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Effect of Ar/O_2 ratio on double-sided electrochromic glass performance

Chien Chon Chen [a], Wern Dare Jheng [b,*]

[a] Department of Energy Engineering, National United University, Miaoli 36003 Taiwan
[b] Department of Mechanical Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan

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Abstract

This paper reports the qualities of WO_3 film and NiO film added to a counter electrode and their use in a double-sided electrochromic glass device. A mixture of argon and oxygen gasses with ratios of Ar/O_2 of 1.5, 2, 3, and 5 were used for the deposition of the working electrode of WO_3 film for EC glass. The structure of double-side EC glass consists of glass/ITO/NiO/electrolyte/WO_3/ITO/glass/ITO/WO_3/electrolyte/NiO/ITO/glass layers. The working electrode of WO_3 film controls the color presented, the applied voltage controls the color depth, and the counter electrode controls the transparency in the bleached state. The double-sided EC glass with double WO_3 films and double NiO films have faster coloration/bleaching rates than do single-sided EC glass. A mixture of Ar/O_2 ratio of 3.0 has the best coloration/bleaching property of the ratios tested. Compared to the single-sided EC glass, the double-sided EC glass has lower transmittance of about 72% and 6% than the 78% and 12% during coloration and bleaching states in the visible light region with +1.5 V and −3.5 V applied.

Keywords: WO_3; NiO; Electrochromic glass; Double sides; Transmittance

1. Introduction

Electrochromic (EC) windows change color when an electrical charge is applied and become transparent and colorless when it is removed. Such devices have multiple layers of heat insulator film of zirconium dioxide (ZrO_2), working electrode of indium tin oxide/tungsten oxide (ITO/WO_3), electrolyte, counter electrode of platinum/ITO (Pt/ITO), and protective glass on both top and bottom. The ZrO_2, WO_3, Pt, and ITO work as heat insulator film, vacuum tube film, electrochromic film, catalytic film, and ion storage film, respectively. This type of electrochromic material is able to sustain reversible and persistent changes of its optical properties upon the application of a voltage [1].

Transition metal oxides such as WO_3 [2], nickel oxide (NiO) [3], molybdenum trioxide (MoO_3) [4], and iridium oxide (IrO_3) [5] have been widely studied for use in electrochromic materials. Among the inorganic compounds, WO_3 thin film has significant advantages over the others in terms of reversibility, stability, and color efficiency. Because of those qualities, WO_3 thin film is one of the most promising EC materials, with good potential for application in large-area displays and light-modifying materials [6,7]. Nickel oxide is an outstanding anodically coloring electrochromic material due to its large span in optical density between fully bleached and fully colored states and low material cost. It is also considered to be a model semiconductor with p-type conductivity because of its wide band-gap energy range of 3.6–4.0 eV [8]. Additionally, NiO_x thin films play an important role as a complementary counter layer to the WO_3 layer for enhancing the coloration efficiency and contrast ratio [9]. Methods for preparing WO_3 and NiO_x films include sputtering [10], spray pyrolysis [11], chemical vapor deposition [12], electrodeposition [13], and sol–gel deposition [14,15].

Among these methods, reactive sputtering is most widely used, and NiO_x films with good electric and optical properties have been thus obtained [16–19]. In this article, we present a systematic way to study and better understand the relationship among electrochromic glass processing parameters (such as film quality and NiO film effects) and performance measurements (such as transparence, color/bleach rate, and color uniformity). In order to get a fast coloration/bleaching rate of EC glass, we made double-sided EC glass that can achieve different degrees of transparency between the dyed and

* Corresponding author.
E-mail address: jen102@ncut.edu.tw (W.D. Jheng).

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bleached states. The double-sided EC glass includes four ITO films, two WO_3 films, and two NiO films. We also vary the ratios of argon/oxygen (Ar/O_2) during physical vapor deposition (PVD) making good WO_3, ITO, and NiO transparent films.

