

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.

single-particle electro-optical imaging | tungsten oxide | single-particle electrochromism | ion-insertion kinetics

The “smart” glass industry is developing window tinting technologies that modulate the amount of visible and infrared radiation transmitted into aircraft, automobiles, and buildings to increase occupant comfort and decrease energy consumption (1–4). Smart windows are typically based on electrochromic tungsten oxide films (5–10), whose tunable optical properties stem from the electrochemical ion-insertion/extraction reaction in Eq. 1. Applying a cathodic potential induces tinting, or coloration, where electrons (e^-) and cations (M^+) (such as H^+ or Li^+) are injected into the transparent WO_3 material, forming a deep blue M_xWO_3 compound. Applying an anodic potential induces bleaching, where electrons and cations are extracted from the colored M_xWO_3 compound, reforming the transparent WO_3 material. State-of-the-art electrochromic smart windows switch from transparent to 90% fully tinted states in 7 to 12 min (11). Since smart windows consume the most energy during the tinting process (12), there is a strong interest in increasing the coloration efficiency (color change per unit charge inserted into the electrochromic material) to decrease the energy required for window tinting:



Electrochromic nanoparticles have unique properties that potentially enable faster tinting rates and longer lifetimes compared with thin films (13, 14). First, nanostructured electrodes enable more ion-insertion reactions per geometric area than planar electrodes. Since more color centers are produced near the solid/electrolyte interface, cations traverse less distance during coloration/bleaching cycles; both effects potentially improve

coloration/bleaching kinetics and electrochemical reversibility. Second, nanoparticles exhibit size-dependent pseudocapacitive electrochemical properties (15). Pseudocapacitive electrochromic nanoparticles increase tinting rates (16–19) due to rapid surface ion-insertion reactions rather than a slow bulk ion-insertion process.

Despite the potential advantages of electrochromic nanoparticles for smart window applications, it is unknown how nanoparticle heterogeneity contributes to particle-dependent coloration efficiency, coloration/bleaching kinetics, and optical-density (OD) magnitude. Particle-dependent electrochromic behavior across square meter-sized windows contributes to spatially nonuniform tinting. In situ optical-based (20–22), electron-based (23), and X-ray-based (24, 25) microscopy techniques have been used to image ion-insertion kinetics and structural transitions in electrochromic metal oxide films and single particles, but it is challenging for the electron and X-ray approaches to study electrochromic properties under device-relevant conditions such as ambient pressure, temperature, and radiation doses.

In this work, we use a single-particle-level optical imaging approach to determine structure–function relationships in

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 electrochromic 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 light-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. 1C 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,

$$\Delta OD(t)_d = OD(t)_d - OD(0)_d = -\log_{10} \left(\frac{I(t)}{I_0(t)} \right) + \log_{10} \left(\frac{I(0)}{I_0(0)} \right), \text{ where } I_0$$

and *I* are the transmitted light intensities through the ITO substrate and WO₃ particle, respectively (indicated by dashed and solid red lines in Fig. 1B–D; also see *Methods*). Fig. 1F shows a representative

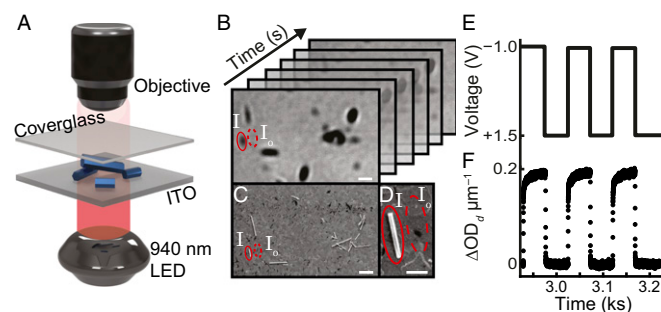


Fig. 1. Single-nanoparticle electrochromism imaging approach. (A) Electrochemical setup for widefield optical imaging of single-nanoparticle electrochromism. Pt counter and Ag/AgCl reference electrodes are not shown for clarity. (B) Optical transmission image stack during a cathodic polarization pulse. The solid and dashed red lines indicate equivalent-sized regions to calculate the light intensity transmitted through a WO₃ nanoparticle (*I*) and ITO substrate (*I*₀), respectively. (Scale bar, 1 μm.) (C) SEM image of the sample region in B. (Scale bar, 1 μm.) (D) Zoom-in of the single nanorod indicated by the solid red lines in B and C. (Scale bar, 500 nm.) (E and F) Potential versus time waveform applied to the *h*-WO₃ NR/ITO electrode (E) and the thickness-corrected ΔOD(*t*)_{*d*} versus time trajectory from the particle (F) in D.

