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Scalable synthesis of improved nanocrystalline, mesoporous tungsten oxide films with exceptional electrochromic performance

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ABSTRACT

Templated sol gel chemistry provides a versatile approach to introduce order and porosity into nanostructured materials. However conventional evaporation induced self assembly techniques are not easily scaled to produce films with sufficient thickness over large areas at the throughput required by electrochromic windows. Here we demonstrate that the principles of sol gel chemistry may be deployed using ultrasonic spray deposition (USD) for scalable synthesis of nanocrystalline WO_3 films with unrivaled electrochromic performance. Systematic manipulation of sol chemistry enabled the production of mesoporous films with high specific surface area (>100 m^2/g), mean pore sizes of $\sim$5 nm, and narrow pore size distributions. Film thickness is found to be proportional to the sol concentration and number of spray passes, and various combinations are shown to produce films capable of modulating $>98\%$ of incident solar radiation in the visible spectrum (450–900 nm). Elimination of haze enables full transmission in the bleached state, while the broadband coloration is attributed to the exceptionally high charge density (>120 mC/cm^2). The materials have good switching speeds which improve with specific surface area, and the long term durability is promising.

1. Introduction

Buildings account for 40% of energy expenditures in the US, more than any other sector including transportation and industry [1]. Windows are responsible for a significant fraction of energy loss in buildings, strongly influencing cooling, heating and lighting requirements. Smart windows employing electrochromics (EC) have the potential to significantly reduce the US energy footprint by up to 5 quads (1 quad $=10^{15}$ BTU) by controlling solar heat gain and lighting through modulation of their optical characteristics (i.e. transmittance, reflectance). The optical transparency of electrochromic materials such as tungsten oxide is reversibly altered due to the insertion/extraction of light ions such as Li^+ or H^+ in response to a small applied voltage [2]. There has been significant progress in the forty years since Deb's pioneering studies [3,4], but current EC applications remain limited to niche markets such as dimmable rear view mirrors and the windows of Boeing's Dreamliner. Further improvements in both performance and cost reduction are required to enable widespread deployment of this technology.

In his recent critical review, Granqvist identified a number of hurdles that must be overcome in order to enable large scale manufacturing of EC smart windows [5]. Prominent among them was that EC films must have nanoporosity over their entire area, which may require that films are produced under non-standard conditions using techniques that are amenable to large-scale manufacturability. Tungsten oxide films with a mesoporous, nanocrystalline morphology are ideal for electrochromic applications [6]. The crystalline phase is preferred over amorphous material for stability concerns [6,7], while high specific area is required for efficient ion intercalation. Templated sol–gel chemistry approaches have been used to produce mesoporous WO_3 with impressive electrochromic properties [8–15]. For example, the highest optical modulation reported to date of $\Delta T=85\%$ was achieved for WO_3 films deposited using sol gel chemistry [14,15], a value that is superior to leading reports from sputter deposited films [16]. Solution-based chemical synthesis also offers the promise of reduced manufacturing costs relative to current state-of-the-art vacuum deposited electrochromics [17]. However, the techniques employed to produce these results such as dip coating [8,11,14], spin coating [9], or film casting [10,15] are generally quite slow and not easily amenable to large scale, in line manufacturing. As such, commercial production of smart windows continues to rely on sputtered WO_3, largely due to its demonstrated reliability for coating large area substrates [2,4].

Our group has been exploring the potential of ultrasonic spray deposition (USD) for the scalable fabrication of EC devices. Advantages of USD include low capital requirements and high

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materials utilization. Moreover, the use of benign solvents such as water and alcohol allows processing to be conducted under ambient conditions. Spray pyrolysis has been demonstrated for the production of high quality transparent electrodes [18] as well a nickel oxide [19], a leading counter electrode in the electrochromic stack [2]. As such one could envision employing USD for in-line production of smart windows.

One approach for the formation of mesoporous, nanocrystalline films is to first produce crystalline nanoparticles, and then assemble them into a mesoporous network [20,21]. This strategy inspired our initial USD approach which employed a two step process. First, crystalline WO_3 nanoparticles (NP) were produced by hot-wire chemical deposition (HWCVD) [22]. The resulting NPs were then suspended in an ethanol solution and sprayed to form mesoporous films using USD [23]. As expected, the electrochromic performance improved as the NP size was reduced [24], but it proved difficult to reduce the NP size beyond 15 nm using HWCVD or envision scaling NP production to the quantities required for large scale manufacturing. More recently we demonstrated that templated sol–gel chemistry could be adapted to USD [25]. In this work a conventional sol–gel chemistry was used [26], with the exception that the sol was applied by USD onto an unheated substrate instead of by spin coating. This may be considered a variant of evaporation induced self assembly (EISA) in which evaporation occurs from individual droplets as opposed to from a film, accelerating the process. It was found that the post-deposition calcination step was critical, and films with fast switching time (<10 s) were obtained by rapid annealing technique in which samples were place directly on a hot plate maintained at 350 °C after the gelation step [25].

