Preparation and properties of all solid-state electrochromic devices based on tungsten oxide nanocomposites

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Abstract

The optical properties of electrochromic materials can change reversibly under an applied voltage. Tungsten oxide has been widely used in various fields because of its excellent electrochromic efficiency. The electrochromic films produced by W18O49 nanowires and WO3 have excellent performance. Compared with WO3 film, the porous structure of the nanowires can make ions rapidly diffuse, provide a larger surface area for the charge transfer reaction, promote electrolyte penetration, and effectively improve the electrochromic efficiency. In this paper, a kind of electrochromic tungsten oxide thin film combining W18O49 nanowires and WO3 was prepared by combining a hydrothermal method and a tungstic acid method. The electrochromic performance of the film was improved considerably by combining the two kinds of thin films. The results show that the optical modulation amplitude is close to ideal (92.5%) and has a fast colour fading (colour 1.7 s and colour fading 1.3 s) effect, a good cycle stability, which is much better than those of the WO3 and W18O49 films. Using lithium perchlorate and PC as raw materials and polyurethane as a photocuring agent, a solid-state electrochromic device based on a tungsten oxide composite film was fabricated by capillarity. The colouring time of the device is 2 s, the fading time is 1 s, and the optical modulation amplitude is 85%.

1. Introduction

At present, electrochromism is mainly used in the field of smart windows, its color matching effect can effectively block the incidence of infrared light, so as to reduce indoor temperature and achieve the effect of energy saving and emission reduction. It can also be used as a rearview mirror to prevent glare and greatly improve driving safety. In the lab, electrochromism is also studied as a supercapacitor, and its color change can be used as a sign of the charge and discharge stage [1–3]. As a electrochromic cathode material, tungsten oxide (WO3) is one of the most promising nonelectrochromic materials. It has the characteristics of a fast response, low cost, good chemical stability and strong adhesion [4, 5]. However, WO3 thin films have a long response time, poor stability and low colouring efficiency, which limit their use. Compared with WO3, W18O49 has more oxygen defects and a larger aspect ratio, which forms a scattered staggered stack to form a hollow structure and provides a channel for ion migration [6, 7]. At present, the preparation methods of W18O49 include the sputtering method, chemical vapour deposition method, sol-gel method, solvothermal method, electrochemical method and solid phase method [8–12]. A single non-electrochromic material has a series of problems, such as a simple colour change effect, slow colour response, long colour change time, small optical control range, and poor cycle stability. To optimize its electrochromic performance, different kinds of nonelectrochromic materials can be compounded to complement each other to prepare inorganic/inorganic composite electrochromic films with better performance.

Rakibuddin et al [13] prepared MoS2/WO3 nanocomposite films by the sol-gel spin-coating method. Compared with pure WO3 films, the composite films had a higher optical contrast (ΔT ~ 75%–60%), better...
colouration efficiency (39.4–51.2 cm²·c⁻¹), and shorter colour-fading time (11 s/8.8 s). Jin-long Wang et al [14] reported a new route for the large-area synthesis of nanowires (NWs), resulting in the formation of multilayer ordered nanowire (NW) networks with tunable conductivity (7–40 Ω·sq⁻¹) and transmittance (58–86% at 550 nm) for the fabrication of flexible transparent electrochromic devices, showing good stability of electrochromic switching behaviours.

Both tungsten oxide particles and tungsten oxide nanowires have excellent electrochromic properties. In this paper, we will explore whether the composite films with the combination of tungsten oxide particles and tungsten oxide nanowires also have excellent properties. And explore the effect of morphology on electrochromic properties.

2. Experimental procedures

2.1. Preparation of WO₃ and W₁₈O₄₉ nanowires

Five grams of tungsten powder was mixed with 20 ml of an H₂O₂ solution with a mass fraction of 30%. After the reaction, centrifugation (6000 rpm, 5 min) was used for filtration, the same amount of anhydrous ethanol was added, heated and stirred at 70 °C to remove excessive hydrogen peroxide, and WO₃ solution was finally obtained. WCl₆ powder (0.25 g) and PVP(C₆H₉NO)₆ (6 mg) were mixed with 500 ml of ethanol, evenly mixed and placed in the reactor for reaction at 180 °C for 12 h. The resulting solution was centrifuged (12000 rpm for 10 min), and the lower precipitate was dissolved in ethanol to obtain a W₁₈O₄₉ nanowire solution.

2.2. Preparation of electrochromic thin films

The WO₃ solution was spun onto ITO glass (4000 r min⁻¹, 30 s). After annealing at 100 °C for 20 min, WO₃ films were obtained.

The W₁₈O₄₉ nanowire solution was spun onto ITO glass (4000 r min⁻¹, 30 s) 6 times. After annealing the spin-coated glass at 200 °C for 30 min, W₁₈O₄₉ nanowire films were obtained.

