A Complementary Electrochromic Device with Highly Improved Performance Based on Brick-Like Hydrated Tungsten Trioxide Film

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Uniform and well adhesive nanostructured hydrated tungsten trioxide (3WO₃·H₂O) films were grown on fluorine doped tin oxide (FTO) substrate via a facile and template-free crystal-seed-assisted hydrothermal method by addition of ammonium sulfate ((NH₄)₂SO₄) and hydrogen peroxide (H₂O₂). X-ray diffraction (XRD) studies indicated that the films are of orthorhombic structure. Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) analysis showed that the film was composed of brick-like nanostructures with a preferred growing direction along (002). The influence of seed layer, (NH₄)₂SO₄ and H₂O₂ on the products were also studied. The film showed good cyclic stability, comparable switching speed and coloration efficiency (30.1 cm² C⁻¹). A complementary electrochromic device based on the film and Prussian blue depicted highly improved color contrast, coloration/bleaching response (1.8 and 3.7 s respectively) and coloration efficiency (164.6 cm² C⁻¹).

Keywords: Electrochromic, Nanostructure, Tungsten Oxide, Complementary.

1. INTRODUCTION

Electrochromism is the phenomenon of reversible changes in the optical properties of a material during electrochemical redox processes, which can be applied in energy-efficient smart windows, antiglare rear-view mirrors and displays.¹⁻¹² A lot of materials exhibit electrochromism, including many transition metal oxides (WO₃, NiO and MoO₃), Prussian blue (PB) and some organic conducting polymers (poly (aniline) and poly (3, 4-propylene-dioxythiophene)).⁸,¹¹⁻¹³ Compared with the amorphous structure, crystalline WO₃ demonstrates better durability in acidic electrolyte due to

substrate and incorporated into an EC device, which is conventionally a multilayer structure with one EC layer countered with one ion storage layer or one complementary EC layer, and one intermediate ion conductor layer. Compared with a single EC layer device, a complementary device depicts improved optical regulation, coloration efficiency and cyclic stability.¹⁹,²⁰

Among various EC materials, tungsten trioxide (WO₃) has attracted intensive attention due to its distinguished EC properties such as high coloration efficiency, good color-memory effect, large color contrast and good cyclic stability.¹,³,¹³,¹⁷ By alternately applying suitable negative and positive electrical voltages, the WO₃ film displays blue color and colorless due to the double injection/extraction of the cations (H⁺, Li⁺) and electrons correspondingly. Compared with the amorphous structure, crystalline WO₃ demonstrates better durability in acidic electrolyte due to
its denser structure that results in a slower dissolution rate. However, bulk crystalline WO₃ particles usually lead to slow switching responses and small coloration efficiency, resulting from the high diffusion resistance of ions. Thus, nanostructured WO₃ films with large specific area and porous morphologies are desired, and faster switching response and better durability are expected.¹⁸ ²² ²³ Up until now, various methods have been reported to fabricate WO₃ films (dense or porous) on various substrates, such as sputtering, chemical vapor deposition, electrodeposition, sol–gel and hydrothermal.²³–³⁵ Hydrothermal synthesis is a facile, cost-effective and environmentally friendly technique, which offers diversity for substrate selection and the possibility of controlling the characteristics (thickness, structure size, morphology and porosity) of the as-prepared films. In fact, WO₃ hydrates (WO₃·xH₂O) or “tungstic acids” are generally obtained in liquid-phase synthesis routes. Compared with the dehydrated WO₃, the hydrothermally grown hydrated WO₃ films have demonstrated improved stability and efficiency,³⁶ ³⁷ and further improvement could be achieved by increasing the porosity and incorporating a suitable complementary layer.

