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# Electrodeposition of nano-granular tungsten oxide thin films for smart window application

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ABSTRACT

Tungsten oxide ($WO_3$) thin films have been electrodeposited in a solution containing tungsten and ethanol–water. The structural, morphological and electrochromic properties of electrodeposited $WO_3$ thin film were studied. The results indicate that electrodeposited $WO_3$ thin film exhibited amorphous nature, closed packed nano-granular morphology, good coloration efficiency of 140.79 $cm^2/C$ and visible high transmittance of 94.63%.

## 1. Introduction

Recently the most promising electrochromic material for smart window application is tungsten oxide ($WO_3$) due to its highest transparency, good coloration efficiency and low response time [1]. $WO_3$ thin films have been prepared by various methods including vacuum evaporation [2], anodic oxidation [3], spray pyrolysis [4], sol–gel synthesis [5], sputtering [6], laser ablation [7] and electrodeposition [8]. As compared to the other methods an electrodeposition method is easy, cost effective and eco-friendly because it operates at low voltage, no need of vacuum, no wastage of chemicals and pollution free. The main advantage of electrodeposition method is that it can control the morphology as well as thickness of sample by applied potential. The most crucial parameters of the electrochromic materials are their optical modulation, response time and coloration efficiency. Electrodeposition of $WO_3$ is not always used since other techniques are better for producing the large areas device fabrication. However, one major benefit of electrodeposition is that preparative route is easy and more than one material can be electrodeposited simultaneously.

In this work, we report electrodeposition of $WO_3$ thin films synthesized by a dc electrodeposition (potentiodynamic) method. The preparative parameters were prudently optimized to obtain high quality $WO_3$ thin film.

## 2. Experimental details

100 ml of 0.5 M peroxotugnstic acid solution (PTA) is synthesized by reacting 9.192 g tungsten metal powder (99% pure, Sigma-Aldrich) with 100 ml of 30% hydrogen peroxide at room temperature. The predominant peroxytungstate in acidic solution is reported to be $W_2O_{11}^{2-}$ or $[(O)W(O_2)_2(O)(O_2)_2W(O)]^{2-}$, where $(O_2)$ denotes a peroxide ligand. Seven-coordination is completed by hydration. Note that W is in its usual $6^+$ state. The anion is formed according to

$$2W + 10H_2O_2 \rightarrow W_2O_{11}^{2-} + 2H^+ + 9H_2O \quad (1)$$

Peroxytungstates are thermodynamically unstable and decompose slowly. Reactions (2) and (3) describe two possible decomposition reactions, generating solid tungsten trioxide and polytungstate, respectively

$$W_2O_{11}^{2-} + 2H^+ \rightarrow 2WO_3 + 2O_2 + H_2O \quad (2)$$

$$6W_2O_{11}^{2-} + 6H^+ \rightarrow W_{12}O_{36}^{6-} + 12O_2 + 3H_2O \quad (3)$$

Fig. 1(a) shows the schematic diagram of the growth mechanism of electrodeposited $WO_3$ thin film. Step 1 and step 2 show tungsten metal powder and hydrogen peroxide respectively, step 3 shows that the tungsten metal powder is dissolved in hydrogen

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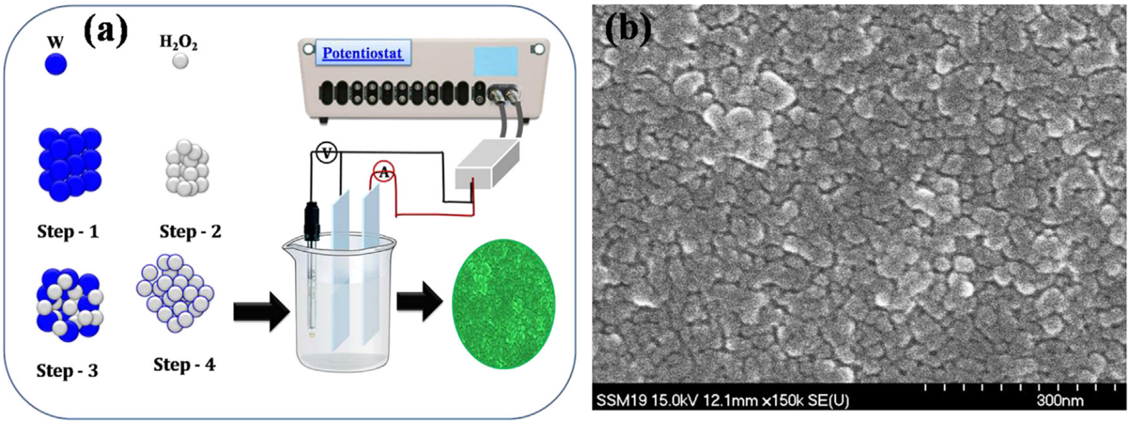

**Fig. 1.** (a) Growth mechanism of electrodeposited $WO_3$ thin film and (b) FE-SEM image of $WO_3$ thin film.

peroxide to form a PTA and in step 4, ethanol and water are added to PTA and reflux the solution 60 °C for 25 min to form a final yellow colored $WO_3$ sol. This final $WO_3$ sol is used for the potentiodynamic electrodeposition. The deposition was carried out by applying dc voltages in the range of ± 1 V at a scan rate of 50 mV $s^{-1}$ for 20 cycles at room temperature (25 °C). $WO_3$ thin film was deposited using three electrode systems, namely counter-electrode is platinum electrode, working electrode is ITO substrate and reference electrode is saturated calomel electrode. Cathodic electrodeposition is usually based on generation of a local high pH near the electrode surface which induces precipitation of metal ions present in solution. This route has been used extensively to deposit, for example, ZnO and $ZrO_2$. The reaction responsible for generation of $OH^-$ can be oxygen reduction, hydrogen evolution, or nitrate reduction. Early transition metal oxides such as $WO_3$, $MoO_3$ and $TiO_2$ can also be electrodeposited [9].