ΔOD(*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.

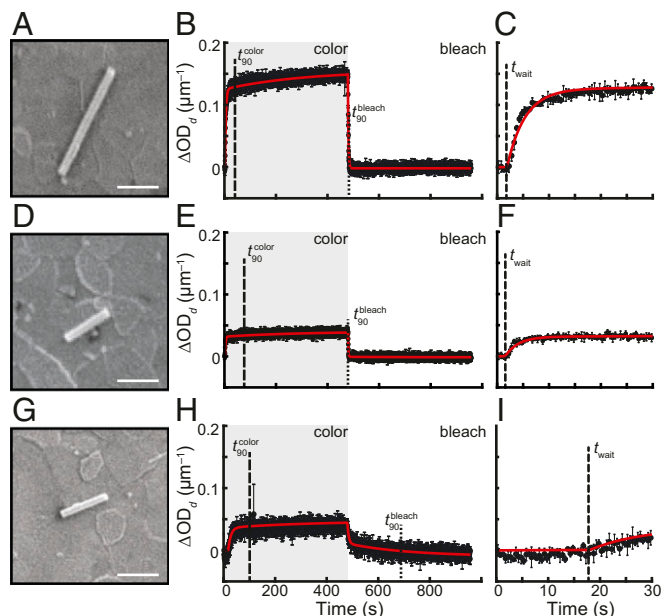
Modeling Coloration and Bleaching Dynamics in Single *h*-WO₃ Nanorods.

Fig. 2 shows representative ΔOD(*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 ΔOD(*t*)_{*d*} trajectories exhibit three distinct features: (i) a particle-dependent waiting time for a change in OD (*t*_{wait}) (Fig. 2C, F, and I), (ii) an abrupt OD burst at short times, and (iii) a steady OD increase at long times (Fig. 2B, 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 particles from *t* = 0 to *t* = *t*_{wait} even though there is no OD change (*SI Appendix*, Figs. S4 and S5). Thus, we attribute the waiting time to Li-ion insertion at optically inactive TC sites.

To explain the OD burst behavior, we analyzed cyclic voltammetry data and concluded that these *h*-WO₃ nanorods exhibit pseudocapacitive electrochemical behavior (*SI Appendix*, Fig. S5B) (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 behavior can be attributed to Li-ion insertion at optically active HW and SW surface sites because we observed that ΔOD(*t*)_{*d*} scales exponentially with *t*, consistent with a capacitive surface charging process. Intercalation pseudocapacitance throughout the nanorod bulk is not expected in these *h*-WO₃ nanorods because bulk pseudocapacitance requires a unique crystalline network (31). The slow OD rise behavior can be attributed to a diffusion-limited Li-ion insertion process at bulk HW and SW sites because we observed that ΔOD(*t*)_{*d*} scales with *t*^{1/2} at long times, in agreement with the Cottrell equation (22). While we do not image directly 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 ΔOD(*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 W⁵⁺ 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 ΔOD(*t*)_{*d*} data (see solid red lines in Fig. 2B, E, and H) yields *t*_{wait}, a rate constant for the surface charge transfer reaction (*k*_{surf}), and the total charge inserted into optically active bulk and surface HW and SW sites (*Q*_{bulk}^{active} and *Q*_{surf}^{active}). In addition, we extract smart window performance metrics such as the particle thickness-corrected maximum change in OD (ΔOD_{*d*}^{max}), the time required to reach 90% of ΔOD_{*d*}^{max} (*t*₉₀^{color}), and the time required to decay from ΔOD_{*d*}^{max} by 90% (*t*₉₀^{bleach}).

