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The influence of sol–gel processing on the electrochromic properties of mesoporous WO_3 films produced by ultrasonic spray deposition

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ABSTRACT

High performance mesoporous tungsten oxide films were deposited by ultrasonic spray deposition using templated sol–gel chemistry. The dynamics of both sol preparation and hydrolysis were investigated by UV–vis spectroscopy. A stable sol was formed after 12 h, while optimum electrochromic performance was obtained for 12 h of hydrolysis. Electrochromic performance is strongly correlated to the annealing conditions, with optimized films displaying coloration efficiency > 50 cm^2/C and switching times < 10 s. FTIR spectroscopy revealed that WO_3 produced under optimized conditions were free of hydroxyl and carbonate impurities. Performance scaled with the specific surface area and nanoscale morphology. The WO_3 films display good long term cycling durability up to 2500 cycles, which was attributed to the high degree of film crystallinity.

1. Introduction

Smart windows employing electrochromic materials to reversibly modulate optical transmission and reflection can significantly improve building energy efficiency [1]. Similar to thin film batteries, electrochromic windows consist of a cathode and anode separated by a solid state electrolyte. Tungsten oxide is the leading cathodic electrochromic material due to its excellent optical properties, coloration efficiency and stability in response to an applied small voltage [2]. There has been significant progress in the forty years since Deb's pioneering studies [3], but further improvements in both performance and cost reduction are required. Developing cost effective synthesis processes are keys for widespread implementation of electrochromic windows.

Solution-based chemical synthesis offers versatility with respect to controlling film composition while also being promising for reducing manufacturing costs relative to current state-of-the-art vacuum deposited electrochromics [4]. Ultrasonic spray deposition (USD) is an attractive technique for large scale, low cost thin film manufacturing of nanostructured thin films [5]. The use of benign solvents enables deposition under ambient conditions, and ultrasonic nebulizer technology addresses the quality and uniformity issues that are a concern with conventional pressure driven sprays [6,7]. Our group has been exploring the potential of this technology for inline fabrication of electrochromic devices. Previously we demonstrated the synthesis of NiO:Li films for use as the complementary electrochromic layer through ultrasonic spray pyrolysis using aqueous mixtures of nickel nitrate and lithium nitrate [7]. The resulting nanocomposite films exhibited strong and efficient optical modulation. In the case of WO_3 the crystalline phase is desired for long term durability, but crystallinity can often impede intercalation relative to amorphous films. Mesoporous films comprised of nanocrystalline domains can provide both high performance and good durability [8]. Initially we produced mesoporous films in a two step process in which WO_3 nanoparticles generated by hot wire chemical vapor deposition (HWCVD) were suspended in water and converted into a film by USD [9]. Solid performance was obtained, but stability was a concern since nanoparticles detached into solution during extended cycling [10]. In addition, control of nanoparticle size and morphology using HWCVD can be challenging.

Sol–gel chemistries combined with sacrificial templating agents is a well-established technique for the formation of mesoporous metal oxide films [11,12]. Mesoporous WO_3 produced using this approach has demonstrated remarkably improved electrochromic properties [13–18]. Moreover, the mesoporous structure does not have to be ordered to produce high levels of performance [17,19]. However, the preparation of high quality submicron films using sol–gel chemistry typically employs either slow dip coating [16,18], spin coating [14,19],

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or evaporation induced self assembly [15,17], which are convenient laboratory techniques but not amenable to large scale production. We recently demonstrated the production of high performance mesoporous tungsten oxide films by adopting sol–gel chemistry to ultrasonic spray deposition [20]. There are three steps to film production: sol formation, hydrolysis, and calcination. In this work the dynamics of the individual steps are studied by UV–vis spectroscopy and correlated to electrochromic performance. Extensive material characterization including FTIR, Raman, selected area diffraction, and electron microscopy are employed to establish structure–property–performance relationships for this material. Finally, the durability of this material is examined by long-term cycling.

2. Materials and methods

2.1. Preparation of sol solution

Triblock polymer Pluronic P123 (poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene), $EO_{20}PO_{70}EO_{20}$), anhydrous ethanol and tungsten hexachloride (WCl_6) were all purchased from Sigma-Aldrich and used without further purification. An inert (Ar-filled) glovebox was used for both reagent storage and sol formation, since the reagents are moisture sensitive. Typical preparation began by dissolving 1 g of the triblock copolymer P123 in 20 ml anhydrous ethanol ($\geq$99.5%). The sol was completed by adding 0.25 g of WCl_6 ($\geq$99.9%) followed by several hours of stirring. The evolution of the sol composition was monitored by UV–vis spectroscopy (Stellernet SD200). After 12 h the sol composition stabilized and was used for ultrasonic spray deposition.