Structural studies of $WO_3$ thin film were carried out by a D2 phaser Bruker X-ray diffractometer ($\lambda = 1.54$ Å). Morphological analysis was investigated by field emission scanning electron microscopy (FESEM S-4700, Hitachi). Elemental analysis is carried out by VG Multilab 2000-Thermo Scientific, U.S.A., K-Alpha. The transmittance is carried out using a UV-1800 Model Shimadzu spectrophotometer. In situ transmittance was recorded using a He–Ne laser ($\lambda = 632.8$ nm), a Si photodiode and a storage oscilloscope.

## 3. Results and discussion

The FE-SEM image shown in Fig. 1(b) illustrates the top side view of $WO_3$ thin film. The FE-SEM image reveals that the $WO_3$ thin film is composed of close-packed nano-grains. The average diameter of nano-grains is about 30–40 nm to form a continuous thin film. Fig. 2(a) presents the X-ray diffraction (XRD) pattern of electrodeposited $WO_3$ film on ITO substrate. XRD pattern exhibits a broad hump in the low $2\theta$ region due to glass and peaks are matched with ITO (JCPDS card # 00-039-1058); there is a broad peak centered at 30°, in addition to the three sharp peaks of ITO glass at 35°, 50° and 59°. This broad peak indicates the amorphous structure of the electrodeposited $WO_3$ film. In general $WO_3$ films with amorphous background are suitable for electrochromic applications. A well crystallized structure is less favorable for ions to diffuse through because of the densely packed atomic structure and due to this lithium ion movement through the film is obstructed by the dense structure leading to a lower response time. X-ray diffraction patterns realized that the film allowed us to confirm that $WO_3$ thin film is amorphous. Fig. 2(b and c) illustrates the W (4f) and O (1s) XPS spectra of the $WO_3$ thin film. The analysis of electrodeposited $WO_3$ thin film indicates a perfect fit to the Voigt curve peaks, which corresponds to the $W^{6+}$ cation. The peak observed at 35.72 eV and 37.88 eV binding energies corresponds to the $W^{6+}$ state in the electrodeposited $WO_3$ thin film. The energy separation between the main peaks of W ($4f_{7/2}$) and W ($4f_{5/2}$) is 2.16 eV which corresponds to the tungsten in the $W^{6+}$ valence state and is also indicative of the nominal stoichiometry of the $WO_3$ thin film [10]. The O (1s) XPS spectrum of the $WO_3$ thin film shown in Fig. 2(c) was deconvoluted with the Voigt curve fitting function following the Shirley background subtraction. The result shows that the lower binding energy peak corresponding to the O (1s) core level of the $O^{2-}$ anions in the $WO_3$ thin film is located at 530.84 eV. This peak is related to the W$=$O chemical bonding. Also the peak at 532.14 eV indicates the presence of more hydroxide groups or water and/or C–O bond originates from the residual adsorbed molecules on the surface of electrodeposited $WO_3$ thin film. Overall these results confirm that the $WO_3$ is formed with some hydrated content. Fig. 2(d and e) shows the actual photograph of bleached and colored states of electrodeposited $WO_3$ thin film respectively. The cyclic voltammetry (CV) technique is employed to investigate the cathodic/anodic behavior of $WO_3$ films. The CV was recorded at a scan rate of 50 mV $s^{-1}$ in 0.5 M $LiClO_4$ +PC electrolyte between the sweep potential ranges from +1.0 to −1.0 V, as shown in Fig. 3(a). The shape of the curve is typical of redox reactions in $WO_3$ thin film, causing coloration and bleaching. It is observed that the cathodic current density of the $WO_3$ thin film was 0.1 mA $cm^{-2}$,when the potential swept from +1.0 to −1.0 V and achieved a value as high as 2.5 mA $cm^{-2}$ as the potential reached to −1.0 V showing deep blue coloration. This progressive increase in the cathodic current density indicates the reduction of the $W^{6+}$ ionic state to the $W^{5+}$ state due to intercalation of $Li^+$ ions towards extreme cathodic potentials as a result of

$\{WO_3 + Li^+ + e^- \rightarrow Li_xWO_3\}$ intervalence charge transfer (IVCT) reaction and eventually responsible for blue coloration. Upon anodic polarization (+1.0 V), oxidation of $WO_3$ takes place with simultaneous deintercalation of $Li^+$ ions and $e^-$ from the film to acquire a transparent (bleached) state as a result of $\{Li_xWO_3 \rightarrow WO_3 + Li^+ + e^-\}$ reaction. It is well known that the area under the curve is directly related to the amount of charge intercalated in the film. Fig. 3(b) displays the switching response characteristics of the electrochromic $WO_3$ thin film. The switching responses, including the coloration ($t_c$) and bleaching ($t_b$) times, are very crucial to the performance of the electrochromic devices. Shorter switching responses represent better performance in the electrochromic devices. The switching response is determined as