Site-selective ion intercalation controls spectral response in electrochromic hexagonal tungsten oxide nanocrystals

Benjamin Z. Zydlewski †, Hsin-Che Lu ‡, Hugo Celio δ, and Delia J. Milliron*,†,‡

†Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States
‡McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States
δTexas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States

Abstract

The electrochromism of tungsten oxide occurs through electrochemical reduction, providing active solar control to smart windows, but control over the spectral response is limited and largely empirical. To determine how specific chemical changes result in the optical absorption processes responsible for coloration, we pair structurally well-defined electrochromic nanocrystals (NCs) with cations of varying ionic radii to limit intercalation into specific crystallographic sites. The localized surface plasmon absorption of hexagonal cesium-doped tungsten oxide (Cs:WO₃) NCs is enhanced, and new absorption features appear, depending on how the cations intercalate into various interstitial voids. These differences were rationalized using X-ray photoelectron and Raman spectroscopies to reveal the chemical and structural changes leading to the observed variations in the electrochemically induced absorption spectra. Smaller cations, Na⁺ and Li⁺, can access additional interstitial sites, leading to a secondary, polaronic mechanism of electrochromism, accounting for enhanced visible light absorption.

Introduction

Electrochromic materials that can dynamically modulate the transmittance of infrared and visible light independently are essential for the development of energy-saving window technologies. Electrochemical charging and discharging modulates the optical properties in response to a potential bias, resulting in reversible coloring and bleaching.¹ By controlling the transmittance of solar radiation, we can limit unwanted heating and regulate natural lighting, improving building energy efficiency.²–⁴ Both amorphous and crystalline forms of tungsten oxide absorb visible and near infrared light when electrochemically reduced, making it one of the most heavily studied materials for electrochromic window technologies.⁵,⁶ More recent research has shown that nanocrystalline forms of tungsten oxide demonstrate localized surface plasmon resonance (LSPR), allowing selective optical modulation in the near infrared.⁷,⁸ LSPR is a property of conductive nanoparticles where the free charge carriers oscillate collectively in resonance with the electric field of incident light, leading to strong absorption.⁹ This absorption occurs throughout the
Infrared for various conductive metal oxides, making it ideal for controlling the transmittance of infrared light in solar radiation. 9

LSPR can be modulated electrochemically through oxidation or reduction, which varies the population of free charge carriers that contribute to light absorption. Electrochemical modulation of LSPR has been described as due to purely capacitive charging, which is a surface property where charge is stored in the electrical double layer at the interface between the electrolyte and electrode surface. The modulation of the LSPR of Sb:SnO2 and Sn:In2O3 NCs has been shown to be mostly independent of the electrolyte cation used, with only small differences between electrolytes containing lithium and tetrabutylammonium (TBA+) cations. Differences in the spectral response arising at more strongly reducing potentials have been ascribed to the irreversible intercalation of lithium and the reduction of either Sb or Sn.10,11 The crystal structures of these materials do not contain easily accessible interstitial voids or channels for cations to diffuse through reversibly during electrochemical cycling. However, plasmonic tungsten oxide NCs do contain cation-accessible interstitial sites. Tungsten oxide exists in various phases, all containing different arrangements of WO6 octahedra. The various crystal phases of tungsten oxide allow for cation intercalation.

Figure 1. a) Crystal structure of hexagonal Cs0.29WO3 viewed along c-axis. b) Crystal structure of hexagonal Cs0.29WO3 viewed along the a-axis. The various interstitial channels are highlighted to show the varying size and location within the crystal structure. The gray, red, and purple spheres correspond to tungsten, oxygen, and cesium, respectively. c) STEM image of Cs:WO3 NCs. The scale bar represents 40 nm. d) X-ray diffraction pattern of Cs:WO3 NCs with reference pattern for bulk hexagonal Cs0.29WO3 (ICSD #56223).
into the interstitial voids between the tungsten octahedra. The impact of ion intercalation on the LSPR of tungsten oxide NCs is not well understood.

