



# Improved coloration contrast and electrochromic efficiency of tungsten oxide films thanks to a surfactant-assisted ultrasonic spray pyrolysis process



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## ABSTRACT

Tungsten oxide thin films are known for their excellent electrochromic efficiency, nevertheless, most of deposition methods reported in the literature are not suitable to produce high quality films and at low cost. In this paper, tungsten oxide thin films have been deposited on FTO-glass substrates by a surfactant-assisted ultrasonic spray pyrolysis. This deposition method, associated to the presence of surfactant, has led to improved electrochromic performance of tungsten oxide films, without excessive production cost.

Tungsten oxide films made by the surfactant-assisted ultrasonic spray pyrolysis show a high specific surface area, which results in one of the highest coloration contrast (83%) ever reported for tungsten oxide thin films. WO<sub>3</sub> thin films also show excellent reversibility (94%), as well as good coloration efficiency (28 cm<sup>2</sup>/C).

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## 1. Introduction

Tungsten oxide has been intensively studied as electrochromic material due to its excellent coloration efficiency and its fast intercalation and extraction kinetics. Nevertheless, several studies pointed out a low reversibility of the film upon lithium insertion and extraction [1–7], leading to poor long-term stability and durability.

Recently, improved electrochromic performances have been obtained by surfactant-assisted ultrasonic spray pyrolysis [8–10]. Ultrasonic spray pyrolysis is a promising and versatile technique to produce homogeneous thin films on large area substrates. Moreover, this technique could be easily transferred to an industrial pilot line without excessive production costs, which is not the case for vacuum deposition techniques.

Li et al. [9,10] have investigated the addition of a non-ionic surfactant (poly(alkeneoxide) triblock copolymer or P123) in the tungsten hexachloride (WCl<sub>6</sub>) precursor solution. Their nanostructured WO<sub>3</sub> films showed excellent coloration efficiency (50.6 cm<sup>2</sup>/C), fast switching kinetics ( $t_c$  6.4 s and  $t_b$  6 s) and improved

robustness and durability. Nevertheless, their deposition process is not suitable for an industrial pilot line, since it consists of spraying the precursor solution at room temperature, followed by a hydrolysis step (12 h in a vapor saturated chamber) and a calcination step (at 300–400 °C).

Tungsten oxide thin films made by surfactant-assisted spray pyrolysis have also been investigated with a mixture of cationic (hexadecyltrimethylammonium bromide) and non-ionic (polyethylene glycol, PEG) surfactants [8,11]. Different nucleation and growth processes have been observed after the addition of those surfactants, due to the variation of the surface tension in the sprayed solution containing surfactants. The resulting films showed enhanced crystalline order and surface area, as well as improved reversibility and coloration contrast in a non-aqueous viscous electrolyte (bis(trifluoromethane sulfonyl) imide in 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide) [8]. Their deposition conditions also limit further industrial use as the films are deposited at moderate temperature (200–250 °C) followed by an annealing post-treatment at high temperature (350 or 410 °C) [8,11].

In the present work, we have investigated the deposition of tungsten oxide films by a single step surfactant-assisted USP process, where the deposition of tungsten oxide takes place directly at 350 °C. We have compared the electrochromic

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performance (durability, reversibility, switching kinetics, coloration efficiency and contrast), the morphology and crystallization of our films formed in this single-step USP process with those reported in the literature.

## 2. Material and methods

### 2.1. Materials

The fluorine-doped tin oxide (FTO)-coated glass substrates were provided by AGC Glass Europe (Planibel GFast, 15  $\Omega$ /square). During the industrial process, the FTO layer is deposited by CVD on 4 mm-thick flat glass, followed by a polishing of the surface. Ammonium metatungstate hydrate (AMT, Alfa Aesar) and polyethylene glycol (PEG, average  $M_n$  400, Sigma-Aldrich) are used without further purification.

### 2.2. Substrate pre-treatment and film deposition

Substrates of 2 cm  $\times$  2 cm are cut from the FTO/glass sheets. The samples are cleaned by successive sonication in acetone and ethanol, during 5 and 10 min, respectively. They are then blown dry with a compressed air stream.

The tungsten oxide films are deposited on FTO substrates with an ultrasonic spray pyrolysis device (ExactaCoat, Sonotek). The precursor solution is made of ammonium metatungstate (0.01 M in double distilled water) and polyethylene glycol, with a mass ratio  $m_{\text{AMT}}:m_{\text{PEG}}$  1:10. This aqueous solution is continuously sprayed through the ultrasonic AccuMist nozzle (operated at 120 kHz) onto pre-heated FTO/glass substrate ( $T=350^\circ\text{C}$ ), which is located 5.5 cm below the nozzle. The solution flow rate is 0.25 mL/min and clean air is used as a carrier gas (6205 Pa). To obtain a full surface coverage, the ultrasonic nozzle is moved in  $x$  and  $y$  directions following a S-shaped pattern (4 mm spacing) at a constant speed (40 mm/s). Six passes are done to reach a thickness of 550 nm (measured by mechanical profilometry). The substrates are maintained 5 min before and after the spraying on the heating plate to reach the desired temperature at the surface of the substrate before spraying and to promote the decomposition of the precursor after spraying.

