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Preparation and properties of electrochromic coatings based on nanoparticle tungsten oxide

Vera V. Abramova,[a] **Alexander S. Sinitskii,***[a] **Eugene A. Goodilin**[a,b] **and Yuri D. Tretyakov**[a,b]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.*
Fax: +7 095 939 0998; e-mail: sinitsky@inorg.chem.msu.ru
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation*

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Optical and electrochromic properties of nanocrystalline tungsten oxide coatings are investigated after deposition and a subsequent treatment at optimal temperatures.

The reversible change of optical properties under an applied voltage was discovered in tungsten oxide,[1] and this material remains the most promising for the production of electrochromic coatings. Recent interest in these coatings is induced by their potential applications like devices for temperature control, smart windows, allowing the throughput of visible light and solar energy to be modulated, anti-dazzling mirrors and information displays with superior angle viewing performance and brightness adapted to the environment.[2–4]

Tungsten oxide films are usually prepared by sputtering,[5] chemical vapour deposition,[6] thermal deposition,[7,8] anodization[9] and wet-chemistry methods[10–13] demonstrating several apparent advantages, such as a low cost at ease deposition of coatings over large areas. Among other chemical methods, the sol–gel technique is most commonly used. In this method, a uniform film is formed onto an appropriate substrate due to the hydrolysis and condensation of a liquid precursor dried in ambient moisture after its deposition *via* dip-coating or spin-coating.[10,12,13] In all the cases, as-deposited tungsten oxides are amorphous transforming into a crystalline state at about 300–400 °C.[7–9,10,12] Both amorphous and crystalline tungsten oxide films have their own advantages and disadvantages in terms of required optical and electrochromic properties.[14,15] Therefore, we report a deposition method for nanocrystalline $WO_3 \cdot 2H_2O$ and the control of optical and electrochromic properties of the coatings by annealing conditions.

The procedure was based on the reaction of soluble tungsten salts with strong acids. Concentrated hydrochloric acid was added dropwise to a 0.1 M aqueous solution of reagent grade $Na_2WO_4 \cdot 2H_2O$ in an ice bath to precipitate tungsten acid. Then, the precipitate was rinsed several times with distilled water until the absence of residual chloride ions. The $WO_3 \cdot 2H_2O$ precipitate was suspended in water, slowly heated and deposited *via* dip-coating onto cleaned glass substrates with a conducting indium-tin oxide (ITO) coating. When varying the concentration of the nanoparticle suspension, withdraw rates and the number of dipping/drying cycles, different thickness of the coatings was achieved.

For analytical purpose, the precursor sol used for coating production was dried in air for several days and thus obtained bulk material was analysed by TGA/DTA (Perkin–Elmer Pyris thermal analyser, air, platinum crucibles) to suggest a scheme of further treatment. In accordance with the TGA results, some of the deposited coatings were slowly heated at a rate of 1 K min^{-1} up to 300 °C in air and annealed at this temperature for 2 h.

The optical properties of coatings were determined in the wavelength range 200–1100 nm using a Perkin–Elmer Lambda 35 double-beam spectrophotometer. The microstructure of the coatings was studied using a LEO Supra VP 50 scanning electron microscope (SEM), an NT-MDT Solver BIO M scanning probe microscope (AFM) and a Nikon Eclipse E600 POL (optical microscopy). The electrochemical measurements (Solartron SI 1287

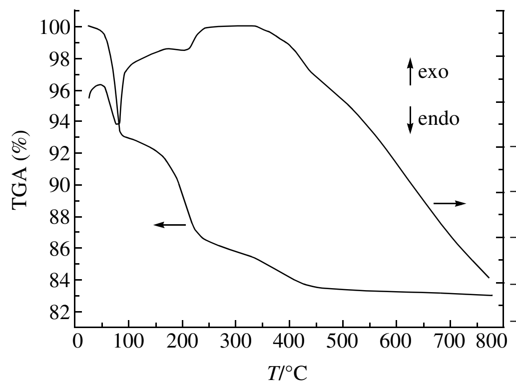

Figure 1 Typical TGA and DTA curves of nanoparticle tungsten oxides (5 K min^{-1} heating rate in air).