2. Experimental

EC glass with a single working electrode device has a configuration of glass/ITO/WO_3/1 M $LiClO_4$-PC/NiO/ITO/glass, and a double working electrodes device has a configuration of glass/ITO/NiO/1 M $LiClO_4$-PC/WO_3/ITO/glass/ITO/WO_3/1 M $LiClO_4$-PC/NiO/ITO/glass. The films of ITO, WO_3, and NiO were deposited by RF magnetron sputtering, and thickness was detected by film detector (ET4000). The ITO film was deposited onto glass using a 4-in. ITO target with a purity of 99.99%. The base pressure of the deposition chamber was kept at 1×10^{-6} Torr. Working pressure was 5×10^{-4} Torr, and sputtering power during deposition was 100 W, 50 V bias, applied for 30 min. In order to obtain a lower resistance of ITO film, the thickness of the ITO film was 530 nm by deposition. The WO_3 thin film was deposited onto ITO (10 Ω/sq) glass by (RF) magnetron sputtering using a 4-inch tungsten metal target with a purity of 99.99%. A mixture of argon and oxygen gasses with ratios of Ar/O_2 of 1.5, 2, 3, and 5 were used for the deposition. The base pressure of the deposition chamber was kept at 1×10^{-6} Torr. Working pressure was set to 5×10^{-3} Torr, and sputtering power during deposition was 100 W for 40 min. The thickness of the WO_3 film was about 140 nm. The NiO thin film was deposited onto ITO (10 Ω/sq) glass by RF magnetron sputtering using a 4-in. nickel tungsten metal target with a purity of 99.99%. A mixture of argon and oxygen gasses with a ratio of Ar/O_2 of 3 was used for the deposition. The base pressure of the deposition chamber was kept at 1×10^{-6} Torr. Working pressure was set to 5×10^{-3} Torr, and sputtering power during deposition was 100 W for 30 min. The thickness of the NiO film was about 50 nm.

EC glass with a size of 5 cm × 5 cm was fabricated by assembling two pieces of ITO glass in the following way. The two electrodes were assembled into a sandwich-type cell and sealed with hot-melt film (SX1170, Solaronix, thickness 0.1 mm), and the electrolyte was injected into the space between the two electrodes with a syringe. The EC glass device was fabricated accordingly. The device was finally sealed with vacuum glue. The optical transmission and reflection spectra were recorded using a UV–VIS–NIR optical photometer (JASCO V570) with an integrating sphere (JASCO ISN-470) in the range of 300–1100 nm. The electrochromic properties were characterized using cyclic voltammetry (CV) with an impedance measuring unit (IM 6) from Zahner. Two electrodes were used to perform the electro-chemical tests in an electrolyte of 1 M $LiClO_4$ in propylene carbonate solution.

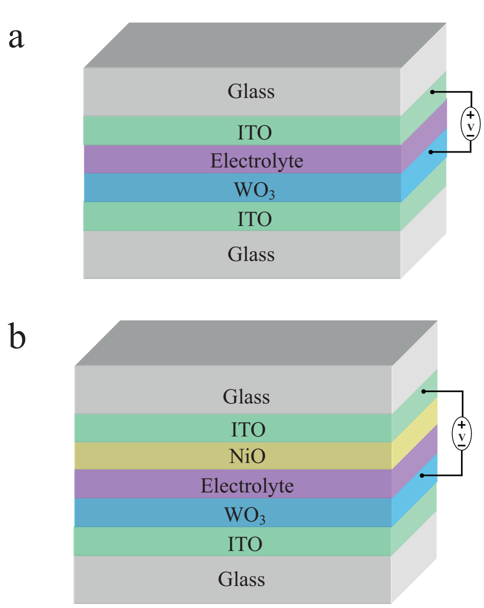

Fig. 1. Schematic diagram of EC electrochromic glass based on WO_3 as working electrode: (a) ITO as counter electrode, (b) NiO/ITO as counter electrode, with negative voltage (−) applied to working electrode and positive voltage (+) to counter electrode.

