

Synthesis and Characterization of Tungsten oxide Electrochromic Thin Films

Yingpeng Zhen^{1*}, Tao Gao¹, and Bjørn Petter Jelle^{1,2}

¹Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway.

²Department of Materials and Structures, SINTEF Building and Infrastructure, NO-7465 Trondheim, Norway.

*Corresponding author: yingpeng.zhen@ntnu.no

Abstract—A radio frequency sputtering method was utilized and developed for tungsten oxide film preparation. The thickness of tungsten oxide film can be controlled at nano scale. Tungsten oxide thin films with thickness of ~36 nm were prepared and investigated. The morphologies and microstructures of the as-prepared tungsten oxide thin films were characterized using X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. Tungsten oxide films utilized in the laboratory changed color from colorless to blue during electrochemical cycles, showing a potential for assembling electrochromic smart windows to modulate the transmitted solar radiations.

I. INTRODUCTION

Electrochromic (EC) smart windows are windows whose optical properties can be adjusted with the change of an external electrical field strength. In the presence of an external voltage, the EC materials can change from a dark colored state (e.g., dark blue) to a transparent state with no color tints. EC smart windows have been developed and utilized in energy-efficient buildings. Using EC smart windows, the amount of solar radiation transmitted through windows can be controlled. Consequently, the energy usage by heating and cooling in buildings can be reduced.

Typically, an EC device (e.g., EC smart windows) consists of five functional layers: two transparent electrical conductor layers to inject and extract charge, an active EC layer, an electrolyte, and an ion storage layer, which may in some cases be another complementary EC layer. This sandwich configuration allows a reversible electrochemical reaction to cycle between the EC layer and the ion storage media, with simultaneous injection of electrons/holes and cations/anions. The overall transparency of the EC layer is changed due to the formation of color centers (or defect complexes) or due to an electrochemical reaction that produces a colored compound; a voltage pulse with opposite polarity makes the device regain its original properties [1].

Tungsten oxide (WO₃) is probably the most studied EC material for smart window applications. We have been working on EC smart windows by using WO₃ [2-5] among others. In this work, we developed a radio frequency sputtering method for WO₃ film preparation. This method can accurately control the thickness of WO₃ films at nano scale. WO₃ thin films with a thickness of about 36 nm were prepared by using radio

frequency sputtering. Subsequently, WO₃ films were utilized to form a working electrode in our laboratory. We found that the WO₃ films exhibit good electrochemical performance.

II. SAMPLE PREPARATION

2.1 Materials

WO₃ sputtering target (diameter 5.08 cm, thickness 0.32 cm) was purchased from AJA International Inc., USA. Substrates for the growth of WO₃ thin films were ITO (tin doped indium oxide, In₂O₃(Sn)) glass slides purchased from Sigma-Aldrich. ITO glass slides have a typical transmittance of about 86% at 550 nm and a surface resistivity of about 70-100 Ω/square. The ITO glass slides were cut to small pieces with typical sizes of about 9.2 mm × 25 mm × 1.1 mm in the laboratory for this work. Reagent grade sulfuric acid (H₂SO₄, 96 wt%) and potassium chloride (KCl, 99%) were also purchased from Sigma-Aldrich. Distilled water was utilized throughout the experiments.

2.2 Sputter Process

WO₃ films with thickness of 36 nm were prepared by radio frequency (RF) magnetron sputtering technique using an AJA sputter and evaporator (model: Custom ATC-2200V, AJA International Inc. USA). Argon (Ar) flow was set as 67 sccm (standard cubic centimeter per minute). Plasma strike pressure was 30 mTorr (≈ 4.0 Pa), and strike power was 50 W. After the plasma was strike on, the pressure was changed and maintained at 3 mTorr (≈ 0.4 Pa) during the deposition process. The sputter rate was about 0.05 nm/s.

2.3 Heat Treatment

Heat treatment is necessary for the WO₃ films. Heat treatment was performed and the as-deposited WO₃ film samples were annealed in air at 400 °C for 5 h in an oven.

III. CHARACTERIZATION

3.1 XRD

X-ray diffraction (XRD) analysis was performed using a Bruker D8 A25 Davinci X-ray Diffractometer (Bruker, Germany) with Cu-Kα radiation and LynxEye™ SuperSpeed Detector for 30 minute. XRD data were collected in the range of 15° - 75° with a step size of 0.013°. The structures of the samples were analyzed using the DIFFRAC.EVA V4.2 software (Bruker AXS, Germany).

