

Electrochromism in thin films of tungsten trioxide-microspheres prepared by aqueous chemical growth

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Abstract. WO₃ thin films were grown on conductive F-doped SnO₂-coated glass through the low temperature, wet chemistry method of Aqueous Chemical Growth. Thin films produced contained microspheres of WO₃ that were 1-2μm in diameter. SEM showed these microspheres to consist of a thick central core on which grew hair-like protrusions with lengths in the 200 - 400 nm range and thicknesses in the 50-100 nm range. X-ray Diffraction analysis revealed WO₃ to be in the hexagonal and cubic phase. TEM and HRTEM confirmed the existence of the hexagonal phase and showed evidence of the existence of lattice fringes in the hair-like protrusions. For electrochromism the WO₃ thin films showed fairly fast, reversible, optical switching speeds (from a deep blue to semi-transparent colour) of less than 20 seconds upon H intercalation in 0.1M H₂SO₄ solution.

1. Introduction

Tungsten trioxide (WO₃) is an n-type, wide band gap semiconductor metal oxide whose I-V characteristics, electrochromic and gasochromic properties have been widely investigated for use as thin films and powders (bulk) in electrochromic prototypes and gas sensors [1,2,3]. Electrochromism is a reversible and visible change in optical properties a material undergoes when an applied voltage of a few millivolts/volts is reversibly applied to the material [2]. Electrochromism in WO₃ arises when WO₃ electrode material (pale yellow/transparent) is cathodically reduced by the insertion of an electron (e⁻). Simultaneous intercalation of the interstitials in a WO₃ matrix with a metal cation M, where M = H⁺, Li⁺ or Na⁺ ions helps in maintaining electrical neutrality in the WO₃ system while forming a blue coloured bronze M_xWO₃ [4,5].



This entirely reversible process represented in equation (1) above, takes place primarily at the surface of the electrochromic material, in this case WO_3 [6]. Being a phenomenon that occurs primarily at the surface of materials with electrochromic potential it is therefore likely to be influenced by processes that result in the increase of the effective surface area available for H^+/e^- insertion/intercalation. Increase in the surface area/volume ratio such as is observed in nanostructured or porous thin films could help in assisting the process of intercalation in tungsten trioxide films [7, 8].

As thin films, several methods have been used to prepare WO_3 among which are thermal evaporation [9], chemical vapour deposition [4,9], electrodeposition [4,9], spray pyrolysis [9] electron beam evaporation [1], magnetron sputtering [9], sol-gel methods [2,4] etc. In recent times [7] emphasis has been on the preparation and use of nanostructured materials in investigating different chemical and physical phenomena such as electrochromism and gas sensing, this because reduction of particle size in such materials gives rise to quantum confinement effects, increase in surface/volume ratio, increase in grain boundaries, increase in electronic band gaps, etc, all of which give rise to new or enhanced properties for these materials.

Soft chemistry methods such as Aqueous Chemical Growth (ACG) [10] give the opportunity of designing metal oxide thin films containing micro/nanostructures whose size, shape and orientation can be rationally influenced by varying parameters such as the concentration, pH and temperature of metal-oxide precursor solutions.

We report here the use of the low-temperature (80-95°C), soft chemistry method of Aqueous Chemical Growth for the growth of porous WO_3 microsphere-containing thin films on FTO-coated glass substrates. The method has as advantage the fact that substrates used did not require seeding or surface modification nor is there any need to use structure directing agents/surfactants rendering the process environmentally friendly with thin films produced suffering from little or no contamination.

2. Experimental

Pale yellow solutions of Peroxotungstic acid (PTA, pH=2.21) were prepared through the action of 30% H_2O_2 (80 mL) on W powder (3g) after which was added to it iso-propanol and de-ionised water in the 1:1 v/v ratio. F-doped SnO_2 (FTO) substrates (1 mm thick), 10mm x 20 mm, cleaned by sequential ultrasonication in solutions of MeOH, acetone and de-ionised water for periods of 5 min each, and dried with N_2 were placed in a Teflon holder designed to hold tightly, back-back, four FTO substrates. This was placed at an angle 70° to the horizontal in Schott® bottles containing the PTA solution and was then tightly sealed and placed in a pre-heated (90-95°C) laboratory oven for 6-24h. Thin films greenish- or pale-yellow in color were seen to grow on the FTO-glass substrates. Upon removal these were washed gently with distilled water and dried in air after which annealing was carried out in air at temperatures of 400°C, for 1-2h so as to improve adhesion of the as-synthesized films to the FTO substrates.