The electrochromism of thin films of tungsten oxide has been studied extensively and the change in the optical properties upon electrochemical reduction has been attributed to the formation of polaronic states or an increased concentration of conduction electrons.\textsuperscript{5,12} Polarons are electronic states in which charge carrier localization is associated with a local lattice distortion. These localized states can hop between neighboring sites of differing valence through the absorption of a photon. The energy required for the charge-transfer between neighboring tungsten octahedra leads to the visible absorption of reduced tungsten oxides. Localized states can form near defect sites such as oxygen vacancies or interstitial cations formed during intercalation. For materials such as tungsten oxide with multiple different interstitial sites that cations can occupy, it is not well understood if specific sites favor charge localization or if their occupation introduces shallow donors that contribute free charge carriers to the conduction band. Distinguishing between optical absorption due to polaronic states and free carrier effects such as the LSPR we observe in tungsten oxide NCs is difficult, but we investigate the extent of charge localization to provide an indication of which mechanism is contributing to the decreased transmittance of tungsten oxide NCs during electrochemical reduction.

Specifically, we look to better understand the electrochromism of tungsten oxide by comparing the electrochromism of hexagonal cesium-doped tungsten oxide NCs (Cs:WO\textsubscript{3} NCs) reduced in electrolytes containing cations of varying ionic radius. It has been previously shown that the coloration efficiency of monoclinic WO\textsubscript{2.72} NCs could be increased by selective intercalation into larger interstitial sites using sodium-based electrolytes compared to electrolytes based on smaller lithium cations.\textsuperscript{13} Sodium ions were inhibited from occupying the small trigonal sites, which contribute only weakly to the optical response, improving the coloration efficiency. Similar results have been shown for hexagonal tungsten oxide nanorods, which showed variations in the amount of achievable coloration based on different surface faceting of the particles which varied the amount of accessible sites for lithium intercalation.\textsuperscript{14} Here, in Cs:WO\textsubscript{3} NCs we reveal that site-selective occupation of interstitial sites based on differential cation size can tune not only the magnitude of the coloration, but can also give rise to dramatically different spectral signatures. We assign these distinct spectral responses to either plasmonic or polaronic absorption, based on extent of charge localization.

**Experimental**

Cs:WO\textsubscript{3} NCs were synthesized using standard Schlenk line techniques under inert atmosphere, as previously described.\textsuperscript{7,15,16} The synthesis involves the injection of tungsten oleate into a hot solution of
cesium oleate at 300°C. The two metal oleates were prepared separately by the reaction of tungsten (IV) chloride or cesium chloride with oleic acid. After injection, the reaction was allowed to proceed for 10 minutes, then the dark blue mixture was cooled quickly to stop the reaction. The NCs were purified after synthesis by precipitating them out of the reaction mixture with isopropanol acting as an antisolvent. The NCs were centrifuged to separate the precipitated NC product and the supernatant was discarded. The mixture was redispersed in toluene and washed again by addition of antisolvent and subsequent centrifugation. The final NC colloid was prepared by redispersing the product in hexane with an approximate concentration of 20 mg/mL. The colloidal NC dispersion was concentrated to 50 mg/mL and used to spin-coat thin films on conductive, tin-doped indium oxide coated glass substrates at 1500 rpm. These films were then annealed in a furnace at 400°C under air to remove the oleic acid ligands that coat the surface of the NCs to improve film conductivity. No structural change was observed using XRD in NC powders annealed under the same conditions, indicating the hexagonal crystal structural and NC morphology are not impacted by the annealing process. These NC thin films were then used as electrodes to study their electrochromic properties.

The electrochromic responses of the NC films were investigated using in situ spectroelectrochemistry. A NC film served as the working electrode in an optically transparent electrochemical cell controlled by a Biologic VMP3 potentiostat, which was placed between fiber optic cables coupled to an ASD Quality Spec Pro visible-near infrared spectrometer. For lithium electrolyte-based experiments, a lithium foil was used as both the counter and reference electrodes. For measurements utilizing other electrolyte cations, a silver/silver cation reference electrode and a platinum foil counter electrode were used. All electrolytes were prepared in propylene carbonate at 0.1 M concentration of metal hexafluorophosphate salt of formula XPF₆, where X is either Li⁺, Na⁺, K⁺, or tetrabutylammonium (TBA⁺). All electrochemical experiments were carried out in an argon glovebox to avoid water or oxygen contamination.