3.2 SEM

A scanning electron microscope (SEM) was utilized to check the surface topography of the samples. The SEM Apreo purchased from Thermo Fisher Scientific (FEI), USA, was utilized in this work.

3.3 FTIR

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 8700 FTIR Spectrometer (Thermo Scientific, USA). The transmittance of the samples were recorded in the wavenumber range 4000 cm^{-1} to 400 cm^{-1} .

3.4. Cyclic Voltammetry Test

The electrochemical properties of the WO_3 films were characterized by cyclic voltammetry (CV) on an AutoLab electrochemical workstation PGSTAT302N (Metrohm Autolab B.V., Netherlands). The WO_3 films were applied as working electrodes (WE). The counter electrode (CE) was a Pt wire. The reference electrode (RE) was Ag/AgCl (3 M KCl). The electrolyte was 0.5 M H_2SO_4 .

3.5. UV-VIS-NIR Spectroscopy

Transmittance of samples was measured in the ultraviolet (UV), visible (VIS) and near infrared (NIR) solar radiation wavelength range (280 -1300 nm) on a UV-VIS-NIR spectrophotometer (PerkinElmer 1050 WB, USA).

In situ coloration and bleaching of the samples were also performed, and a constant potential of -0.3 V and 0.3 V (vs. Ag/AgCl (3 M KCl)) was used to color and bleach the samples, respectively. Firstly, the potential of -0.3V was applied in the 1st hour. Subsequently, the potential of +0.3 V was applied in the 2nd hour. Furthermore, the recycled potentials of -0.3 V and +0.3 V were applied for 1h alternately. The coloration and bleaching state processes were recorded at the wavelength of 555 nm.

IV. RESULTS AND DISCUSSION

4.1 XRD

Fig. 1 shows XRD results of the as-prepared samples. Fig. 1a is almost identical to Fig. 1b, which suggests that the WO_3 films deposited on the ITO glass were probably amorphous, e.g., no new peaks appearing compared to the ones for the ITO substrate. However, after the heat treatment the XRD pattern in Fig. 1c showed several new peaks, indicating the recrystallization of WO_3 at elevated temperatures. The newly formed crystalline phase may be assigned to monoclinic WO_3 (PDF 00-043-1035) based on the observed strong reflections.

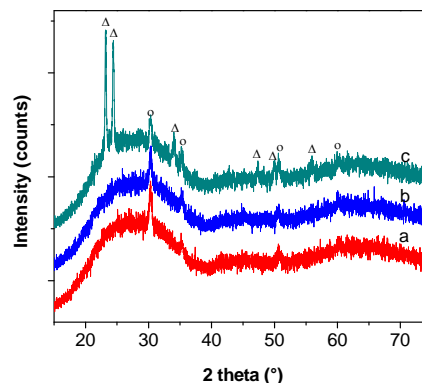


Fig. 1. XRD results of (a) ITO glass substrate, (b) WO_3 films before heat treatment, and (c) WO_3 films after heat treatment. Open circles (o) denote the reflections of ITO (PDF 04-019-3926). Open triangles (Δ) denote the reflections of monoclinic WO_3 (PDF 00-043-1035).

4.2 SEM

The SEM results are shown in Fig. 2. Fig. 2a shows that the as-prepared WO_3 film before heat treatment had a flat, smooth surface. After the heat treatment, window ice-like crystals were formed (Fig. 2b). That means heat treatment can help the crystal formation on the surface of the ITO glass.

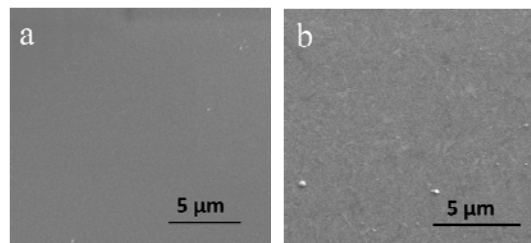


Fig. 2. SEM images of samples. (a) WO_3 thin films deposited on ITO glass substrates before heat treatment, (b) WO_3 thin films deposited on ITO glass substrates after heat treatment.

