Dual-Band Electrochromism: Plasmonic and Polaronic Mechanisms

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Abstract: Electrochromic windows that dynamically absorb incident solar irradiation are envisioned as smart technology devices that can reduce power consumption in buildings and accelerate progress toward sustainable development. While regulating the visible light in interior spaces to suite the comfort of occupants, electrochromic windows also offer thermal control by controlling the flux of solar energy, including infrared radiation. The ability to selectively modulate visible and the infrared solar transmittance is denoted as dual-band electrochromism. Dual-band control can be achieved by employing materials that absorb light in different spectral regions when electrochemically charged, with light absorption due to either a polaronic or a plasmonic mechanism, depending on the charging conditions. In this perspective, we discuss how adopting a plasmonic or a polaronic approach can affect the performance of an electrochromic device in terms of different quantitative figures-of-merit, and the challenges and opportunities for designing better dual-band electrochromic devices in the future.

Introduction: Since the inception of human civilization, there has been a constant striving to invent, sometimes for necessity and sometimes for pleasure or convenience. Some inventions are at the nexus of both necessity and pleasure and these have the potential to transform our way of life. Electrochromic (EC) smart windows are one such invention, which may widely replace traditional static windows and will significantly enrich our experience of windows as they mediate our interaction with the natural environment. Commercial EC windows change their transmittance of visible light on demand when an electric potential is applied.[1] Such windows can now be commonly observed in passenger airplanes and modern skyscrapers.[2] In fact, EC windows and their components already constitute a market greater than 1.4 Billion USD, which is likely to grow to over 2.7 Billion USD by 2027.[3]

Although these commercial EC windows modulate mostly visible light transmittance, the solar radiation arriving on the Earth's surface contains, besides ultraviolet, visible and infrared radiation in an almost equal ratio.[4] While visible light is useful to illuminate interior spaces, infrared radiation is not visible yet still contributes to solar heat gain in buildings. A large amount of energy is consumed to regulate interior temperatures, cooling during warm weather and heating during cold spells that could be reduced by dynamically modulating solar transmittance with smart windows. In the ideal case, solar heating and daylighting could be controlled independently since our needs for heating and lighting vary in an uncorrelated fashion. This challenge motivates the development of *dual-band electrochromic windows* that selectively regulate the transmittance of two different regions (bands) of the electromagnetic spectrum, namely, the visible and the solar infrared.[5] Unlike a traditional EC window which switches through intermediate tints between two end points (colored and bleached), dual-band EC devices aim to independently control the transmittance of the visible and the infrared regions enabling switching between at least three different modes, denoted bright, cool and, dark modes (Figure 1). The bright mode has high transmittance for both visible and infrared radiation (maximizing daylighting and solar heating), while the cool mode blocks infrared radiation selectively while still allowing most of the visible light to transmit. The dark mode limits the transmittance of both visible and infrared radiation to

minimize solar heat gain and control glare.[5] Switching between these modes and intermediate states can be controlled by applying a small electric potential and adjusted to suit the comfort and preferences of building occupants and to decrease energy use for lighting and thermal control. EC devices require minimal power to switch and little to none to maintain their optical state, so energy savings are made without compromise. In contrast to the multifunctionality of dual-band EC technologies, visible tinting and solar heat gain modulation are intrinsically coupled in conventional EC windows, resulting in compromising trade-offs[1, 6-9] between daylighting and thermal control.

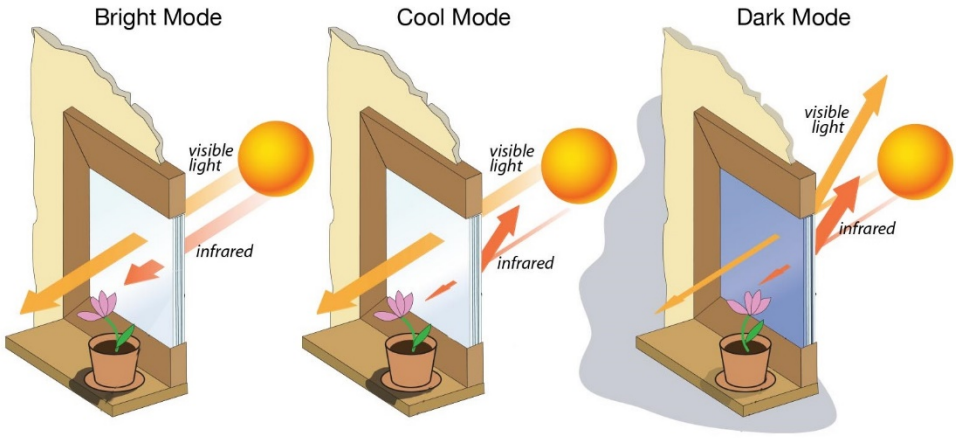

Figure 1: The three different modes of a dual-band electrochromic window allowing independent control over the transmittance in the visible and the infrared regions. Reprinted with permission from reference 5. Copyright 2013 Nature Publishing Group.

In EC devices, electrochemical reactions introduce charge carriers in the active materials that trigger the reversible change of their transmittance. To enable the different modes of a dual-band EC window, the device should be capable of absorbing both the visible and the infrared radiation independently, typically controlled by applying different potential biases. To achieve distinct spectral responses, it is beneficial to leverage different light absorption mechanisms that depend on the nature of the electrochemically introduced charge carriers. These distinct mechanisms can significantly influence the performance attributes of the EC device.