The relevant electrochemical potential window for the reversible color change of Cs:WO₃ NCs was determined by monitoring the change in transmittance as a function of the applied potential using chronoamperometry (Figures S1 and S2). The potential window and charge capacity found using chronoamperometry were used to determine the appropriate current density to achieve an approximate 1C charging rate of the NC films in each of the four electrolytes. Films were charged with a constant current, and absorbance spectra were taken at set time intervals, corresponding to known amounts of stored charge (Figures S3 and S4). The ratio of incremental changes in optical density to stored charge determine the coloration efficiency. All absorbance measurements were taken in transmittance mode and backgrounded.
with a clean piece of ITO coated glass in the electrochemical cell filled with electrolyte. The OD changes are then referenced to the fully transparent state.

X-ray diffraction (XRD) of the NC sample was done by precipitating a powder from a dispersion in hexane through the addition of excess isopropanol. The dried powder was mounted on a cryoloop with mineral oil for measurement. A Rigaku R-Axis Spider with a Cu Kα source was used to collect the diffraction pattern.

Scanning transmission electron microscopy (STEM) was used to image the NCs. A carbon-coated copper grid was coated with the NC sample by dropping 20 μL of a 1 mg/mL dispersion in hexane. After drying overnight in a vacuum desiccator, the sample was imaged using a Hitachi S5500 microscope in STEM mode.

X-ray photoelectron spectroscopy (XPS) was used to assess changes in the electronic state of tungsten as the NC films were reduced. Films were prepared for XPS by electrochemically reducing them at a set potential for 10 minutes, followed by washing of the films with dimethyl carbonate to remove excess electrolyte. The potential used to reduce the films corresponds to the lowest potential used to reversibly color the films. Films were transferred from a glovebox to the XPS using an air-free capsule that mechanically couples to a semi-automatic interface on the XPS. This interface evacuates the capsule via differential pumping to prevent air exposure during the transition from high pressure to ultra-high vacuum (patent 9945761). Preventing air exposure allowed for the transfer of the films to the XPS chamber without

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**Figure 2.** a) UV-Vis-NIR absorption spectra a colloidal dispersion and film of h-Cs:WO3 NCs. b) Change in optical density of h-Cs:WO3 NC films reduced in electrolytes consisting of 0.1 M XPF₆ (X = Na, Li, TBA, K) in propylene carbonate.
contamination or discharging due to contact with water or oxygen. The photoemission spectra of the films were measured using a Kratos X-ray Photoelectron Spectrometer – Axis Ultra DLD using an Al Ka source.

Raman spectroscopy was performed using a Horiba LabRAM Aramis instrument using a 50x microscope objective and a 532 nm laser as the excitation source. NC dispersions were drop-cast on aluminum foil substrates. Electrochemically reduced samples were prepared in an Ar glovebox and transferred in a sealed container to measure the ex situ Raman spectra.