SEM images of the thin films' surface morphologies were obtained using a LEO-Stereo Scan 440 Scanning Electron Microscope. X-ray Diffraction Analysis (XRD) was obtained with the Bruker AXS D8 ADVANCE X-Ray diffractometer, using $\text{Cu K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$. X-ray tube current and voltage were set at 40mA and 40kV respectively. Optical characterization of the WO_3 -FTO substrates before and after calcinations and post- H^+ intercalation was carried out in air, at room temperature, this within the 200-1100 nm spectral range (UV-Vis-NIR region), using a CECIL 2100 series spectrophotometer. H^+ intercalation (via electrochemical redox reactions) on a calcined sample of WO_3 -FTO was carried out in a degassed 0.1M H_2SO_4 liquid electrolyte using a three electrode electrochemical cell powered by ECOCHEMIE's AUTOLAB PGSTAT 302N potentiostat-galvanostat, with WO_{3-x} -FTO as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode.

3. Results And Discussion

3.1. Surface morphology and chemical analysis by SEM, TEM, EDS

SEM (figure 1a,b) and TEM (figure 1c,d) revealed that microspheres with hair-like protrusions were formed on the FTO-coated glass substrates. The microspheres whose diameters were generally in the 1-2 μm range with hair-like protrusions, consisted of a thick central core, non-transparent to high voltage electron beams in a TEM, around which grew the hair-like nanoscaled protrusions/rods, 20-50 nm in thickness and 200-500 nm in length.

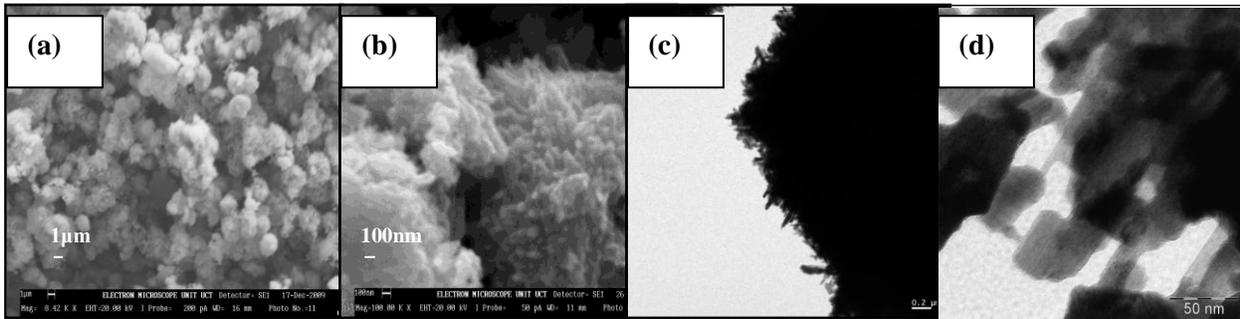


Figure 1. SEM image of microsphere in WO_3 thin films on FTO (a) 8500 X (b) 20000 X; (c) TEM image of WO_3 microsphere (d) TEM image of hair-like protrusions on microspheres.

3.2. Crystal structure determination using X-ray diffraction analysis, HRTEM and SAED

X-Ray Diffraction (figure 2a) analysis showed the WO_3 in the thin films on FTO were in the hexagonal phase with strong reflections in the (100), (001), (110), (200), (201), (220), (221), (311), (401) planes that could be indexed to JCPDS Card no:01-072-1147. XRD suggested that though the thin film contained WO_3 in an amorphous phase it was predominantly crystalline.

