

ELECTROCHROMIC AND STRUCTURAL CHARACTERISTICS OF MESOPOROUS WO₃ FILMS PREPARED BY A SOL-GEL METHOD

B. D. Alexander*¹, R. Solarska¹ and J. Augustynski¹

¹Département de Chimie Appliquée et Minérale, Sciences II, Université de Genève, quai E.-Ansermet 30, CH-1211 Genève, Suisse; E-Mail: bruce.alexander@chiam.unige.ch

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Abstract: Mesoporous WO₃ films have been prepared from the sol-gel method. Modification of the preparation method has been shown to exert a critical influence on the structure of the resultant films. A relationship between the structure and performance of the films shall be discussed.

Tailoring of microporous and mesoporous oxide films have recently attracted attention given their abundant potential applications in heterogeneous catalysis, chemical separation, optoelectronics, sensors, batteries and photonic and electrocatalytic materials. This interest has also been extended to metallic oxides with charge transport and transfer functionalities.[1,2]

It is already possible to prepare such oxide films using wide array of deposition techniques. Amongst these, the sol-gel method provides some of the largest possibilities of controlling film morphology and, importantly, porosity. Traditionally, sol-gel processing either involves acidic metal salts or acidification of a basic metal salt, followed by condensation, evaporation of the solvent and finally annealing at relatively high temperature. One alternative to this approach is the use of metal alkoxides as precursor species, which undergo condensation to form a sol after an initial hydrolysis. Clearly, the porosity and particle size of sol-gel derived oxides are affected by the choice of the precursor and the processing conditions, especially the annealing temperature. For example, change of processing conditions from acidic to basic will normally favour formation of mesoporous instead of microporous films. Addition of a structure-directing species to either the sol or the gel can induce structural ordering of the oxide films during heat treatment. Nevertheless, the elevated temperature of annealing required for the formation of well-crystallized films often causes the collapse of the template-mediated, ordered mesostructures.

Nanostructured WO₃ films a few microns thick have displayed promising photoelectrochemical properties as efficient photoanodes for water splitting under visible light illumination.[3,4] These films are also potentially interesting electrochromic materials due to their nanocrystalline nature, which affords an open and porous structure.[5] The present study reports the fabrication of WO₃ films from tungstic acid and tungsten (VI) ethoxide precursors, with structure-directing organic additive. The effects of the choice of precursor and annealing temperature are closely monitored by Raman and SEM microscopies. The formation of a complex between tungstic acid and the hydrophilic poly(ethylene glycol) clearly effects the crystallization process of WO₃ leading first to the formation of metastable hexagonal tungsten trioxide at *ca.* 200°C. It is only above 400°C that conversion into the stable monoclinic form of WO₃ starts, in conjunction with the combustion of the remaining carbonic matter. Films prepared using the tungsten (VI) ethoxide/PEG precursor follow a similar structural trend although the formation of the monoclinic phase is pushed to higher temperatures.

The prepared WO₃ films combine excellent transparency to wavelengths larger than 550 nm with the short diffusion path for intercalating cations (Li⁺, H⁺). Here, changes in optical properties and the degree of electrochromic optical modulation are presented for the WO₃ films obtained using both tungstic acid and tungsten (VI) ethoxide precursors annealed over a range of temperatures. The structural modifications of WO₃ observed using Raman microscopy are related

to electrochromic colouration efficiency (CE) of the films, *i.e.* $CE = \Delta OD/q$, where ΔOD is the change in optical density on going from bleached to coloured films and q is the charge inserted during the colouration process. Previously it was considered that films of amorphous WO_3 were most efficient electrochromic materials. Although we report good colouration efficiencies for the amorphous WO_3 films prepared from both tungstic acid and tungsten (VI) ethoxide precursors ($35 \text{ cm}^2/\text{C}$ for in $H_2SO_{4(aq)}$ and $80 \text{ cm}^2/\text{C}$ in $LiClO_4$ in propylene carbonate), we note that the highest colouration efficiencies are found in the well-crystallised monoclinic films, which combine good adherence with mechanical stability. This might appear in contradiction with previously reported good electrochromic characteristics of amorphous WO_3 films but this result can be explained by the increased porosity of the monoclinic films and the lingering presence of organic species in the WO_3 films annealed at lower temperatures.

Monitoring changes in the Raman spectra of the films upon insertion of H^+ or Li^+ enables the discussion of the mechanism of colouration. The Raman spectrum of coloured amorphous WO_3 films after ion insertion has already been reported,[6] however that of monoclinic WO_3 is not yet understood and shall be discussed.

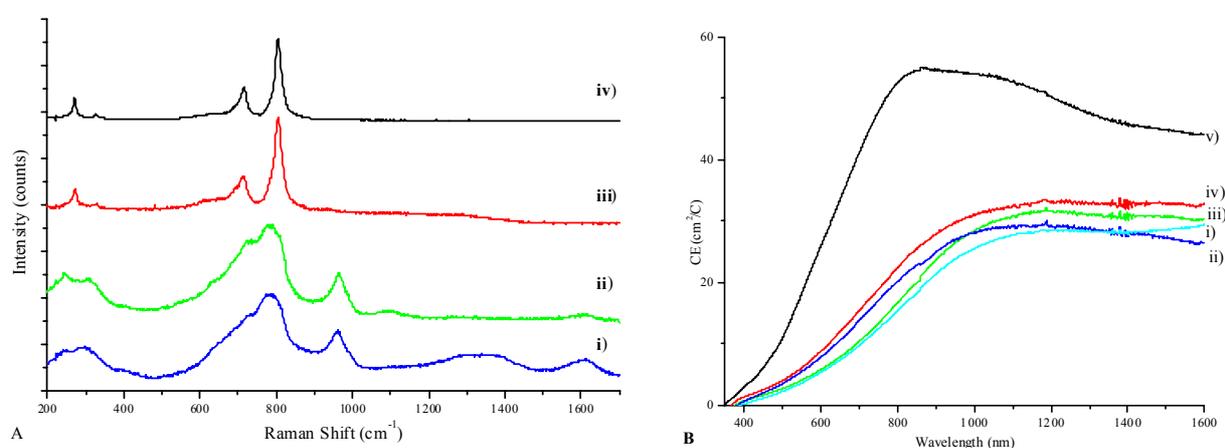


Fig. 1. A: Raman spectra of WO_3 films derived from tungstic acid/PEG precursor deposited on conducting glass substrates. Films annealed at i) 350°C ; ii) 400°C ; iii) 500°C and iv) 550°C .

B: Colouration efficiency (CE) of *ca.* $0.4 \mu\text{m}$ thick WO_3 films prepared from tungstic acid/PEG precursor in $1 \text{ M } H_2SO_{4(aq)}$. Films annealed at i) 250°C ; ii) 300°C ; iii) 350°C ; iv) 400°C and v) 500°C .

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