Influence of single-nanoparticle electrochromic dynamics on the durability and speed of smart windows

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Nanomaterials have tremendous potential to increase electrochromic smart window efficiency, speed, and durability. However, nanoparticles vary in size, shape, and surface defects, and it is unknown how nanoparticle heterogeneity contributes to particle-dependent electrochromic properties. Here, we use single-nanoparticle-level electro-optical imaging to measure structure–function relationships in electrochromic tungsten oxide nanorods. Single nanorods exhibit a particle-dependent waiting time for tinting (from 100 ms to 10 s) due to Li-ion insertion at optically inactive surface sites. Longer nanorods tint darker than shorter nanorods and exhibit a Li-ion gradient that increases from the nanorod ends to the middle. The particle-dependent ion-insertion kinetics contribute to variable tinting rates and magnitudes across large-area smart windows. Next, we quantified how particle–particle interactions impact tinting dynamics and reversibility as the nanorod building blocks are assembled into a thin film. Interestingly, single particles tint 4 times faster and cycle 20 times more reversibly than thin films made of the same particles. These findings allow us to propose a nanostructured electrode architecture that optimizes optical modulation rates and reversibility across large-area smart windows.

Significance

“Smart” windows reduce electricity consumption associated with cooling buildings by blocking thermal radiation from the sun, or heat, from entering buildings. However, state-of-the-art smart windows require 7 to 12 min to modulate between transparent and dark states. Nanomaterials have the potential to tint faster and more efficiently than bulk materials, but it is unclear how structural differences among nanoparticles influence their optical modulation behavior. Here, we identify champion particles that tint the fastest and block the most radiation by watching single nanoparticles in a model smart window device. In addition, we observed that interfaces between particles contribute to long-term device degradation. These findings allow us to propose a new nanoparticle-based window design that optimizes tinting rates and promotes long-term stability.

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Conflict of interest statement: R.C.E. and J.B.S. filed a provisional patent based on the findings in this study.

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Data deposition: The raw image files and codes to analyze the data have been deposited in the Mountain Scholar repository, https://hdl.handle.net/10217/195014

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pseudocapacitive hexagonal WO₃ nanorods and quantify the impact of particle–particle interactions on electrochemical dynamics. Our measurements revealed a particle-dependent waiting time for coloration due to Li-ion insertion at optically inactive surface sites. Longer nanorods tend to tint darker because they store more Li-ion color centers at surface step sites, and an internal electric field drives Li-ion transport from the nanorod ends toward the middle. The particle-dependent waiting time, coloration rates, and magnitudes contribute to unwanted spatial and temporal tinting performance across large-area electrochromic windows. In addition, we discovered that particle–particle interfaces contribute to long-term irreversible tinting in nanoparticle-based electrochromic smart windows.

Results and Discussion

Single-Particle Electrochromism Imaging Approach. Fig. 1 shows the experimental methodology for imaging Li-ion insertion/extraction processes in single hexagonal WO₃ nanorods (h-WO₃ NRs) (average length = 1.02 ± 0.54 μm and width = 0.10 ± 0.04 μm; SI Appendix, Fig. S1). Each nanorod is a single crystal with well-defined {1000} surface facet orientations for the sidewalls (SI Appendix, Fig. S1B). We assembled a h-WO₃ nanorod-coated tin-doped indium oxide working electrode (h-WO₃ NR/ITO) into a three-electrode microfluidic electrochemical cell and mounted it on the stage of an inverted optical microscope (Fig. 1A). A 940-nm long-emitting diode (LED) illuminates the sample, and an electron-multiplying charge-coupled device camera acquires images that are synchronized with the current-time response of the electrochemical cell (Fig. 1B). The WO₃ nanorods appear as dark objects against a bright background in optical transmission images because the particles absorb and scatter incident light. Ex situ scanning electron microscopy (SEM) imaging confirms that the dark objects in optical images are either isolated or clustered h-WO₃ NRs (Fig. 1 C and D).