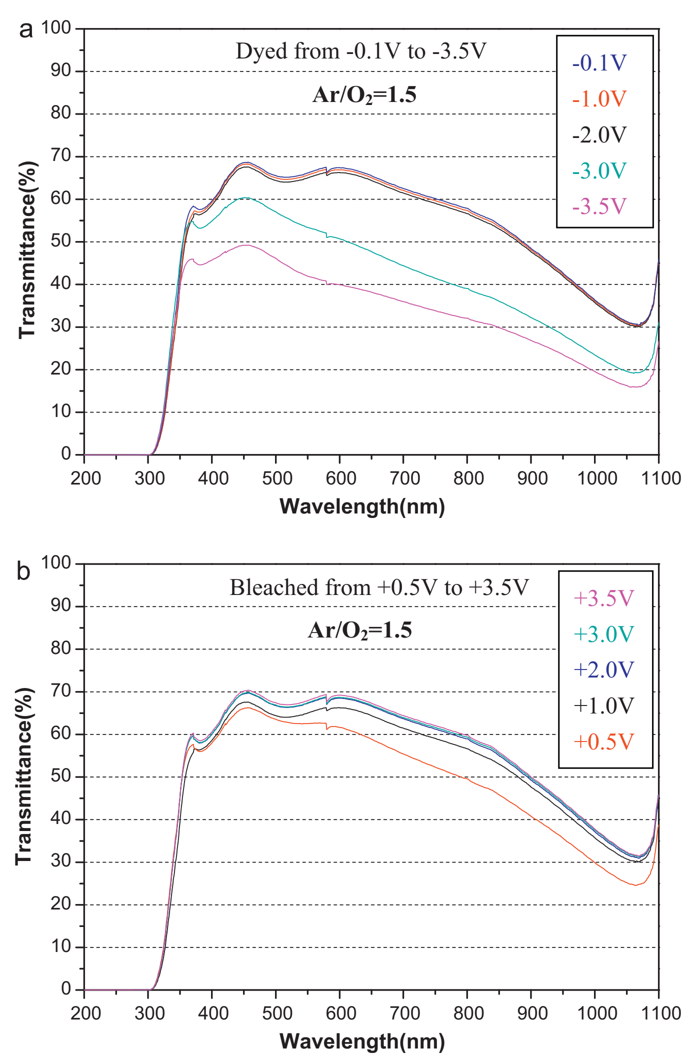

Fig. 2. Transmission spectra of EC glass with Ar/O_2 ratio of 1.5 for WO_3 film deposition under (a) dyed state from −0.1 V to −3.5 V applied, and (b) bleached state from +0.5 V to +3.5 V.

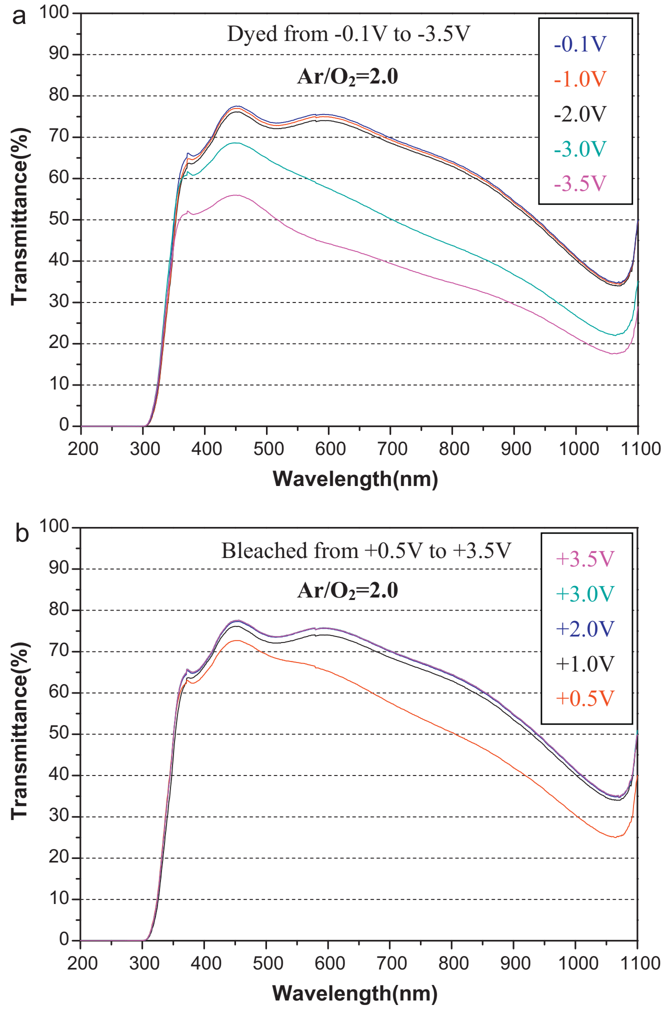

Fig. 3. Transmission spectra of EC glass with Ar/O_2 ratio of 2.0 for WO_3 film deposition under (a) dyed state from −0.1 V to −3.5 V applied, and (b) bleached state from +0.5 V to +3.5 V.