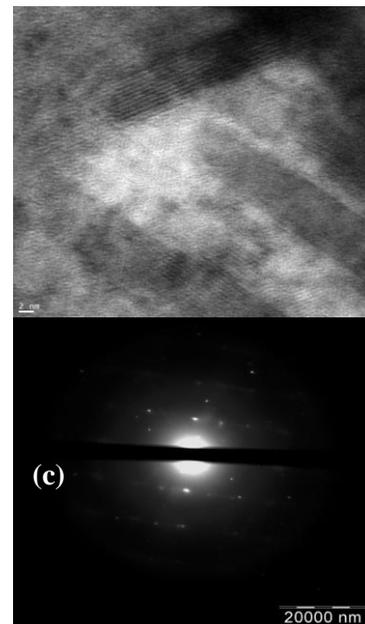
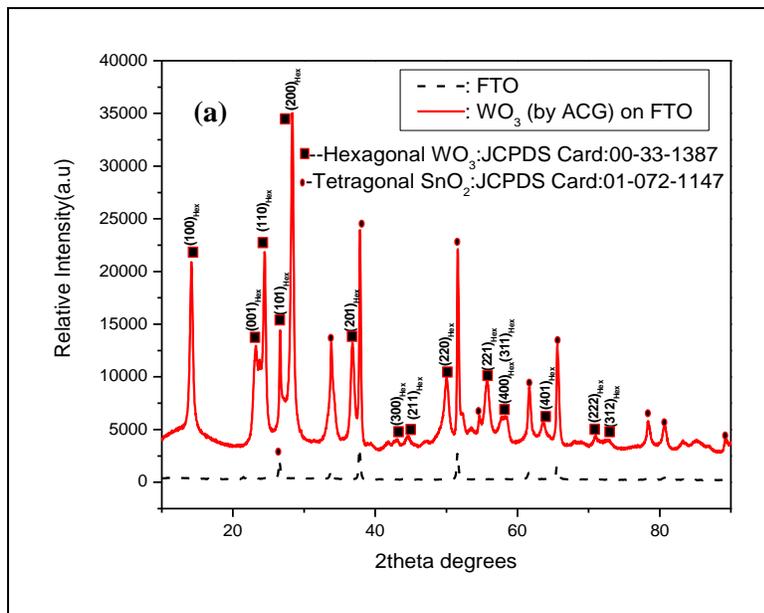


Figure 2. (a) XRD profile of hexagonal-WO₃ on FTO; (b) HRTEM depicting lattice fringes on nanosized hair-like protrusion; (c) SAED on single crystal of WO₃ hair-like protrusion.

Regular diffraction spots observed in SAED (figure 2c) carried out on the hair-like protrusions confirm the single crystalline nature of the fragments observed. From HRTEM (figure 2b) the lattice fringes were estimated to be 0.304 nm which is close to the value for interplanar spacing between the (200) planes in hexagonal WO₃. In WO₃, W atoms are octahedrally coordinated with O atoms to form WO₆ octahedra which join by sharing O corner atoms. Open channels within the octahedra provide interstitial sites for ion insertion [5,6].

3.3. Electrochromism via cyclic voltammetry

Cyclic Voltammetry (figure 3a) was carried out on the WO₃ coated FTO substrate in a 0.1M H₂SO₄ solution, between potentials of -1000mV to +1000 mV and scan rates ranging from 50-200mV/s. When compared to bare FTO (dashed red line) the presence of WO₃ on FTO allowed for high H⁺ intercalation and high charge transfer as porous WO₃ coated-FTO with high surface area incorporates much higher charge density than bare FTO. The application of a negative (reduction) potential caused the formation of a tungsten bronze which was intensely blue coloured (see inset) and could be ascribed to optical intervalence charge transfers that take place as electrons hop between W^{VI}, W^V and W^{IV} metal ions post the double insertion of electrons and protons into interstitial sites present in WO₆ octahedra [4]. Reverse oxidation (positive potential) resulted in de-insertion of the H⁺ and e⁻ yielding a semi-transparent thin film. When taken out of the electrolyte the intensely blue coloured WO₃ thin film bleached in under 1h returning to the traditional pale yellow colour of bulk WO₃.