Effect of Particle Size and Surface Structure on OD Magnitude and Dynamics. Fig. 3A shows a positive Pearson correlation coefficient between ΔOD_{*d*}^{max} and nanorod length; on average, longer nanorods tint darker than shorter nanorods. However, particles



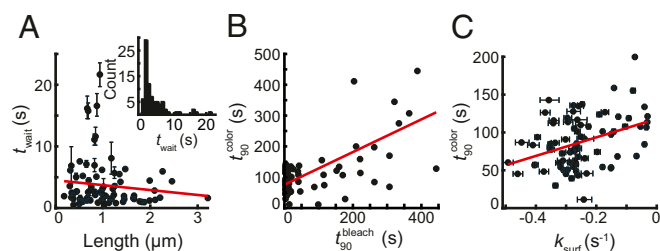


Fig. 4. Coloration and bleaching kinetics at the single particle-level. (A) Waiting time for optical modulation versus nanorod length ($\rho = -0.11 \pm 0.07$). Inset shows the distribution of waiting times. (B) Coloration versus bleaching kinetics; t_{90}^{color} versus t_{90}^{bleach} ($\rho = 0.65 \pm 0.04$). (C) t_{90}^{color} versus k_{surf} ($\rho = -0.38 \pm 0.06$). The black circles in A–C represent data from single nanorods and red line is a linear fit to show the general trend. Error bars in A and C are defined in *SI Appendix, section 16*.

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 t_{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 $h\text{-WO}_3$ 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 microns 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 $h\text{-WO}_3$ 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 $h\text{-WO}_3$ nanorods and Fig. 5B and C shows its normalized $\Delta\text{OD}(t)$ response (black trace) compared with the average trajectory of 98 isolated $h\text{-WO}_3$ 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. 5B and C) and qualitatively reversible electrochromic behavior (Fig. 5D). For large nanoparticle clusters (Fig. 5E–H) and the thin-film electrode (Fig. 5I–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_{90}^{color} , t_{90}^{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_{90}^{color} and t_{90}^{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 $h\text{-WO}_3$ nanorods, the irreversible bleaching effect onsets for two particle-sized clusters due to (Li-W^{5+}) color

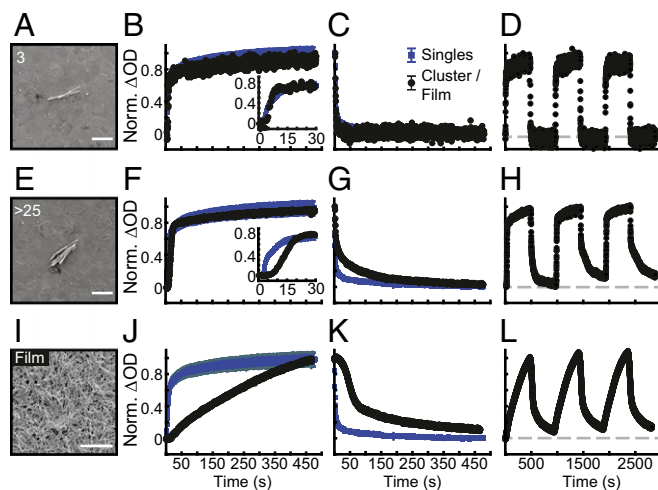


Fig. 5. Electrochromic dynamics and reversibility of nanorod clusters and thin films. (A) SEM image of a particle cluster containing three nanorods. (B and C) $\Delta\text{OD}(t)$ trajectory of the cluster in (A, black trace) compared with the average trajectory of 102 single nanorods (blue trace). (D) $\Delta\text{OD}(t)$ trajectory for the cluster in A during three consecutive color and bleaching cycles. The dashed horizontal line in D represents ΔOD at 0 s. 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 .)

