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A simple method for the fabrication of WO_3 films with electrochromic and photocatalytic properties

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ABSTRACT

This work proposes a simple and inexpensive method for the deposition of WO_3 films with electrochromic and photocatalytic properties. It consists of preparing a precursor solution of WO_3 powder in H_2O_2, allowing the precursor to age for a period of 1 to 2 months and then spraying it on an appropriate substrate. Changes in the crystallinity of the WO_3 particles within the precursor were observed during aging. They were taken advantage of for the preparation of homogeneous WO_3 films of optical quality. The films thus prepared are amorphous, stable, with good adherence on the substrate. They exhibit favorable electrochromic properties, such as a high Li ion diffusion coefficient (of about 5×10^{-10} cm^2/s) and reversible coloration with efficiencies of 132 cm^2/C at 389 nm, 48.9 cm^2/C at 534 nm and 52.4 cm^2/C at 800 nm. These films were also used as photo-anodes for the photocatalytic degradation of methylene blue (MB) in a NaOH aqueous solution with promising results. Effective degradation of MB was observed with the lowest half-life time of 55 min recorded for a NaOH concentration of 0.8 M.

1. Introduction

Tungsten oxide is a compound that has attracted considerable research interest lately, due to its properties that include electrochromism, photochromism, gas sorption and photocatalysis [1,2]. Many applications have been envisaged for it, such as smart windows, switchable mirrors, displays and gas sensors, some of which have already been commercialized [3,4].

WO_3 thin films have been developed in the past with the use of physical vapor deposition (thermal, electron beam gun evaporation and sputtering [1,2]) and by chemical methods such as sol–gel, spin coating, electrodeposition and spray pyrolysis [5–8].

Of these, chemical methods are straightforward, versatile and require less expensive equipment. They yield a large variety of film morphologies depending on the pre- and post-deposition conditions, starting materials, solution chemistry [8–11] and thermal treatment of the films [8,12]. They are also well suited for coating of large areas [4].

For the preparation of tungsten oxide films with chemical methods, various starting materials can be used, such as tungsten hexachloride (WCl_6) or tungsten oxytetrachloride ($WOCl_4$) for the formation on chloro-alcoxides [7], metallic tungsten (W), tungsten carbide (WC) or sodium tungstate (Na_2WO_4) that can be diluted in aqueous solutions of hydrogen peroxide to form peroxotungstic acid [7,13–15]. Of these, chlorides are reactive and corrosive and need special care in their treatment, while the formation of peroxotungstic acid is a strong exothermal reaction and requires continuous cooling. A much simpler route is the dilution of tungsten oxide in H_2O_2 that has been used in the past by our group for the preparation of opaque, nanostructured WO_3 films [16].

In the present paper, the WO_3–H_2O_2 method is further advanced by allowing the aforementioned precursor solution to age prior to deposition. The aged precursor solution is then sprayed on appropriate substrates. Aging of a different precursor was found to significantly affect the resulting film properties in electrodeposited WO_3 films, as was reported in our earlier work [17,18]. Here the aging effect is taken advantage of in order to prepare homogeneous films of optical quality. It was found that aging of the precursor for up to 2 months leads to the deposition of homogeneous WO_3 films with favorable electrochromic and photocatalytic properties.

2. Experimental details

2.1. Precursor solution

For the preparation of the precursor solution, 0.36 g of WO_3 powder (Aldrich, 99.995%) was dissolved into 20 mL of 15% H_2O_2. With vigorous agitation a yellow-greenish solution was obtained. The solution was unstable and precipitation occurred when the agitation stopped. Heating at 80 °C for about half an hour was used to increase the viscosity of the solution. The solution was aged by storage at room temperature in a sealed bottle.

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2.2. WO_3 film deposition

The precursor solution was used for the growth of WO_3 films either immediately after its preparation or after aging which varied from 1 to 4 months. Low-cost equipment were used for the spray deposition: a hand-held electrical air compressor to create suction, a spray nozzle (airbrush), a hot plate for placing the substrates and a magnetic stirrer for mixing the precursor solution prior to spraying. A schematic representation of the spray deposition set-up appears in Fig. 1a.

A commercial SnO_2:F coated glass product with the trade name K-glass was used as substrate. It is produced by spray pyrolysis with a thickness of 200 to 500 nm [19]. K-glass pieces 2.5 cm × 4 cm in size were used.

In spray deposition, film thickness and homogeneity can be controlled by adjustment of numerous parameters such as nozzle-to-substrate distance, spreading of the solution jet, substrate temperature and number of repetitions. In the present work the nozzle-to-substrate distance was kept constant to 21 cm, the substrate temperature was kept to 80 °C (to avoid "boiling" of the solution upon contact with the glass) and the thickness was varied by spraying on the same substrate more than once. Each spray pulse had a duration of 1 s and a solid film was allowed to form (by drying of the precursor) before the next spray pulse was effected. The precursor drying took a few minutes for every spray pulse.

2.3. Instrumentation and experimental techniques

The thickness of the films was measured using an Ambios XP-1 profilometer. Step height measurements between film-coated and uncoated areas were conducted to determine film thickness. This instrument was also used to assess the surface morphology and roughness of the films.