Results and Discussion

The hexagonal crystal structure of cesium-doped tungsten oxide leads to anisotropy in nanocrystal morphology (Figure 1a-c). The XRD pattern confirms that the NCs are the hexagonal phase of tungsten oxide with the cesium cations located in hexagonal channels (Figure 1d). The presence of these cations is crucial to stabilizing the otherwise metastable hexagonal crystal structure. The cesium cations also act as interstitial dopants, with the excess charge of the cations being compensated by electrons in the conduction band of the material. Various alkali metal doped tungsten oxide phases, commonly known as tungsten bronzes, have been shown to be metallic conductors due to the high concentration of free electrons generated by the interstitial cations. When nanocrystalline materials with high charge carrier concentrations are illuminated, these electrons oscillate in resonance with the electric field of light, producing localized surface plasmon resonance. LSPR in conducting metal oxide NCs results in strong absorption of near infrared (NIR) light (Figure 2a). The LSPR of the dispersion of NCs shows two distinct peaks, which correspond to two unique plasmon modes, a result of the anisotropy in particle shape and electronic structure (effective mass and damping) between the two unique crystallographic directions of the hexagonal crystal structure. The LSPR spectrum of the NCs broadens when they are deposited as a film due to plasmonic coupling between the NCs, but the bimodal structure is still apparent (Figure 2a). The NIR peak of the LSPR and wide bandgap, in the UV, allows for high transparency in the visible region, with only the tail of the LSPR spilling over into red edge of the visible, leading to the blue coloration of the NCs. After the removal of the surface-capping ligands by annealing in a furnace under air, the NC films can be reversibly electrochemically cycled to induce an electrochromic response, while recovering the transparent state upon oxidation. The change in optical density (OD) with electrochemical reduction varies depending on the electrolyte cation used to compensate the injected charge (Figure 2b). TBA+ electrolytes have been previously used to enforce a purely capacitive charging mechanism. In our case, capacitive charging in a TBA+ electrolyte results in a modulation spectrum (ΔOD) that matches very closely to the LSPR of the pristine material. Comparing this response to the electrochromism due to intercalation of the smaller cations, we see significant differences in the spectral line shape.
The differences in spectral line shape between the samples reduced in each of the electrolytes suggest that there are different electrochromic mechanisms depending on which interstitial sites are occupied. Films reduced in Li$^+$ and Na$^+$ electrolytes show similar spectral line shapes, while the same can be said for films reduced in K$^+$ or TBA$^+$ electrolytes. If the occupation of the various interstitial sites in the hexagonal crystal lattice contributed equally to the electrochromism, one would expect changes only in the magnitude of the optical density change (ΔOD), but not in the line shape. The overall line shape of the ΔOD spectra of the films reduced in K$^+$ or TBA$^+$ electrolytes show similar shape to the LSPR spectrum of the NC film prior to annealing as shown in Figure 2a. This similarity suggests that the electrochromism in these films is the result of purely LSPR modulation. The LSPR modulation in other metal oxide NC systems is consistent with the results shown here, where there is minimal LSPR peak shift, but substantial LSPR intensity increase with electrochemical reduction. The minimal LSPR peak shift is attributed to the filling of a depletion layer near the surface of the NCs, which results in only modulation of the LSPR active volume, but not the overall carrier concentration. The films reduced in Li$^+$ or Na$^+$ electrolytes show a significant modulation in the visible region (12,500-25,000 cm$^{-1}$), which is not present for the films reduced using the larger cations. The increased modulation in the visible region suggests that the intercalation of the smaller cations results in a secondary mechanism of electrochromism.

To understand how the intercalation of different sized cations influences the electrochromic spectral response, we must first consider the size of the interstitial sites in the hexagonal lattice. The hexagonal crystal structure has three interstitial voids that vary in size. The first are the large hexagonal channels that run along the c-axis of the crystal structure. The second are the smaller trigonal channels that run parallel to the c-axis as well. The last set of pathways ions can potentially diffuse through are the square channels that run orthogonal to the other two. To compare the approximate size of these different voids in the material, a circle was inscribed in the channel and the radius was used to compare the relative sizes of the different sites (Figure 1a and 1b). The approximate sizes are 236 pm, 78 pm, and 129 pm for the hexagonal, trigonal, and square sites, respectively. The ionic radii of the four cations used in this study are 60 pm, 95 pm, 133 pm, and 494 pm for Li$^+$, Na$^+$, K$^+$, and TBA$^+$, respectively. Comparing the relative sizes of the ionic radii to the sizes calculated for the different sites in the material, we expect certain cations to be inhibited from diffusing through certain sites. The ionic radius of the lithium cation is small enough that it is expected to be able to freely diffuse through all the sites. The opposite can be said for TBA$^+$. Its much larger size limits its ability to intercalate into the material at all, which restricts it to purely surface charging. Na$^+$ is small enough that it is expected to be able to diffuse through the square and hexagonal channels, while K$^+$ is only expected to be able to diffuse through the hexagonal channels. Based on this analysis and the observed electrochromism, it appears that the ability for Li$^+$ and Na$^+$ to diffuse through and
occupy sites within the smaller square or trigonal channels leads to a secondary mode of absorption during electrochemical reduction.

The optical properties of hexagonal cesium tungsten oxide that have been reported include both plasmonic and polaronic excitations, but it has not been shown that these two different mechanisms can be activated based on different electrochemical reduction pathways.\textsuperscript{21} It has been hypothesized that the higher energy absorption, greater than approximately 12,500 cm\textsuperscript{-1} is the result of polaron formation in the material. The slightly lower energy excitations that appear further in the NIR have been assigned to LSPR.\textsuperscript{15} It has also been shown that varying amounts of cesium occupation in the hexagonal crystal structure primarily impacts the extinction of the lower energy optical transitions, suggesting the cesium primarily contributes free electrons to the conduction band, amplifying the plasmonic absorption. Theoretical calculations of hexagonal tungsten oxide with varying occupation of the hexagonal channels with alkali metal cations is consistent with our theory. Those calculations indicate that cations occupying the hexagonal sites donate free electrons; in NCs these electrons would result in LSPR, as we observed.\textsuperscript{22} Machida et al. reported that varying oxygen content led to variation in the extinction of the material at higher energy. They hypothesized that the higher energy extinction was due to the increased oxygen vacancy concentration leading to an increased amount of polaronic states.\textsuperscript{21,23} This idea of different electronic states, associated with distinct charge compensating defects, leading to different optical absorption processes can correspondingly rationalize the cation-dependent electrochromic modulation spectra we observe.

