Fast fabrication of a WO$_3$·2H$_2$O thin film with improved electrochromic properties†

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By using electrochemical activated FTO glass as both a substrate and catalyst, we developed a facile and fast method to fabricate a WO$_3$·2H$_2$O thin film with a thickness of ~100 nm. Due to the specific layered crystal structure of the dihydrated phase and the good contact with the transparent conductive oxides (TCOs) layer, the as-prepared WO$_3$·2H$_2$O thin film achieved a fast coloration/bleaching response speed ($t_{c,90\%} = 3.2$ s, $t_{b,90\%} = 1.2$ s), excellent cyclic stability, wide optical modulation range up to 53.8% and a high coloration efficiency of 107.8 cm$^2$ C$^{-1}$. A solid-state electrochromic device with a size of 5 cm × 5 cm was also fabricated, exhibiting high transparency contrast and good reversibility between the bleached and colored states.

Introduction

During the past few decades, intelligent materials have attracted increasing amounts of attention for their great advantages in various areas, especially in the electronic industry. Electrochromic (EC) materials, which can change their optical properties (reflected time, transmittance, and absorbance) through reversible color changes in response to a small electric potential difference, are one of the most important branches of intelligent materials, and have promising applications in energy-efficient smart windows, automatically dimming rear-view mirrors, and optical displays. The widely studied electrochromic materials can be divided into bipyridilium salts (known as viologen), conducting polymers (e.g., polythiophene, polyaniline) and inorganic metal oxides (WO$_3$, IrO$_2$, NiO). Among these EC materials, tungstic trioxide (WO$_3$) was widely studied and can switch between colorless and a blue color reversibly by alternately applying a small positive and negative voltage. The electrochromic mechanism of WO$_3$ is based on the reversible oxidation/reduction reactions induced by electrochemical double injection/extraction of both positive ions (H$^+$, Li$^+$, Na$^+$) and electrons into/outside the host lattice, namely the reversible transition of W$^{6+}$ and W$^{5+}$. Generally, WO$_3$ films are fabricated on transparent conductive substrates (e.g., FTO, ITO, and conductive plastic) to work as a host electrode in EC devices. To improve the performance of EC devices, many techniques have been developed to fabricate WO$_3$ EC films, including chemical vapor-phase deposition(CVD), sputtering, electron-beam deposition, thermal evaporation, spray pyrolysis, electrochemical anodization, sol–gel and especially the hydrothermal method. For instance, Wang et al. and Zhang et al. have prepared 1D nanostructured WO$_3$ films by a facile hydrothermal process with NaCl and (NH$_4$)$_2$SO$_4$ as the capping agent, respectively. These WO$_3$ films exhibited fast coloration/bleaching switching and high coloration efficiency. Lately, Jiao and Sun et al. fabricated a plate-like hydrated WO$_3$ film via a crystal-seed-assisted hydrothermal approach with Na$_2$SO$_4$ as the capping agent, the film have achieved a faster switching response ($t_{c,90\%} = 4.3$ s, $t_{b,90\%} = 1.4$ s) and increased coloration efficiency (112.7 cm$^2$ C$^{-1}$). However, all the above methods have some disadvantages which limit the application of WO$_3$ EC films to some degree, including high energy consumption, rigorous preparation conditions, expensive equipment needs, or introduction of toxic and dangerous reagents. For these reasons, it is an urgent need to develop faster, simple and effective ways to synthesize tungsten oxide films with enhanced EC properties.

In this report, we present a convenient and fast way to fabricate a WO$_3$·2H$_2$O thin film at room temperature in an open system by using the freshly electrochemical activated FTO glass as both substrate and catalyst. The reaction mechanism was investigated in detail by studying the intermediate samples. The as-prepared WO$_3$·2H$_2$O thin film exhibits enhanced electrochromic properties in terms of fast coloration/bleaching response speed, excellent cyclic stability, wide optical modulation and high coloration efficiency. Moreover, a solid-state EC device with a size of 5 cm × 5 cm was also fabricated and its electrochromic performance is discussed.

† Electronic supplementary information (ESI) available: chronoamperometry movie for the alternating coloration/bleaching response for 1 s. See DOI: 10.1039/c2jm33622g
Experimental section

Materials

All solvents and chemicals used in the present work were of analytical grade and used without any purification. Sodium tungstate dihydrate (Na₂WO₄·2H₂O), hydrochloric acid (35%), oxalic acid dihydrate (H₂C₂O₄·2H₂O), potassium hydroxide, potassium chloride and sulfuric acid (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). All aqueous solutions were freshly prepared with deionized water.

