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# Electrochromic films produced by ultrasonic spray deposition of tungsten oxide nanoparticles

Chi-Ping Li [a], Colin A. Wolden [a], Anne C. Dillon [b], Robert C. Tenent [b,*]

[a] Materials Science Program, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA
[b] National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO 80401, USA

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ABSTRACT

Crystalline tungsten oxide nanoparticles (NPs) were synthesized by hot-wire chemical vapor deposition (HWCVD) and subsequently employed to form electrochromic thin films using ultrasonic spray deposition. Particle morphology may be tuned using HWCVD synthesis parameters including filament temperature, substrate temperature, and oxygen partial pressure. The electrochromic performance of films derived from three sets of NPs was characterized by performing cyclic voltammetry in direct registry with measurements of optical transmission. The coloration efficiency scaled with the specific surface area, and values obtained from films derived from HWCVD NPs were as high as 38 $cm^2/C$, comparing favorably with leading $WO_3$ films produced by sputtering. The HWCVD-based material formed continuous films that were mesoporous in nature, while the larger commercial NPs did not form homogeneous coatings. In addition to size, XRD and Raman analysis revealed a correlation between performance and the presence of the ε-monoclinic crystal phase.



## 1. Introduction

It is estimated that 30% of the energy used by buildings in the United States is lost through windows. "Smart windows" are capable of modulating their optical characteristics based on an external stimulus and be employed to tailor heat transfer and lighting conditions within a structure. One example of this type of device incorporates an electrochromic material that allows modulation of optical properties by application of a small voltage [1,2]. The active portion of such a smart window typically consists of two electrochromic thin films separated by an electrolyte. Transparent conducting oxides (TCOs) are used to reversibly bias these structures, shuttling $Li^+$ ions back and forth to modulate the transparency. Tungsten oxide is the leading cathodic electrochromic material, with NiO serving as a complementary material that not only displays anodic coloration but also serves as the ion storage layer.

It is estimated that implementation of such structures could reduce US energy consumption by 6%, an annual savings worth ~$30B. Despite this potential high manufacturing costs have limited the widespread deployment of this technology. Sputtering is the leading deposition approach [3,4], but it is difficult to further reduce costs using this high vacuum technique. Our group has been examining the potential of ultrasonic spray deposition (USD) as a cost effective alternative for large scale manufacturing of smart windows [5]. USD is scalable process that is conducted at atmospheric pressure. It is a green manufacturing technology that employs environmentally benign solvents and has very efficient precursor utilization. Concerns about uniformity and quality that plagued conventional pressure driven sprays have been assuaged by the advent of piezoelectric-based ultrasonic nebulization, which generates atomized droplets with a narrow size distribution. In principle, USD could be used to sequentially deposit a complete electrochromic device using an in-line process. USD has been used extensively for TCO synthesis [6–8], and we recently reported on its use for deposition of electrochromic NiO [9]. The focus of this work is the formation of electrochromic tungsten oxide films.

The films described in this work were produced using a two step process in which $WO_3$ nanoparticles (NPs) are first produced by hot wire chemical vapor deposition (HWCVD) [10]. This simple technique has been shown to produce NPs in large quantities [11]. Previous efforts employed electrophoresis to assemble $WO_3$ films from these materials. These films displayed very high coloration efficiency and excellent durability [11,12]. However, electrophoresis is slow and difficult to scale to large areas. The goal of this work was to demonstrate the viability of USD for large scale deposition of $WO_3$ films using NPs. Films were produced using three types of $WO_3$ NPs, and the performance of the resulting films is correlated with the properties of the individual starting materials.

## 2. Experiment

### 2.1. Preparation of tungsten oxide films

Tungsten oxide nanoparticles were produced by HWCVD using a system that has been described previously [13]. Briefly,

* Corresponding author.
*E-mail address:* Robert.Tenent@nrel.gov (R.C. Tenent).

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a tungsten wire is placed in a quartz tube and resistively heated in an $Ar/O_2$ gas mixture. $WO_3$ NPs are deposited on the wall of the quartz tube, which is independently held at a controlled temperature using a clam shell furnace. The relationship between HWCVD conditions and the resulting morphology has been discussed previously [10,13]. In general, NP size increases when more oxidizing conditions and/or higher temperatures are used during synthesis. Important parameters include filament current ($I$), $O_2$ partial pressure, wall temperature ($T_w$), and the duration of the batch process ($\tau$). In this work we compare the electrochromic performance of films produced using 3 types of NPs. Representative TEM images are shown in Fig. 1. Small NPs were produced by HWCVD using $I=13$ A, 4% $O_2$, $T_w=25$ °C, and $\tau=15$ min. This recipe produced as-deposited NPs that were roughly spherical in shape, with diameters on the order of 5–15 nm (Fig. 1a). Fig. 1b displays the morphology of the small NPs after annealing. The basic shape is retained, but the particles are somewhat larger, which is attributed to oxidation as described in more detail below. Fig. 1a and b are characteristic of the morphology changes observed during annealing of HWCVD NPs. Larger nanoparticles were synthesized under more oxidizing conditions: $I=14$ A, 16% $O_2$, $T_w=300$ °C, and $\tau=45$ min. This material contains a mixture of ~20 nm spheres as well as a significant fraction of nanorods, nominally 200 nm in length (Fig. 1c). Finally, commercial NPs purchased from Skyspring Nanomaterials, Inc. were used as a control. These NPs were largely spherical in shape, with diameters in the range of 60–80 nm (Fig. 1d).