electrochemical interface) were carried out in a transparent three-electrode cell containing a 1 M H_2SO_4 solution, a tungsten oxide coating deposited onto the ITO glass substrate as a working electrode, a platinum counter electrode and a standard Ag/AgCl reference electrode. In all the electrochromic measurements, a transparent electrochemical cell connected to the electrochemical interface was located inside the spectrophotometer, so that electrochromic properties were measured *in situ*. X-ray powder diffraction (XRD) experiments were performed using a Guinier camera FR-552 with filtered CuKα radiation and Ge as an internal standard. The JCPDS-PDF2 database was used to carry out the phase analysis.

According to the XRD results, the as-prepared tungsten oxide was crystalline corresponding to the known $WO_3 \cdot 2H_2O$ phase (JCPDS-PDF2 file 18-1419). This is contradictory to the previously described results because, usually, no crystalline phase was observed below 300–400 °C.[7–9,10,12] The coating heat-treated at 300 °C looses water forming the $WO_{2.95} \cdot 0.05H_2O$ phase (JCPDS-PDF2 file 6-210).

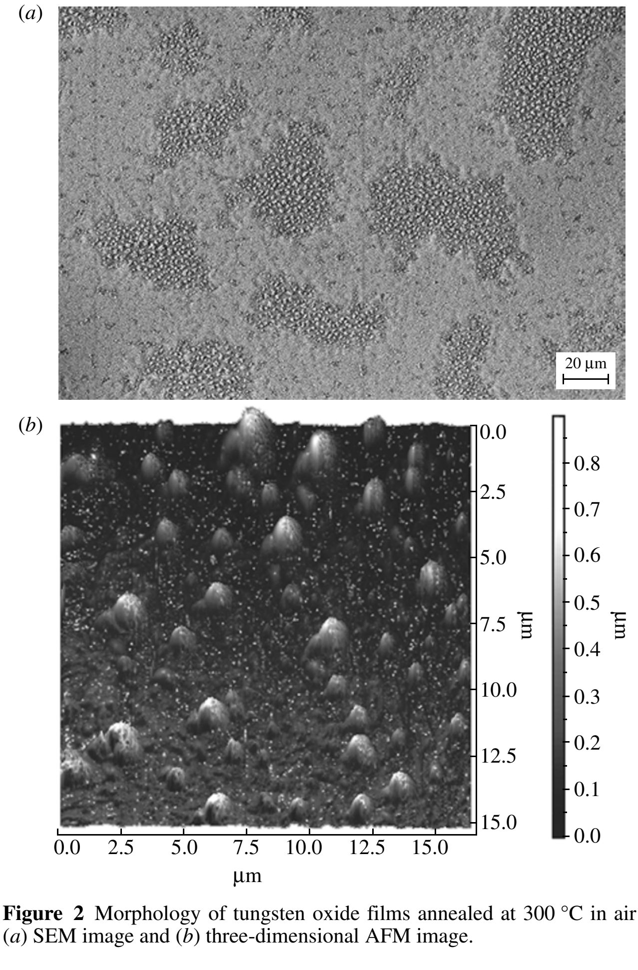

Figure 2 Morphology of tungsten oxide films annealed at 300 °C in air: (*a*) SEM image and (*b*) three-dimensional AFM image.

