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Research note

The optical and electrochromic properties of tungsten oxide thin layer: the effect of deposition time

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Abstract

Tungsten oxide (WO_3) thin layers were prepared on Fluorine Tin Oxide glass using the electrodeposition method. WO_3 layers were evaluated as a function of the deposition time (480 s, 600 s, 660 s and 720 s). SEM results showed that by increasing the deposition time, a gradual decrement in cracks on their surface occurred. The electrochromic properties of the WO_3 thin layers were investigated in a nonaqueous $LiClO_4$–PC electrolyte by means of optical transmittance, cyclic voltammogram (CV) measurements. The WO_3 thin layer with the deposition of time 600 s exhibited a noticeable electrochromic performance with the variation of transmittance being up to 58.26% at 633nm. The CV measurements also revealed that the WO_3 thin layer with the deposition time of 600 s had a high electrochemical reaction activity and reversibility due to its highly porous structure.

Keywords: tungsten oxide, electrochromic properties, electrodeposition, cyclic voltammogram

1. Introduction

Electrochromic (EC) materials modulate their optical properties depending on charge (electrons and ions) insertion /extraction in the EC materials [1,2]. The optical modulation of EC materials in the visible and infrared regions has received much attention since 1980, both in the science and industry. Tungsten oxide (WO_3) is one of the most promising materials for the spacecraft thermal control or the military camouflage against IR sensors due to its chemical stability and UV radiation resistance[3]. EC device is comprised of an EC active layer, an electrolyte, and an ion storage layer. EC active layer is an active layer inserting or extracting ions, resulting in the coloration and bleaching. WO_3 is an EC material which has been widely investigated as an active EC electrode (working electrode). Ions like H^+ or Li^+ in the electrolyte are intercalated into the WO_3 thin layer to reduce WO_3 to M_xWO_3, a blue colored state, when a negative electric field is applied. Under positive electrical field, i. e., oxidation state, the reduced M_xWO_3 is oxidized and returned to the WO_3 original form, which is as follows [4, 5].

$$\underset{\text{Clear}}{WO_3 + xLi^+ + xe} \rightleftharpoons \underset{\text{Dark blue}}{Li_xWO_3}\ , \tag{1}$$

EC devices can be used for transmittance modulation, reflectance, thermal emittance and scattering, thus opening new venues for applications in optical technology, including smart windows for energy efficient building [6]. The advantages of EC materials include their open circuit memory, high coloration efficiency and low electric power [7]. WO_3 thin layers have been synthe sized using several methods such as sol–gel [8], electrodeposition synthesis [9, 10], template method [11], anodic oxidation [12], chemical vapor deposition [13], electro spinning [14], electron beam evaporation [15], hydrothermal oxidation [16], atmospheric pressure plasma jet [17], etc. In this work, electrodeposition method was employed to prepare WO_3 thin layers with high porous and high surfaces. Our aim was to investigate the EC properties of electrodeposited WO_3 thin layers as a function of the deposition time (480 s, 600 s, 660 s, 720 s) in order to study the morphology of these thin layers, as well as their optical and electrochemical properties.

2. Experimental details

2.1. Deposition of the WO_3 thin layer

To prepare the peroxotungstic acid solution, 3.25 gr of tungsten metal powder (99% pure) was dissolved in 20 ml 30% H_2O_2 (Qualigens) and 2 ml distilled water to obtain a clear solution. This solvent was kept at a low temperature (2°C) for 8 days. The solution was then mixed with the same amount of anhydrous ethanol at room temperature under continuous