To induce the coloration and bleaching process according to Eq. 1, cathodic and anodic voltage pulses were applied to the h-WO₃ NR/ITO electrode in a propylene carbonate electrolyte containing 1.0 M LiClO₄ (Fig. 1E). We calculate the particle thickness (d) corrected change in OD, \( \Delta OD(t)_d = OD(t)_d - OD(0)_d = -\log_{10} \left( \frac{I(t)}{I_0} \right) + \log_{10} \left( \frac{I(t)}{I_0} \right) \), where \( I_0 \) and \( I \) are the transmitted light intensities through the ITO substrate and WO₃ particle, respectively (indicated by dashed and solid red lines in Fig. 1 B–D; also see Methods). Fig. 1F shows a representative \( \Delta OD(t)_d \) trajectory from the single nanoparticle in Fig. 1D, where the OD expectedly increases and decreases during cathodic and anodic voltage pulses. The widefield imaging approach measures hundreds of nanoparticles in a single experiment. We observed that 9% (9 of 102) of single particles showed no optical modulation and 6% (6 of 102) of single particles showed anomalous tinting behavior during cathodic polarization cycles (SI Appendix, Fig. S2). The potential significance of the inactive and anomalous particles will be discussed below.

Modeling Coloration and Bleaching Dynamics in Single h-WO₃ Nanorods. Fig. 2 shows representative \( \Delta OD(t)_d \) trajectories for three isolated nanorods with similar widths (0.11, 0.16, and 0.10 μm) and different lengths (1.64, 0.52, and 0.67 μm). The \( \Delta OD(t)_d \) trajectories exhibit three distinct features: (i) a particle-dependent waiting time for a change in OD (\( t_{wait} \) (Fig. 2 C, F, and I)), (ii) an almost linear rise in OD at short times, and (iii) a steady OD increase at long times (Fig. 2 B, E, and H). To explain the particle-dependent waiting time, we consider that h-WO₃ has three Li-ion binding sites: hexagonal windows (HWs), square windows (SWs), and trigonal cavities (TCs) (SI Appendix, Fig. S3) (26–29). Balaji et al. showed that Li ions fill TC sites first, but only HW and SW sites contribute to coloration in macroporous hexagonal WO₃ films (28), in agreement with electronic structure calculations (27). For these h-WO₃ NRs, ensemble-level electro-optical, electrochemical current, and Raman spectroscopy measurements show that Li ions and electrons are injected into the WO₃ NRs from the electrolyte (30). Pseudocapacitance is a faradaic capacitive charging process that is associated with rapid charge transfer reactions at or near the electrode surface (16). The OD burst response, which can be attributed to Li-ion insertion at bulk versus surface sites, we distinguish the rapid surface Li-ion insertion reaction (i.e., pseudocapacitance) from the slow bulk Li-ion insertion process, respectively, in agreement with the literature (17, 18, 32–35).

To quantitatively analyze the \( \Delta OD(t)_d \) trajectories of 102 individual h-WO₃ NRs, we developed a time-dependent electrochromism model that accounts for (i) \( t_{wait} \), (ii) the pseudocapacitive OD burst, and (iii) the slow OD rise (see Methods). In this model, Li-ion insertion at reduced W³⁺ sites are responsible for coloration as we observe no W⁴⁺ species in X-ray photoelectron spectroscopy measurements (SI Appendix, Fig. S6) (36). Fitting Eq. 2 in Methods to the \( \Delta OD(t)_d \) data (see solid red lines in Fig. 2 B, E, and H) yields \( t_{wait} \) as a rate constant for the surface charge transfer reaction (\( k_{wait} \)). The total charge inserted into optically active bulk and surface HW and SW sites \( (Q_{active}^{SW} + Q_{active}^{HW}) \). In addition, we extract short window performance metrics such as the particle thickness-corrected maximum change in OD (\( \Delta OD_{max}^{SW} \)), the time required to reach 90% of \( \Delta OD_{max}^{SW} \) (\( t_{bleach} \)), and the time required to decay from \( \Delta OD_{max}^{SW} \) by 90% (\( t_{bleach} \)).