Prussian blue [PB, iron (III) hexacyanoferrate (II)], a synthetic coordination-compounded transition metal hexacyanometallates, is a well-known anodically colored EC material. It is reported that an electrodeposited PB film exhibits electrochromism between blue and colorless with a fast response (~less than 100 ms) and a high durability after 5 × 10⁶ cycles.³⁸ However, the PB film shows little absorption in the IR region which hinders its applications in energy efficient smart windows. The combination of WO₃ and PB in a complementary device has demonstrated improved optical modulation, response speed and coloration efficiency. For example, Kraft and Rottmann reported large-area laminated EC glass composed of electrodeposition of WO₃ and PB counter electrode were sandwiched together with hot-melt Surlyn spacers. A liquid electrolyte composed of Na₂WO₄·2H₂O (0.065 g) was dissolved into 20 mL of de-ionized water and then H₂O₂ (0.2 g) and (NH₄)₂SO₄ (0.045 g) was added into the solution under intense stirring. Pure HCl was dropped into the above solution until the pH value reaches 1.5. For the purpose of comparison, solutions without adding H₂O₂, (NH₄)₂SO₄ or both were also prepared. The as-prepared solutions were transferred into autoclaves as hydrothermal precursors. The seed coated FTO glasses were lie at the bottom of the autoclaves and the hydrothermal growth was performed at 180 °C for 18 h. High transparent films were grown on the substrate after washing away the adhered precipitate by di-water. Then the films were dried in atmosphere.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Crystal Seeds Layers, Precursor and Hydrothermal Treatment

The procedures for preparing crystal seeds layers are similar to our previous report, which can be found elsewhere.³⁴ In a typical experiment for preparing the precursor, Na₂WO₄·2H₂O (0.065 g) was dissolved into 20 mL of de-ionized water and then H₂O₂ (0.2 g) and (NH₄)₂SO₄ (0.045 g) was added into the solution under intense stirring. Pure HCl was dropped into the above solution until the pH value reaches 1.5. For the purpose of comparison, solutions without adding H₂O₂, (NH₄)₂SO₄ or both were also prepared. The as-prepared solutions were transferred into autoclaves as hydrothermal precursors. The seed coated FTO glasses were lie at the bottom of the autoclaves and the hydrothermal growth was performed at 180 °C for 18 h. High transparent films were grown on the substrate after washing away the adhered precipitate by di-water. Then the films were dried in atmosphere.

2.2. Electrodeposition of PB and Preparation of EC Device

The electrodeposition of PB film was carried out by a conventional three-electrode system, where a clean FTO glass (1.5 × 2 cm²) served as the working electrode, a platinum sheet as the counter electrode, and a Ag/AgCl/1 M KCl as the reference electrode. The electrodeposition bath contained 10 mM K₃Fe(CN)₆, 10 mM FeCl₃ and 0.1 M KCl and the electrodeposition was carried out by applying a constant cathodic current density of 50 μA cm⁻² for 130 s. Then the WO₃ (hydrated) working electrode and PB counter electrode were sandwiched together with hot-melt Surlyn spacers. A liquid electrolyte composed of 0.3 M LiClO₄ in γ-butyrolactone (γ-BL) was introduced between the two electrodes by capillary action. Finally the cell was sealed by epoxy with a structure of FTO[hydrated (WO₃)]γ-BL (LiClO₄)][PB][FTO].

2.3. Characterizations

The phases of the as-grown films were identified by X-ray powder diffraction (XRD, Siemens), using Cu Kα(λ = 0.15406 nm) radiation. The phase structures were characterized by Raman spectroscopy (Renishaw in Via). X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos AXIS spectrometer with monochromatic Al-Kα (1486.71 eV) X-ray radiation. The morphologies of the as-prepared thin films were observed by field emission scanning electron microscope (FESEM, JSM 6340). High-resolution transmission electron microscopy
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A (HRTEM) image was obtained by a JEM-2100 microscope using an accelerating voltage of 200 kV. Thicknesses of the films were measured by a TENCOR P-10 Surface Profiler. The UV-vis transmittance spectra were measured using a UV-vis spectrophotometer (JESCO V670). Electrochemical measurements were performed by a three-electrode system (VersaSTAT 3F Potentiostat/Galvanostat) with 0.3 M LiClO₄ in γ-BL as the electrolyte, Pt sheet as the counter electrode and Ag/AgCl/1 M KCl as the reference electrode.

