficient spectra of the chemically deposited WO_3 film in the bleached and colored states.

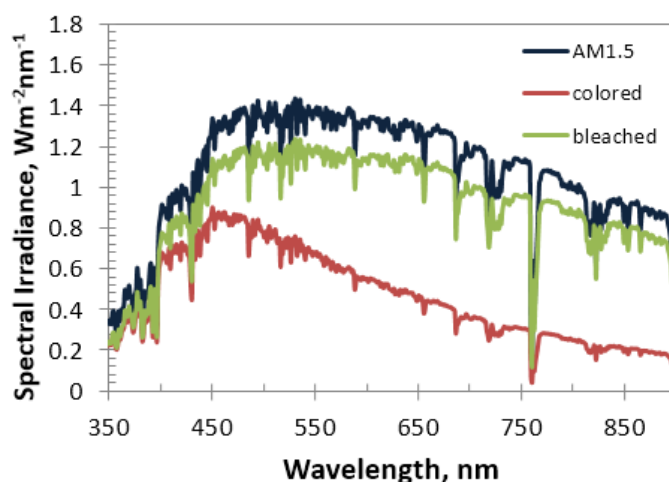


Figure 10. Spectral intensity of the transmitted AM 1.5 solar irradiance spectrum through the WO_3 film in bleached and colored states

Conclusions

Tungsten oxide thin films investigated in this work were deposited onto FTO coated glass substrates by chemical bath deposition method. The method is simple, economical, and has benefit of being easily realizable from the point of view of industrialization, especially on large area devices, with the required electrochromic properties. The obtained films exhibited good electrochromic properties. They were stable and exhibited excellent reversibility, with color changed from originally colorless into deep blue when negative potential was applied, and back to colorless when the potential was reversed. Transmittance difference of more than 60 % was achieved in the red region of the visible spectrum. Also, by controlling the coloring potential, intermediate states of coloration were achieved. Optical energy gaps were evaluated from the transmittance measurements for the both, bleached and colored states of the films, assuming a direct semiconductor transition mechanism. The coloration efficiency (at 700 nm) was found to be $22.11 \text{ cm}^2\text{C}^{-1}$, the value higher compared with those obtained for electrodeposited and sol-gel coated WO_3 thin films, but lower compared to the values obtained for sputtered WO_3 thin films. The switching times between transparent and blue states of the WO_3 thin film were found to be 9.3 s for coloring, and 1.2 for bleaching. The maximum light intensity modulation ability of the films, as the AM 1.5 spectrum is taken for an input, was calculated to be about 50 % which is considerable value which makes chemically deposited tungsten oxide thin films suitable for application in electrochromic devices.

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