Effect of Particle Size and Surface Structure on OD Magnitude and Dynamics. Fig. 3A shows a positive Pearson correlation coefficient between \( \Delta OD_{max}^{SW} \) and nanorod length; on average, longer nanorods tint darker than shorter nanorods. However, particles
Fig. 2. Quantitative analysis of single-nanoparticle OD trajectories. (A) SEM image of a single WO$_3$ nanorod (length = 1.64 μm, width = 0.11 μm). (B) ∆OD(t$_{90}$) trajectory of the same nanorod in A. The ∆OD(t$_{90}$) data points and error bars represent the mean and SD of three consecutive cathodic (−1.0 V vs. Ag/AgCl) and anodic (+1.5 V vs. Ag/AgCl) potential cycles. The dashed vertical lines represent $t_{\text{color}}$ (67.78 s) and $t_{\text{bleach}}$ (4.33 s). The solid red line represents the fit to the data using Eq. 2 in Methods. (C) ∆OD(t$_{90}$) trajectory in B from t = 0 to 30 s, showing $t_{\text{wait}}$ = 1.78 s. (D-F) Same data as A-C, but for a shorter WO$_3$ nanorod (length = 0.52 μm, width = 0.16 μm) with longer $t_{\text{color}}$ (115.53 s), $t_{\text{bleach}}$ (3.33 s), and slightly longer $t_{\text{wait}}$ (2.78 s). (G-I) Same data as A-C, but for a shorter WO$_3$ nanorod (length = 0.67 μm, width = 0.10 μm) with longer $t_{\text{color}}$ (96.78 s), $t_{\text{bleach}}$ (209.33 s), and much longer $t_{\text{wait}}$ (18.03 s). (Scale bars, 500 nm.)

Fig. 3. Correlation between OD magnitude and nanorod structural properties. (A) The particle thickness-corrected change in OD (∆OD$^{\text{max}}$) versus nanorod length (Pearson correlation coefficient $\rho = 0.34 \pm 0.06$, n = 98 particles). (B and C) Charge inserted into optically active surface sites per electrochemically active surface area of the nanorod Q$^{\text{Surf}}$ versus length ($\rho = 0.52 \pm 0.05$, n = 83 particles) and bulk charge per unit volume Q$_{\text{Bulk}}$ versus length ($\rho = 0.33 \pm 0.07$, n = 83 particles). (D and G) SEM image of a single nanorod. The distance between all vertical black and red lines are 200 nm. The nanorod end segments beyond the vertical black lines were not analyzed. (Scale bar, 1 μm.) (E) Representative ∆OD(t) trajectories measured from the middle (hollow green circles) and end segments (hollow and solid blue squares) on the single nanorod in D. (F) ∆OD$^{\text{max}}$ versus distance from nanorod centroid calculated from the trajectory analyses in E. The red line represents a linear fit to the segmented data. Error bars are the SD of ∆OD within the segment. (G) ∆OD$^{\text{max}}$ of 13 single particles versus its slope parameter defined in F. The red line is a linear fit to show the general trend ($\rho = 0.73 \pm 0.31$).
the large hexagonal tunnels accommodate more Li ions than the small trigonal cavity tunnels (45) and (ii) Li-ion transport is more efficient in the large, open hexagonal tunnels than in the smaller trigonal tunnels (43). Regardless of the underlying reason why \( \tau_{\text{wait}} \) and optically inactive surface charge is independent of length, the large variation in waiting times, from 100 ms to 20 s (Fig. 4A, Inset), is significant because particles with longer waiting times decrease coloration efficiency; no OD change occurs even though charge is inserted into the nanorods.

A particle’s maximum OD is not correlated with its coloration and bleaching kinetics; particles that tint faster do not necessarily tint darker (SI Appendix, Fig. S11). Instead, Fig. 4B shows that coloration and bleaching kinetics are strongly correlated (i.e., positive Pearson correlation coefficient), indicating that particles that color faster also bleach faster. The optical modulation times are extremely heterogeneous; some nanoparticles achieve 90% OD modulation in 12 s, whereas other nanoparticles require 275 s. The strongest predictor of fast coloration in these h-WO\(_3\) NRs is fast pseudocapacitive charge-transfer kinetics (Fig. 4C). The trend in Fig. 4C suggests that Li-ion insertion at the WO\(_3\) electrolyte interface, rather than Li-ion diffusion in the WO\(_3\) interior, accounts for large heterogeneities in coloration/bleaching kinetics at the single-particle level, likely due to the particle-dependent stepped-surface structure (e.g., SI Appendix, Fig. S7).

While our approach does not measure electrochemical current at the single nanoparticle level, this apparent experimental limitation does not restrict the conclusions regarding the structure-function relationships of our study. Regardless of the electrochemical current flow into single particles, we still measured that longer nanorods tint darker than shorter nanorods and longer nanorods exhibit a color center gradient. These structure/property relationships hold regardless of the electrochemical current into the nanoparticles. Importantly, all of the above observations were made from single particles that are attached to the same ITO electrode, immersed in the same electrolyte, and located only micron apart.