Preparation of the WO₃·2H₂O thin film

The synthesis of the WO₃·2H₂O thin film can be summarized as a three-step procedure as shown in Fig. 1a. It starts from the electrochemical activation of commercially available FTO conductive glasses. The FTO conductive glasses (2.5 cm × 3 cm in size) were first ultrasonically cleaned with acetone, ethanol and deionized water, each for 30 min, respectively. After drying, two pieces of the cleaned FTO conductive glasses were dipped in 0.1 M KOH solution, and were used as the anode and cathode electrodes, respectively. By applying a direct voltage of 6 V for 10 s, the cathode FTO conductive glass was successfully activated. The second step involves the fast formation of a blue WO₃ film on the activated FTO conductive glass within 15 min. Briefly, Na₂WO₄·2H₂O (3.3 g) was dissolved into 50 mL of deionized water and then 3 M HCl was slowly added into the Na₂WO₄ solution to adjust the pH value to 1.2, resulting in the formation of a yellowish tungstic acid sol. Subsequently, 10 mL of the newly formed tungstic acid sol was mixed with an equal amount of 0.6 M H₂C₂O₄ aqueous solution and then 1 g KCl was added as a capping agent. A transparent and colorless precursor solution was thus obtained. After that, the activated FTO conductive glass in the first step was dipped into the precursor solution and maintained for about 15 min. It was found that the surface of the activated FTO glass changed from brown to dark blue and was stable even after being washed with deionized water, indicating the successfully self-coating of the tungstic acid sol on the substrate. After drying in air, the coated substrate was annealed in air at 300 °C for 1 h, resulting in the formation of the final product.

For a comparison, another WO₃-based film was prepared by simply dip-coating the newly obtained yellowish tungstic acid sol on a cleaned unactivated FTO conductive glass, also followed by annealing at 300 °C for 1 h in air.

Characterizations

The composition of the as-prepared products was characterized by an X-ray diffractometer (X’Pert PRO, PANalytical B. V., the Netherlands) with radiation of a Cu target (Kα, λ = 0.15406 nm) at 40 kV and 40 mA. The morphologies of the films were characterized by field-emission scanning electron microscopy (FESEM, Sirion 200, FEI, Netherlands), and the elements distributions were analysed by energy-dispersive X-ray spectroscopy (EDS). Electrochromic properties of the as-obtained WO₃ films were measured on an electrochemical workstation (CS350, Wuhan CorrTest Instrument Co., Ltd). Cyclic voltammetry (CV) and chronoamperometry (CA) tests were performed in a conventional three-electrode electrochemical cell with 0.1 M H₂SO₄ aqueous solution as the electrolyte. The WO₃ thin film was contacted as the working electrode, and an Ag/AgCl electrode and Pt wire were used as the reference and counter electrodes, respectively. The transmittance spectra were measured by a UV-vis spectrophotometer (UV-2500, Shimadzu). The colouration/bleaching switching characteristics of the electrochromic films were recorded by transmittance changes at a wavelength of 670 nm with alternately applying a potential of ±0.5 V, 30 s for each state.

Results and discussion

Structure and morphology

The blue curve shown in Fig. 1b is the XRD pattern of the final annealed product obtained on the activated FTO substrate. Besides the peaks from the FTO substrate, all the other peaks (marked with stars) can be easily indexed to monoclinic WO₃·2H₂O, indicating the formation of pure product (JCPDS no. 18-1419). To systematically investigate the formation process of the WO₃·2H₂O product, the compositions of the intermediate samples formed during the three-step procedure were also studied by XRD and the corresponding XRD patterns are depicted in Fig. 1b. From the XRD patterns, we can see that compared with pure FTO glass, a trigonal tin phase (JCPDS no. 89-4898) presented after electrochemical activation, indicating the formation of tin crystals on the cathode substrate. As for the sample before annealing, the XRD pattern only shows the presence of amorphous peaks beside the peaks from the FTO glass, indicating that the blue film coating on the substrate is amorphous WO₃. The XRD pattern of the comparison film...
coated on the unactivated FTO substrate also indexed to monoclinic WO$_3$·2H$_2$O, while the intensity of the peaks were weaker than the WO$_3$·2H$_2$O film obtained on the activated FTO substrate, indicating much poorer crystallinity (Fig. S1, ESI†). Fig. 1c shows the crystal structure of monoclinic WO$_3$·2H$_2$O, which is composed of distorted WO$_6$(OH)$_2$ octahedrons in corner-sharing mode. Each single WO$_6$(OH)$_2$ unit is coordinated by four W–O bonds, a shorter terminal W–O bond and a longer W–(OH)$_2$ bond.\(^\text{28,41}\) Between the layers the second water molecule (structural water) is incorporated into the lattice to increase the distance of the lattice. The Raman spectrum of the annealed WO$_3$·2H$_2$O film was investigated and is shown in Fig. S2, ESI†, which confirmed the presence of monoclinic WO$_3$·2H$_2$O.

