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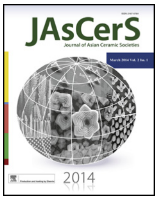

# Electrochromic response of $WO_3$ and $WO_3$-$TiO_2$ thin films prepared from water-soluble precursors and a block copolymer template

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ABSTRACT

Electrochromic tungsten trioxide ($WO_3$) thin films are attracting renewed attention as transmittance-controllable windows for use in automobile, aircraft, and building applications. In order to achieve high electrochromic performance, high cycle stability, and high reliability, the microstructure and compositional homogeneity of $WO_3$ thin films have to be optimized. In this study, non-doped $WO_3$ and $TiO_2$-doped $WO_3$ thin films were fabricated from water-soluble precursors of tungsten and titanium, and their electrochromic response was investigated. Amorphous $WO_3$ and $TiO_2$-doped $WO_3$ thin films were fabricated by calcining the spin-coated films at 573 K. The use of a PEO-PPO-PEO block copolymer as a porogen facilitated the redox reactions occurring on the thin film/electrolyte interface. Although the effect of $TiO_2$-doping on the cycle stability of $WO_3$ thin films has not been fully elucidated, this study demonstrated that $TiO_2$ doping up to 15 mol% effectively enhanced the cycle stability.

## 1. Introduction

Tungsten trioxide ($WO_3$) thin films are potential candidates for use in photochromic devices [1], chemical sensors [2,3], supercapacitors [4], photocatalysts [5], and electrochromic devices [6]. A recent review article [7] describes many practical and potential applications of $WO_3$ thin films. Electrochromic devices comprising $WO_3$ thin films have recently attracted renewed attention since they are promising candidates for transmission-controllable windows, i.e., smart windows, which are mounted in modern automobiles, aircrafts, and buildings.

Electrochromism and aforementioned characteristics of $WO_3$ are a result of the redox reactions between $W^{6+}$ and $W^{5+}$ ions at the $WO_3$/electrolyte interface, as expressed by Eq. (1)

$$WO_3 + xe^- + xM^+ \leftrightarrow M_xWO_3 \tag{1}$$

where $M^+$ represents a monovalent cation such as $H^+$, $Li^+$, or $Na^+$. For greater contrast and faster response of an electrochromic $WO_3$ thin film, reaction (1) needs to proceed at higher rates. Hence, the microstructure of $WO_3$ thin films has to be optimized to enable faster reaction rates. Among a large variety of methods for fabricating $WO_3$ thin films including sol–gel [6,8], electrodeposition [9], sputtering [10], hydrothermal [11], and chemical vapor deposition (CVD) [1], liquid-phase deposition of $WO_3$ from alcoholic [12–14] or aqueous solutions [15,16] seems to be advantageous because it is possible and easy to fabricate porous thin films with micro- or macrosized pores. Highly porous $WO_3$ thin films have a large surface area for reaction (1) to proceed, implying that they can show a fast electrochromic response and deep contrast in the coloration/bleaching cycles. The most widely used porogens have been polymers such as poly(ethyleneglycol) (PEG) and block copolymers, leading to porous $WO_3$ thin films with enhanced electrochromic response [12–14,17,18].

Another aspect to be considered for $WO_3$ thin films is the lifetime or cycle stability. The degradation of the electrochromism of $WO_3$ thin films upon repeated coloration/bleaching cycles has been attributed to the crystallization of $WO_3$ and/or $LiWO_3$. $TiO_2$ doping has long been known to improve the cycle stability of $WO_3$ thin films [19], believed to occur because the incorporation of $TiO_2$ hinders the rearrangement of $[WO_6]$ octahedra for crystallization. However, as far as the thin films prepared by liquid-phase deposition techniques are concerned, $TiO_2$ doping has not necessarily been successful. For example, Lin et al. [20] prepared $TiO_2$-$WO_3$ thin films from ethanol solutions of peroxotungstic acid (PTA) and titanium tetra-n-butoxide, $Ti(O\text{-}n\text{-}Bu)_4$, and reported that $TiO_2$ doping up to 22% elongated the lifetime of $WO_3$ but slowed the

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electrochromic response. Paipitak et al. [21] prepared $TiO_2$-$WO_3$ thin films from aqueous solutions of PTA and Ti(O-n-Bu)$_4$ and found that $TiO_2$ doping by more than 15% deteriorated the coloration/bleaching contrast. They did not assess the cycle stability. Zayim [22] reported that $TiO_2$ doping did not improve the cycle stability at all. Other studies on the preparation of $TiO_2$-$WO_3$ thin films by liquid-phase deposition did not evaluate the effect of $TiO_2$ doping on the cycle stability [23,24]. Therefore, the effect of $TiO_2$ doping has not been fully elucidated. In addition, the effect of $TiO_2$ doping should be strongly dependent on the process of thin film fabrication.

In this study, $WO_3$ and $WO_3$-$TiO_2$ thin films were prepared from water-soluble precursors of both oxides and a block copolymer as the porogen, and their electrochromic properties and cycle stability were evaluated by cyclic voltammetry and iterative chronoamperometry.

## 2. Experimental

Non-doped $WO_3$ thin films were prepared using PTA as the tungsten source and a PEO-PPO-PEO block copolymer (P123, BASF, Ludwigshafen, Germany) as the porogen. PTA was prepared by dissolving approximately 3.0 g of metallic tungsten powder (99.9%, Kojundo Chemical Laboratory, Saitama, Japan) in a mixture of 10 cm$^3$ of 35% $H_2O_2$ and 10 cm$^3$ of pure water at room temperature. The tungsten powder gradually dissolved in the diluted $H_2O_2$ evolving heat and bubbles to form a transparent, yellow solution. After cooling to room temperature, the supernatant solution was condensed in a rotary evaporator until it became a dry gel. The $WO_3$ content in the dry PTA gel was determined using a thermogravimetric analyzer (EVO-II, Rigaku, Tokyo, Japan). Typically, the $WO_3$ content in the PTA gel differed from batch to batch and ranged from 60 to 70 mass%.