To investigate the differences in the electronic state of tungsten during electrochemical reduction, we turned to XPS. The electrochromism occurs due to the injection of electrons into the material, but what electronic states result and how these contribute to the optical response of hexagonal tungsten oxide is debated in the literature.\textsuperscript{22,24} For plasmonic electrochromism, these electrons occupy the conduction band of the material, which increases the electron concentration or volume of LSPR active material, leading to increased LSPR extinction. For polaronic electrochromism, the electrons are localized on WO\textsubscript{6} octahedra by distorting the surrounding crystal lattice. The optical response is the result of the hopping of these electrons to nearby octahedra of differing valence state through the absorption of a photon. The electrochromic mechanism is thus correlated with the degree of charge localization, which was probed using XPS to determine if the electronic states depend on the intercalation sites occupied by the cation during reduction.
Using XPS to compare the changes in electronic state of tungsten with electrochemical reduction, we identified some key differences between the films reduced in different electrolytes. The W 4f photoemission spectra for a pristine film and films reduced in electrolytes containing Na\(^+\) or K\(^+\) are shown in Figure 3 with the fitting parameters reported in Table 1. The W 4f photoemission spectra for films reduced in TBA\(^+\) and Li\(^+\) are shown in Figures S5 and S6. Mirroring the similarities between the optical spectra of the samples, the films reduced in K\(^+\) and TBA\(^+\) electrolytes show very similar W 4f spectra. Likewise, the other two films reduced in Li\(^+\) or Na\(^+\) electrolytes have similar W 4f spectra. Compared to a pristine NC film, the films reduced in Li\(^+\) or Na\(^+\) electrolytes show a much more significant change in the W 4f photoemission spectra, with much greater intensity at lower binding energy. Tungsten 4f photoemission spectra consist of spin-orbit doublets with an energy splitting of 2.1-2.2 eV.\(^{25,26}\) These parameters were used to fit the photoemission spectra to multiple doublet components, indicating the presence of different tungsten electronic states. After fitting the spectra to deconvolute different W electronic states, the Li\(^+\) and Na\(^+\) films show a lower binding energy doublet in addition to the two doublets observed in the spectra of films reduced in K\(^+\) and TBA\(^+\) electrolytes. Based on the W 4f photoemission spectra there is a significantly larger amount of reduced tungsten for the Li\(^+\) and Na\(^+\) intercalated tungsten oxide.

Figure 3. Ex situ W 4f XPS of electrochemically reduced Cs:WO\(_3\) NC films. a) NC film reduced in Na\(^+\) electrolyte. b) NC film reduced in K\(^+\) electrolyte. c) Pristine NC film prior to any electrochemistry. The spectra show 2-3 distinct doublets representing electronic states. They are labeled from highest to lowest binding energy W\(^A\), W\(^B\), and W\(^C\), respectively.
The interpretation of multi-peak structures in the photoemission spectra of metal oxides is actively debated. The first interpretation is that each component represents localized valence states, with a distribution of different states throughout the tungsten oxide octahedral network. The second interpretation is that the multiple components are derived from final-state effects due to interactions of the core-holes generated during photoemission with the valence electrons. Both interpretations have merit and reliable methods of differentiating between these two effects are not well established. Based on the photoemission spectra, there are two possible interpretations to the differences in the electronic state of tungsten in each sample and how it relates to the mechanisms for electrochromism.