3. RESULTS AND DISCUSSION

The X-ray powder diffraction patterns of the bare FTO substrate and the as-prepared thin film are illustrated in Figure 1(a). The pattern of the substrate is indexed to tin oxide layer. For the hydrothermally grown film, characteristic peaks of hydrated WO₃ were obtained. All the diffraction peaks can be well indexed to orthorhombic 3WO₃·H₂O (H–WO₃) phase with lattice constants of \( a = 7.345 \), \( b = 12.547 \) and \( c = 7.737 \) Å, agreeing well with the standard diffraction pattern (JCPDF 87-1203). And no impurity peaks were observed on the pattern, implying high purity of the H–WO₃ film. The sharp peaks indicate the good crystalline quality of the as-fabricated film. The X-ray photoelectron spectroscopy (XPS) and Raman spectra of the nanobrick H–WO₃ film were also investigated and shown in Figures 1(b) and (c), respectively. All the peaks appeared on the spectra can be well assigned to be H–WO₃ and no other impurities were detected, coincide with the XRD result. The orthorhombic 3WO₃·H₂O phase contains two type of structure unites: one is conducted by six oxygen atoms surrounded one centered W atom that shares the six corner oxygen atoms with adjacent octahedra, and the other is containing a coordinate water molecule with a prolonged W–OH₂ bond and a shorted W=O bond (shown in Fig. 1(d)). It is clear that the EC performance of WO₃ is closely related to its level of crystallization. Crystalline WO₃ films with large surface area and porous morphologies are expected to achieve a good stability, high coloration efficiency values and fast response.

Figures 2(a) and (b) show the top-view SEM images of the as-synthesized H–WO₃ film under different

Fig. 1. (color online) (a) XRD patterns of the bare FTO substrate and the as-synthesized thin films. (b) Wide scanning XPS spectra of the as-prepared nanobrick film. (c) Raman spectra of the film. (d) Schematic illustration of the orthorhombic 3WO₃·H₂O structure.
Fig. 2. (a) and (b) FESEM images of the H–WO₃ thin films under different magnifications. (c) TEM image of the nanobrick scratched from the film. (d) SAED pattern of the nanobrick. (e) HRTEM image of the nanobrick.

magnifications. It can be seen that the film is composed of brick-like nanostructures with average size of ∼100 nm, forming a rough surface. These nanobricks gather together and grow along various directions, leading to the formation of a lot of pores which could increase the surface area of film. Through these pores, ions in the electrolyte can insert into or extract from the film more easily and efficiently, resulting from the reduced length of ion diffusion path.

One nanobrick with integral shape (length: ∼320 nm) shows vertically joint angles. Figure 2(d) depicts the selected area electron diffraction (SAED) pattern of this nanobrick. Regular diffraction spots are obtained, proving it is single crystalline. The nanobrick has preferential growing direction along c axis, corresponding to crystal planes of (002). The HRTEM image in Figure 2(e) from the edge of this nanobrick shows its crystal lattices of 0.38 nm, corresponding to the d-spacing of (002) planes, in good agreement with Figure 2(d). Clear lattice fringes also indicate its single crystal quality.