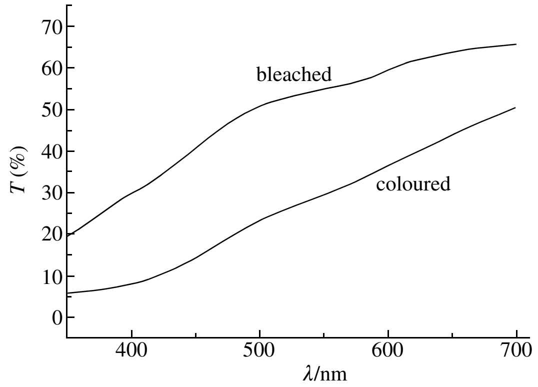

Figure 3 Optical transmission spectra of bleached and coloured nanoparticle tungsten oxide coatings annealed at 300 °C.

Thermal analysis curves for nanoparticle tungsten oxide (Figure 1) suggest a two-step process. In the first step, rapid water desorption takes place between room temperature and ~100 °C; this process corresponds to the endothermic peak at 55 °C. In the second step, there is a subsequent weight loss accompanied by an endothermic peak at 170 °C corresponding to the removal of chemically bonded water molecules. The weight loss is almost completed at 470 °C. The composition of as-prepared and annealed nanoparticle tungsten oxides can be estimated as $WO_3 \cdot 2.9H_2O$ and $WO_3 \cdot 0.4H_2O$, respectively, so these values are consistent with the results of XRD analysis.

The surface of as-prepared tungsten oxide coatings is relatively smooth and covered with isolated aggregates of tungsten oxide nanoparticles [Figure 2(*a*)]. The annealing process has no essential influence on the surface morphology since no microcracks were found to appear due to water removal, whereas the mechanical properties of the coatings were improved. The roughness of the coating surface was analysed using AFM [Figure 2(*b*)] for several regions of the surface. The in-plane size of WO_3 nanoparticle aggregates lies in a micron range while their height was under 800–900 nm.

Before optical measurements, a +1 V voltage was applied to the WO_3-coated ITO substrate until a maximum of transmittance was obtained. After that, the tungsten oxide coatings were successfully coloured and bleached by reversing the applied voltage. The optical properties were modulated by proton intercalation or deintercalation into the tungsten oxide upon the application of voltage across the outer electrodes. The process can be illustrated schematically by the reaction

$$WO_3 + xH^+ + xe^- \rightleftharpoons H_xWO_3,$$

where WO_3 is considered to be transparent, whereas H_xWO_3 absorbs light in the visible spectrum range.

Typical optical transmission spectra measured for both bleached and coloured states are shown in Figure 3. The transmission in the visible range was significantly different for the coatings in bleached or coloured states though the shape of the spectra had

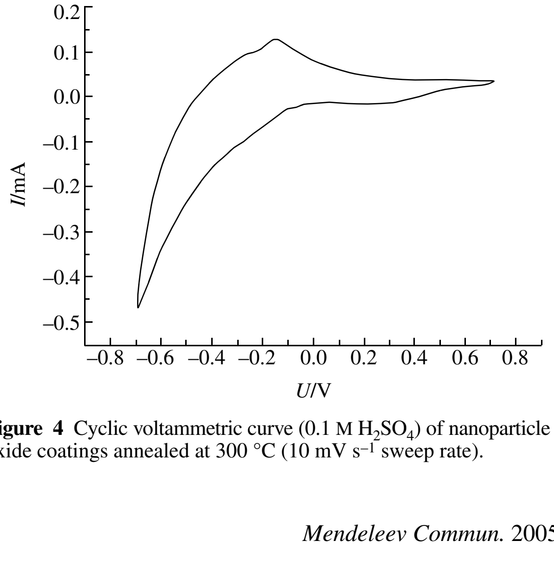

Figure 4 Cyclic voltammetric curve (0.1 M H_2SO_4) of nanoparticle tungsten oxide coatings annealed at 300 °C (10 mV s^{-1} sweep rate).