Fig. 2a shows the plane-view SEM image of the as-obtained WO$_3$·2H$_2$O film, which presents a smooth and compact surface except for some tiny cracks caused by the annealing treatment. The line-scanning elemental map on the boundary of the WO$_3$·2H$_2$O film is shown in Fig. 2b. From the image, we can see that the intensity of WM and WL (M and L represent the second and third electronic shell of W element) increase along the scan line in the product layer, while the intensity of the Sn element (SnL) decreases in the obtained product layer, and C (CK) and O distribute uniformly along the scan line. The increase of W and decrease of Sn further confirm the formation of the WO$_3$·2H$_2$O thin film on the substrate.

For comparison, the morphologies of the pure FTO substrate and the intermediate products on the activated FTO substrate were also characterized, as shown in Fig. 2c–f, respectively. It revealed that the pure FTO substrate has a rough surface with sharp edges and corners (Fig. 2c), while it became smooth after the cathode electrochemical activation (Fig. 2d). Fig. 2e and f exhibited the plane-view and boundary line-scanning elemental map of the blue amorphous WO$_3$ film before annealing. It can be observed that the surface morphology and elemental distribution of the blue amorphous WO$_3$ film are similar to the WO$_3$·2H$_2$O thin film. However, the difference is that the intensity of C and O increase along the scan line due to the presence of C$_2$O$_4$\(^2−\) in the unannealed tungsten oxide film. Furthermore, from the cross-sectional view images of the WO$_3$·2H$_2$O film and intermediate products (the insets of Fig. 2a, d and e), we found that the thicknesses of the oxide layers for the three films are 719 nm, 615 nm and 708 nm, thus the thickness of the WO$_3$·2H$_2$O layer can be calculated to be about 100 nm.

Combined with the analysis of the XRD patterns and SEM images of the WO$_3$·2H$_2$O film, and the intermediate products, the formation mechanism of the WO$_3$·2H$_2$O thin film was proposed, including the electrochemical activation reaction and the precipitation of WO$_3$ from the WO$_4$\(^2−\) solution at room temperature. The electrochemical activation is a redox reaction as follows:

\[
\text{Anode: } 4\text{OH}^- - 4e^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \uparrow + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Cathode: } \text{SnO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Sn} + 4\text{OH}^- \quad (2)
\]

\[
\text{Total reaction: } \text{SnO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Sn} + 2\text{H}_2\text{O} \quad (3)
\]

During this process, SnO$_2$ nanocrystals with sharp edges (Fig. 2e) on the cathode FTO substrate were partly reduced to form ultrafine beta Sn crystals, as shown in Fig. 2d.

The precipitation of WO$_3$ from the WO$_4$\(^2−\) solution can be described according to the following well-known reactions:\(^\text{41,42}\)

\[
\text{Na}_2\text{WO}_4 + 2\text{HCl} \rightarrow \text{H}_2\text{WO}_4\cdot n\text{H}_2\text{O} (\text{sol}) + 2\text{NaCl} \quad (4)
\]

\[
\text{H}_2\text{WO}_4\cdot n\text{H}_2\text{O} + x\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{WO}_3\cdot x\text{H}_2\text{C}_2\text{O}_4\cdot (n+1)\text{H}_2\text{O} \quad (\text{peroxytungstic acid}) \quad (5)
\]

\[
\text{WO}_3\cdot x\text{H}_2\text{C}_2\text{O}_4\cdot (n+1)\text{H}_2\text{O} + x\text{Sn} \rightarrow \text{WO}_3\cdot (n+1)\text{H}_2\text{O} \downarrow + x\text{SnC}_2\text{O}_4 + x\text{H}_2\uparrow \quad (6)
\]

\[
\text{WO}_3\cdot (n+1)\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot 2\text{H}_2\text{O} + (n-1) \text{H}_2\text{O} \quad (7)
\]

Tungstic acid hydrate was synthesized by adding HCl solution to a Na$_2$WO$_4$ solution to form the WO$_3$ sol at room temperature. Then the sol was dissolved by adding the proper amounts of H$_2$C$_2$O$_4$, and the polytungstic acid coordination complex was thus formed. Once the electrochemically activated FTO substrate was dipped into the complex solution, the Sn layer started to react with the polytungstic acid, resulting in the formation of a blue amorphous tungsten trioxide hydrate film. Meanwhile, the Sn element was oxidized into Sn$^{2+}$. During this process, the newly formed Sn particles acted as a catalyst to lower the reaction potential barrier for the precipitation of the tungsten trioxide hydrates. On the other hand, as a capping agent, KCl was also conductive to promote the formation of amorphous tungsten oxide film. After a calcination process, the blue amorphous tungsten trioxide hydrate film was crystallized to form the monoclinic WO$_3$·2H$_2$O thin film.
Electrochemical and electrochromic properties