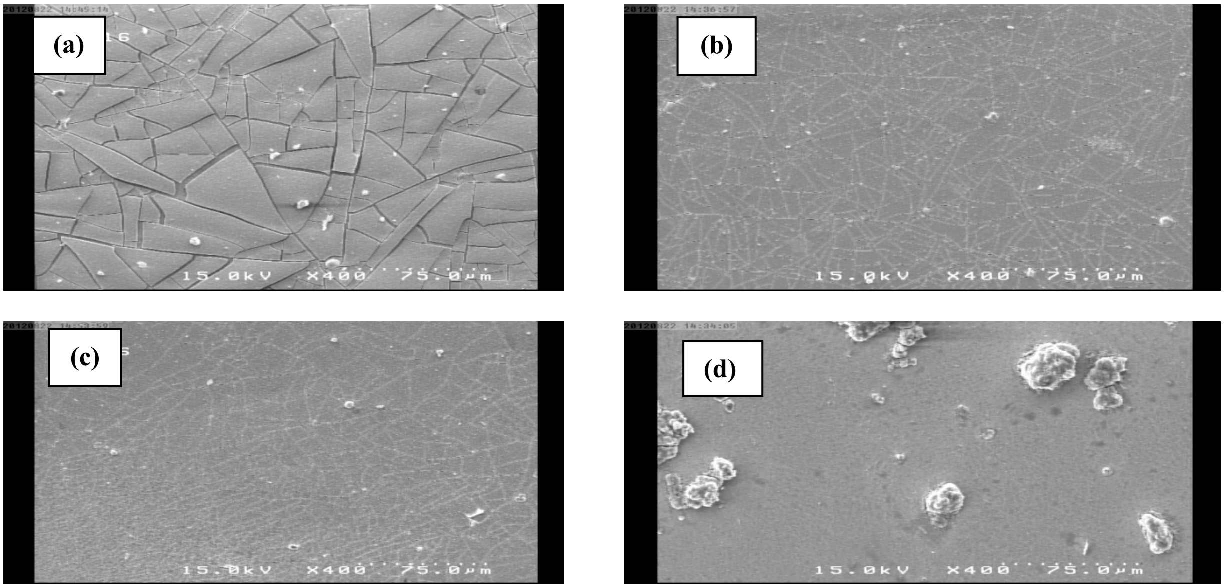

Figure 1. SEM images of WO_3 thin layers with different deposition times (a) 480 s, (b) 600 s, (c) 660 s and (d) 720 s.

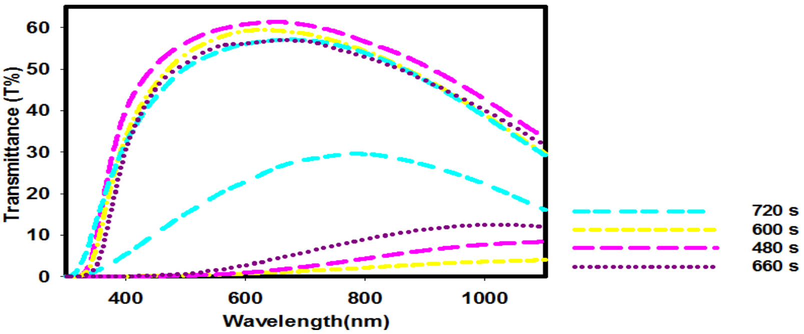

Figure 2. (color online) Optical transmittance spectra of the WO_3 thin layer with different deposition times in the colored and bleached states within the $300 \leq \lambda \leq 1100$ nm range.

stirring. The liquid was heated to 60°C for 30 min before deposition. The solution was then changed to a bright yellow liquid.

The layers were deposited under potentiostatic conditions in a three-electrode electrochemical cell with a fluorine thin oxide (FTO) coated on the glass substrate with the dimensions 2.5×2.5 cm^2 as the working electrode, a Saturated Calomel Electrode (SCE) as the reference electrode, and a platinum sheet serving as the counter electrode. The working electrode was subjected to a constant cathodic potential of -493 mV for different times (480 s, 600 s, 660 s, 720 s) at the room temperature.

3. Deposition of the NiO thin layer

NiO thin layer was prepared using the Chemical Bath Deposition (CBD) method. The solution for CBD was obtained by mixing 40 ml of 1 M nickel sulfate, 30 ml of 0.25 M potassium persulfate and 10 ml of aqueous ammonia at the room temperature. FTO coated on glass substrates was masked with a polyimide tape to prevent deposition on the nonconductive sides. The FTO samples were placed in the freshly made solution and kept at 20°C for 60 min to deposit the precursor layer under constant stirring. Then they were washed with deionized water. After removing the tape masks, the coated samples were dried at 75°C and annealed at the temperature of 300°C in air for 1.5 h.

The surface morphology was observed by field emission scanning electron microscopy (FESEM; Hitachi S-4160). To measure the layers optical transmittance the UV spectrum was performed using a UV-1800 PC Shimadzu spectrophotometer. Transmission spectra were recorded for the colored and bleached thin layers in the 300-1100 nm wavelength range with respect to air. The Cyclic Voltammogram (CV) was used to measure the EC properties of the thin layers. The measurements were performed in a three-electrode electrochemical cell between -1.5 and +1.5 V, where a WO_3 thin layer was deposited on the FTO coated glass substrate was used as the working electrode. SCE was selected as the reference electrode and the Pt foil was used as the auxiliary electrode. In this research, lithium perchlorate in propylene carbonate with the 1M density (1M $LiClO_4$-PC) was used as an electrolyte solution with the scan rates of 50 mv/s (BEHPAJOOH, BHP2063+).