P123 was dissolved in water to obtain a concentration of 10.0 mass%. The PTA gel was dissolved in the P123 solution so that the mass ratio of P123:$WO_3$ varied from 0:100 to 400:100. The formulation details of the coating solutions are shown in Table 1. The non-doped $WO_3$ thin films prepared from each solution (described later) are denoted as W($x$), where $x$ stands for the mass percentage of P123 with respect to that of $WO_3$, as shown in Table 1.

Glass slides coated with F-doped tin oxide (2 cm × 4 cm) were used as the substrates, which are denoted as FTO substrates. The coating solutions containing PTA and P123 were spin-coated onto the FTO substrates at 1000 rpm for 30 s. The coated substrates were dried at room temperature overnight, and then, calcined at 573 K for 12 h. The heating rate was 1 K/min. The calcination temperature was determined so that P123 was completely burnt off and $WO_3$ remained amorphous.

$TiO_2$-doped $WO_3$ thin films were prepared by substituting 10–40 mol% of $WO_3$ with $TiO_2$. For the preparation of $TiO_2$-doped $WO_3$ thin films, a water-soluble titanium lactate solution (TC-310, Matsumoto Fine Chemical Co., Ltd., Chiba, Japan), which contained 13.7 mass% $TiO_2$, was used as the titanium source. The coating solutions were prepared based on the formulation of the solution for W(100). Required amounts of PTA and TC-310 were dissolved in 1.0 cm$^3$ of the 10.0 mass% P123 solution so that the molar ratio of W:Ti could be varied from 90:10 to 60:40. The solutions were spin-coated on the FTO substrates and calcined in the same manner as the non-doped $WO_3$ films. The resultant films are denoted as W($1-x$)Ti($x$), where $x$ indicates the molar percentage of $Ti^{4+}$.

The film thickness was measured with a surface profiler (Dektak 3000, Veeco Instruments Inc., NY, USA). The electrochemical properties of the thin films were characterized by cyclic voltammetry and chronoamperometry using a potentio/galvanostat (Versastat 3, Toyo Corp., Tokyo, Japan) at room temperature. In both cases, the electrolyte was propylene carbonate containing 1.0 mol/dm$^3$ of $LiClO_4$, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl pair. The cyclic voltammetry data were recorded at scanning rates of −1.0 to +1.0 V at 50 mV/s. For the chronoamperometry, the potential of the thin films was switched 200 times between −1.0 and +1.0 V at an interval of 5 s.

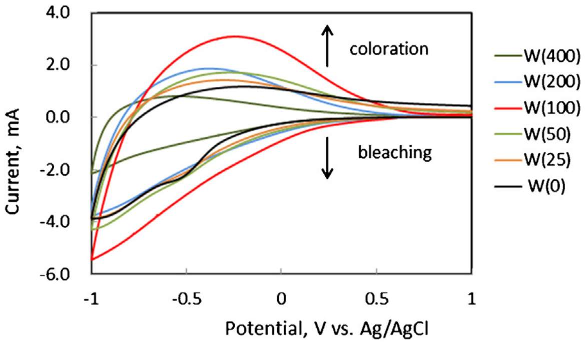

**Fig. 1.** Cyclic voltammograms of non-doped $WO_3$ thin films prepared from solutions containing various P123/$WO_3$ ratios.

## 3. Results and discussion

### 3.1. Non-doped $WO_3$ thin films

Fig. 1 shows the cyclic voltammograms (CVs) of the non-doped $WO_3$ thin films prepared from solutions containing various P123/$WO_3$ ratios. The area surrounded by each loop corresponds to the electric charge involved in reaction (1). The as-prepared $WO_3$ films were colorless, but they became deep blue upon reduction because of the absorption of optical energy in the visible light region through the d-d transition of the 5d electron in the $W^{5+}$ ions. The larger the area of the CV loop, the higher is the contrast. The thickness of the resultant films was 200 ± 30 nm. However, since all the solutions had different viscosities and $WO_3$ concentrations, the exact thickness and the mass of $WO_3$ on each substrate may be different for different films. Therefore, the electrochromic properties of "as-prepared" thin films will be compared. W(100) showed the largest CV loop, indicating that W(100) would show the highest electrochromic contrast. The addition of P123 increased the area of the loop from samples W(0) to W(100). It has been well established that polymers added into precursor solutions of thin films can act as porogens and increase surface area [12–14,17,18]. Therefore, in the present case, too, the addition of P123 should have increased the surface area of $WO_3$ films from W(0) to W(100). However, excessive addition of P123 decreased the area of the CV loops for W(100) to W(400) because of too high a porosity and a decrease in the mass of $WO_3$ in the film.

Fig. 2(a) and (b) shows the chronoamperograms of the non-doped $WO_3$ thin films for a single coloration/bleaching cycle. Although the coloration was not complete within 5 s, as indicated by the fact that the current did not return to zero, the bleaching was almost complete within 2 s, as indicated by the currents returning to almost zero. This implies that these $WO_3$ films showed a relatively fast bleaching response, compared to previous reports in which coloration/bleaching lingered for more than several tens of seconds. The quick response is due to the pores introduced by P123.

Here, the addition of P123 did not result in ordered mesopores, as determined from X-ray diffraction analysis, which was carried out over $2\theta$ angles ranging from 1.5° to 40°. However, non-ordered mesopores were indicated because there was a heap in the low angle region (1.5–3°) (Fig. 3). No diffraction peaks assignable to crystalline $WO_3$ were observed.

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