**Role of Particle–Particle Interfaces on Electrochromic Dynamics and Reversibility**

To probe whether the electrochromic properties of nanoparticle building blocks are maintained in thin-film electrodes, we studied how electrochromic dynamics and reversibility scale with the number of particle–particle interactions as the building blocks are assembled into a thin-film electrode. To do so, we compared single particle \( \Delta \text{OD}(t) \) trajectories to those measured from particle clusters containing two, three, four, or five h-WO\(_3\) nanorods. In addition, we measured \( \Delta \text{OD}(t) \) trajectories of large clusters (25 to 100 particles) and a thin-film electrode. For example, Fig. 5A shows an SEM image of a cluster containing three h-WO\(_3\) nanorods and Fig. 5B and C shows its normalized \( \Delta \text{OD}(t) \) response (black trace) compared with the average trajectory of 98 isolated h-WO\(_3\) nanorods (blue trace).

**SI Appendix**, Fig. S12 shows representative SEM images and \( \Delta \text{OD}(t) \) responses for all cluster sizes. The three-particle cluster showed similar \( \Delta \text{OD}(t) \) dynamics compared with single particles (Fig. 5 B and C) and qualitatively reversible electrochromic behavior (Fig. 5D). For large nanoparticle clusters (Fig. 5 E–H) and the thin-film electrode (Fig. 5 I–L), the \( \Delta \text{OD}(t) \) kinetics and reversibility deviate from the single particle building blocks.

To quantify the role of particle–particle interactions on tinting dynamics and reversibility, we extracted \( t_{\text{clus}}^{\text{color}}, t_{\text{clus}}^{\text{bleach}}, \) and the fraction of electrochromic cycles that do not return to the original transparent state for 298 clusters and 894 cycles (SI Appendix, section 15). Cluster size-dependent coloration magnitude was not analyzed because OD depends on cluster thickness and it was difficult to measure cluster thickness via SEM and atomic force microscopy imaging. Fig. 6A shows that \( t_{\text{clus}}^{\text{color}} \) and \( t_{\text{clus}}^{\text{bleach}} \) are independent of particle–particle interactions in the small cluster limit (two to five particles), but then both parameters increase for large clusters and the thin-film electrode. The electrochromic dynamics of small particle clusters are unaffected presumably because each particle within the cluster remains in contact with the ITO electrode and the liquid electrolyte. As the number of particle–particle interactions increases (i.e., for 25- to 100-particle clusters and the thin-film electrode), the optical modulation kinetics decrease because electrons and Li ions must traverse multiple particle–particle interfaces. On the other hand, an alternative possibility is that one anomalous single particle in one large nanoparticle cluster dominates the OD(t) response because we observed that the OD(t) kinetics of anomalous particles are strikingly similar to large clusters and the thin-film electrode (SI Appendix, Fig. S2). However, it remains unclear to what extent a single anomalous particle impacts the kinetics and reversibility of an entire cluster.

While tinting rates are independent of particle cluster size in the few particle regimes, the frequency of irreversible bleaching cycles increases monotonically with particle–particle interactions (Fig. 6B). In other words, large particle clusters remain tinted following an anodic polarization treatment. This persistent tinting effect has been attributed to ion trapping in WO\(_3\) thin films (46). For these h-WO\(_3\) nanorods, the irreversible bleaching effect onset for two particle-sized clusters due to (Li-W\(_{3+}\)) color.

**Fig. 5.** Electrochromic dynamics and reversibility of nanorod clusters and thin films. (A) SEM image of a particle cluster containing three nanorods. (B and C) \( \Delta \text{OD}(t) \) trajectory of the cluster in (A, black trace) compared with the average trajectory of 102 single nanorods (blue trace). (D) \( \Delta \text{OD}(t) \) trajectory for the cluster in A during three consecutive color and bleaching cycles. The dashed horizontal line in D represents $\Delta \text{OD} = 0$; E–L are the same as A–D, but for a large 25- to 100-particle cluster and a thin-film electrode, respectively. (Scale bars: A and E, 1 μm; I, 10 μm.)
nanorods were





color cycles versus particle cluster size. The total number of clusters analyzed for sizes 2, 3, 4, 5, and >25 were 134, 72, 41, 32, and 19, respectively. Error bars in A–C represent the standard error of the mean. (D and E) SEM image of a two-particle cluster with side-by-side (area contact) configuration and top-and-bottom (point contact) configuration. (Scale bars, 1 μm.) (F) Fraction of irreversible coloration and bleaching cycles for 81 side-by-side clusters (243 total cycles) and 30 top-and-bottom clusters (90 total cycles).