Transmission electron microscopy (TEM) pictures of the dried precursor were taken using a JEOL JEM 2100 microscope at 160 kV. A drop of the precursor solution was placed on a carbon coated copper substrate (grid) and was allowed to dry prior to the measurements.

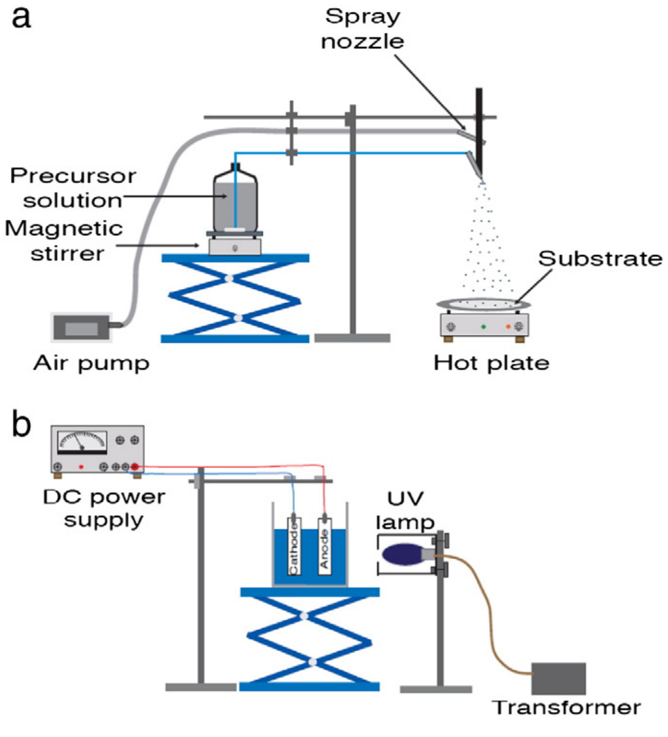

Fig. 1. Schematic representation of the experimental set-up. (a) Spray deposition of WO_3, (b) photocatalysis experiments.

Scanning electron microscopy (SEM) pictures of the films were taken using a JEOL 6300 microscope at 20 kV.

In order to assess the electrochemical properties of the films, cyclic voltammetry and Galvanostatic Intermittent Titration (GITT) were performed using the following instruments: a potentiostat–galvanostat (AMEL, model 2053), a function generator (AMEL, model 586) and a noise reducer (AMEL NR 2000). The electrochemical cell used for these experiments has already been described elsewhere [20]. This cell allows for the insertion of a Pt wire serving as the reference electrode, close to the WO_3/K-glass (working electrode). A K-glass piece was used as counter electrode. The cell was sealed by o-rings and filled with the 1 M $LiClO_4$-PC liquid electrolyte. During the cyclic voltammetry tests, the potential between the working (WO_3/K-glass) and the reference (Pt) electrode was varied linearly in the range (−0.8 V, +1.4 V) at a rate of 20 mV/s.

During the GITT experiments, a series of 100 square current pulses with amplitude of 0.2 mA and duration of 5 s were fed into the electrochemical cell, each followed by an equilibration period of 30 s. The potential between working and reference electrodes (corresponding to the electromotive force of the film) versus the inserted charge density was measured.

The chemical diffusion coefficient of Li^+ was calculated using the formula [18]:

$$D = \frac{4L^2}{\pi\tau}\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \qquad (1)$$

where ΔE_s is the change in the steady-state voltage as a result of the current pulse, ΔE_t is the total change in overvoltage during the pulse, τ is the duration of each pulse and L is the film thickness. Eq. (1) can be applied to our electrochemical systems provided that the following conditions are observed [21]:

(a) Negligible change in the WO_3 molar volume with Li^+ intercalation.
(b) Small current values to justify the approximation $dE/dx \approx \Delta E/\Delta x$, i.e. the substitution of a first derivative by a finite difference.
(c) During the current pulse the overvoltage E is proportional to $t^{1/2}$.
(d) $\tau \ll L^2/D$.

The experimental parameters were set so as to meet these conditions.

The "intercalation parameter" x in the Li_xWO_3 films was calculated using the following expression [21]:

$$x = \frac{\left(\frac{I\tau}{q_e}\right)N_{pulse}}{\left(\frac{N_A}{M}\right)\rho PDSL} \qquad (2)$$

where I and τ are the current and the duration of each pulse respectively, q_e is the elementary charge, N_{pulse} is the pulse number, N_A the Avogadro number and M, ρ, PD, S, and L are the molecular weight, bulk density, packing density, area and thickness of the WO_3 film, respectively.

Electrochromic (EC) devices of the form K-glass/WO_3/liquid electrolyte/K-glass were fabricated, incorporating the prepared WO_3 films. The liquid electrolyte used in all experiments was 1 M lithium perchlorate dissolved in propylene carbonate ($LiClO_4$-PC). In order to construct the electrochemical cells, two pieces of K-glass (a plain one and one with the deposited tungsten oxide film) were used, each having dimensions of 2.5 cm by 4 cm. The two pieces of glass were arranged facing each-other and a cavity was formed between them using silicone. The cavity was then filled with the 1 M $LiClO_4$-PC liquid electrolyte and sealed with silicone [17]. Electrical contacts were created at the edge of each piece of glass using copper adhesive tape.

The electrochromic devices thus fabricated were also subjected to a galvanostatic coloration process. Certain amounts of electric charge,