The W 4f photoemission spectra of NC films that have been electrochemically charged show significant populations of tungsten in more reduced states. All NC films show a doublet ($W^B$) of varying intensity 1.4-1.5 eV lower in binding energy than the highest energy W 4f doublet ($W^A$). In addition to $W^B$, films reduced in Li$^+$ and Na$^+$ electrolytes show another doublet ($W^C$) 2.2 eV lower in binding energy than $W^A$. The XP spectra of these films also show higher intensity in both low binding energy doublets, indicating a much larger population of both reduced tungsten states compared to the other samples. The more dominant presence of reduced tungsten species could be interpreted as a greater amount of charge stored on tungsten cations in the material. Differing amounts of charge localization helps explain the differences in the electrochromic line shapes between samples. Greater charge localization as a function of lithium-ion intercalation has been used to explain increased visible light electrochromism in niobium oxide NCs as well.\textsuperscript{27} This supports our hypothesis that the visible light absorption of Cs:WO$_3$ NCs comes from the localization of charge during the double injection of electrons and cations into the material. The small increase in reduced tungsten species for films reduced in K$^+$ and TBA$^+$ electrolytes could either be due to a small amount of the reduction of surface tungsten atoms, or it could be the result of final-state effects that become more influential at higher carrier concentrations.

The presence of multiple components in photoemission spectra of metallically conductive oxides has also been attributed to final-state effects, which result from interactions between the core-holes created during photoemission and the electrons near the Fermi level.\textsuperscript{28-30} Final state effects lead to two different components in the photoemission spectra, the higher binding energy unscreened component, and the lower binding energy screened component. The screened component results from interactions with the electrons in the conduction band, resulting in a slightly lower binding energy. The splitting has been attributed to the screening of the photoelectron through the excitation of a plasma oscillation of the conduction electrons, with the energy difference corresponding to the bulk plasma energy.\textsuperscript{31-33} The consistent energy difference between component $W^A$ and $W^B$ of 1.4-1.5 eV is similar to the bulk plasmon energies measured by electron energy loss spectroscopy for metallically conductive oxides such as MoO$_2$, WO$_2$, and Na$_x$WO$_3$, which also
show similar multi-component Mo 3d and W 4f PES spectra, respectively.\textsuperscript{34,35} It has also been shown that the relative intensity of the screened final state increases in intensity relative to the unscreened component with increasing carrier concentration in other doped metal oxides, which is also consistent with the increased intensity of W\textsuperscript{B} relative to W\textsuperscript{A} when comparing the pristine and reduced samples.\textsuperscript{36} Considering the impact of final state effects, the individual spin-orbit doublets in Figure 3 are not a result of isolated, reduced tungsten species within the material, but a result of the increased concentration of conduction band electrons occupying the tungsten 5d-derived band. Consistent with this accumulation of charge, there is increased intensity near the Fermi level in the valence band photoemission spectra following reduction (Figure 4).

The relatively low intensity of the screened component compared to the unscreened component could be explained by the presence of a depletion layer devoid of free charge carriers near the oxide surface, which for other metal oxides has been shown to be of similar nanometer length scales as the probe depth of XPS.\textsuperscript{37-39} The filling of a depletion layer near the NC surface explains the relative increase in intensity of the small band near the Fermi level compared to the valence band as the material is reduced (Figure 4). This small band increases in intensity, but the valence band does not noticeably shift in energy, indicating that the Fermi level is not increasing with electrochemical charging, while the depletion layer near the surface is being reduced in size. The narrowing of the depletion region places more weakly bound conduction electrons within the photoelectron escape depth, resulting in the increased intensity we observe.

The filling of a depletion layer has also been used to explain the limited shift in the LSPR peak position of metal oxide NCs, including Cs:WO\textsubscript{3} NCs, upon chemical or electrochemical reduction. The LSPR intensity increases following electron transfer to the NCs with little to no peak shifts, which is unexpected based on the relationship between the plasma frequency and carrier concentration.\textsuperscript{10,19} The modulation of LSPR in Cs:WO\textsubscript{3} NCs has been modeled previously as the filling of a shell depleted of conduction electrons near the surface of the material, both when chemically reduced with hydrazine and when electrochemically reduced in non-aqueous electrolytes.\textsuperscript{7,15} The electronic changes we observed using XPS and the

![Figure 4. Valence band photoemission spectra of Cs:WO\textsubscript{3} NC films reduced in electrolytes containing various cations. The spectra are normalized to the intensity of the valence band.](image-url)
changes in the optical properties are consistent with the filling of a depletion layer near the NC surface during electrochemically reduction.