Fig. 6. Role of particle–particle interactions on electrochromic dynamics and reversibility. (A) Σc and Σb versus particle cluster size. f, nanorod thin film; L, large clusters (>25 particles). (B and C) Fraction of irreversible bleaching (C) and color (B) cycles versus particle cluster size. The total number of clusters analyzed for sizes 2, 3, 4, 5, and >25 were 134, 72, 41, 32, and 19, respectively. Error bars in A–C represent the standard error of the mean. (D and E) SEM image of a two-particle cluster with side-by-side (area contact) configuration and top-and-bottom (point contact) configuration. (Scale bars, 1 μm.) (F) Fraction of irreversible coloration and bleaching cycles for 81 side-by-side clusters (243 total cycles) and 30 top-and-bottom clusters (90 total cycles).

To explore how interfacial contact area between nanorods influences electrochromic reversibility, we analyzed the electrochromic reversibility of two-particle clusters with area versus point contact configurations. Fig. 6D shows a representative SEM image of a two-particle cluster where the nanorods align in a side-by-side configuration. Fig. 6E shows a two-particle cluster in a top-and-bottom configuration where one nanorod lays on top of another particle. The side-by-side configuration has a larger particle–particle contact area than the top-and-bottom configuration (see additional examples in SI Appendix, Fig. S13). Two-particle clusters with side-by-side contacts exhibit less irreversible coloration and more irreversible bleaching behavior than clusters with point contacts (see blue bars versus patterned white bars in Fig. 6F). We attribute the increase in irreversible electrochromic behavior to the large interfacial contact area that introduces more extrinsic ion-trapping sites between two nanorods. The coloration reversibility difference between the different cluster configurations is likely due to differences in the electron injection pathway. The electron-injection pathway for the side-by-side configuration is similar to isolated nanorods; the ITO electrode contacts each nanorod in the cluster along the entire nanorod sidewall (Fig. 6A). The pathway for the top-and-bottom configuration occurs at the nanorod end points (either at the nanorod–nanorod interface or the ITO–nanorod interface). It is possible that electron-injection efficiency at the nanorod–nanorod interface decreases with cycle number due to the accumulation of trapped ions at the solid–solid interface.

Two-particle clusters with large-area contacts modulate from the bleached state to the colored state more reversibly than from the colored state to the bleached state (Fig. 6F). We observed the opposite effect for two-particle clusters with point contacts; the cluster modulates from the colored state to the bleached state more reversibly than from the bleached state to the colored state. The exact origin of these trends is currently unknown since the ion-trapping sites and mechanisms are likely different in the coloring and bleaching processes (48). It is possible that the different particle–ITO and particle–particle contacts for each cluster configuration influence the coloration and bleaching reversibility differently. In summary, our measurements reveal underlying electro-optical processes that contribute to performance heterogeneity across large-area electrochromic nanoparticle films. First, the particle-dependent waiting time for coloration contributes to a delay time for window tinting and diminishes electrochromic coloration efficiency. The overall performance effect is that the window tints gradually in space and time as particles stochastically switch one-by-one from the transparent to colored state. Second, individual nanoparticle building blocks can tint up to 400% faster than a nanoparticle film assembled from the same building blocks. Finally, ion-trapping sites are introduced at particle–particle interfaces that cause long-term optical performance degradation. We propose to overcome these challenges using a mesoporous thin-film architecture, where fast-switching electrochromic nanoparticles are deposited onto a high surface area transparent conductor (SI Appendix, Fig. S14). This strategy would enable total light absorption with single layers of WO3 particles, thereby avoiding deleterious particle–particle interactions. Our single particle electrochromism imaging approach can be generally applied to transition metal oxides (49, 50), graphite (51, 52), and Ni(OH)2 battery materials (53) whose optical properties change during ion insertion. Single particle electro-optical imaging of ion-insertion/extraction processes can guide applied research related to batteries, fuel cells, electrochemical capacitors, and sensors.

Methods

Materials Synthesis and Characterization. Hexagonal WO3 nanorods were synthesized via a hydrothermal reaction following Wang et al. (37). Ensemble-level structural characterization (SI Appendix, section 1) shows that these nanorods have a hexagonal crystal structure, and we assume that the particles have a square rectangle morphology (average length = 1.02 ± 0.54 μm and width = 0.10 ± 0.04 μm; n = 258 particles), in agreement with Wang et al. (37).

