Inorganic-Alone Solid-State Electrochromic Device for Application as Visible Near Infrared Region Electronic Curtain

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A prototype inorganic material-based solid-state electrochromic device (ECD) using an active WO₃ layer has been demonstrated followed by testing its potential application in blocking infrared (IR) radiation. A cost-effective hydrothermal method has been used for fabricating WO₃-based electrodes. Prior to application, the structural and morphological characterization of the WO₃ has been done using X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. A solid-state ECD has been fabricated in a sandwiched geometry with a supporting gel electrolyte. The solid-state inorganic ECD displays a color contrast of more than 40% at 600 nm wavelength while toggling between transparent (OFF state) and blue (ON state) colors under a bias of as low as 2.5 V making it a power-efficient device. The device is capable of maintaining its absorbance switching for longer than 2400 s without altering its absorbance rate. The device is capable of blocking IR radiation with more than 100% in its ON state as compared to its OFF state. A power-efficient electrochromic performance has been reported from an inorganic-alone solid state ECD while displaying its potential as an electronic curtain.

1. Introduction

Tungsten oxide (WO₃) is often considered the first material to display electrochromic properties as discovered by S. K. Deb in 1969. Bias-dependent reversible change in the optical appearance of a material is termed as “electrochromism” and the devices working on this principle are commonly known as electrochromic devices (ECDs). Electrochromic materials and devices are conjectured for multifunctional applications encompassing energy storage devices (battery, supercapacitor), sensors, solar cells, photocells, etc. The domain of electrochromic materials and devices seems to be a snowballed research area spanning its wings in different dimensions to attract scientists from various research areas. The ECDs have been potentially useful in antiglare mirrors, smart windows, display systems, and other related applications. As mentioned earlier, in spite of being the first ever material to be discovered with bias-dependent color change property of WO₃, an application-oriented device could not be demonstrated and thus needs to be revisited because of the robust nature of inorganic material.

After the successful demonstration of electrochromic properties in WO₃, oxides of titanium, nickel, cobalt, vanadium, and other inorganic materials have been explored for their potential in electrochromism. With successive progress of electrochromism in inorganic materials, organic, organometallic, coordination network complex, and herbal materials have been parallelly used for making ECDs. By and large, it seems that almost every category of material has been explored for electrochromic application till now. Recent research development focuses on improving ECD performance in terms of switching speed, color contrast, stability, and other performance parameters. This is done by adapting various device paradigms including hybrid device design, incorporation of the counter material, or graphene or other 2D material in device geometry. The inclusion of a counter electrode with inherent electrochromic property is proven to be an efficient method in enhancing ECD’s performance while giving an additional color appearance under appropriate bias conditions.

Often inorganic materials have been studied for their electrochromic performance in an electrolytic medium. Another research interest lies in the study of the electrochromic performance of inorganic material in solid-state device form, which has not been much explored. It has two-fold benefits: i) it will allow to study the electrochromic performance of an inorganic material as a single entity and especially their infrared absorbance characteristic which furthermore can be utilized for making infrared shielding devices, and ii) it will provide an opportunity to understand their electrochromic performance alone and this will help in designing efficient hybrid devices.

In this work, solid-state ECD with a WO₃ layer on fluorine-doped tin oxide (FTO)-based glass electrode has been designed using an active WO₃ layer has been demonstrated followed by testing its potential application in blocking infrared (IR) radiation.
and a gel electrolyte layer is used to finish the device in a cross-bar geometry. The electrochromic performance of the device has been evaluated by measuring its color contrast, cyclability, and switching time. The device shows color switching in the visible region as well as in the near-infrared region of the electromagnetic spectrum. The device shows encouraging performance and can be used as a switchable electronic curtain to be switched between colored and transparent states in less than one second. Moreover, the device was found capable of shielding the “heat” component from the optical spectrum by suppressing the transmission of the infrared component by a small bias of 3 V.

2. Results and Discussion

Hydrothermally grown WO₃ films were characterized for their structural properties using various techniques as discussed here. XRD analysis of as-fabricated WO₃ film on the FTO electrode has been done for phase purity of the film using Cu Kα radiation of 1.5 Å wavelength in Bragg Brentano geometry. The XRD pattern depicted in Figure 1a shows peaks originating from WO₃ and FTO marked with alphabets w and f, respectively. The peaks positioned at 13.8°, 23.4°, and 27.7° (denoted with the alphabet “w” in Figure 1a) correspond to (100), (002), and (200) diffraction planes, respectively. This is in good agreement with values of WO₃ peaks given in JCPDS no. 85-2460 as shown in Figure S1, Supporting Information. Different vibrational modes of WO₃ have been studied using Raman spectroscopy as shown in Figure 1b. The Raman stoke peak at 291 cm⁻¹ corresponds to δ(W=O–W) vibrational mode, peak at 778 cm⁻¹ belongs to θ(W–O–W) vibrational mode, and W = O vibrational mode originates from the peak at 947 cm⁻¹ while peak positioned at 701 cm⁻¹ belongs to FTO substrate.[34–37] The surface morphology of the WO₃ film has been characterized using SEM as shown in Figure S2, Supporting Information. The presence of various oxidation states of WO₃ has been detected using XPS as discussed in the following in detail.