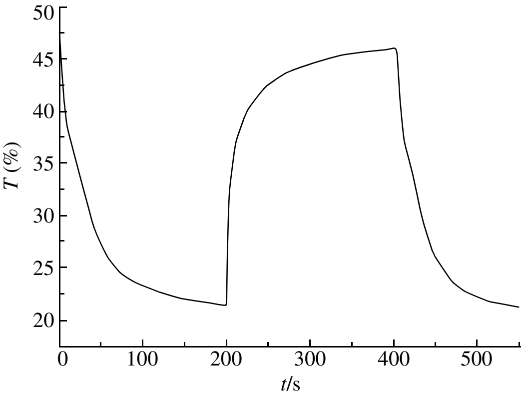

Figure 5 Variation in the transmittance at 550 nm as a function of time for nanoparticle tungsten oxide coatings annealed at 300 °C (a voltage step between –0.8 and +0.8 V). The voltage changes polarity for each 200 s.

no apparent changes. The cyclic voltammogram measurements carried out on tungsten oxide coatings after several initial cycles of stabilization and optimization (Figure 4) correspond to an applied potential varying between 0.8 and –0.8 V (colouration) and back to 0.8 V (bleaching) at a sweep rate of 10 mV s^{-1}. The slightly defined anodic peak is situated around 0.2 V. The curve did not change over a large number of cycles suggesting a good self-consistency and reproducibility of the data.

A typical transmission–time curve for tungsten oxide coatings (Figure 5) represents the transmission at 550 nm corresponding to a voltage step applied to annealed 5–10 μm thick coatings. All the samples were coloured at –0.8 V and bleached at 0.8 V. The maximum transmission difference of about 25% between bleached and coloured states was reached with a time step of about 200 s. This full-switching time is longer than that reported recently[7,8,10–12] since most of the results there were reported for thin films (thickness less than 1 μm) of an amorphous or semicrystalline nature, in which a faster optical switching is presumably expected. This means that a slower colouration–bleaching process for nanoparticle tungsten oxide coatings in this work might take place due to a decreased intercrystalline electronic conductivity.

The optical transmittance spectra of as-deposited and heat-treated coatings (Figure 6) obviously evidence that the coatings exhibit a high transmission both in as-deposited and annealed states (especially, regarding their thickness and nanocrystalline nature). The annealed coatings exhibit a higher transmittance in the whole spectral region, probably, because of a shrinkage of the heat-treated oxide film.

The influence of annealing on the electrochromic properties of tungsten oxide coatings can be easily revealed by a comparison of colouration efficiencies (CE):

$$\mathrm{CE} = \frac{\Delta(\mathrm{OD})}{Q} = \frac{1}{Q}\log\,(T_\mathrm{b}/T_\mathrm{c}),$$

where Δ(OD) is the variation in optical density, Q is the charge density (C cm^{-2}), T_b and T_c are the values of transmission in the bleached and coloured states, respectively. It was found that the temperature treatment increases CE for tungsten oxide coatings from 8.5 to 15 C cm^{-2}.

Thus, tungsten oxide nanoparticle coatings exhibit such values of major functional parameters that make them a promising electrochromic material when considering an improved transmission rate and a low cost.

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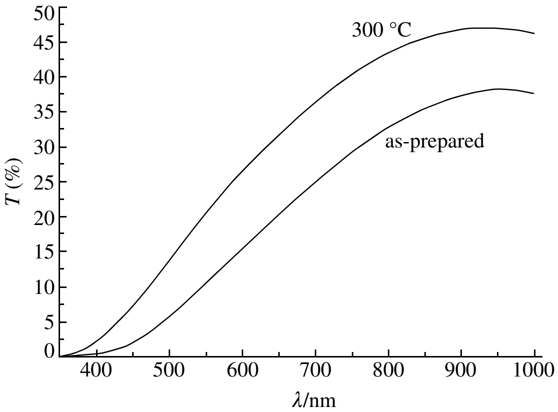

Figure 6 Optical transmittance spectra for nanoparticle tungsten oxide coatings as-deposited and annealed at 300 °C.

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