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RESEARCH ARTICLE

Electrodeposited Tungsten Trioxide (WO_3) Thin Films for Electrochromic Applications

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ABSTRACT: The need of smart and innovative technology with energy saving approach is the main and serious concern while dealing with fastest growing urbanization and civilization. The smart technologies like electrochromic supercapacitors are beneficial in multifunctional way by providing energy storage systems with visual and reversible colour changes in many applications such as smart windows, electrochromic goggles, automotive mirrors, sunroofs, displays and so on. Herein, nanoporous WO_3 thin film is prepared by using cathodic electrodeposition technique and used to study electrochromic as well as electrochemical properties. The bi-functionality of the electrode was confirmed by electrochemical tests including CV, GCD, EIS and chrono methods. The film shows greater coloration efficiency up to 52.61 cm^2/C with an aerial capacitance 2.8 mF $/cm^2$. Also, film shows faster switching kinetics as faster coloration and bleaching times like 1.88 and 2.6 s respectively. Hence, electrodeposited WO_3 can be a good candidate for bi-functional electrochromic supercapacitors.

Keywords: Electrochromism, Electrochromic Supercapacitors, Electrodeposition, Tungsten Trioxide thin films

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1. INTRODUCTION

Currently, the world is grappling with the effects of climate change. Energy conservation and environmental protection stand as paramount tasks on a global scale. From an environmental perspective, mitigating severe climate change and reducing the emission of greenhouse gases, namely global warming, necessitates minimizing pollution from the built sector. Approximately 40% of greenhouse gas emissions originate from the building sector [1]. Greenhouse gas radiations are main reason of global warming and climate change. For energy conservation, electrochromic smart devices help to store energy with visual color changes on application of certain voltage. In the field of smart devices electrochromic technologies e.g., smart windows have gained more consideration because of their energy saving with thermal control ability benefits in the multi-application device [2]. The phenomenon in which the optical properties (absorbance/transmittance/reflectance) of material changes reversibly via electrochemical redox reaction under the effect of applied potential or current is termed as electrochromism [3]. The electrochromic supercapacitor is bifunctional application of tungsten trioxide (WO_3) which integrate electrochemical energy storage with electrochromic effect.

The WO_3 is cathodic coloration material change its color on the application of cathodic potential. Commonly used metal oxide Electrochromic materials are WO_3, NiO and V_2O_5. Among them WO_3 and NiO are a research hotspot of ESCs in recent years due to their feasibility as a bifunctional device. Electrochromic Supercapacitors mainly consist discoloration function, charge and discharge states and energy saving ability due to this they are demanded and have many expectations in recent years [4].

The transition metal oxides are most popular electrochromic materials with having partially filled d orbital with multiple oxidation states. Tungsten trioxide (WO_3) is an n-type semiconductor having 2.6 -3.0 eV band gap which is best electrochromic material possess high coloration efficiency with fast color switching [5]. The Tungsten trioxide has different types of crystal structures according to their formation at specific temperatures. The crystal structure of WO_3 consist of Tungsten atom at the central position and six oxygen atoms are surrounded to this

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central atom making it octahedral in geometry. As the oxygen vacancies are created at the time of reduction of W^{6+} ions the optical properties of Tungsten trioxide changes. The change in color is due to reversible intercalation and de-intercalation of ions in the WO_3 thin film. The electrochemical reaction of tungsten trioxide (WO_3) can be written as follow:

$$WO_3 + x\,(M^+ + e^-) \rightarrow M_x\,WO_3 \qquad (1)$$

Where, M is H^+, Li^+, K^+, Na^+, and so on, which are intercalated ions and e^- are donating electron. On the application of reducing potential, W^v sites are generated which are responsible for electrochromic effect.

$$\underset{\text{Transparent}}{WO_3} + x\,(M^+ + e^-) \rightarrow \underset{\text{Blue}}{M_x\,W^{VI}_{(1-x)}\,W^{V}_{x}\,O_3} \qquad (2)$$

Various deposition techniques are used for preparation of tungsten trioxide thin films which includes spray pyrolysis, hydrothermal method, spin-coating, sol-gel, chemical bath deposition, electrodeposition, and so on [6]. Among all these techniques electrodeposition methods have many advantages such as ease and fast process and by applying voltage we can controls the size, shape and thickness of the samples.