To investigate the growth mechanism of the H–WO₃ films, the effects of seed layer, H₂O₂ and (NH₄)₂SO₄ on the products were also studied. Figures 3(a) and (b) show the SEM images of products grown without seed layer under different magnifications, while other conditions remain the same with Figure 2. Irregular bricks with different sizes rather than a film are obtained. These bricks are stacked disorderly and adhered to the substrate surface. This result indicates that crystal-seed-layer offers the nucleation sites for the growth of bricks, which is crucial on organizing these bricks into an ordered film system on the substrate. Figures 3(c) and (d) depict the SEM images of film grown without addition of (NH₄)₂SO₄. Thick yellowish film composed of gathered blocks with irregular shape and sizes are prepared. The nanoblock film shows a good adhesion to the substrate. The above result implies that (NH₄)₂SO₄ has a capping effect on the product. Figures 3(e) and (f) show the morphologies of products grown without addition of H₂O₂. Accumulated nanospheres with uniform sizes (∼80 nm) were synthesized. These nanospheres stacked intricately on the substrate are easily washed away by di-water. It seems that H₂O₂ has some chelating effect on directing the condensation of the [WO₆] and [WO₅–H₂O] octahedrons through the peroxo group. Moreover, it plays a role in linking the nucleus to the seed-layer coated surface. From the above result, it can be seen that H–WO₃ films can only be obtained on seed-layer-coated substrate with the addition of H₂O₂. The growth mechanism of the brick-like nanostructured film can be explained according to the following reactions:

Na₂WO₄ + 2HCl → H₂WO₄↓ + 2NaCl

H₂WO₄ + xH₂O₂ → WO₃·xH₂O₂·H₂O

(Peroxopolytungstic acid)
Fig. 3. (a) and (b) SEM images of the product grown without seed layer under different magnifications. (c) and (d) The product grown without addition of (NH₄)₂SO₄. (e) and (f) The product grown without addition of H₂O₂.

\[ \text{WO}_3 \cdot x\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O} \rightarrow \text{WO}_3 \cdot 1/3\text{H}_2\text{O} (\text{nucleus}) \]
\[ + (x + 2/3)\text{H}_2\text{O} + x/2\text{O}_2 \uparrow \]  
\[ \text{WO}_3 \cdot 1/3\text{H}_2\text{O} (\text{nucleus}) \rightarrow \text{WO}_3 \cdot 1/3\text{H}_2\text{O} (\text{nanobrick}) \]
\[ \text{(capping agent: (NH}_4\text{)}_2\text{SO}_4) \]  

H₂WO₄ precipitate was formed immediately after addition of HCl solution. Then it was rapidly dissolved by the existing hydrogen peroxide (H₂O₂) in the precursor and peroxopolytungstic acid (WO₃·xH₂O₂·H₂O, PTA) was obtained. The peroxy group of the H₂O₂ behaves as a chelating agent on directing the condensation of the [WO₆] and [WO₅–H₂O] octahedrons.\(^{36,37}\) It decreases the functionality of aqueous precursors toward condensation and prevents precipitation. Without the addition of H₂O₂, H₂WO₄ precipitate composed of numerous small clusters were formed and these clusters were further developed into nanospheres after hydrothermal process under high temperature. PTA can be easily decomposed at high temperature and a layer of WO₃·1/3H₂O crystal nucleus was formed from the decomposition of PTA, and the seed-coating substrate acted as nucleation and growth sites. Without seed layer, irregular bricks attaching on the substrate surface rather than a film are obtained. Although there is no chemical reaction between the (NH₄)₂SO₄ and tungstic acid, the (NH₄)₂SO₄ will act as structure-directing and dispersing agents through both the anions (SO₄²⁻) and cations (NH₄⁺) on the condensation of [WO₆] and [WO₅–H₂O] octahedrons. The brick-like nanostructures were grown eventually from the WO₃·1/3H₂O
nucleus under the capping effect of (NH$_4$)$_2$SO$_4$, while block-like films were obtained without (NH$_4$)$_2$SO$_4$. Figure 4 schematically summarizes the formation process of as-prepared products under different hydrothermal conditions.

The thicknesses of the as-grown nanobrick films can be controlled by altering the concentration of precursor solution. A thicker film can be obtained under higher concentration. Moreover, the effects of the amount of (NH$_4$)$_2$SO$_4$ and H$_2$O$_2$ on the products were also investigated and shown in Figure 5. When the amount of (NH$_4$)$_2$SO$_4$ increased to 0.1 g, some irregular particles were obtained and attached on the surface of substrate (shown in Figs. 5(a and b)), which may be due to the high ionic strength of the solution. While thin film made up of irregular microbricks was obtained when the amount of H$_2$O$_2$ was increased from 0.2 to 0.4 g (shown in Figs. 5(c and d)), with similar morphology to the previous reports.$^{23}$