First, the W₁₈O₄₉ nanowire solution was spinner coated on ITO glass (4000 r min⁻¹, 30 s), annealed at 200 °C 5 times. Then, WO₃ solution was applied to the nanowire film at 4000 r min⁻¹ for 30 s. After annealing at 100 °C for 20 min, WO₃/W₁₈O₄₉ composite films were obtained.

2.3. Preparation of electrolytes

Five grams of anhydrous lithium perchlorate powder was mixed with 20 g of polycarbonate, and the electrolyte was obtained after stirring at 60 °C. The solid electrolyte precursor was obtained by adding light curing resin to the electrolyte.

2.4. Fabrication of electrochromic devices

Tape was stuck on both sides on the surface of the ITO conductive glass. To paste the good film and the glass stagger at certain positions, the electrolyte precursor droplets in the location of the two pieces of glass should not coincide. Fill the electrolyte precursor into the interlayer of two pieces of glass. After the precursor solution was completely full of interlining, with ultraviolet light electric parts, the precursor liquid electrolyte layer formation was cured.

2.5. The performance test

Scanning electron microscopy (SEM) was used to analyse the surface morphology of the films. The surface roughness and particle diameter of the film were observed by atomic force microscopy (AFM). The crystallization of thin films was analysed by x-ray diffraction (XRD). X-ray diffraction (XRD) was used to detect the photoelectron spectra of the W level of the sample. A UV-visible light spectrometer was used to measure the transmittance of the sample in the same band under different conditions. Electrochemical analysis of the sample was performed using an electrochemical workstation.

3. Results and discussion

The XRD pattern of the WO₃/W₁₈O₄₉ composite film is shown in figure 1. The diffraction peak of the W₁₈O₄₉ film (figure S1 available online at stacks.iop.org/MRX/8/095703/mmedia) can be attributed to the WO₃ phase, and it is most obvious in the direction of 2θ = 010 [15]. The electrochromic performance of metal oxides is closely related to the degree of crystallization. In general, crystal metal oxides have a better cycling stability than amorphous metal oxides [16–18]. Therefore, W₁₈O₄₉ film may improve the crystallinity of the WO₃/W₁₈O₄₉ composite film.
The WO₃/W₁₈O₄₉ composite film is made of WO₃ and W₁₈O₄₉ films (figure S2). The SEM images of the WO₃/W₁₈O₄₉ composite film without any cracks are shown in figures 2(a) and (b). At the same time, there were cracks in the WO₃/W₁₈O₄₉ composite film. The SEM images of cracks are shown in figures 2(c) and (d). To further explore the structure of the WO₃/W₁₈O₄₉ composite film, EDS scanning was performed. Figure 3 shows the EDS image of cracks in the WO₃/W₁₈O₄₉ composite film (figure 2(d)), where O, W and C represent film components and In represents Ito. It can be seen from the EDS figure that W is mainly distributed in the WO₃ film, and there is a small amount of W at the crack, but the content is much lower than that of the WO₃ film. A large amount of In was observed at the fracture, which was similar to the EDS observation of nanowires. Through EDS image analysis of the film cracks, it can be found that the WO₃/W₁₈O₄₉ composite film was based on the W₁₈O₄₉ nanowire film, and almost all the nanowires were covered by WO₃ particles. The surface composition and chemical valence of the WO₃/W₁₈O₄₉ composite films were detected by XPS. The characteristic peaks of W4f are located at 38.6 eV and 35.5 eV (figure 4), which indicates that the valence state of tungsten is W⁶+ [19]. The element distribution table of the WO₃/W₁₈O₄₉ composite film is shown in table S1.

Through the above analysis of the surface morphology and structure of the sample, a schematic diagram of the composite film can be obtained (figure 5).

As shown in the insets of figure 6(d), at 760 nm, the optical modulation amplitude of the WO₃/W₁₈O₄₉ composite film is 92.5%. It is much larger than that of the WO₃ film (58%) and W₁₈O₄₉ film (45%). The three
Figure 3. The EDS image of cracks in the WO$_3$/W$_{18}$O$_{49}$ composite film: (c) C; (d) O; (e) W; (f) In.

Figure 4. The XPS of the WO$_3$/W$_{18}$O$_{49}$ composite film.

Figure 5. The schematic diagram of the composite film.
kinds of films have a faster response time. The optical modulation amplitude of WO3/W18O49 nanowire films at 760 nm is much higher than that of the other two kinds of films. The transmission spectral curves of the WO3 film and W18O49 nanowire thin film at 760 nm are shown in figure S4. In addition, the transmittance difference at 760 nm is almost constant after multiple switches, indicating that the electrochromic film is relatively stable.