In this present work, we report that WO_3 thin films synthesized by potentiostatic dc electrodeposition method on FTO glass substrates. The effect of deposition time and the influence of pH on electrochromic performance of WO_3 thin films was studied. The electrochromic properties caused by charge intercalation/de-intercalation of ions was studied by using cyclic voltammetry, Chronoamperometry and Chronocoulometry. The thin films of tungsten trioxide were characterized by using X-Ray Diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Raman spectroscopy to study structural purity, surface topography and qualitative compositional analysis. The aim of this research is to study structural, morphological and Electrochromic properties of WO_3 thin films prepared by a simple electrodeposition method and their possible application for supercapacitor.

2. EXPERIMENTAL DETAILS

2.1. Chemicals and materials

Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), Hydrogen peroxide (H_2O_2, 30%) and perchloric acid ($HClO_4$, 60%) were used as precursors for electrodeposition bath solution. Distilled water was used throughout the experiment as solvent. Fluorine doped tin oxide (FTO) as conducting glass substrates were used as current collector and washed with acetone, ethanol and double distilled water for 15 minutes in each prior to the electrodeposition.

2.2. Preparation of WO_3 thin films

Tungsten Trioxide were synthesized by dissolution of 0.0125M of sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) and Hydrogen peroxide (H_2O_2, 30%) in 125 ml of double distilled water. After the drop-wise addition of $H_2O_2$the precursor solution was constantly stirred for 15 min., after that the pH of this precursor solution was adjusted between pH 1.8 to pH 1.2 which was acidified using perchloric acid ($HClO_4$). Then obtained solution were stirred for 15 min. This prepared solution was used as an electrolyte during electrodeposition in a three-electrode electrochemical cell.

For the electrode position of WO_3 thin films the FTO (Fluorine doped tin oxide) substrates were cleaned with double distilled water, acetone and ethanol under ultrasonic irradiation. After drying in air, FTO substrates were used for electrodeposition. Electrodeposition was carried out at room temperature (27°C) using a three-electrode cell using potentiostat (Metrohm's Multi Autolab M204) equipment in an electrochemical set up, with an Ag/AgCl as the reference electrode, a platinum wire as counter electrode and Fluorine doped tin oxide (FTO) coated glass as the working electrode. Films of WO_3 were deposited under various potantiostatic conditions, by varying deposition time (td) at constant cathodic potential of -0.63V for different samples. Just after taking electrodeposition the samples were rinsed with deionized water were appeared as dark blue and dried at room temperature and further annealed at 350°C for 60 min.

3. RESULTS AND DISCUSSION

3.1. Structural, morphological and compositional properties

X-ray diffraction technique was utilized to study structural purity, phase identification and crystallite size. X-ray diffractogram of the prepared sample is shown in the Figure 1(a). The most intense peaks are corresponding to the FTO is due to the lower thickness of the film which is maintained for the clear transmittance at the bleached state. The cubic crystal structure of the prepared sample is confirmed by comparing observed peaks having 2θ values 23.67°, 33.64°, 41.46°, 54.57°, 60.25° and 78.06° with JCPDS 00-046-1096 and are in good agreement with corresponding dhkl planes with miller indices (200), (220), (222), (420), (422) and (611) respectively. The calculated crystallite size ranges between 163 to 418 nm.

Raman spectroscopy is used for the analysis of Raman spectra of electrodeposited WO_3 thin films. The complex signals of Micro- Raman spectra of (WO_3 thin films) electrode is shown in Figure 1(b) which is in the range of 200 cm^{-1} to 1200 cm^{-1}. From spectral analysis of micro-Raman spectra, the stretching of W-O band on WO_3 appears at weak peak of maximum intensity at 556.7 cm^{-1}. Also, at 270.1 cm^{-1} the presence of asymmetric stretching in W-O bond was observed. While the peaks at 556.7 cm^{-1} and 637.4 cm^{-1} gives antisymmetric stretching vibrations of (W^{6+}-O) bond [5].