Cyclic voltammograms (CVs) normalized to the geometric area of the H–WO$_3$ film and PB film electrodes are shown in Figure 6(a), measured in 0.3 M LiClO$_4$ in γ-BL as the electrolyte with a scan rate of 0.1 V/s. The PB film shows typical oxidation and reduction peaks at 0.23 V and −0.37 V, respectively, similar to the report.$^{40}$ The H–WO$_3$ film shows oxidation peak at −0.34 V. Compared with the H–WO$_3$ film, the PB film has a higher current density, implying faster ions intercalation/deintercalation kinetics. During each scan, both films will reversibly change their colors from colorless to blue. For H–WO$_3$, this behavior is resulting from Li$^+$ and electron transfer between W$^{6+}$ and W$^{5+}$ according to the following reaction:

$$\text{WO}_3 \cdot 0.33\text{H}_2\text{O}^{\text{bleach}} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{WO}_3 \cdot 0.33\text{H}_2\text{O}^{\text{blue}} \quad (5)$$

while for PB, the EC mechanism can be explained as follows:

$$\text{Fe}^{(III)}_4\text{[Fe}^{(II)}\text{(CN)}_6]_4^{\text{blue}} + 4e^- + 4\text{Li}^+ \leftrightarrow \text{Li}_4\text{Fe}^{(II)}_4\text{[Fe}^{(II)}\text{(CN)}_6]_4^{\text{colorless}} \quad (6)$$
The cyclic stability of the H–WO₃ film was also investigated by multiple cycles and shown in Figure 6(b). No significant shape change was observed, and only a small current reduction was found after 2000 cycles, indicating an excellent cyclic stability. According to the report, PB films also demonstrate outstanding stability. The long term cyclic stability is crucial for applications in energy efficient smart windows to compensate its relatively high cost.

Transmittance spectra of the complementary device and single PB layer device at bleached and colored state were compared (shown in Fig. 7(a)), operated under ±0.8 V in γ-BL electrolyte (0.3 M LiClO₄). The single PB layer device shows obvious broad optical modulation between bleached and colored states, especially in the range of 470 nm to 850 nm, similar to the reports. The complementary device depicts a comparable high transmittance level at bleached state, indicating a highly transparent state of as-grown H–WO₃ films. When the device is colored, lower transmittance in the whole range is achieved, resulting from the complementary color contrast of H–WO₃ films. As a result, the complementary device demonstrates an improved optical regulation and an increased color contrast. Moreover, the complementary device shows a larger modulation in the infrared light due to a high absorbance and reflectance of crystalline H–WO₃ films, which property is highly desired in energy saving windows applications since a large amount of heat energy in infrared light is blocked from entering into the interior building. Transmittance spectra of the as prepared H–WO₃ film and the film at colored/bleached states were investigated and shown in Figure 7(b). The transmittance decreases obviously at the colored state above 400 nm compared to the bleached state. And a larger modulation in the infrared light region was observed compared with the single PB layer device. Moreover, the transmittance at bleached state is very close to the as-prepared state, indicating good reversibility of the film. Compared with the complementary device, the single H–WO₃ film device shows smaller transmittance regulation, resulting in the indistinctive optical contrast between colored complementary device and single PB layer device.

Figure 8(a) shows the in-situ switching transmittance response of the complementary device at 632.8 nm, conducted by ±0.8 V for 30 s. Obvious color changes between transparent and blue can be seen during the switching. A maximum transmittance modulation (ΔT) of ~30% between coloration and bleaching is achieved at this
wavelength, agreeing well with the transmittance spectra shown in Figure 7. The response time is extracted as the time for 90% transmittance change. The coloration time ($t_{c,90\%}$) is found to be 1.8 s and bleaching time ($t_{b,90\%}$) is 3.7 s, respectively, both are much faster than the previous reported values. It is clear that the fast switching speed of the complementary device is mainly due to the fast switching kinetics of PB film, which account for the primary optical regulation. Although H–WO$_3$ films contribute a small complementary color contrast, it is crucial in regulating infrared light. The coloration/bleaching responses of the H–WO$_3$ films were also investigated and shown in Figure 8(b). A slower response of $t_{c,90\%} = 51.5$ s, $t_{b,90\%} = 11.5$ s and a smaller transmittance modulation ($\sim 13\%$) is found. However, the switching response is much faster than the reported microbrick and nanorods WO$_3$ films. Fast switching speed is due to the small thickness and large surface area that resulting in a short diffusion path for ions.