Table 1. XPS fitting parameters for films electrochemically reduced in various conditions

<table>
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<th>Reduction Condition</th>
<th>W^A 4f 7/2 BE (eV)^a</th>
<th>W^A 4f 7/2 FWHM^b</th>
<th>W^B 4f 7/2 BE (eV)^a</th>
<th>W^B 4f 7/2 FWHM^b</th>
<th>W^C 4f 7/2 BE (eV)^a</th>
<th>W^C 4f 7/2 FWHM^b</th>
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<td>Pristine</td>
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<td>0.99</td>
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<td>1.08</td>
<td>34.3</td>
<td>1.08</td>
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<td>-</td>
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<tr>
<td>Na^+</td>
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<td>34.6</td>
<td>1.62</td>
<td>33.9</td>
<td>0.99</td>
</tr>
<tr>
<td>Li^+</td>
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<td>1.66</td>
<td>34.6</td>
<td>0.98</td>
<td>33.9</td>
<td>0.73</td>
</tr>
</tbody>
</table>

a The W 4f 5/2 peaks were constrained to 2.14 eV higher than the W 4f 7/2 components based on the splitting observed in the pristine sample, which is consistent with literature values.  

b The FWHM for the W 4f 5/2 component was constrained to be equal to the FWHM of the W 4f 7/2 component.

Final-state effects account for the increase in intensity of W^B in the photoemission spectra of the reduced films compared to the pristine material, which is consistent with the increased LSPR intensity in the UV-Vis-NIR spectra with reduction. Accounting for W^A and W^B as unscreened and screened final states due to the conduction band electrons, we assign W^C as a more strongly localized state resulting from cation intercalation. Most likely, the lowest binding energy W^C corresponds to a polaronic state that involves a lattice distortion and localization of the electronic charge, which would change the local electronic environment and shift the W 4f binding energy. When comparing the photoemission peaks, we note that W^C is much narrower compared to the other two components in Figure 3a, indicating a longer lifetime of that state, which is expected for a more localized state (Table 1). Significant charge localization is also expected to be correlated with structural rearrangements of the tungsten octahedra.

In addition to the changes in the electronic properties of hexagonal tungsten oxide with electrochemical reduction, we monitored structural changes using Raman spectroscopy (Figure 5). The pristine NCs prior to any electrochemical reduction show multiple Raman modes between 50-150 cm\(^{-1}\), 200-350 cm\(^{-1}\), 650-800 cm\(^{-1}\), and 850-1000 cm\(^{-1}\). These modes correspond to lattice modes, \(\delta(O-W-O)\), \(\nu(O-W-O)\), and \(\nu(W=O)\), respectively. The most prominent differences between the reduced and pristine
13 films occur in the ν(O-W-O) modes located between 650-800 cm$^{-1}$. For the Li$^+$ intercalated film, there are significant changes to the peaks corresponding to this mode, with the two peak structure present in the pristine sample merging into one broad peak. The merging of the two peaks indicates an increase in symmetry of the tungsten octahedra with lithium intercalation, as the two peak structure is a result of the differing O-W-O bond lengths in the different crystallographic directions.\textsuperscript{41,42} In addition to this, the lower frequency Raman peak corresponding to the δ(O-W-O) mode decreases in intensity and broadens. The last major difference is in the higher energy peaks related to the ν(W=O) modes. This double bond stretching mode has been assigned to terminal tungsten oxygen bonds, occurring both for tungsten ions near oxygen vacancies and due to surface termination of the tungsten octahedra.\textsuperscript{41,43} Both of these structural motifs are plausible contributors for our samples, considering the high surface area of nanocrystalline samples and the prevalence of oxygen deficiencies in various tungsten oxide phases. The ν(W=O) modes shift to lower energy in all reduced samples relative to the pristine sample, which could be related to the reduction of tungsten cations in the material. Reduction of tungsten to lower oxidation states cause an increase in W-O bond length and softening of that bond, due to the lower charge of the tungsten.