4.3 FTIR

FTIR results of the samples are shown in Fig. 3. Fig. 3a is the FTIR spectrum of the ITO glass, which is in agreement with previous reports [6]. Fig. 3b shows no new absorbance from the FTIR spectrum of the WO_3 films before the heat treatment. The WO_3 films after heat treatment showed two new absorptions at about 980 and 710 cm^{-1} (Fig. 3c), which are corresponding to $\text{W}=\text{O}$ and $\text{O}-\text{W}-\text{O}$ stretching vibrations from the newly formed crystalline WO_3 [7]. These absorptions only happened in the crystalline WO_3 film, which is not seen in amorphous WO_3 films.

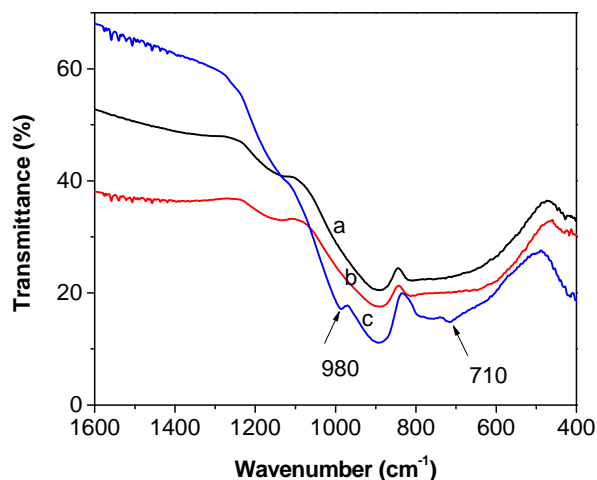


Fig. 3. FTIR spectra of (a) ITO glass, (b) WO₃ film coated on ITO glass before heat treatment, and (c) WO₃ film coated on ITO glass after heat treatment.

4.4 Cyclic Voltammetry

1) Influence of Scan Rate

The kinetic and thermodynamic behaviors of as-prepared WO₃ films after heat treatment were investigated by cyclic voltammetry (CV), which was carried out between -0.3 V and 0.3 V vs. Ag/AgCl at scan rates ranging from 5 to 100 mV/s.

Fig. 4 shows the CV curves. A cathodic current peak emerged at around -0.2 V and an anodic current peak appeared at around 0.05 V when the scan rate was 20 mV/s. These two potentials were accompanied by the coloration (from colorless to blue) and bleaching (from blue to colorless) of the WO₃ films, respectively.

With an increasing scan rate, the anodic potential shifted to higher voltages and the cathodic potential shifted to lower voltages, indicating an increased polarization at higher sweep rates due to kinetic limitations associated with the H⁺ diffusion through the active material [8]. The cathodic current peak turned to be hard to find when the scan rate was higher than 60 mV/s.

2) Durability of As-Prepared WO₃ Films

Cycling stability of the as-prepared WO₃ films was evaluated and the results were shown in Fig. 5. No obvious changes were observed during the first 200 scans, whereas the film began to decompose after about 250 scans. The decomposition is due to the acidic environment with oxygen in the electrolyte. Increasing the cycling voltage to 0.5 V reduce stability of the WO₃ films. For example, the film began to decompose after about 120 scans.

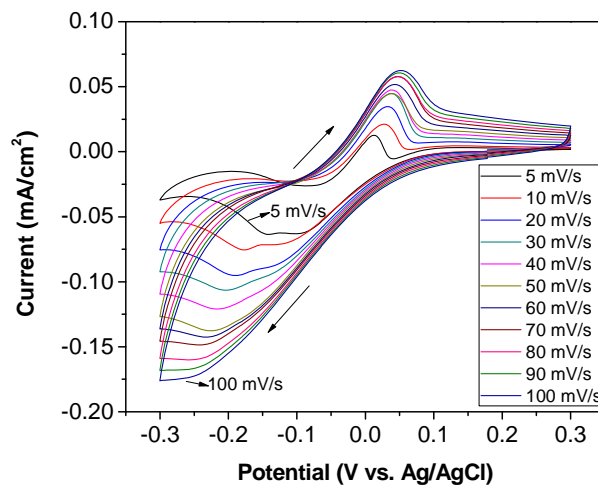


Fig. 4. CV scans of a WO₃ thin film deposited on ITO glass substrate after heat treatment. WE: WO₃ films, CE: Pt wire, RE: Ag/AgCl (3 M KCl), electrolyte: 0.5 M H₂SO₄. Scan rates were 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s.