Full survey scan of XPS spectra from 0 to 800 eV binding energy is given in Figure 2a which clearly indicates the formation of WO₃. The full survey XPS scan indicates the presence of W, O, and N in the WO₃ film. The presence of W and O peaks is obvious due to the chemical composition of WO₃, whereas the N₁s peak is a signature of the defect in WO₃.[38,39] Figure 2b shows high-resolution scan of the 4f shell of WO₃ with two distinctive peaks at 35.7 and 37.8 eV arising from spin–orbit coupling of W-4f⁷/₂ and W-4f⁵/₂ states, respectively, corresponding to W⁶oxidation states. Peaks positioned at 36.4 and 35.08 eV also arise from the interaction of W-4f⁷/₂ and W-4f⁵/₂ states, respectively, and give rise to the W⁵oxidation state.[40] The W₄d signal shows two peaks arising from the binding energy of 247.5 and 260 eV as shown in Figure 2c and their separation is 12.5 eV suggesting a W⁶oxidation state.[41,42]

Peak positioned at 530 eV contributes to the oxygen present in the WO₃ structure while the other at 532 eV signifies residual oxygen presence due to surface contamination as shown in Figure 2d. Moreover, the ratio of W⁶ and W⁵ is found to be 1:0.22 according to integrated areas from Figure 2b. After normalization, the chemical formula obtained using XPS (from Figure 2b,d) is W₀.₈₂⁺⁶ W₀.₁₈⁺⁻⁵ O₂.₃₁ which is in good agreement with the ideal WO₃ formula.[40,43] All these characterization techniques confirmed the presence of WO₃ uniformly deposited on the FTO substrate. Fabrication of a solid-state ECD comprising WO₃ film with gel electrolyte using appropriate device geometry is discussed in the following in detail.

The solid-state device geometry consists of two FTO electrodes in a sandwich geometry with WO₃ on the FTO electrode as active material (upper FTO electrode in Figure 3a) and lithium perchlorate in the polyethylene oxide (PEO) gel matrix as an electrolyte. The WO₃ containing FTO electrode is connected to the positive terminal while the other FTO electrode is connected to the negative terminal of a battery. The as-fabricated device contains WO₃ film which is composed of W⁶ and W⁵ as discussed earlier and the same has been depicted in Figure 3a, which is the initial state of the device. When a bias of -3 V is applied to the device, ion insertion is accompanied by the flow of charge balancing electrons in the WO₃ crystal structure and leading to the reduction of W⁶ ions to W⁵, and this process is shown in Figure 3b. Under this situation, the WO₃ film is in its reduced state and indicated by R-WO₃ (Figure 3b), and this state is termed as ON state of the device. The presence of W⁵ ions leads to coloration of WO₃ film.[44] When the external bias is changed to 2.5 V, without altering polarity of the device or battery, the reduced WO₃ film regained its original configuration with the dominance of W⁶ ions in the WO₃ film as shown in
Figure 3c, and this state is termed as OFF state of the device. Oxidation and reduction processes induced by external bias lead to a change in the ionic configuration of WO$_3$ film which effectively changes color of the device and is thus responsible for electrochromic alteration of the WO$_3$ film. Quantification of color appearance of the device, under different bias conditions, has been done using in situ absorbance spectroscopy as discussed in the following in depth.

Real images of the device under two operating states ON ($-3\ V$) and OFF (2.5 V) are shown in Figure 4a,b respectively. In situ bias-dependent absorbance spectroscopy of the device has been done in UV-visible–near infrared (NIR) wavelength region as shown in Figure 4c. The device is initially transparent to naked eyes as observed from the black curve in Figure 4c and does not absorb much in the NIR wavelength region. With the bias of $-3\ V$, as per the polarity arrangement shown in Figure 3b, the device changed its appearance from transparent to blue color as evident from red curve of Figure 4c. The reduction of W in WO$_3$ film, due to an applied external bias leads to coloration of the device and the same is reflected in red curve of Figure 4c. The device regained its initial transparent appearance with an applied bias of 2.5 V (blue curve, Figure 4c) and retraced its initial state’s black curve as shown in Figure 4c. Under this situation, a bias of 2.5 V initiated a redox reaction in the already reduced form of WO$_3$ and which turns WO$_3$ to its initial state as reflected in the blue curve of Figure 4c. The device has an optical contrast of more than 40% at 600 nm
wavelength. Previous works on electrochromic property of WO₃ film are limited to their optical properties in an electrolytic medium as evident from the work by D. S. Dalavi et al. where the achieved transmittance modulation is 88.5% at 550 nm wavelength in 0.5 M LiClO₄ of propylene carbonate electrolyte. The work done by H. Kim et al. reported transmittance modulation of 44% at 800 nm wavelength from a WO₃-based device. One of the interesting features of the device is that it absorbed more than 100% of NIR wavelength region in its ON state as compared to its OFF state. This will be an important factor in utilizing the device’s potential for heat shield and espionage applications. The device’s electrochromic performance between ON and OFF states has been measured using in situ spectroelectrochemistry as discussed in the following in detail.