### 2.3. Characterization methods

The morphology of tungsten oxide films has been characterized by scanning and transmission electron microscopies (SEM and TEM) and atomic force spectroscopy (AFM). The SEM micrographs were recorded at 15 kV, on a FEG-SEM XL30 microscope (FEI). All samples were coated by a thin layer of gold (sputtering) before any measurement. The TEM micrograph was recorded on a TECNAI G2 Twin microscope (FEI, 200 kV), scratched  $\text{WO}_3$  films were deposited on a copper grid. The morphology of the films was examined by AFM under ambient conditions using a Digital Instruments Nanoscope III microscope (Veeco). The image acquisition was performed in tapping mode – over a 25  $\mu\text{m}^2$  surface – with a super sharp – improved super cone probe (TeamNanotec).

X-ray diffraction (XRD) has been used to study the crystallization of the coatings. XRD was performed in theta-theta geometry on a Bruker D8 parallel beam diffractometer with  $\text{Cu K}_{\alpha}$  radiation. The diffractogram was recorded in the range of  $20^\circ < 2\theta < 70^\circ$  with a step width of  $0.02^\circ$  and at a scan rate of 1 s/step. The PDF4+ database (International Center for Diffraction Data) has been used to index the diffractogram.

All electrochemical measurements were carried out on a Biologic SP200 Potentiostat/Galvanostat. The coloration efficiency and the switching kinetics of the films were investigated by coupling

chronoamperometry (CA) with in situ measurement of the optical transmission. The measurements were performed using an optical glass cell (3-G-40), a silver-silver nitrate microelectrode (CHI 112, 0.01 M  $\text{AgNO}_3$ , 0.54 V/ENH) as the reference, a platinum wire (CHI 115) as the counter electrode, the  $\text{WO}_3$  films on FTO substrate playing the role of the working electrode. Lithium perchlorate (0.5 M) in propylene carbonate was used as electrolyte. The system comprising cell, electrolyte and FTO glass was used to define the 100% of optical transmission.

The films were first colored by applying a potential of  $-1.74$  V/Ag– $\text{AgNO}_3$  during 3 min, the potential was then changed to  $+1.06$  V for 3 min leading to the bleaching of the films. The transmission of the films during this double-step chronoamperometry was measured at 550 nm, using a Lambda 750 spectrometer (Perkin Elmer). The coloration and bleaching times correspond to the duration required to reach 90% of the total transmittance change.

Long-term cyclic voltammetry (CV) was carried out at a sweep rate of 20 mV/s and for a potential ranging from  $+1.4$  to  $-1.4$  V/Ag–AgCl. A silver-silver chloride electrode (non-aqueous media, 0.20 V/ENH) was used as the reference; the potential range is therefore similar to our chronoamperometry analyses ( $+1.06$  V to  $-1.74$  V/Ag– $\text{AgNO}_3$ ).

The UV-visible spectra of the films, in their bleached and colored states, were recorded from 360 to 780 nm. A potential of  $-1.74$  V/Ag– $\text{AgNO}_3$  was maintained for 20 s allowing the acquisition of the UV-visible spectrum of colored films. The potential was then fixed at  $-1.06$  V/Ag– $\text{AgNO}_3$  for 20 s and the spectrum of bleached  $\text{WO}_3$  films was measured.

The optical quality of the films was estimated by the haze number, using a Hazemeter (Pacific Scientific XL-211 Hazegard System). The haze measurement procedure is defined by the ASTM D1003 standard and is taken for the illuminant C.

Colorimetric determinations were done based on the CIELAB 1976 system ( $L^*/a^*/b^*$ ). The chromaticity coordinates ( $a^*$  and  $b^*$ ) and luminance ( $L^*$ ) data were calculated from the transmittance spectra of the tungsten oxide films in their colored and bleached states. The luminance ( $L^*$ ) characterizes the brightness of the films and is comprised between 0 (black) and 100 (white). The color of the films is defined by their  $a^*$  and  $b^*$  coordinates:  $-a^*$  value tends toward green and  $+a^*$  value tends toward red, while  $-b^*$  value tends toward blue and  $+b^*$  value tends toward yellow.

## 3. Results and discussion

### 3.1. Morphology and crystallization

The SEM micrograph (Fig. 1a) shows a full coverage of the FTO substrate, tungsten oxide films made by a surfactant-assisted USP are homogeneous, crack- and pinhole-free. Those films are dense, without porosity, as shown by the TEM micrograph (Fig. 1b). By spraying the solution at room temperature, following by hydrolysis and calcination steps, Li et al. have obtained mesoporous  $\text{WO}_3$  films, made up of spherical-shaped clusters with pores size around 8–20 nm [9,10]. In our case, the addition of PEG surfactant in the USP process has not led to the formation of porous films since the decomposition temperature of polyethylene glycol is well below our USP deposition temperature of  $350^\circ\text{C}$ .

Nevertheless, the addition of surfactant is essential to form high quality films. Indeed, Bertus et al. [8,11] have shown that the addition of surfactant in the precursor solution involves a decrease of the surface tension and the formation of smaller droplets and in larger amount. The AFM image (Fig. 1c) confirms the presence of small particles closely packed, with a granular morphology. Furthermore, the interactions between the polyethylene glycol and the

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