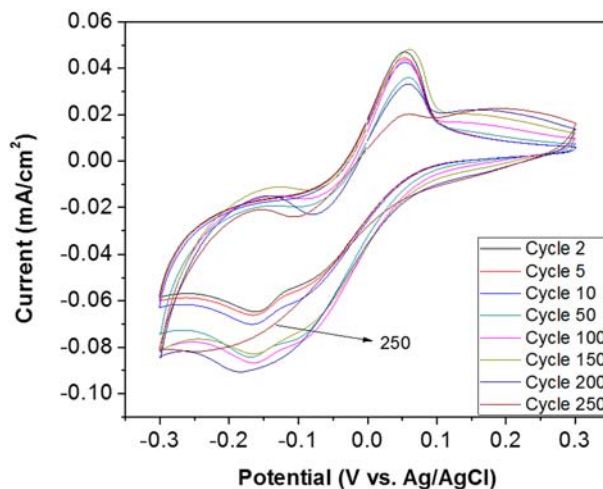


Fig. 5. CV scans of a WO₃ thin film after heat treatment. Scan rate is 20 mV/s.

4.5 UV-VIS-NIR Spectroscopy

UV-VIS-NIR spectroscopy was utilized to characterize the WO₃ films. As shown in Fig. 6, the transmittance spectrum in the wavelength range 280 to 1300 nm of the WO₃ thin film at the colored state was compared with that of the bleached state. The colored and bleached samples were obtained from as-prepared samples after Autolab procedure chrono amperometry experiments. A potential of -0.3 V was applied to the colored samples for 3600 s. Similarly, a potential of +0.3 V was applied to the bleached samples for 3600 s. Fig. 6

shows the spectrum of the bleached state (a) and the colored state (b) in the 4th cycle. The largest transmittance difference ΔT was 59.1% at wavelength $\lambda=1300$ nm, whereas ΔT was around 20% at $\lambda=555$ nm.

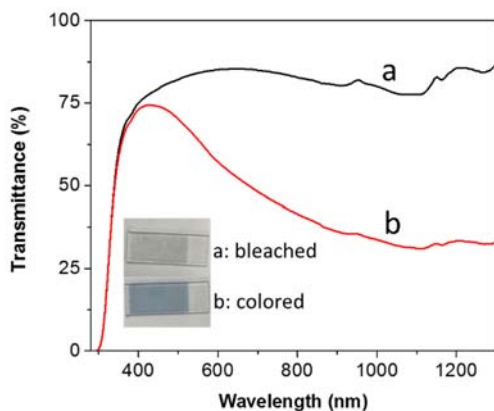


Fig. 6. Transmittance spectra of a WO_3 thin film electrode at (a) bleached state at +0.3 V and (b) colored state at -0.3 V. Inset shows an optical photo of the corresponding sample states.

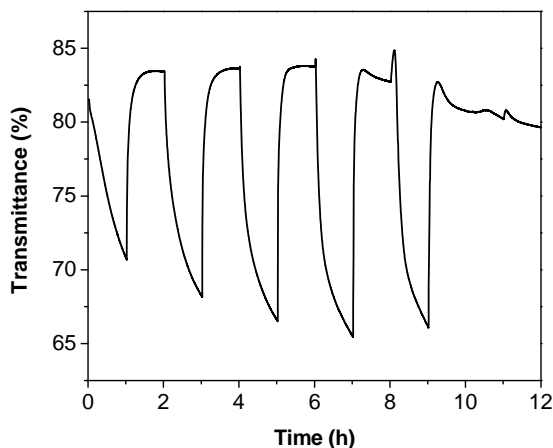


Fig. 7. Transmittance of 36 nm WO_3 thin film electrode response to Autolab procedure chronoamperometry: potentials -0.3 V for 1 h and 0.3 V for 1 h. Transmittance spectra was recorded at 555 nm.