Single-Nanoparticle Electrochromism Measurements and Image Analysis. All electrochemical measurements were performed in 1 M LiClO4 in propylene carbonate in a three-electrode microfluidic electrochemical cell using a Pt wire counter electrode and a Ag/AgCl reference electrode. The electrochemical cell was mounted on the stage of an inverted optical microscope (Olympus IX73; Fig. 1A). Detailed flow cell preparation and electro-optical imaging procedures are provided in SI Appendix, section 14. Transmission image stacks (54) were processed using a home-written MATLAB program (SI Appendix, section 15). The raw data and image processing codes required to reproduce the OD trajectories are available to download from https://lib.colostate.edu/find/csu-digital-repository/.

Modeling ΔOD(t), Trajectories. SI Appendix, section 16 describes the electrochemical model to determine the optically active and inactive surface charge as well as detailed fitting procedures. Briefly, ΔOD(t) is proportional to the time-dependent concentration of (Li-W+) color centers, Δc(t), according to ref. 55:

$$\Delta \text{OD}(t) = \Delta c(t) |_{\lambda = 940} / d ,$$

where με is the molar absorption coefficient of WO3 at 940 nm (1 x 10^6 cm/mo/l) (45). For these h-WO3 NR/ITO electrodes, Δc(t) is equal to the
sum of the integrated Li-ion fluxes into optically active surface \( \left( \frac{\partial n_{\text{surf}}}{\partial t} \right) \) and bulk \( \left( \frac{\partial n_{\text{bulk}}}{\partial t} \right) \) sites and is given by refs. 36 and 56.

\[
\Delta c(t) = \int_{t_{\text{surf}}}^{t} \frac{\partial n_{\text{surf}}}{\partial t} \, dt + \int_{t_{\text{bulk}}}^{t} \frac{\partial n_{\text{bulk}}}{\partial t} \, dt
\]

where \( A \) is the amplitude of the pseudocapacitive Li-ion flux, \( k_{\text{surf}} \) is the rate constant for the surface charge-transfer reaction, \( Q_{\text{max}} \) is the total charge transferred during the bulk Li-ion intercalation reaction, and the fitting parameter, \( D = Q_{\text{max}} V_{\text{DLi}} / \sqrt{\varepsilon} \), where \( D_{\text{Li}} \) is the Li-ion diffusion coefficient in \( \text{WO}_3 \). We assume that \( D_{\text{Li}} \) is independent of the Li-ion insertion content (36). \( H(t - t_{\text{wait}}) \) is the Heaviside function that switches on the fast pseudocapacitive coloration term to fit the OD burst feature that onsets at \( t_{\text{wait}} \).