3. Results and discussion

Fig. 1 shows a schematic diagram of electrochromatic glass, comprising transparent substrates (glass), working electrode (ITO/WO_3), ion conductive layer (1 M $LiClO_4$-PC), and (a) a general structure using ITO as counter electrode, (b) a modified structure using NiO/ITO as counter electrode, with negative voltage (−) applied to working electrode and positive voltage (+) to counter electrode. The electrochromic film, WO_3, can serve as an interaction host for hydrogen (H^+) or lithium (Li^+) ions from the electrolyte of 1 M $LiClO_4$-PC. When a negative voltage (−) was applied to the device, the color of the transparent film of WO_3 changed to blue (the dyed state). When a positive voltage (+) was applied to the device, the blue film of WO_3 again became transparent (the bleached state). In this electrochromatic glass device, the working electrode of WO_3 film controls the color presented, the applied voltage controls color depth, and the counter electrode controls the transparency in the bleached state. NiO has better properties than ITO for EC glass devices because NiO can restrict hydrogen or lithium ions holding the counter electrode, making a transparent counter electrode in the bleached state.

The WO_3 film, which controls color depth and thus the dyed or bleached states, is the most important film in EC glass. The quantity of oxygen affects the quantity of defects in WO_3. A higher quantity of defects in WO_3 film results in a deeper color in the dyed state, while too much hydrogen or lithium ion doping in WO_3 film can cause ion retention in WO_3 film in the bleached state. Therefore, to obtain a high quality of reversible reaction in EC glass requires careful control of the quantity of defects in WO_3 film. Figs. 2–5 present transmission spectra of EC glass produced with Ar/O_2 ratios of 1.5, 2.0, 3.0, and 5.0 for WO_3 film deposition under (a) dyed state, with −0.1 V to −3.5 V applied, and (b) bleached state, from +0.5 V to +3.5 V. The average transmittance value from 380 nm to 760 nm wavelength was used to evaluation the transmittance property of EC glass in the visible region. Fig. 2 shows that with the relatively low Ar/O_2 ratio of 1.5 during WO_3 film formation, EC glass has a lower transmittance at −3.5 V applied for dyed,

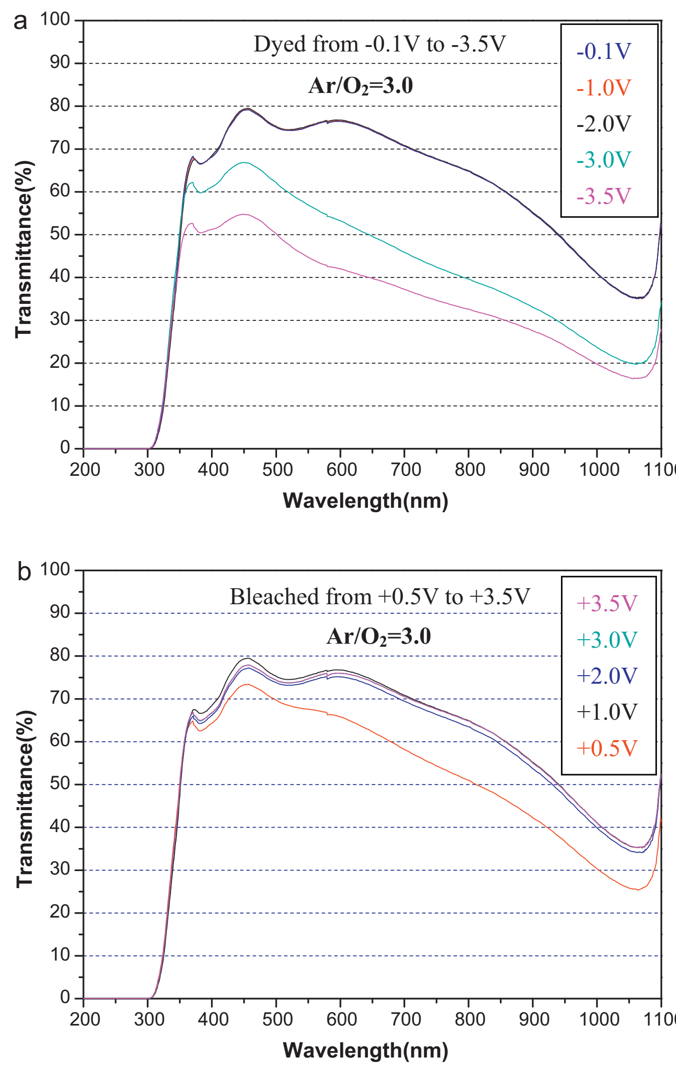

Fig. 4. Transmission spectra of EC glass with Ar/O_2 ratio of 3.0 for WO_3 film deposition under (a) dyed state from −0.1 V to −3.5 V applied, and (b) bleached state from +0.5 V to +3.5 V.