2.2. Preparation of gel films

The stable green sol described above was transferred to a syringe and delivered to the ultrasonic spray nozzle at a flow rate of 0.25 ml/min using Fluid Metering Inc. VMP TRI Pulseless "Smoothflow" pump. The ultrasonic spray system was obtained from Sono-Tek Corporation and consisted of a model 8700-120 spray head that operated at a frequency of 120 kHz. The spray nozzle had a 0.230 in. diameter conical tip and 0.015 in. diameter orifice that was fitted with the impact system for gas-driven spray delivery. The atomized mist was entrained in a stream of nitrogen whose flowrate was fixed at 6.9 slm using an electronic mass flow controller (Omega FMA 1818). This aerosol was directed onto FTO-coated glass (TEC-15, Pilkington) positioned 5 cm below the nozzle under ambient conditions. Before deposition, all substrates were cleaned with an isopropanol-soaked clean-room wipe, blown dry with nitrogen, and then placed in an oxygen plasma (800 mtorr, 155 W) for 5 min. Samples were mounted on a computer controlled stage which rastered them through the deposition zone ten times, producing uniform, iridescent blue films with the desired thickness of $\sim$400 nm. Samples were then transferred into a chamber saturated with water vapor for hydrolysis. The transparency changes during hydrolysis of the gel films on FTO substrates were also monitored by using UV–vis spectroscopy.

2.3. Preparation of tungsten oxide thin films

The final step is calcination, where samples are heated in air to remove residual solvent and the polymer template while completing the oxidation and crystallization of the WO_3. Two different techniques were explored for the critical calcination step. "Fast" annealing describes samples placed directly onto a hot plate set at the desired temperature for a duration between 0.5 and 2 h. Samples calcined using the "slow" annealing procedure were placed in an oven that was ramped at 5 °C/min from ambient to the desired temperature and then held there for 1 h. After calcination the samples were removed and allowed to naturally cool down to room temperature. Samples were annealed at three different annealing temperatures (300, 350, 400 °C) using both the slow and fast approaches.

2.4. Electrochromic performance

Electrochromic performance was evaluated by cycling films in an electrolyte composed of 1 M $LiClO_4$ dissolved in propylene carbonate in a test cell housed in an Ar-purged glovebox. Cyclic voltammetry and potential cycling measurements were made using a BioLogic VMP3 multichannel potentiostat. A diode laser (670 nm) coupled to a detector (Thor Labs, Inc. DET100A) was used to collect optical transmission in direct registry during cycling. The contribution of a clean FTO substrate was background subtracted, so that the reported optical response reflects only contributions from the WO_3 film. Cyclic voltammetry (CV) was performed using a 20 mV/s scan rate between 2 and 4 V vs. Li/Li^+. Switching kinetics was measured using chronoamperometric cycling between 1.7 and 4.2 V vs. Li/Li^+, and the switching speed is defined as the time required to achieve 90% of the full optical change. The durability tests were performed by cycling at a constant current density of 39 $\mu A/cm^2$ between 2 and 3 V.

2.5. Materials characterization

Raman spectroscopy was performed on films using the 488 nm line of a 15 mW argon ion laser. The additional analysis described below was performed on WO_3 powder that was obtained by scraping material from glass substrates using a stainless steel blade after the final calcination step. For FTIR the powder was mixed with KBr powder and spectra were obtained from a Thermo 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector using a resolution of 4 cm^{-1}. Samples for transmission electron microscopy (TEM) and selected area diffraction (SAD) were produced by suspending particles in ethanol using sonication and placing a drop on a TEM grid and allowing the solvent to evaporate. The nanoscale morphology was examined by transmission electron microscopy (TEM, FEI CM200) of scraped powder. Selected-area electron diffraction (SAD) patterns of the WO_3 particles were carried out in the same instrument with an accelerating voltage of 200 kV. N_2 physisorption was performed using a Micrometrics ASAP 2020 after samples were degassed at 250 °C under vacuum for 4 h.

3. Results and discussion

3.1. Film preparation and electrochromic performance

Fig. 1(a) shows photographs of the sol solution at selected stages of preparation. The color changes during sol formation were monitored by UV–vis transmission measurements, and the spectra obtained at each time step in Fig. 1(a) are displayed in Fig. 1(b). The ethanol/P123 mixture is transparent, but immediately turns yellow upon the addition of tungsten chloride, due to formation of hydrogen chloride. After stirring for 20 min the solution again becomes transparent as the W^{5+} alkoxide begins to form. Continued stirring results in absorption in the red portion of the spectrum, which is attributed to the formation of blue W^{5+} alkoxide, $WCl_3(OC_2H_5)_2$ from the reaction of tungsten hexachloride with ethanol [21,22]. The overall reaction can be described as followed equation [23]:

$$WCl_6 + 2.5C_2H_5OH \rightarrow WCl_3(OC_2H_5)_2 + 0.5CH_3CHO + 3HCl \quad (1)$$