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1. N. L. Stan, L. Pedebelski, H. M. Yang, B. Pease, Electrochromic dynamic windows for office buildings. Int. J. Sustain. Built. Environ. 1, 125–139 (2012).
2. N. DeForest et al., United States energy and CO\(_2\) savings potential from deployment of near-infrared electrochromic window glazings. Build. Environ. 89, 107–117 (2015).
3. A. Georg, A. Georg, W. Graf, V. Wittwer, Switchable windows with tungsten oxide. Vacuu 82, 730–735 (2008).
4. P. M. S. Monk, Charge movement through electrochromic thin-film tungsten trioxide. J. Phys. Chem. C 111, 2419–2424 (2007).
5. R. J. Mortimer, Electrochromic materials. Appl. Phys. Lett. 30, 201–202 (2000).
6. S. K. Deb, Opportunities and challenges in science and technology of \( \text{WO}_3 \) for electrochromic and related applications. Sol. Energy Mater. Sol. Cells 92, 245–258 (2008).
7. A. Georg, A. Georg, W. Graf, V. Wittwer, Switchable tungsten oxide windows. J. Phys. Chem. C 111, 2371–2376 (2007).
8. P. Yang, Electrochromic thin-film electrochromic devices for energy efficiency and human comfort in buildings: A critical review. Electroact. 25, 1170–1182 (2018).
9. G. Cai, J. Wang, P. S. Lee, Next-generation multifunctional electrochromic devices. Acc. Chem. Res. 49, 1469–1476 (2016).
10. Z. Xie et al., Determining the key parameters and materials for energy efficiency and comfort in buildings: A critical review. Electroact. 25, 1170–1182 (2018).
11. P. Skol et al., Electrochromic materials for energy efficiency and solar conversion efficiency of tungsten diselenide photoanodes. J. Phys. Chem. C 112, 14306–14312 (2008).
12. B. Miao et al., Large scale hydrothermal synthesis of monodisperse hexagonal \( \text{WO}_3 \) nanowire and the growth mechanism. Mater. Lett. 147, 12–15 (2015).
13. J. J. Martin, A. F. Armitage, Effect of growth rate on quartz defects. J. Cryst. Growth 62, 203–206 (1983).
14. X. Zhou et al., Quantitative super-resolution imaging uncovers reaction reactivities on single nanocrystals. Nat. Nanotechnol. 7, 237–241 (2012).
15. J. Bisquert, G. García-Belmonte, F. Fabregat-Santiago, Modelling the electrical potential distribution in the dark in nanoporous semiconductor electrodes. J. Solid State Elec- tromicroscopy of an operating lithium-ion battery. Electrochem. Solid State Lett. 4, 15225 (2015).
16. C. G. Granqvist, “Nano-particle electrochromic dynamics on the durability and speed of smart windows. J. Mater. Res. 9, 435–448 (2016).
17. B. Sun et al., High surface area tunnels in hexagonal \( \text{WO}_3 \). Nano Lett. 15, 4834–4838 (2015).
18. G. A. Naklsson, L. Berggren, A.-L. Larsson, Electrochromic tungsten oxide: The role of defects. Sol. Energy Mater. Sol. Cells 94, 315–328 (2008).
19. K. H. Cheng, A. J. Jacobson, M. S. Whittingham, Hexagonal tungsten trioxide and its intercalation chemistry. Solid State Ion. 5, 355–358 (1981).
20. R.-T. Wen, C. G. Granqvist, G. A. Naklsson, Eliminating degradation and uncovering ion trapping dynamics in electrochromic \( \text{WO}_3 \) thin films. Nat. Mater. 14, 996–1001 (2015).
21. C. Lian et al., Preparation of hexagonal ultrathin \( \text{WO}_3 \) nanoribbons and their electrochromic performance as an anode material in lithium ion batteries. Nano Res. 9, 435–448 (2016).
22. K. H. Cheng, A. J. Jacobson, M. S. Whittingham, Hexagonal tungsten trioxide and its intercalation chemistry. Solid State Ion. 5, 355–358 (1981).
23. C. G. Granqvist, “Devices with solid inorganic electrolytes and ion conductors” in Handbook of Inorganic Electrochemical Materials, C. G. Granqvist, Ed. (Elsevier Science B.V., Amsterdam, The Netherlands, 1995), chap. 29, pp. 473–488.
24. Z. Y. Liu et al., Characterization of carbon corrosion-induced structural damage of PEM fuel cell cathode electrodes caused by local fuel starvation. J. Electrochem. Soc. 152, 1189–1196 (2005).
25. D. Manka, E. Evers-Tiffée, Electro-optical measurements of lithium intercalation/de-intercalation at graphite anode surfaces. Electrochim. Acta 186, 642–653 (2015).
26. Y. Luo, W.-B. Cai, X.-K. Xing, D. A. Scherson, In situ, time-resolved Raman spectroscopic study of an operating lithium-ion battery. Electrochim. Solid State Electrochem. Lett. 7, E1–E5 (2004).
27. A. J. J. J. Eberard, D. A. Scherson, Microelectrode electrodes and single particle micro-batteries: Electrochemical and in situ microraman spectroscopic studies. Acc. Chem. Res. 46, 1192–1205 (2013).
28. J. B. Sambur et al., 2019 Data associated with the manuscript: Influence of single nanoparticle electrochromic dynamics on the durability and speed of smart windows. Mountain Scholar. https://hdl.handle.net/10217/195014. Deposited 16 May 2019.
29. J. Scammanders, A. Urbano, B. Gardes, The Beer-Lambert law for electrochromic tungsten oxide thin films. Mater. Phys. Chem. 61, 143–146 (1999).
30. R. S. Candall, B. W. Faughnan, Dynamics of coloration of amorphous electrochromic films of \( \text{WO}_3 \) at low voltages. Appl. Phys. Lett. 28, 95–97 (1976).