

Influence of polyethylene glycol template on microstructure and electrochromic properties of tungsten oxide

M. Deepa*, M. Kar, D.P. Singh, A.K. Srivastava, Shahzada Ahmad

National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi 110012, India

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Abstract

Electrochemical synthesis of tungsten oxide (WO_3) thin film nanostructures by potentiostatically controlling the surface aggregates formed at the electrode–electrolyte interface, in the presence of a polymeric template (polyethylene glycol 400, PEG) from a plating sol of peroxotungstic acid (PTA) is presented. The nanoparticulate morphology of the WO_3 film changes drastically upon varying PEG content in the precursor sol; from an amorphous structure with randomly distributed pores for a film derived from a PTA sol with PEG:ethanol in a 3:7 volume ratio, to a mesoporous, nanocrystalline material with hybrid structures encompassing spherical grains and nanorod-like shapes with a triclinic modification for a film formed in a sol with PEG:ethanol in a 1:1 volume ratio. This approach highlights the role of the PEG proportion in controlling crystal growth, assembly patterns and pore structure. The film derived from the sol with PEG:ethanol in a 1:1 volume ratio exhibits superior transmission modulation and coloration efficiency as compared to the film obtained from a sol with PEG:ethanol in a 3:7 volume ratio. While the latter film deteriorates rapidly within 35 color-bleach cycles, the former film sustains more than 3500 cycles, without significant degradation. This film also exhibits fast switching between the clear and blue states; these are repercussions of the mesopore structure and the interconnected nanocrystallite phase.

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1. Introduction

The design of mesoporous transition metal oxide networks by use of molecular self-assembly templating technique with silicate MCM-41 or its analogues [1] has reached a stage where researchers are combining diverse processes which include colloidal crystal templating, sol–gel, zeolite, cluster and polymer chemistry [2,3]. The optical, electronic and electrochemical properties of these compounds strongly depend on the size and shape of the corresponding nanoparticles and film porosity. The choice of (a) an appropriate organic, inorganic or a hybrid structure directing agent and (b) post-deposition annealing conditions permit control over the material microstructure to optimize the same for specific applications. Tungsten oxide (WO_3) is one such indirect gap semiconducting

material and studies on WO_3 are mainly aimed at the formation of high surface area, mesoporous, transparent thin films, in view of their use as photoanodes in solar cells, cathodes in electrochromic windows and in photocatalyses [4–6]. Despite a significant number of attempts on surfactant-assisted production of WO_3 [6,7], there are hardly any reports on electrodeposition of high quality electrochromic films of WO_3 from a polyethylene glycol (PEG)–peroxotungstic acid (PTA) sol. Here, we describe a methodology to produce electrochemically active mesoporous thin films of WO_3 from an electrolyte containing peroxotungstate species as the inorganic precursor, PEG as the wetting reagent as well as the surfactant. By combining the principles of electrodeposition and templating, this strategy manipulates the surfactant–inorganic co-assemblies only in the thin interfacial region by potentiostatically tuning the surface charge densities and thus allowing the production of nanostructured films [8,9]. This technique affords better control over wetting, degree of penetration, wall thickness, sample shrinkage and grain size thereby

*Corresponding author. Tel.: +91 11 25742610/25742611x2283; fax: +91 11 25726938/25726952.

E-mail address: m_deepa@mail.nplindia.ernet.in (M. Deepa).

allowing the formation of more uniformly structured materials [10] as compared to the electroless sol–gel or electrodeposition from a neat PTA sol.

In previous attempts, WO₃ films have been spin coated or drop cast from a sol encompassing PEG mixed either with WCl₆–C₂H₅OH [11] or with colloidal polytungstic acid [4,12]. PEG has never been utilized in conjunction with PTA and, therefore, the use of this formulation for deposition of WO₃ films either by electrochemical means or by spin/dip coating techniques remains hitherto unexplored. Unlike sol–gel derived films, which are predominantly amorphous in the as-deposited state [13,14] and have poor chemical stability, films generated from surfactant-mediated electrochemical syntheses, are nanocrystalline at room temperature (RT) and are insoluble in aqueous and organic media [8,9]. In addition, we also observed that the assembly patterns of the oxide change upon varying PEG content in the plating sol as rod-like structures emerge in the film, which shows the role of PEG in controlling crystal growth and pore structure. The structural attributes of the films were found to govern their electrochemical and optical properties. Recently, use of sodium dodecyl sulfate as a templating agent for WO₃ has been reported [9], but in spite of having the advantages of a two-step route, the limited window of use (~7 days at 5 °C) of the precursor sol, after which films of desired quality are not obtained rendered the sol unsuitable for large-area applications. A low-cost approach entails the use of a sol that must not particulate or gel preferably for a few months or longer upon repeated platings. The PEG based sol, on the other hand, has a shelf lifetime of more than 6 months at low temperatures, which renders it ideal for commercial use as well. The sol also enables the formation of mesoporous WO₃ films of high cosmetic quality and outstanding performance characteristics.