The broad high intense peak at 801.5 cm^{-1} represents stretching of (W^{6+}= O) bond. The weak peak at 270.1 cm^{-1}

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not always observed in amorphous WO_3. The diffusion of ions due to stretching of chemical bonds between oxygen atoms occurred at the porous surface of WO_3 film. The phenomenon of electrochromism occurred when the process of insertion and extraction of ions into the WO_3 thin film started and there is reduction of W^{6+} to W^{5+} state. The peaks observed at 270.1, 556.7, 637.4 and 801.5 cm^{-1} represents the stretching and bonding between the tungsten metal cations and oxygen atoms respectively which indicates the pure formation of WO_3 [7].

The scanning electron microscopy was used to capture surface morphology and to confirm the formation of nanoparticles. The captured images at different magnifications shows the porous nature with interconnected nanoparticles with size ranging between 100 to 200 nm and some of the particles with larger size up to 400 nm. The porous morphology offers more voids for the easy ion intercalation and de-intercalation which is beneficial for active and fast electrochemical activity. The more active surface area offered by the observed porous structure with nanoparticles exhibits more surface-active sites and enhance the electrochromic performance by enhancing redox activity. Figure 2 (a-c) shows the images taken at different magnification. The compositional analysis was done by Energy Dispersive Spectroscopy (EDS) at lowest magnification which covering larger area for scanning as shown in Figure 2 (d). The qualitative confirmation of the presence of tungsten and oxygen is confirmed with respective atomic and mass percent.

3.2. Electrochemical analysis

3.2.1 Cyclic Voltammetry

Cyclic Voltammetry is an electrochemical measurement technique commonly used to know the value of deposition potential of metal oxides and to study the electrochemical behaviour of dissolved metal ions which gets absorbed on electrode surface in an electrolyte.

Table 1. A table of the properties of the various samples.

Samples	Temperature (°C)	Concentration (ppm)	Ref.
A	20	2	[7]
B	25	45	[8]
C	40	100	[9]