The device shows an optical contrast of more than 40% at 600 nm wavelength between its ON (2.5 V) and OFF (2.5 V) states as observed in Figure 4c. The device switches back and forth between ON and OFF states for more than 1200 s as shown in Figure 5a. The device took 0.8 s to switch from ON to OFF state and 2.1 s to go to its ON state such that there is a 90% transmittance change as shown in Figure 5b. A time interval of 5 s is chosen for switching between two states to give sufficient time to saturate the transmission curve such that no information is lost during continuous cyclic switching. It can be rationalized that the device shows compatible performance in the domain of inorganic material-based solid-state ECDs as shown in Table 1 and this is even without the support of any counter electrode to support its redox reaction responsible for reversible electrochromism. Furthermore, the device shows an excellent capability of shielding IR reaction and thus potentially be useful as a heat shield device for espionage and camouflage applications.

3. Conclusion

An inorganic solid-state ECD comprising WO₃ and a gel electrolyte shows IR shielding properties when the device is turned ON with an applied bias of only −3 V. The asymmetric stacked solid-state device, consisting of WO₃ and gel electrolyte (LiClO₄ + PEO), shows efficient reversible color switching between transparent and dark blue-colored states under 2.5 V (OFF) and −3 V (ON), respectively. The device stops transmission of significant amount of IR radiation present in the optical spectrum when the device is in its ON state. In addition to the infrared region, the device shows a color contrast of ≈43% in the visible region (600 nm) making it suitable for visible–NIR electronic curtains. The device has stable absorbance switching for more than 500 consecutive voltage pulses without degradation in its electrochromic performance. On the whole, the present study suggests that the WO₃-alone-based ECD has the potential of being used as an IR radiation blocker and thus seems to be a good candidate for real applications in military, space, and smart windows/buildings.

Table 1. Performance comparison of present work with other inorganic-based solid-state electrochromic devices.

| S. No. | Active component | ΔA | Switching time [s] | Applied voltage [V] | References |
|-------|-----------------|----|--------------------|---------------------|------------|
| 1.    | WO₃ nanorod     | 0.5 | 0.8/2.1            | 2.5/−3             | This work |
| 2.    | WₓOₓ₂Oₙₓ      | 0.3 | 8                  | 1.5/1              | Li et al. [46] |
| 3.    | WO₃₂H₂O        | 0.6 | 9                  | ±3                 | Liang et al. [47] |
| 4.    | WO₃            | 0.24| Not reported       | ±2.5               | Zhang et al. [48] |
| 5.    | Cu₂O₃          | Not reported | 3          | −0.1/−0.8        | Wang et al. [49] |
| 6.    | Prussian blue and TiO₂ | 0.30 | 3                  | 0.6/−0.2          | Seelant et al. [50] |
| 7.    | Prussian blue and poly(butyl viologen) | 0.58 | 10                 | 0.8/1.7           | Fan et al. [51] |
| 8.    | Prussian blue and Co₂O₃ | 0.4  | 2                  | 2/−1.5            | Chaudhary et al. [52] |
4. Experimental Section

Commercially available chemicals from Alfa Aesar™ and Sigma Aldrich™ were purchased and used as received. The chemicals that were used are tungstic acid (H₂WO₄, 99%, Sigma Aldrich), thiourea (SC(NH₂)₂, 99%, Sigma Aldrich), hydrogen peroxide (H₂O₂, 30 wt%, Merck), hydrochloric acid (HCl, 32%, Merck), acetonitrile (CH₃CN, AR, Sigma Aldrich), and maleic acid (C₄H₄O₄, LR, Sigma Aldrich). FTO-coated glass substrates were purchased from Macwin™. Tungsten oxide (WO₃) films were hydrothermally synthesized on FTO substrates. Details of WO₃ synthesis and procedure of device fabrication are provided in Supporting Information. Lambda 750 (Perkin-Elmer make) spectrophotometer was used for UV–vis measurements. Supra55 Zeiss microscope was used for performing scanning electron microscopy (SEM) characterization. X-ray diffraction (XRD) was done using Rigaku X-ray diffractometer (Cu Kα radiation of 1.54 Å wavelength) while for X-ray photoelectron spectroscopy (XPS) instrument of Leybold Heraeus company was used. Raman spectroscopy measurement was done using LABRAM-HR (Horiba) spectrometer and all electrochemical measurements were carried out using a Keithley-2450 source meter.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The author declares no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrochromic devices, hydrothermal, infrared, solid-state, tungsten oxide

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