4. Results and discussion

4.1. Surface morphology of the layers

Figure 1. depicts the SEM micrograph of the surface of layers deposited with different deposition times (480 s, 600 s, 660 s, 720 s). The surfaces of the layers were fairly uniform with only a few large aggregates of WO_3 particles on them. SEM results showed that by increasing the deposition times, a gradual decrease in the cracks appeared and there was an increase in the aggregates of WO_3 particles on their surface. Therefore, the layer deposited with time 480 s, in contrast to the layers deposited for longer times, showed a better open structure.

5. Optical properties of the layers

Figure 2. shows the optical transmittance spectra within the

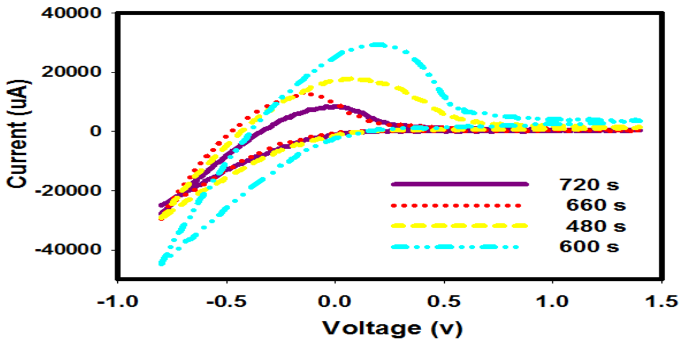

Figure 3. (color online) Cyclic voltamogram for WO_3 thin layers with different deposition times.

Table 1. Transmittance modulation for the WO_3 thin layers with different deposition times in the 633 nm wavelength.

Deposition time (s)	480	600	660	720
Transmittance modulation (%)	59.81	58.26	53.09	32.86

$300 \le \lambda \le 1100$ nm wavelength range for the WO_3 thin layers with different deposition times at the 10th cycle, in the colored and bleached states. Transmittance modulation is summarized in table 1 for the WO_3 thin layers with different deposition times.

Table 1. reveals that the highest value of transmittance modulation was 59.81% and 58.26% for thin layers with the deposition time of 480 s and 600 s, respectively; this was lower for the layers with other deposition times. It is usual for a structure with more cracks to allow better penetration of lithium ions. The visible transmittance of the layer with the deposition time of 480 s was ~62.4%, which was dropped to ~50% in the solar region due to an increase in the reflectance from the underlying the FTO substrate near the infrared region. This value was higher than the reported ΔT values for WO_3 thin layers deposited by cathodic electrodeposited using a peroxytungstate deposition bath of the $Na_2WO_4{\cdot}2H_2O$ salt (that was a complex in distilled water with concentrated hydrogen peroxide added), exhibiting a ΔT =58.7% at λ=700 nm [18]. The high transmittance (T~63%) in the visible range was retained for WO_3 thin layers deposited by sol-gel and it was dropped to ~42-44% in the solar region due to an increase in the reflectance from the underlying FTO substrate near the infrared region [19]. Electrochemical measurements on WO_3 thermal evaporation layers of tungsten trioxide powder exhibited a ΔT_{vis} = 34.5% [20].

6. Electrochromic performance of the layers

Figure 3. shows CV for different WO_3 thin layers with different deposition times (480 s, 600 s, 660 s, 720 s). All data presented here were obtained with the same sweep rate of 50 mV/s after 9 consecutive coloration-bleaching cycles using the electrolyte solution 1 M $LiClO_4$-PC.The coloration current, an indicator of the speed of Li^+ intercalation in the thin layers, was higher with the lowest negative values on the CV plots. From this Figureure, it was apparent that the highest value of the coloration current was achieved for the layers deposited with the deposition time of 600 s; this was because the most aggregations were on the surface of deposited layer.

WO_3 thin layer with the deposition time of 480 s yielded a lower coloration current because this layer had few aggregates on its surface. The highly porous structure o the f layer when deposited with the deposition time of 600 s facilitated electrolyte penetration into the particles and shortened the ions diffusion path within the bulk of tungsten oxide. Meanwhile, the intercrossing network could provide many paths for the double injection/extraction of ions and electrons to/ from the layer. All these contributed to the improvement of the optical and EC performance. These properties could make the layer with the deposition time of 600 s an interesting option in making efficient EC windows. On the other hand, figure 3 also shows that the area of the CV was decreased when the deposition time was increased. The decrease of the CV area could be attributed to the reduction and narrowing of the cracks observed in the SEM images (Figure 1), hence reducing the ion mobility. Both reduction and oxidation peaks of the layer with the deposition time 600 s were stronger than those of the other layers. Therefore, the layer with the deposition time of 600 s had a higher insertion/extraction capacity for electrons and ions.