Fig. 7 shows the colored and bleached process which was recorded at $\lambda=555$ nm from 0 to 12 h. Firstly, the potential of -0.3V was applied in the 1st hour. Subsequently, the potential of +0.3 V was applied in the 2nd hour. Furthermore, the recycled potentials of -0.3 V and +0.3 V were applied from the third hour to the 12th hour. The WO_3 film changed color from colorless to blue by the negative potential and was bleached by the positive potential. The bleached transmittance reached a steady value (84%) for each cycle, whereas the colored transmittance value turned to be lower and lower from first to the 4th cycle. That is, the colored process had not completed during 1 h. The 5th transmittance value was higher than its former one due to influence of some degradation, which

happened after around 8 h. The film lost its color changing properties almost completely after 10 hours, i.e. the film has been degraded. It seems the system can not stand the acidic environment with oxygen in the electrolyte for a prolonged time. However, this may be solved by fabricating an oxygen-free EC device (e.g. using a glovebox in the laboratory).

V. CONCLUSIONS

In this work, a radio frequency sputtering method was developed for WO_3 film preparation in order to control the thickness of films accurately at nano scale. WO_3 thin films with a typical thickness of about 36 nm were prepared and their structural and physical properties were investigated. The films before heat treatment were amorphous. However, crystals were formed during heat treatment. The amorphous films could not change color under applied potential, whereas the crystalline films demonstrated good EC abilities.

The EC properties were investigated using cyclic voltammetry analysis and UV-VIS-NIR spectroscopy. At a scan rate of 20 mV/s, the color of the WO_3 films changed at around -0.2 V and bleached at around 0.05 V. The WO_3 films could be cycled for 200 times between the potentials -0.3 V to 0.3 V.

ACKNOWLEDGMENTS

This work has been supported by the Research Council of Norway and several partners through "The Research Centre on Zero Emission Buildings" (ZEB) (project no. 193830). The authors gratefully acknowledge The Research Council of Norway for the support to the Norwegian Micro- and Nano-Fabrication Facility, NorFab (project no. 245963/F50).

REFERENCES

- [1] T. Gao, B.P. Jelle and A. Gustavsen, "Nanoelectrochromics with applied materials and methodologies", *Zero Emission Buildings-Proceedings of the Renewable Energy Research Conference*, Trondheim, Norway, pp. 61-71, 2010.
- [2] B. P. Jelle and G. Hagen, "Transmission spectra of an electrochromic window based on polyaniline, prussian blue and tungsten oxide", *Journal of the Electrochemical Society*, vol.140, pp. 3560-3564, 1993.
- [3] T. Gao, B. P. Jelle and A. Gustavsen, "Synthesis and characterization of sodium tungsten bronze nanorods for electrochromic smart window applications", in *Nanotechnology (IEEE-NANO), 13th IEEE Conference*, pp. 1093-1096, 2013.
- [4] T. Gao and B. P. Jelle, "Visible-light-driven photochromism of hexagonal sodium tungsten bronze nanorods," *Journal of Physical Chemistry C*, vol. 140, pp.13753-13761, 2013.
- [5] B. P. Jelle, G. Hagen and Ø. Birketveit, "Transmission properties for individual electrochromic layers in solid state devices based on polyaniline, prussian blue and tungsten oxide", *Journal of Applied Electrochemistry*, vol. 28, pp. 483-489, 1998.
- [6] L. Meng and M. P. Dos Santos, "Properties of indium tin oxide (ITO) films prepared by r.f. reactive magnetron sputtering at different pressures", *Thin Solid Films*, vol. 303, pp. 151-155, 1997.
- [7] M. F. Daniel, B. Desbat, J. C. Lassegues, B. Gerand and M. Figlarz, "Infrared and Raman study of WO_3 tungsten trioxides and $\text{WO}_3 \cdot x\text{H}_2\text{O}$ tungsten trioxide hydrates", *Journal of Solid State Chemistry*, vol. 67, pp. 235-247, 1987.
- [8] P. Hu, J. Ma, T. Wang, B. Qin, C. Zhang, C. Shang, J. Zhao and G. Cui, "NASICON-structured $\text{NaSn}_2(\text{PO}_4)_3$ with excellent high-rate properties as anode material for lithium ion batteries", *Chemistry of Materials*, vol. 27, pp. 6668-6674, 2015.