Fluorine-doped tin oxide (FTO)-coated glass samples were used as substrates (Pilkington, 20 Ω/□). Prior to deposition the substrates were cleaned with isopropanol, dried with nitrogen, and subjected to a 5 min oxygen plasma treatment (800 mTorr, 155 W). Tungsten oxide nanoparticles were dispersed in ethanol (99.5%) at a concentration of 7 mg/ml using sonication, and it was found that these solutions were stable for over 2 h before any settling was observed. A commercial ultrasonic spray system (Sono-tek) was used to deposit the $WO_3$ NPs onto the FTO glass substrates. A syringe pump was used to deliver the solution to the nozzle at a flow rate of 0.25 ml/min, and the spray head was modulated at 120 kHz. The resulting mist was entrained in a stream of $N_2$ flowing downward at a flow rate of 6.9 l/min, impinging on the substrates located 5.5 cm below the nozzle. This geometry created a coating zone that was ~2 cm in diameter, and a computer-controlled susceptor rastered the substrates at a speed of 3.8 cm/s through this zone, making 10 passes under the stationary nozzle to form a complete film. The susceptor has the capability to be resistively heated, but all films discussed here were deposited at ambient temperature. Following deposition the samples were annealed in air for 2 h at 300 °C.

### 2.2. Characterization

The size and shape of tungsten oxide nanoparticles were examined by transmission electron microscopy (TEM, Philips CM200). The surface morphology of tungsten oxide films was studied using a field emission scanning electron microscope (FESEM, FEI Quanta 3D FEG Dual Beam). Cross-section samples were produced using the focused ion beam capability of this instrument. The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method with nitrogen in the $P/P_0$ range of 0.05–0.35 (Micrometrics ASAP 2020). The samples were degassed at 300 °C in vacuum for more than 4 h prior to the measurement. X-ray photoelectron spectroscopy (XPS) was used to analyze tungsten oxide films *ex situ*. A Kratos system with an Al Kα X-ray source was employed. The base pressure of the analysis chamber was $<10^{-9}$ Torr, and high resolution spectra of individual binding states were recorded using a sweep time of 60 s at

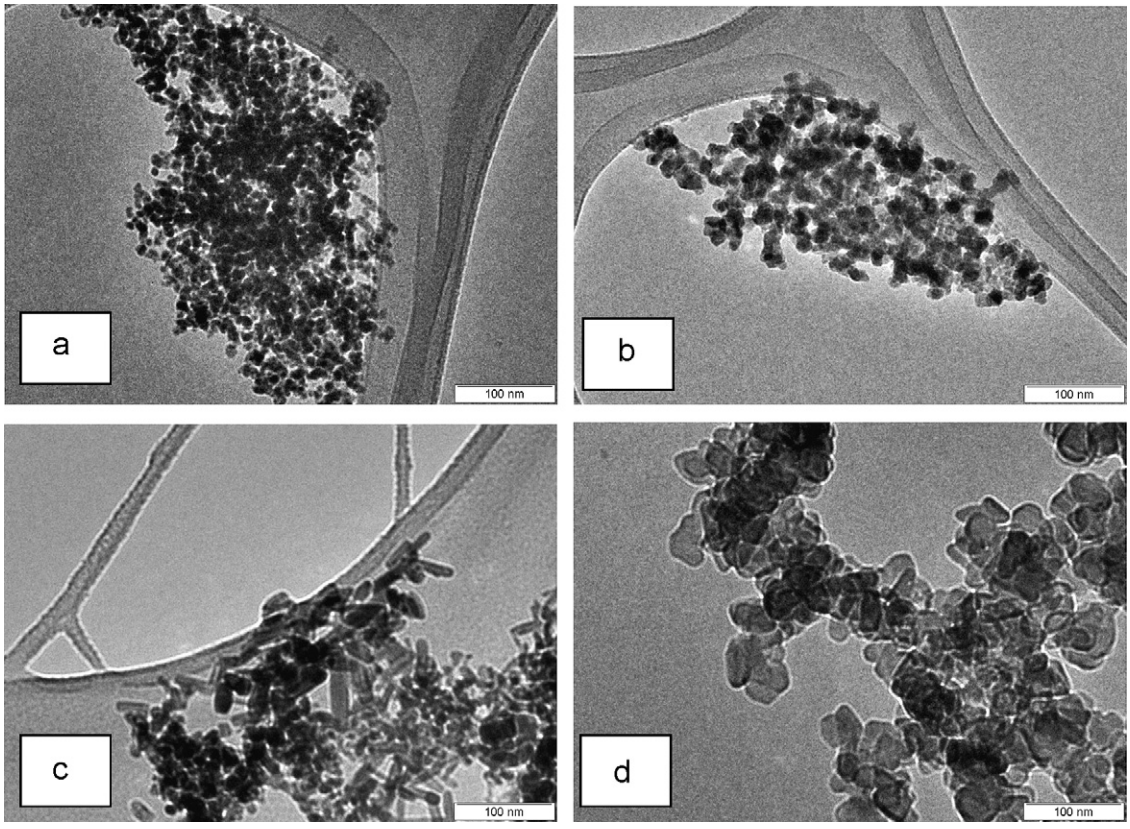


**Fig. 1.** Representative TEM images of (a) small HWCVD NPs before annealing, (b) small HWCVD NPs after annealing, (c) large HWCVD NPs after annealing, and (d) as-received commercial $WO_3$ nanoparticles.