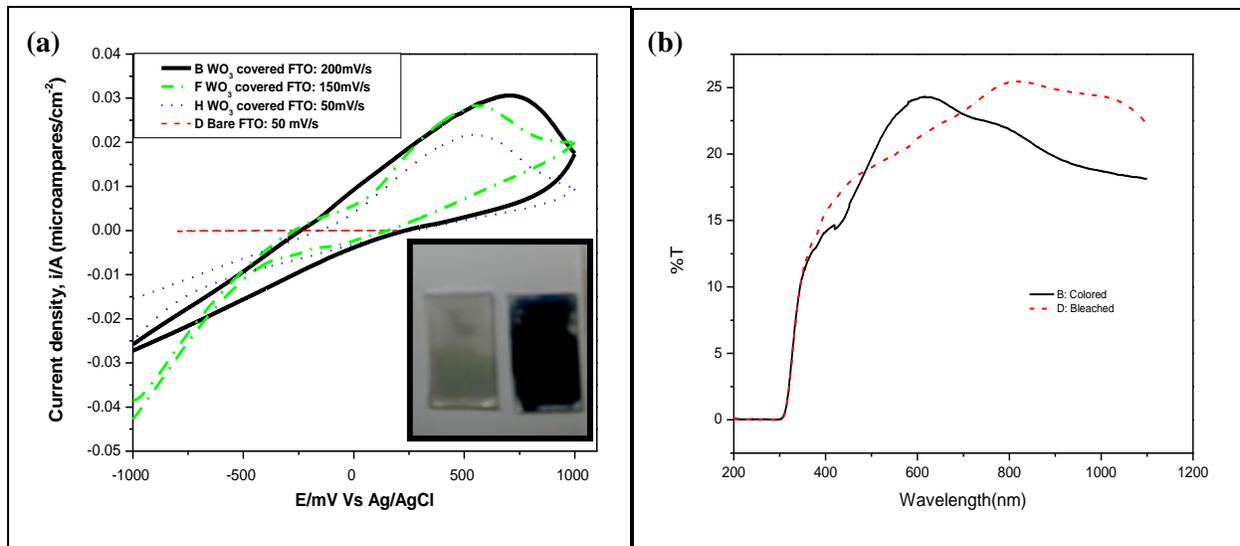


Figure 3. (a) Cyclic Voltammetry on WO₃ on FTO (b) Optical transmission in coloured and bleached state; Digital photographs of WO₃-FTO substrates(inset) showing WO₃ in the coloured (blue) and bleached state (pale yellow).

Optical modulation switch on application of a redox potential was observed to be fairly rapid (15-20 secs). With all optical transmission measurements having been carried out of the electrolytic medium, maximum modulation between the coloured and the bleached states, for the thin film investigated in figure 3b,

amounted to ~6-7% in the Near IR (700-1200 nm). The anodic peak potential (positive scan) as well as the anodic peak current density in brackets were observed to increase from 519.6 mV (0.022 $\mu\text{A}/\text{cm}^2$), 558.3 mV(0.028 $\mu\text{A}/\text{cm}^2$) to 705 mV(0.031 $\mu\text{A}/\text{cm}^2$) with increase in scan rates from 50 mV/s, 150 mV/s to 200 mV/s. Fast diffusion kinetics within the thin films could be ascribed to both the use of an electrolyte containing highly mobile H^+ and the presence of amorphous WO_3 which promotes fast diffusion of H^+ [4]. The cyclic voltammograms in figure 3a show that the switch from coloured to bleach state was not entirely reversible especially as the anodic potential is observed to increase with the increase in scan rate, an indication of slow insertion kinetics which leads to irreversibility [10]. The inset in figure 3a shows that film adhered poorly to the surface. The poor stability of the films could be attributed to semi-compactness due to the partially amorphous nature of the films.

4. Conclusions

Predominantly crystalline WO_3 thin films consisting of microspheres with nanoscale hair/rod-like protrusions were prepared on FTO, by a low cost and environmentally benign, low temperature method of Aqueous Chemical Growth then annealed at 400°C. XRD, SAED showed the annealed films to contain WO_3 in the hexagonal phase. Cyclic voltammetry in acidic electrolyte showed that the films experienced fast diffusion kinetics of H^+ to and from the WO_3 thin film. Reversible optical modulation was seen to occur in less than 20 seconds.

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