Coloration efficiency (CE) of the complementary device and single WO$_3$ film device was also investigated and compared at $\lambda = 632.8$ nm (shown in Fig. 8(c)). CE, a crucial

Fig. 9. Photographs of the complementary device at bleached state (a) and (b) colored state. Single H–WO$_3$ layer device at bleached (c) and (d) colored state under $\pm 0.8$ V, respectively.
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characteristic parameter for evaluating EC materials, is defined as the variation in optical density (OD) per unit of charge (Q) inserted into (or extracted from) the films, which can be calculated from the following equations:

\[ CE = \frac{\Delta OD}{\Delta Q} \]  
\[ \Delta OD = \log(T_b/T_c) \text{ or } \log(T_c/T_b) \]

where \( T_c \) and \( T_b \) refer to the transmittance of the film in its colored and bleached states, respectively. The CE value is extracted as the slope of the line fitted to the linear region of the \( \Delta OD \) versus \( \Delta Q \) curve. A high value of CE indicates that the EC film exhibits a large optical modulation with a small charge inserted (or extracted), which is related to the porosity, crystal sizes and phase structures of the film. For the complementary device, the CE value is calculated to be 164.6 cm²C⁻¹, which is larger than the reported value (~140 cm²C⁻¹).15,16 The OD variation is dramatic initially with the insertion of ions, then it gets smaller and smaller and finally gets stabilized after more ions inserted into the films. An inflection point at ~0.008 C cm⁻² is observed, and the OD quickly gets stabilized after it. For the single H–WO₃ film (Fig. 8(d)), a comparable switching response (~140 cm²C⁻¹) is obtained, which is comparable to the reported value.34

Photographs of the complementary EC device and the single H–WO₃ film device are shown in Figure 9. The complementary device made up of H–WO₃ and PB film is fabricated and demonstrates highly improved EC performance. This device shows much faster coloration/bleaching response (\( t_c,90\% = 1.8 \) s, \( t_b,90\% = 3.7 \) s), larger CE value (164.6 cm²C⁻¹) and increased color contrast. The complementary device is prospectively applied in smart windows and displays, and the as-synthesized H–WO₃ films may find more applications in gas sensors and electronic devices.

4. CONCLUSIONS

Uniform and highly adhesive nanobrick H–WO₃ films were assembled on FTO glass substrate by a facile and template-free crystal-assisted hydrothermal method. The effects of seed-layer, (NH₄)₂SO₄ and H₂O₂ on the products are studied. The seed-layer and H₂O₂ are vital in assembling the nanostructures into a thin film on the substrate, and both (NH₄)₂SO₄ and H₂O₂ have influences on the products’ morphologies. The as-synthesized orthorhombic H–WO₃ films show good cyclic stability, comparable switching response (\( t_c,90\% = 51.5 \) s, \( t_b,90\% = 11.5 \) s) and CE value (30.1 cm²C⁻¹). A complementary device made up of H–WO₃ and PB film is fabricated and demonstrates highly improved EC performance. This device shows much faster coloration/bleaching response (\( t_c,90\% = 1.8 \) s, \( t_b,90\% = 3.7 \) s), larger CE value (164.6 cm²C⁻¹) and increased color contrast. The complementary device is prospectively applied in smart windows and displays, and the as-synthesized H–WO₃ films may find more applications in gas sensors and electronic devices.

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References and Notes


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