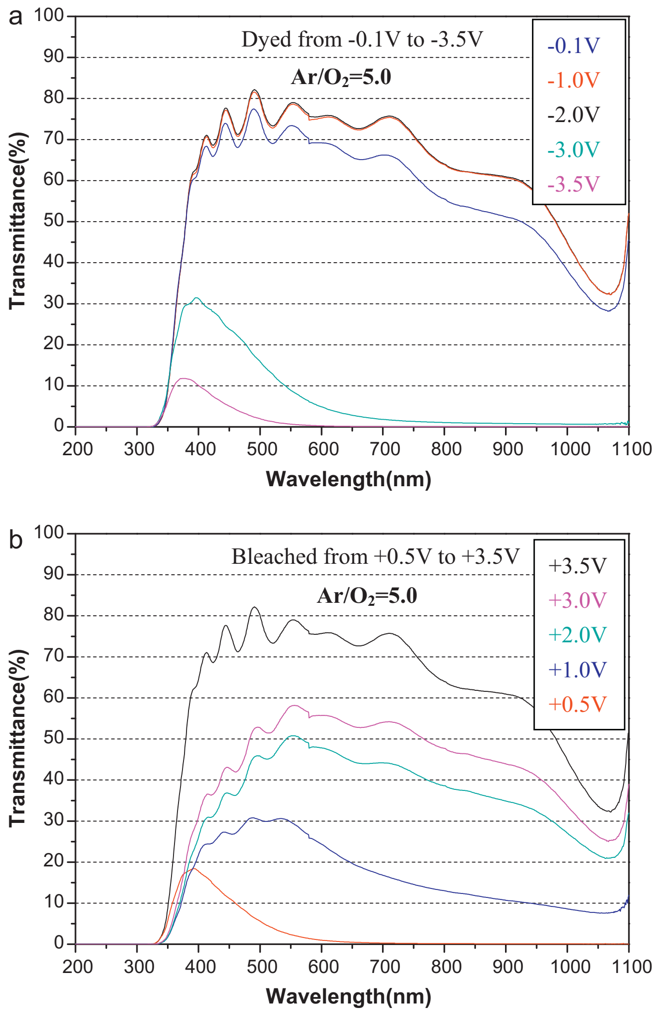

Fig. 5. Transmission spectra of EC glass with Ar/O_2 ratio of 5.0 for WO_3 film deposition under (a) dyed state from −0.1 V to −3.5 V applied, and (b) bleached state from +0.5 V to +3.5 V.

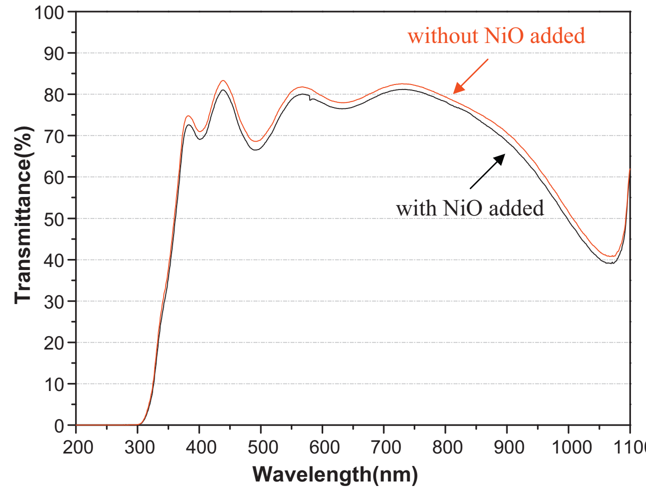

Fig. 6. Transmission spectra of EC glass with NiO added as counter electrode, which affected transparence by less than 1%.