Fig. 1 displays the transmission spectra of a mesoporous WO_3 film produced by USD previously in both its bleached and colored state as well as its optical modulation [27]. This level of performance is representative of current state-of-the-art material [5,28]. The optical modulation reaches 75% in the near infrared but decreased as the wavelength is reduced, dropping precipitously below 600 nm. Transmission losses in the bleached state are attributed to haze, which arises due to scattering from either surface roughness or the presence of voids or agglomerates within the film [29]. The contribution of these scattering losses increase as the wavelength is reduced. In the colored state the transmission is controlled by the degree of ion intercalation. We found that the electrochromic performance correlates with the nanostructure and the specific surface area of the nanocrystalline films [27]. However the specific surface area of the best material in our previous study was just 18 m^2/g, whereas values as high as 145 m^2/g have been reported for mesoporous WO_3 synthesized

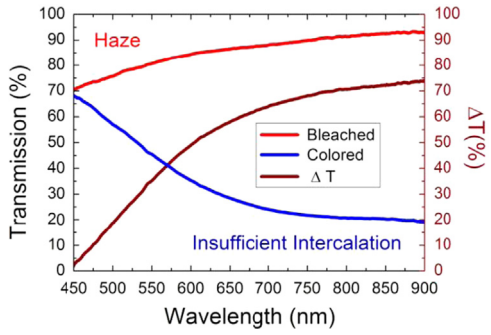

Fig. 1. Optical transmission in the bleached and colored states (left) and the resulting optical modulation (right) as a function of wavelength from WO_3 obtained in our previous work [27]. This performance is characteristic of current state-of-the-art WO_3, and shows the contributions of haze and insufficient intercalation that limit performance.

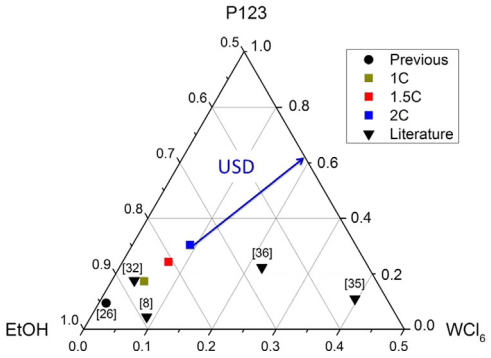

Fig. 2. Ternary phase diagram (wt%) comparing the sol compositions explored in this work with those previously reported in the literature. The arrow indicates the concentrating effect that occurs during ultrasonic spray deposition.

from the conventional sol–gel processes [12], so substantial room for further improvement remains.

It is well known that the shape and size of the mesoporous networks produced by soft templating may be directed through the control of parameters such as sol composition. The volume fraction of the block copolymer can be used for the rationale control of nanostructure [30], and optimization of this critical parameter has been used successfully to control porosity and increase specific surface area in a number of different material systems [10,31,32]. For well-studied materials such as silica and titania the relationship between sol chemistry and resulting nanostructure has been extensively explored, and comprehensive phase diagrams are available [33,34]. Such systematic studies have not been reported for WO_3. Fig. 2 provides a ternary phase diagram for this sol composition, which is comprised of WCl_6 and the commonly used triblock copolymer Pluronic P123 dissolved in ethanol. Our previous USD work employed a sol that was ~95 wt% ethanol, due to concerns about maintaining low viscosity to ensure a well-dispersed mist using the ultrasonic nebulizer. Fig. 2 includes sol compositions previously reported in the literature for this chemistry [8,35–37]. Though none of these studies reported on the sensitivity to sol composition, presumably there was some level of optimization and these points provided guidance for the present study. Although there is substantial variation, the previous reports all used sols with both higher concentration and elevated WCl_6:P123 ratios. Comparison of these studies also suggests that the pore size decreased as the sol concentration was increased. Within this region we found that optimum performance was obtained at the compositions indicated by the squares in Fig. 2. The WCl_6:P123 ratio in each case was 0.595 by mass, an increase from the value of 0.25 used in our previous work [25]. With the WCl_6:P123 ratio fixed, the impact of the total concentration in ethanol was also examined. In this work we examined sols with WCl_6 concentrations of 1.5, 2.25 and 3 mM, which are denoted on the diagram and throughout this work as 1C, 1.5C and 2C, respectively. The viscosity of the sol increased linearly with concentration, and it was found that the 2C concentration level was the practical limit for producing uniform films without clogging of the ultrasonic nebulizer or degradation of mist quality. However, we note that during USD process the sol is further concentrated along the pathway indicated by the arrow in Fig. 2 due to ethanol evaporation.

The sol concentration significantly impacts the morphology and nanostructure of the tungsten oxide films, as well as their electrochromic performance. We first describe the physical characteristics of the resulting films as a function of sol concentration, confirming their mesoporous, nanocrystalline nature through electron microscopy, selected area diffraction, and physisorption studies. Next we demonstrate that the thickness of the resulting