For the electrochemical characteristics, the CV of the WO3/W18O49 electrode was measured in the potential range of $\\pm 1 \text{ V}$, and the CV curve at a scanning rate of 0.1 V/s is shown in figure 6(c). The peak current and the area enclosed by the curve of the voltammetry cycle curve of the WO3/W18O49 composite film are much larger than those of the other two films (figure S5), which indicates that the capacity of accommodating embedded ions is obviously higher and the discoloration performance is better [20, 21]. The results agree with the optical properties. CA and CC tests were conducted on the film with potential steps from $-1$ to $1 \text{ V}$ for 400 cycles. Figure 6(a) shows the CA characteristic curve of the WO3/W18O49 composite film. The maximum current value in the colouring process is 40 mA, which is less than 120 mA in the fading process. This shows that the film resistance in the colouring process is great, and the reaction is difficult to complete. The current value in the fading process is high, the resistance is low, the fading reaction is easy, and the colouring reaction time should be longer than the fading reaction [22, 23]. Compared with WO3 and W18O49 films (figure S6), the maximum current of discoloration increases significantly, which indicates that the film resistance is small. With the increase in the number of cycles, the end-point current of the colouring reaction basically remains unchanged, which indicates that the device has good cycle stability. Figure 6(b) is the CC characteristic curve. It can be seen from the curve that from the beginning to the end of the cycle, with the increase of the number of cycles, the amount of charge movement is less, and the difference between the amount of charge needed for the first and last reaction is very small, showing good cycle stability, which is consistent with the curve shown in figure 6(a).

The improvement of its electrochromic performance is mainly due to the unevenness of the nanowires, which destroys the compactness of the WO3 film and enables the film to fully contact the electrolyte. The porous space between the nanowires provides a larger surface area for the charge transfer reaction, while tungsten oxide particles increase the roughness of the nanowire film surface, which provides a larger surface area for the charge transfer reaction [24].

4. Optical properties of devices

Capillary encapsulation is used to make the electrolyte precursor diffuse into the interlayer of two pieces of glass, and ultraviolet radiation is used to illuminate the electrical parts to solidify the precursor solution to form an electrolyte layer. Solid-state electrochromic devices with three kinds of thin films are obtained. The photographs of the solid-state electrochromic devices is shown in figure 7. Figure 8 shows the structure of the solid
electrochromic device with the WO₃/W₁₈O₄₉ composite film and ITO film at the bottom, LiClO₄/PC (propylene carbonate) as the counter electrode and light cured resin as the consolidation agent.

Figure 9 shows the transmittance spectra of electrochromic devices made of WO₃/W₁₈O₄₉ composite films in the visible light band under the coloured state (FIGURE S8). At a voltage of 2.5 V, the optical transmittance of the WO₃/W₁₈O₄₉ composite film devices in the visible spectral band is higher than that of WO₃ and W₁₈O₄₉ thin film devices, and the colour of the W₁₈O₄₉ thin film device is the lightest. The transmittance of the device is almost the same as that of the film in the whole wave band, which indicates that the manufacturing process of the device has no great influence on the transmittance of the film.

The memory performance of an electrochromic device is usually obtained by measuring the change curve of the transmittance at a specific wavelength with time after removing the voltage. Figure 10 shows that the transmittance of the device will slowly rise with the advancement of time. The transmittance at 760 nm increases from 17% to 50% at 2 h, and the transparency is nearly restored at 4 h. With the increase in memory time after power off, the modulation range gradually decreases to 0.
5. Conclusions

In this paper, WO$_3$/W$_{18}$O$_{49}$ composite films were prepared by the tungstic acid method and hydrothermal method. The colour transmittance is close to 10%, and the colour response time and fading response time are 1.7 s and 1.3 s, respectively. The colouration efficiency is much higher than that of WO$_3$ films and W$_{18}$O$_{49}$ nanowire films. The improvement of the electrochromic performance is mainly because the unevenness of the nanowires destroys the compactness of the WO$_3$ film so that the film can fully contact the electrolyte. Meanwhile, the tungsten oxide particles increase the roughness of the surface of the nanowires, providing a larger surface area for the charge transfer reaction. A solid-state electrochromic device based on a WO$_3$/W$_{18}$O$_{49}$ composite film was prepared by using lithium perchlorate and PC as raw materials and polyurethane as the curing agent. The colouration response time of the device was 2 s, and the fading response time was 1 s. The difference in the fading transmission rate at 760 nm reached 85%. Not much different from the thin film response time. This paper shows that the two morphologies of tungsten oxide materials can effectively combine and play a role in the electrochromic process, which is of guiding significance for improving the performance of tungsten oxide-based electrochromic devices. Further, if the advantages of both can be more effectively used to prepare composite films, for example, making nanowires into a grid to reduce the contact area between nanowires can effectively reduce the contact resistance, or particles can be more flat stacked in the grid can effectively increase the integrity of the composite mode, the performance of the device will be better.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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