Fig. 3 shows the cyclic voltammetry (CV) and chronoamperometry (CA) curves of both the WO$_3$-2H$_2$O thin films on the activated FTO substrate and the comparison WO$_3$ film on inactivated FTO substrate, respectively, which was carried out in 0.1 M H$_2$SO$_4$ solution at a scan rate of 50 mV s$^{-1}$. As can be seen from Fig. 3a, the as-prepared WO$_3$-2H$_2$O thin film shows a much higher current density than the comparison WO$_3$ film over the same time period. To investigate the cycling stability of the as-prepared WO$_3$-2H$_2$O thin film, the CV test was periodically measured for 1000 cycles. Fig. 3b presents the CV curves for the 1st, 500th and 1000th cycle, respectively. It revealed that the current density of the WO$_3$-2H$_2$O thin film only slightly decreases during the initial 500 cycles, and then remains stable in the subsequent 500 cycles. The Raman spectrum of the WO$_3$-2H$_2$O thin film after 500 cycles was characterized as shown in Fig. S3, ESI†. From the comparison of the electrochromic film before and after 500 CV cycles, we found that the WO$_3$-2H$_2$O phase has become the WO$_3$ phase during a slow dehydration process. Although the WO$_3$-2H$_2$O phase has changed to WO$_3$ phase, the slight decrease of current density after 1000 cycles still indicates the very good cyclic stability of the WO$_3$-2H$_2$O thin film. During the CV test, reversible color changes from colorless to blue by cyclic anodic/cathodic polarization can be observed. The coloration/bleaching process is in accordance with a double intercalation/deintercalation of both H$^+$ and electrons into/out of the WO$_3$ films following the reaction:

\[ \text{WO}_3 \cdot 2\text{H}_2\text{O} + x\text{H}^+ + xe^- \rightarrow \text{H}_x\text{WO}_3 \cdot 2\text{H}_2\text{O} \]  

When applying the negative voltage on the WO$_3$ electrochromic layer, electrons and H$^+$ were inserted into the WO$_3$ film,

![Graphs and images](image_url)

**Fig. 3** (a) CV curves of the WO$_3$-2H$_2$O thin film and the comparison WO$_3$ film coated on inactivated FTO substrate in 0.1 M H$_2$SO$_4$ with a scan rate of 50 mV s$^{-1}$ (b) CV curves of the WO$_3$-2H$_2$O thin film for the first, 500th and 1000th cycle, respectively. (c) Chronoamperometry curves of both films by alternately applying a potential of ±0.5 V, 10 s for each state.

**Fig. 4** The UV-vis transmittance spectrum and photographs of the WO$_3$-2H$_2$O thin film colored at potentials of 0, −0.1, −0.3 and −0.5 V, respectively.
the change of transmittance. Moreover, when applying a potential of +0.5 V, the color of the WO$_3\cdot$2H$_2$O thin film quickly changes from blue (colored state) back to colorless (bleached state), revealing excellent color reversibility.

Based on the UV-vis transmittance spectrum of the WO$_3\cdot$2H$_2$O thin film, we measured its transmittance switching characteristic by scanning at ±0.5 V for 30 s. The corresponding in situ coloration/bleaching transmittance response was investigated at a fixed wavelength of 670 nm. As shown in Fig. 5a, an obvious color changes can be observed during the potential switching, and the WO$_3\cdot$2H$_2$O thin film shows a much faster response and larger transmittance modulation than the comparison WO$_3$ film (also shown in Fig. 5a). As an important criterion for judging a WO$_3$ EC film, the coloration/bleaching time extracted for a 90% transmittance change are calculated to be 3.2 s ($t_c$) and 1.2 s ($t_b$) for the WO$_3\cdot$2H$_2$O thin film. On the other hand, the comparison WO$_3$ film on the unactivated FTO substrate exhibited longer coloration/bleaching times of 10.5 s and 7.4 s, respectively, confirming the excellent response of the as-prepared WO$_3\cdot$2H$_2$O thin film.