and a higher transmittance at +3.5 V applied for bleached, in the visible light region. However, under lower working voltages, for example −0.1 V, −1.0 V, −2.0 V, −3.0 V, +0.1 V, +1.0 V, +2.0 V, and +3.0 V, the EC glass has lower electrochromic properties. Figs. 3 and 4 show that using Ar/O_2 ratios of 2 and 3 during WO_3 film formation yields EC glass with transmittance of about 71% in the visible light region with +3.5 V applied. Fig. 5 shows that using an Ar/O_2 ratio of 5 during WO_3 film formation yields EC glass with transmittance of about 73% and 0% in the visible light region with +3.5 V and −3.5 V applied. However, the sample in that figure cannot return to the transparent state when the applied voltage is lower than +0.5 V. Even when the applied voltage is increased to +3 V, the EC glass has just about 53% transmittance in the visible light region. Based on the above results, when the Ar/O_2 ratio is lower than 3, the EC glass has a higher transmittance with the dyed state in the visible light region. Excessive O_2 causes formation of a dense WO_3 film (too few crystal defects in the WO_3 film) during PVD. On the other hand, when the Ar/O_2 ratio is higher than 3, the WO_3 film has a residue color in the bleached state (too many crystal defects in the WO_3 film). Therefore, the Ar/O_2 ratio should be controlled to between 2 and 3 to form a suitable WO_3 film for EC glass. In addition, the WO_3 film can have suitable crystal defects or doping positions for H^+ and or Li^+. Also, NiO can restrict hydrogen or lithium ions held in the counter electrode, making a transparent counter electrode in the bleached state. The transmittance of the Ar/O_2 ratios of 1.5, 2.0, 3.0, and 5.0 are about 69%, 76%, 78%, and 75% under the bleached state and about 40%, 43%, 41%, 0% under the dyed state at 600 nm, −3.5 V, +3.5 V applied. The Ar/O_2 ratio of 5.0 has 0% transmittance under the dyed state; however, the EC glass is irreversible because of a heavy residue color in the WO_3 film.

Electrochromism of NiO films is generally accepted as the coloration and transition from a bleached to a colored state. It is related to a charge-transfer process between $Ni^{3+}$and Ni^{2+} associated with the OH^- ions or H^+ ions. Furthermore, NiO film can reduce the residue color in the counter film when EC glass is under the bleached state. Fig. 6 presents the transmission

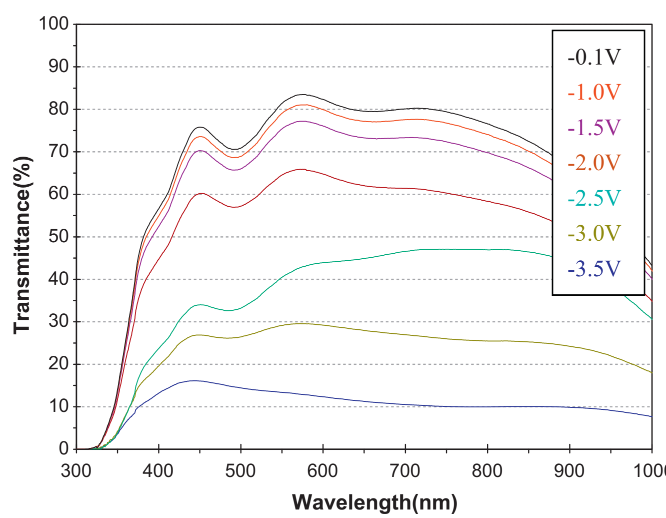

Fig. 7. Transmission spectra of EC glass with NiO as counter electrode and Ar/O_2 ratio of 3.0 for working electrode of WO_3 film deposition under dyed state from −0.5 V to −3.5 V applied.

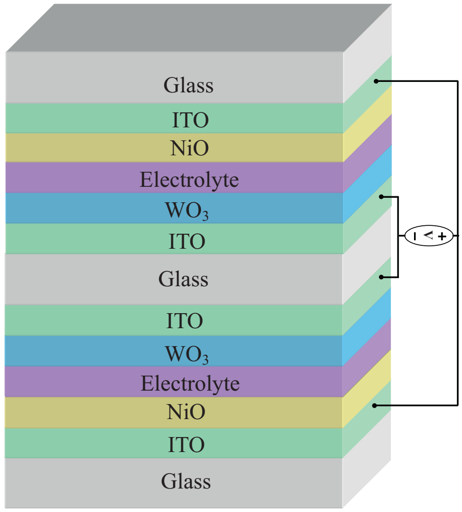

Fig. 8. Schematic diagram of double sides EC electrochromic glass based on double WO_3 as working electrodes and double NiO as counter electrodes, with negative voltage (−) to working electrode, and positive voltage (+) applied to counter electrode.