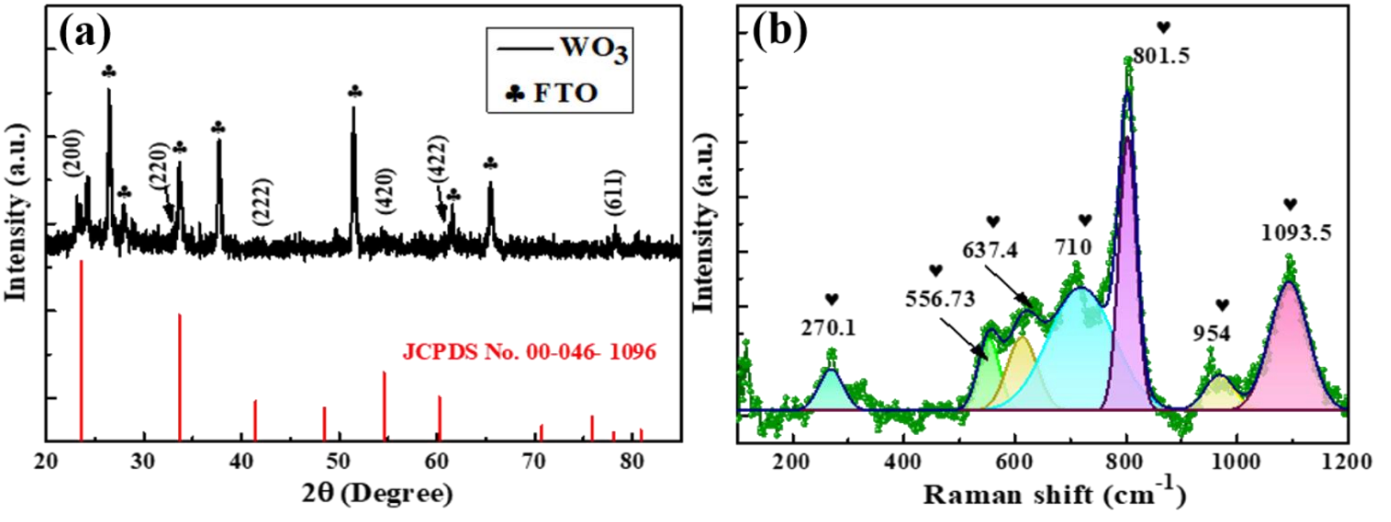

Fig. 1. (a) XRD and (b) deconvoluted micro-Raman spectra of WO_3 thin films.

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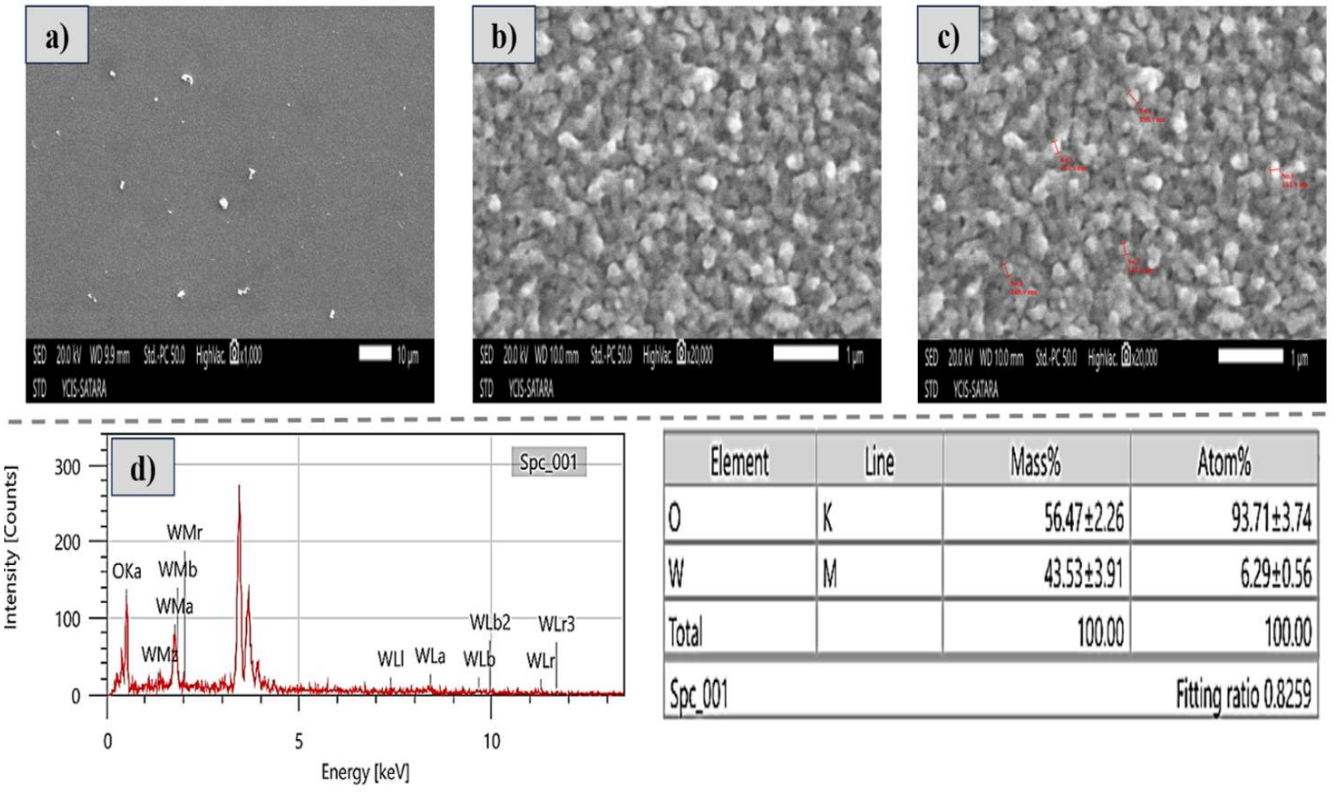