The fast coloration/bleaching kinetics of the WO$_3\cdot$2H$_2$O thin film is not only attributed to the proton diffusion coefficient but is also related to the interface cohesiveness between tungsten oxide and the transparent conductive oxide (TCO) layer.** As described in the fabricating process of the WO$_3\cdot$2H$_2$O thin film, an in situ reaction occurred as soon as the electrochemically activated FTO conductive glass was dipped in the polytungstic acid solution and the as-obtained tungsten oxide film was quite stable after washing with water. So it can be concluded that the tungsten oxide has tightly bonded to the transparent FTO conductive layer, which can enhance the coloration and bleaching response by promoting the electron transfer rate between the electrochromic layer and TCOs layer. Furthermore, the optical modulation of the WO$_3\cdot$2H$_2$O thin film is up to 53.8% at 670 nm, which is higher than 30.4% of the comparison WO$_3$ coated film. The switching responses of the WO$_3\cdot$2H$_2$O thin film under ±0.1 V and ±0.3 V were also investigated, as shown in Fig. 5c, and the value of optical modulation are 11.9% and 36.0%, respectively.

Another important criterion for judging an electrochromic film is the coloration efficiency (CE), which is defined as the change in optical density (OD) per unit of charge (Q) inserted into (or extracted from) the EC films. It can be calculated from the formulas as follows:

\[
CE = \frac{\Delta(OD)}{\Delta Q} \quad (9)
\]

\[
OD = \log \left( \frac{T_b}{T_c} \right) \quad (10)
\]

where $T_b$ and $T_c$ refer to the bleached and colored transmittance of the EC film, respectively. Fig. 6 shows a plot of the in situ...
optical density (OD) at the absorbance wavelength of 670 nm versus the inserted charge density (Q) at a potential of −0.5 V. The CE is extracted as the slope of the line fits to the linear region of the curve. The value is calculated to be about 107.8 cm² C⁻¹ for the WO₃·2H₂O thin film, which is much higher than the comparison WO₃ coated film (CE = 46.6 cm² C⁻¹). The high CE value indicates that the WO₃·2H₂O thin film exhibits a large optical modulation with a small charge inserted (or extracted).

To demonstrate the performance of the as-prepared WO₃·2H₂O thin film in a real EC device, a simple transmissive type of sandwich-like solid-state EC device was fabricated as shown in Fig. 7a. The WO₃·2H₂O thin film was the electrochromic layer (work electrode), and the Pt layer was operated as the counter electrode, which was prepared by coating the FTO glass with the correct amount of H₂PtCl₆ solution and then calcining in air at 450 °C for 30 min. The gel electrolyte was obtained by immobilizing the H₂SO₄ solution in a polyvinyl alcohol (PVA) matrix with stirring at 85 °C until the gel becomes transparent. When both the EC layer and Pt layer were coated with a thin H₂SO₄–PVA (either content ~10 wt%) gel layer, the device was assembled and then glued into a solid state after air-drying at room temperature for 4 h. The photographs in Fig. 7b show the large scale sample of the as-fabricated solid-state EC device (5 cm × 5 cm) under the bleached state with anodic potential (+0.5 V), and the blue-colored state with cathodic potential (−0.5 V), which depicted a high contrast between the bleached and colored states. Fig. 7c shows the switching response of the solid-state EC device under ±0.5 V at 670 nm. It can be found that the EC device has a high transparency change (ΔT = 27.5%), and the coloration time (tₐ) and bleaching time (tₑ) are calculated to be 14.2 s and 2.2 s, respectively. Clearly, the large-area device also presents a durable and reversible performance.

**Conclusions**

In summary, a high quality WO₃·2H₂O thin film was efficiently fabricated on electrochemically activated FTO conductive glass by a facile dipping process at room temperature, followed by annealing treatment. Compared with the common WO₃ film coated on inactivated FTO substrate, the WO₃·2H₂O thin film exhibited a significantly improved electrochromic performance due to the high proton diffusion coefficient and strong interface contact between the EC layer and TCOs layer. This as-prepared sample showed fast coloration/bleaching response speeds (tᵢₐₙₓₙ = 3.2 s, tᵦₙₓᵦₙ₋ₓ = 1.2 s), high transparency contrast (ΔT = 53.8%) at 670 nm and the coloration efficiency was calculated to 107.8 cm² C⁻¹. The fast fabricated WO₃·2H₂O thin film was also assembled into a solid-state electrochromic device with a large area of 5 × 5 cm², exhibiting good cyclic reversibility and high optical modulation under a pulsing voltage of ±0.5 V. Considering the current results, the WO₃·2H₂O thin film, with a facile preparation process and improved EC behaviour, will impact current EC technologies and have promising applications for energy-efficient smart windows and large-scale optical displays.

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**Notes and references**


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