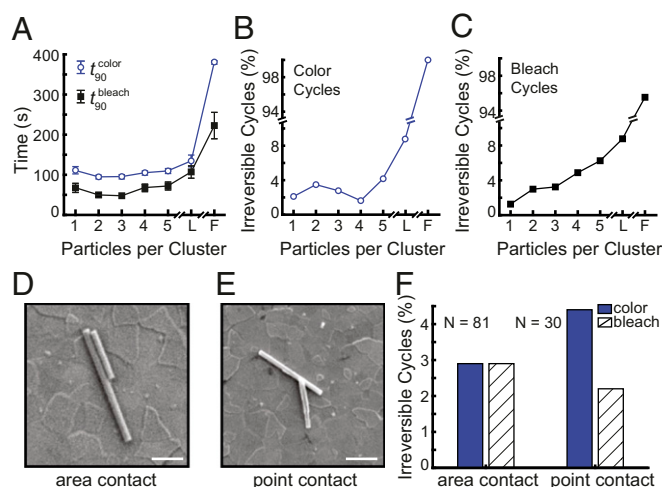


Fig. 6. Role of particle–particle interactions on electrochromic dynamics and reversibility. (A) t_{90}^{color} and t_{90}^{bleach} versus particle cluster size. F, nanorod thin film; L, large clusters (>25 particles). (B and C) Fraction of irreversible bleaching (C) and color (B) cycles versus particle 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).

centers that remain trapped at the nanorod–nanorod interface. The interfacial trapping sites could be due to Li-ion insertion at W = O surface sites on neighboring particles (47), leading to a more stable LiO_x -type interaction (SI Appendix, Fig. S7C). While the exact trapping site is currently unknown, our results show that extrinsic ion-trapping sites are introduced at particle–particle interfaces; the trapping site is not intrinsic to the nanorod. On the other hand, electrochromic coloring reversibility is independent of particle–particle interactions in the single and few particle cluster regimes and then abruptly increases for large clusters and the thin-film electrode (Fig. 6C). This trend could be due to the trapped (Li-W^{5+}) color centers at particle–particle interfaces that decrease the number of available Li-ion binding sites in consecutive 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 WO_3 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 $\text{Ni}(\text{OH})_2$ 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 WO_3 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 = $1.02 \pm 0.54 \mu\text{m}$ and width = $0.10 \pm 0.04 \mu\text{m}$; $n = 258$ particles), in agreement with Wang et al. (37).

Single-Nanoparticle Electrochromism Measurements and Image Analysis. All electrochemical measurements were performed in 1 M LiClO_4 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 $\Delta\text{OD}(t)_d$ 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, $\Delta\text{OD}(t)_d$ is proportional to the time-dependent concentration of (Li-W^{5+}) color centers, $\Delta c(t)$, according to ref. 55:

$$\Delta\text{OD}(t)_d = \Delta c(t) \varepsilon_{940} / d, \quad [2]$$

where ε_{940} is the molar absorption coefficient of WO_3 at 940 nm ($1 \times 10^6 \text{ cm}^2/\text{mol}$) (45). For these $h\text{-WO}_3$ NR/ITO electrodes, $\Delta c(t)$ is equal to the

sum of the integrated Li-ion fluxes into optically active surface ($J_{\text{surf}}^{\text{active}}$) and bulk (J_{bulk}) sites and is given by refs. 36 and 56.

$$\Delta c(t) = \int_{t_{\text{wait}}}^t J_{\text{surf}}^{\text{active}}(t) dt + \int_0^t J_{\text{bulk}}(t) dt + \\ = H(t - t_{\text{wait}}) \left(-\frac{A}{k_{\text{surf}}} [\exp(-k_{\text{surf}} t) - \exp(-k_{\text{surf}} t_{\text{wait}})] \right) + 2D\sqrt{t}, \quad [3]$$

where A is the amplitude of the pseudocapacitive Li-ion flux, k_{surf} is the rate constant for the surface charge-transfer reaction, Q_{max} is the total charge transferred during the bulk Li-ion intercalation reaction, and the fitting

parameter, $D' = Q_{\text{max}} \sqrt{D_{\text{Li}^+}} / d\sqrt{\pi}$, where D_{Li^+} is the Li-ion diffusion coefficient in WO_3 . We assume that D_{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_{wait} .

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