Element	Line	Mass%	Atom%
O	K	56.47±2.26	93.71±3.74
W	M	43.53±3.91	6.29±0.56
Total		100.00	100.00
Spc_001			Fitting ratio 0.8259

Fig. 2. (a - c) SEM images at different magnifications and (d) EDS of the of WO_3 thin films.

Figure 3 (a) represents the typical Cyclic Voltammetry curve of WO_3 thin film which is obtained by applying the potential in the range from -1.0 to 1.0 V vs. Ag/AgCl at different scan rates 10 mV/s, 20 mV/s, 40 mV/s, 80 mV/s and 100 mV/s respectively. The electrolytic bath is composed of 1M H_2SO_4 solution. From CV curve the charge kinetics of H+ ions insertion and extraction at working electrode (WO_3 thin film) was analyzed from peak current density. At the time of reduction, the W^{6+} ions get convert into W^{5+} ions with colored state of WO_3 thin film while at oxidation the extraction of metal ions takes place i.e., bleached state (W^{5+} to W^{6+}).

The cathodic peak current observed at -0.002 m /cm^2 and the anodic peak current is observed at 0.004mA/cm^2. In the CV curve the anodic peak represents the insertion of H^+ ions into the film and cathodic peak due to extraction of H^+ ions. Also, the reduction peak intensity depends on scan rate. The areal capacitance is calculated from the following equation (3)

$$C_A = \frac{\int IdV}{A \times dV \times \vartheta} \quad (3)$$

The areal capacitance of electrodeposited WO_3 thin film is found to be 2.8 mF /cm^2 it gives information about film capable of charge storage. This obtained value still higher than some of the previous reports such as porous WO_3 (2.57 mF/ cm^2 at 0.05 mA/ cm^2) [8], bilayer WO_3 /$ZnWO_4$ (0.23 mF/cm^2 at 0.05 V/s) [9].

3.2.2 Electrochemical impedance spectroscopy (EIS)

To study the charge transfer kinetics and to measure impedance characteristics, EIS was performed and the measured values are plotted in the following Figure 3(b). The Nyquist plot reveals the charge transfer resistance (Rct) and equivalent series resistance (Rs) having the values 4.98 and 37.60 Ω respectively. The lower value of the observed resistances beneficial for electron mobility which enhance the electrochemical activity favouring in enhanced performance. The inset figure shown the presence of semicircle at the higher frequency region displaying its contribution in the reaction.

3.2.3 Chronoamperometry (CA) and Chronocoulometry (CC)

The response characteristic of current-time is studied by using chronoamperometry. The CA measurement was recorded at ±1 V for 10 s per step to measure response time for color-bleach switching effect. The film shows faster coloration and bleaching times as 1.88 and 2.6 s respectively as shown in the Figure 3(c). The faster response with higher transient current density reveals the advantages of the porous structure by enabling faster ion diffusion with more active sites for H^+ ionic activity.

Chronocoulometry studies have been carried out to study the charge mobility i.e., the amount of charges intercalated (Qi) and deintercalated (Qdi).