The EC performance mostly depends on two parameters: the coloration efficiency (CE) and the change in optical density (ΔOD). CE is calculated by ΔOD charges intercalated per unit electrode area. ΔOD and CE were calculated using the following relations:

$$\Delta OD(\lambda)=\mathrm{Log}\left[T_{bleached}(\lambda)/T_{colored}(\lambda)\right] \tag{2}$$

$$CE(\lambda)=\Delta OD(\lambda)/Q \tag{3}$$

, where $T_{bleached}$ and $T_{colored}$ are the transmittance in the bleached and colored states, respectively. Q is the intercalated charge density, which corresponds to the ratio of the inserted charge over the device area.

Figure 4 shows the precise comparison of CE in the WO_3 thin layers with different deposition times. WO_3 thin layer with the deposition time of 600 s showed a higher CE in the visible region, as compared to other layers; however, it presented a lower CE in the near infrared wavelengths. The high value of CE indicated that the EC thin layer exhibited large optical modulation with a small charge inserted or extracted. The high CE observed for the 480 s layer in Figure4 could be attributed to the large cracks of the WO_3 layer, which provided more surface area and direct paths for the process of Li^+ intercalation or de-intercalation.

CE decreased as a function of wavelength and acquired the minimum values of $CE_{VIS} = 98.4\ cm^2\ C^{-1}$ and $CE_{\mathbf{NIR}} = 79.3\ cm^2\ C^{-1}$ for the WO_3 thin layer with the deposition time of 600 s. The relatively high W^{5+} content in this layer could be responsible for its large EC efficiency. This value ($CE_{VIS} = 98.4\ cm^2\ C^{-1}$) was higher than the reported CE values for the WO_3 thin layers deposited by cathodic electrodeposition, such as A.J. MOREet al (CE~87.95 cm^2C^{-1}) [21],T. Pauporte et al (CE=62-66 cm^2C^{-1})[22], and M Deep *et al.* [23] (CE=70 cm^2C^{-1}).

It was obvious that the thin layer deposited with the time of 600 s offered the best changes for transmission modulation, absorption in the colored state, and coloration efficiency.

7. Conclusion

The WO_3 thin layers were successfully prepared by the electrodeposition technique. The CE of the layers was found to be considerable, making them suitable in the production of

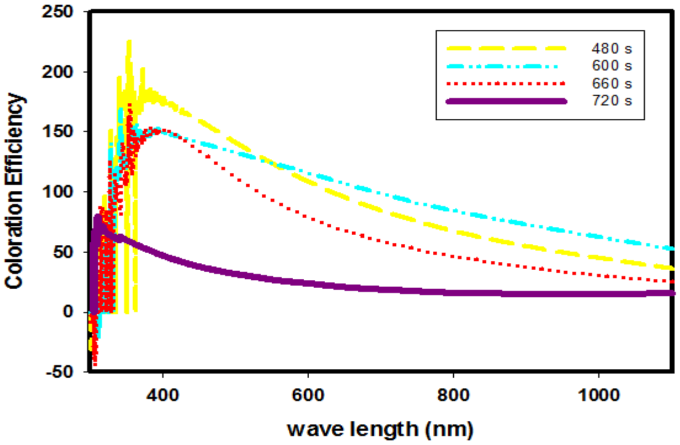

Figure 4. (color online) Coloration efficiencies of WO_3thin layers with the deposited times of 480 s, 600 s, 660 s and 720 s within the $300 \leq \lambda \leq 1100$ nm range.

WO_3 based on EC devices. The open structure of the layer with the deposition time 600 s showed high transmission modulation ($\Delta T \sim 58.26\%$) and coloration efficiency (CE =98.4 $cm^2\ C^{-1}$ at λ = 638 nm). The poor performance of the layers deposited with the time of 660 s and 720 s was related to the dense structure. Therefore, the electrochemical reversibility for the redox processes involving the insertion and extraction of lithium ions was attained only for the layer with the deposition time of 600 s. This layer also exhibited an excellent transmittance modulation effect in the visible region. The surface morphology of the layers was investigated. The results indicated that the layer with the deposition time of 600 s had remarkable reversible EC properties and its EC reversibility was also very good in the visible region.

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