We hypothesize that the electrolyte-dependent differences in electrochromic properties of hexagonal cesium tungsten oxide are the result of different electronic states that result from the intercalation sites occupied during electrochemical reduction. Based on the optical and XPS data, the intercalation of potassium, which is expected to be limited to the hexagonal tunnels in the material, coincides with the injection of free electrons. These electrons expand the plasmonic volume within each NC, resulting in the increased extinction of the LSPR, a response which is almost identical to that for films reduced in an
electrolyte containing TBA+. Charging with TBA+-based electrolytes is capacitive and gives rise to an increased population of free electrons. The spectral change in films reduced in these two electrolytes is consistent with a purely plasmonic modulation of the extinction. The optical response to intercalation of the two smaller cations deviates from the LSPR line shape, which we ascribe to the formation of polaronic states due to intercalation into interstitial sites inaccessible to larger cations. We hypothesize that the ability of these smaller cations to diffuse through the square channels and occupy sites within these voids leads to visible light electrochromism. The similar capacities observed in lithium and sodium electrolytes point to the same type of intercalation sites being accessible. The coloration efficiency, which is the amount of optical density change per unit of injected charge, is also dependent on the electrolyte cation used. The coloration efficiency at longer wavelengths in the NIR is similar across all electrolytes, with only lithium showing a slightly higher coloration efficiency, which could be related to its expected ability to diffuse through the small trigonal channels in the material or the ability to more readily diffuse around cesium cations blocking pathways through the hexagonal channels. In the visible range, the coloration efficiency is substantially different between the smaller cations (Li+ and Na+) and the larger cations (K+ and TBA+). The smaller cations have colorations efficiencies between 40-50 cm²/C, while the larger cations have coloration efficiencies between 12-15 cm²/C (Table S1). The higher coloration efficiency in the visible range for Li+ and Na+ is consistent with our hypothesis that polaronic electrochromism leads to enhanced visible light modulation due to the intercalation of these smaller cations. Prior literature has suggested that even though Li+ has a smaller ionic radius than the spacing of the trigonal channels in the crystal structure, it is still not able to diffuse through these smaller channels. Although, prior work done by Heo et al. suggested that the ability for Li+ to more freely diffuse through these smaller channels allowed for the increased capacity observed in Li+ electrolytes compared to Na+ ones for monoclinic tungsten oxide nanorods. Na+ is believed to be unable to diffuse through these trigonal sites due to the larger size of the cation. Due to the similar observed capacities of the material in these two electrolytes, we believe that the ability for these two cations to diffuse through the square channels in the material leads to the increased capacity, with the trigonal channels being too small to allow for ion diffusion for the hexagonal crystal structure.

The ability for these smaller cations to access more sites in the material suggests an explanation for the differing electrochromic properties for NC films reduced in these electrolytes. The occupation of these sites leads to an increase in the lowest binding energy W 4f peak seen by XPS, corresponding to a more reduced state of tungsten. The more reduced state then contributes to the higher energy optical transitions observed in the UV-Vis-NIR spectra. This understanding illustrates that selecting cations for intercalation into specific interstitial sites is a viable design strategy to tune the spectral response of electrochromic materials. This approach can be used in combination with tuning the morphology of NCs to control the
spectral line shape of the electrochromism to tailor it to solar radiation, customize the optical tint, and better optimize spectrally selective NIR blocking smart windows to enable for increased building energy efficiency.

**Conclusion**

The mechanisms for electrochromism of various phases and morphologies of tungsten oxide have been heavily debated in the last several decades, but these results demonstrate that multiple different mechanisms may be operative depending on the interaction between intercalating cations and the electronic states and crystal lattice. The presence of a different spectral line shapes for films reduced in Li+ and Na+ electrolytes suggests that, in addition to the increase in free electrons, some portion of the injected electrons localize. These localized electrons on tungsten cations lead to a higher energy optical absorption feature due to polaronic hopping, or charge transfer between different tungsten species in the material. The presence of localized electrons is evidenced by the increase in lower binding energy components in the W 4f photoemission spectra for these films. Complementary experiments to probe the overall change in tungsten oxidation state (e.g. by near-edge X-ray absorption spectroscopy) would help validate these connections between the reduction conditions, the electronic state of the material, and the electrochromic spectral response.46

The distinct spectral response based on the electrolyte cation used opens new possibilities for tuning the spectral selectivity of smart window devices to overlap with the different regions of solar radiation. This strategy can be further used to understand and control the electrochromic properties of other intercalation-based materials that have multiple different sites for cation intercalation.27 By using cations that limit intercalation into only select sites, we have shown that we can improve spectral selectivity for NIR light, while still maintaining high transparency in the visible region. This is enabling for smart window technologies that allow for selective blocking of NIR radiation, which leads to excess heat, while still maintaining high transparency for visible light to reduce lighting costs.4

**Author Information**

*Email: milliron@che.utexas.edu*

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