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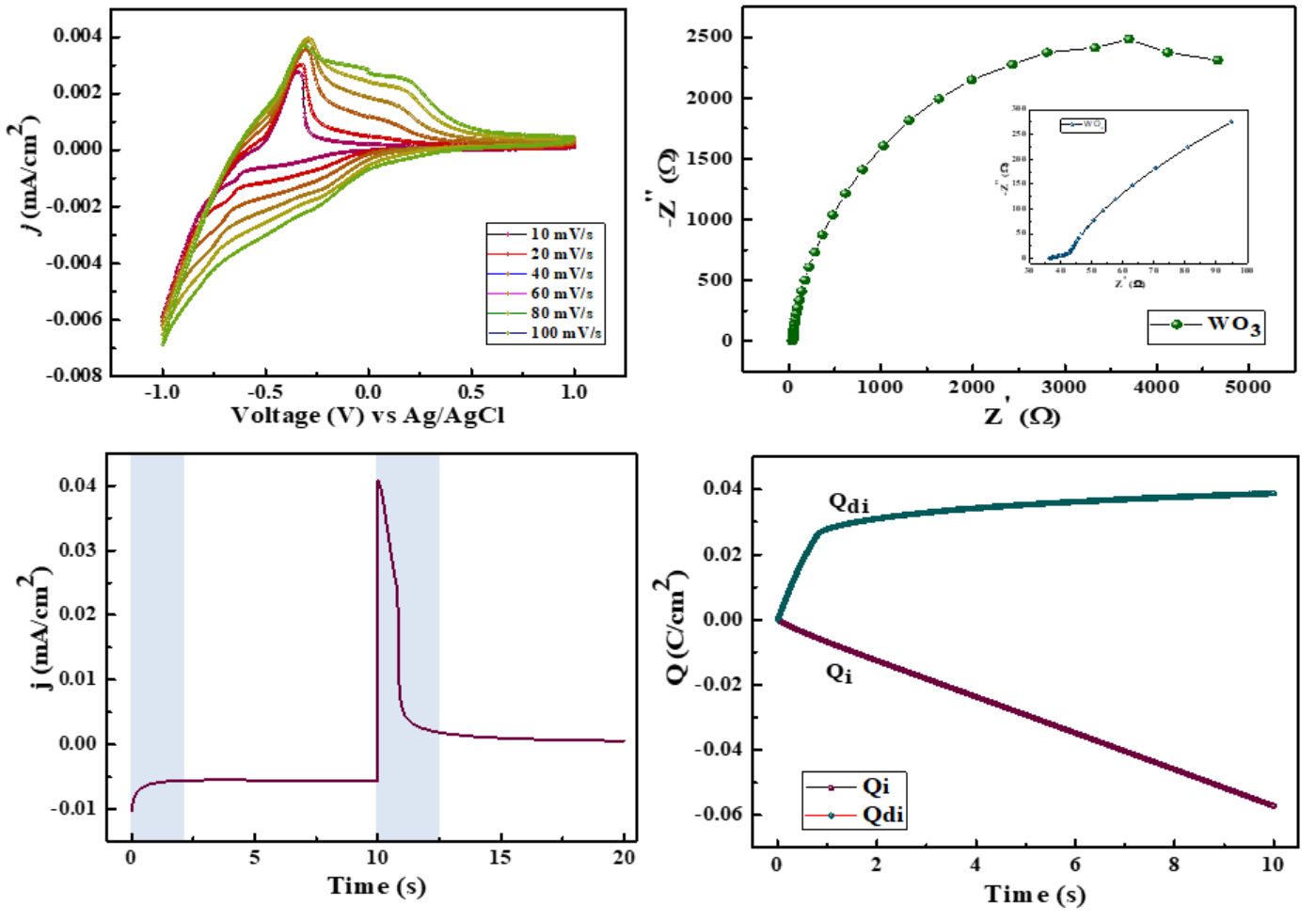

Fig. 3. a) Cyclic voltammetry curves at different scan rates from 10 to 100 mV/s, b) Nyquist plot of the sample with inset showing semicircle at high-frequency region, c) Chrono-amperometric curve at ±1 V for 10 s per step, and d) Chrono-coulometry curve showing charge intercalated and de-intercalated.

The same step potential of ±1 V is applied and Qi/ Qdi is calculated and used for the further calculation to study the performance of the prepared sample. Figure 3(d) shows the Chronocoulometry curve indicating the charge kinetics.