2. Experimental

2.1. Tungsten oxide film deposition

Tungsten electrolytes (0.5 M) were prepared by dissolution of 11.0 g of W metal powder in 120 mL of H₂O₂ (30%). Subsequent to excess peroxide decomposition with Pt black, addition of 100 mL of polyethylene glycol 400 (PEG) and absolute ethanol in (i) 3:7 and (ii) 1:1 volume ratios, yielded the clear pale yellow plating sols (1.2 ≤ pH ≤ 1.5). Ethanol has been used instead of ultra-pure water, to drive the inorganic/organic co-assembly, as wetting characteristics of ethanol are superior to that of water [15]. Potentiostatic electrodeposition was performed in a three-electrode electrochemical cell in the two solutions with a platinum sheet as the auxiliary electrode, an SnO₂:F-coated glass substrate as the working electrode and the reference electrode was Ag/AgCl/KCl. The primary electrode was subjected to a constant cathodic potential of –0.45 V for 30 min at room temperature. The optimization of the deposition potential and efficiency of deposition

have been described in detail elsewhere [16,17]. The pale blue colored WO₃ films thus obtained were immediately rinsed with deionized water and dried in air. For transmission electron microscope (TEM) measurements, the films obtained from a solution containing PEG and ethanol in a 1:1/3:7 volume ratio were deposited on carbon coated 3.05-mm diameter nickel grids. Repeated platings from the precursor sol (containing PEG:ethanol in a 1:1 volume ratio) did not cause the sol to gel or particulate for 6 months, when stored at 5 °C.

2.2. Characterization techniques

X-ray diffraction (XRD) patterns of the virgin films were recorded in the 2θ range from 3° to 70° with a Bruker AXS D8 advance diffractometer, using Cu Kα (λ = 1.5406 Å) radiation and the angle of incidence 0.5°. Film thickness and refractive index measurements were made with a Rudolph ellipsometer at λ = 546.1 nm, using incident angles of 50° and 70°. TEM (JEOL JEM 200 CX, 200 kV) was employed for examining the microstructural features. A scanning electron microscope (SEM, LEO 440) was used for studying the surface morphological characteristics. Transmittance (T) spectra for virgin, colored and bleached WO₃ films, were recorded ex situ in the 300–2000 nm wavelength range with respect to air in the reference beam in a UV-3101 PC SHIMADZU spectrophotometer. A constant current density of 0.3 mA cm^{–2} was applied for 60 s to color and bleach the films as this ensured the same concentration of the inserted and extracted species (18 mC cm^{–2}). Switching time characteristics between the colored and bleached states for WO₃ films were recorded by multiple step chronoamperometry with an indigenously developed microprocessor controlled setup, which is described in Ref. [18]. Cyclic voltammetry (CV) for the films was performed in a classical three-electrode electrochemical cell within ±1 V, wherein a WO₃ film deposited on SnO₂:F coated glass substrate acted as the working electrode, Ag/AgCl/KCl was employed as the reference electrode, a Pt rod was used as the auxiliary electrode and the electrolyte was 1 M LiCF₃SO₃ in gamma butyrolactone.

3. Results and discussion

3.1. Structural and microstructural features

X-ray diffractograms of virgin WO₃ films are illustrated in Fig. 1. The XRD pattern of the film (Fig. 1a) obtained from a PTA sol containing PEG:ethanol in a 3:7 volume ratio reveals an extremely broad hump with a peak centered at 2θ = 8° and d = 11.5 Å and no other distinctive peaks which is typical of an amorphous structure. The diffractogram of the film derived from the PTA sol encompassing PEG:ethanol in a 1:1 volume ratio shows a cluster of three peaks at d = 3.84, 3.76 and 3.66 Å corresponding to the (0 0 1), (0 2 0) and (2 0 0) crystallographic

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