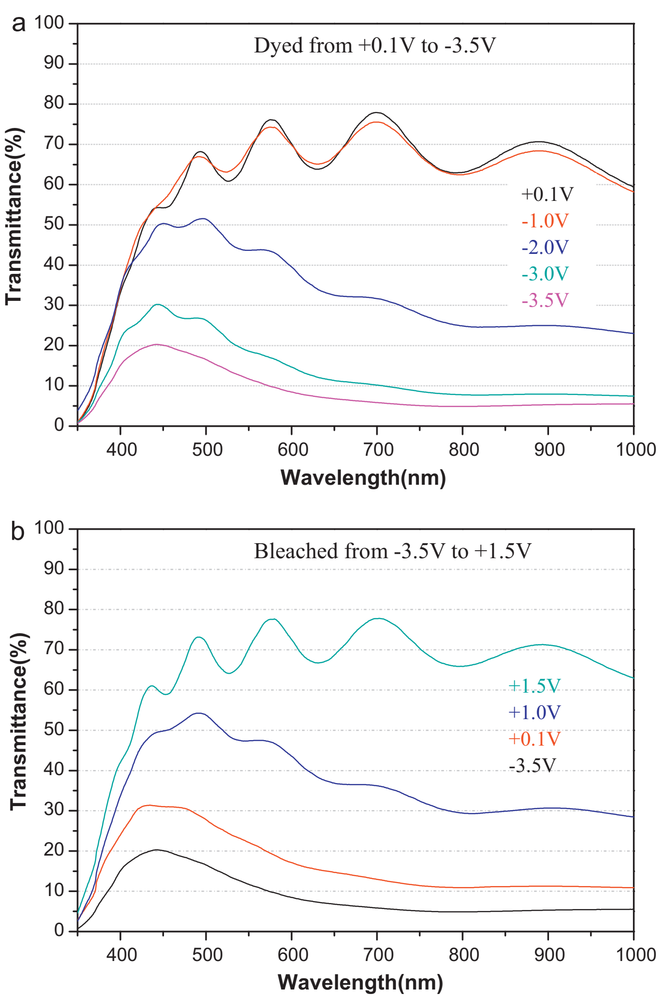

Fig. 9. Transmission spectra of double-sided EC glass under (a) dyed state from −0.1 V to −3.5 V applied, and (b) bleached state from +0.5 V to +3.5 V.

spectra of EC glass with NiO added as counter electrode, which affects transparency by less than 1%. Fig. 7 presents transmission spectra of EC glass with NiO as counter electrode and an Ar/O_2 ratio of 3.0 for working electrode of WO_3 film deposition under the dyed state with −0.5 V to −3.5 V applied. The EC glass has transmittance of about 78% and 12% in the visible light region with −0.1 V and −3.5 V applied. In addition, the color depth can be controlled carefully with the applied voltage.

In order to obtain a greater difference in EC glass transmittance between the dyed and bleached states, we produced double-sided EC electrochromic glass. Fig. 8 presents a schematic diagram of the double-sided EC electrochromic glass, the structure of which was glass/ITO/NiO/1 M $LiClO_4$-PC/WO_3/ITO/glass/ITO/WO_3/1 M $LiClO_4$-PC/NiO/ITO/glass. The double WO_3 is the working electrodes, and double NiO is the counter electrodes, with negative voltage (−) applied to the working electrodes and positive voltage (+) to the counter electrodes. Fig. 9 presents the transmission spectra of double-sided EC glass under (a) the dyed state, with −0.1 V to −3.5 V applied, and (b) the bleached state, with +0.5 V to +3.5 V applied. The EC glass has transmittance of about 72% and 6% in the visible light region with +1.5 V and −3.5 V applied.

4. Conclusions

A double-sided electrochromic device with a structure of glass/ITO/NiO/1 M $LiClO_4$-PC/WO_3/ITO/glass/ITO/WO_3/1 M $LiClO_4$-PC/NiO/ITO/glass was fabricated using ITO, NiO, WO_3 film, and $LiClO_4$-PC electrolyte. The films of ITO, WO_3, and NiO were deposited by triple-gun sputtering, which can produce high quality films. The NiO film can restrict hydrogen or lithium ions held in the counter electrode, making a transparent counter electrode in the bleached state, and a deep glass color can be controlled carefully with the applied voltage. The characteristics of the double-sided EC glass were determined using UV–VIS–NIR and CV equipment. The average transmittance of double–sided EC glass in the colored and bleached states was 6% and 72% in the visible light range, respectively.

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