3.3. UV-VIS-NIR Spectroscopy

To examine change in optical properties (i.e., transmittance) of prepared sample for colored and bleached states by applying ±1 V for 10 sec each, UV-Visible- NIR spectroscopy was recorded within wavelength range of 300 nm to 1100 nm and is shown in Figure 4. The main two parameters which used to study the electrochromic properties are optical modulation i.e., the change in transmittance or absorbance on colored and bleached states and second parameter is coloration efficiency termed for amount of charge required to alter optical properties. The observed optical modulation for the prepared sample is about 68.8% which is attractive as far as previous literature is concern.

The coloration efficiency is the ratio of change in optical density to the amount of charges intercalated or deintercalated which is calculated from following equation 4.

$$CE = \frac{\Delta OD}{Q_i} \quad (4)$$

And the change in optical density is calculated from

$$\Delta OD = \log\left(\frac{T_b}{T_c}\right) \quad (5)$$

where Qi is charges intercalated during electrochromic process, Tb and Tc are transmittance of the film at bleached and colored states.

The calculated coloration efficiency from the films ability to change color is 52.61 cm^2/C which found improved from some previously reported for WO_3. The improved results with having good efficiency with large optical modulation at very less synthesis time is due to the nanostructured porous morphology with open voids resulted into the faster and easy

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ion transport and more electroactive sites for electrochemical reaction. The observed results suggest WO_3 for capable electrode in many electrochromic devices including bifunctional electrochromic supercapacitor.

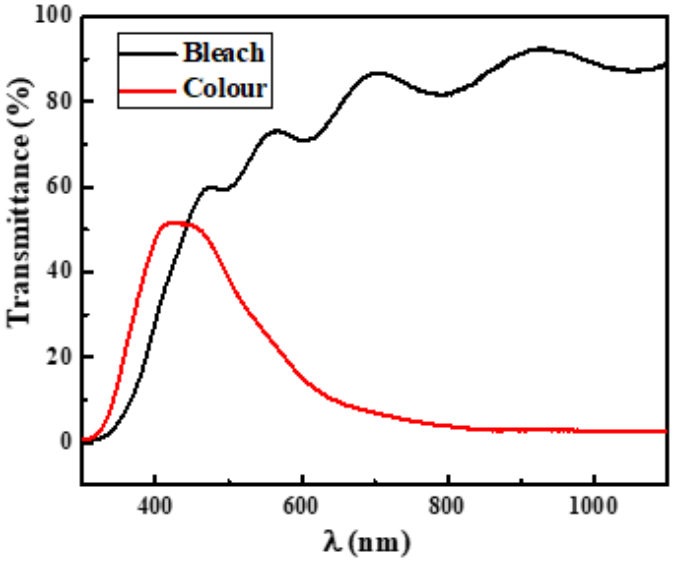

Fig. 4. Transmittance spectra of WO_3 film in colored and bleached states.

4. CONCLUSIONS

In this work, we have successfully synthesized electrodeposited tungsten trioxide (WO_3) thin films by controlling the pH of the electrolyte. The phase confirmation was achieved using X-ray diffraction (XRD) analysis, which validated the successful formation of the desired WO_3 phase. Scanning electron microscopy (SEM) images revealed the formation of nanoparticles and porous structures, indicating a well-controlled electrodeposition process. Electrochemical analysis demonstrated the bifunctional capability of the electrode. It exhibited a high coloration efficiency of 52.61 cm^2/C and significant charge storage capacity, with an areal capacitance of approximately 2.8 mF/cm^2. Additionally, the optical modulation was found to be 68.8%, and the electrode showed faster-switching kinetics with coloration and bleaching times of 1.88 and 2.6 seconds, respectively. These results indicate that electrodeposition is an efficient method for depositing electrochromic WO_3. The process offers uniform and chemically stable growth on conducting substrates, which is beneficial for various multifunctional applications. The combination of high coloration efficiency, substantial charge storage capacity, and rapid switching kinetics underscores the potential of electrodeposited WO_3 thin films in advanced electrochromic devices. Future work can explore the scalability of this method and its integration into commercial electrochromic applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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