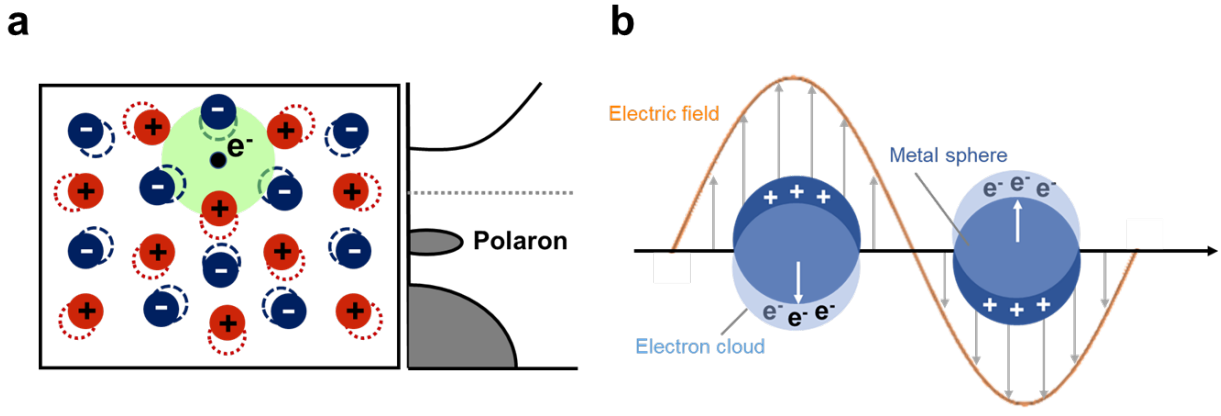

Figure 2: General schematic illustrating (a) polaron formation. (b) plasmonic light absorption.

Two common mechanisms exist for light absorption in different spectral regions, polaronic and plasmonic, depending on the extent to which charge carriers are spatially localized.[10] Metal oxides, which are the most popular active materials for EC smart windows, can exhibit either of these mechanisms.[11] Polaron formation involves the localization of electronic charge associated with distortions in the surrounding crystal lattice (Figure 2a). The localized charges are typically balanced by intercalated ions from the electrolyte, so this mechanism almost always results from Faradaic charging. Meanwhile, plasmonic absorption involves the collective polarization of spatially delocalized charge carriers by interaction with light. Such electronic charging can be balanced by ion intercalation or surface charge, including formation of an electrochemical double-layer.[12-14]

Polaronic absorption has been proposed to describe the optical absorption change of several transition metal oxides (and polymers)[15] triggered by redox reactions. At a reducing potential, one can observe the reduction of metal ions along with the intercalation of counter ions from the electrolyte (such as H^+ or Li^+) into the material for charge balance. The inserted electrons localize and trigger a displacement of surrounding ions from their equilibrium position, producing a potential well that stabilizes the inserted electrons (Figure 2a). The energetic stabilization can lead to the formation of an electron polaron band below the conduction band minimum, resulting in new absorption transitions, primarily in the visible region. When an oxidizing potential is applied, the formation of the localized states can be reversed along with the deintercalation of the counter ions. The polaronic mechanism thus results in a reversible transmittance change in transition metal oxides, which can serve as one of the spectrally selective absorption bands for EC windows. Since this is a Faradaic process involving the redox reaction of metal ions, besides the charge transfer reaction, the switching kinetics and cycling durability of dual-band EC windows operating on a polaronic mechanism depend on the kinetics of ion intercalation and the rate of diffusion of ions in the EC materials. [16-17, 18]

On the other hand, when delocalized charge carriers in a material interact with photons, they cause increased absorption and scattering of radiation at wavelengths dependent on the carrier density. This plasmonic interaction of light with free electrons gives metals their characteristic luster. Similarly, metal oxides with a large density of delocalized electrons (still less than classical metals) are highly reflective of near-infrared light.[15] However, in nanomaterials of metals or doped metal oxides, the free electrons undergo collective, confined oscillations at resonant frequencies producing strong absorption at a characteristic localized surface plasmon resonance (LSPR) frequency (Figure 2b).[19] While films of conductive nanomaterials can also exhibit reflectance at longer wavelengths of near-infrared light, the LSPR absorption is more pronounced and more likely to overlap substantially with solar infrared radiation. Nonetheless, by changing the applied potential, the plasma frequency and corresponding LSPR wavelength can be shifted, which, along with changes in the intensity of absorption, enables switching between different modes of EC window operation. The expected shift in LSPR wavelength with applied potential is distinctly different from the polaronic mechanism where a change in potential is expected to change only transmittance and not the peak energy of absorption.[20]

Since plasmonic and polaronic materials operate on different fundamental mechanisms, both electrochemically and in terms of light-matter interaction, the performance of dual-band EC devices based on these two types of materials can differ significantly. In this perspective, we will discuss the basic architecture of dual-band EC devices, how plasmonic or polaronic mechanisms can affect their performance parameters, and present analysis of the performance trade-offs

associated with these mechanisms. To conclude, we will discuss the challenges remaining for development of dual-band EC windows and the apparent opportunities to improve their performance.

Dual-Band Electrochromic Device: Design

Irrespective of the mechanism of operation, a typical dual-band EC device is assembled using five components and bears similarity with a traditional single-band EC device, in design (Figure 3).[11] To fabricate an EC device, first a thin layer (100-1000 nm) of EC active material (working electrode) is deposited on a transparent conducting oxide (TCO) substrate such as fluorine-doped tin oxide glass or Sn-doped indium oxide (ITO) glass. Since, the molar absorption coefficients for plasmonic materials are much greater than polaronic materials, a much smaller thickness of the active layer is generally required for plasmonic materials as compared to polaronic material to absorb the same intensity of light.[21-22] Even with the same thickness of the electrochromic layer, a difference in the internal microstructure of the film brings about significant difference in the spectral response of a plasmonic and a polaronic material. While polaronic absorption is immune to changes in the morphology and structural arrangement of the active material, plasmonic absorption is very sensitive to changes in the mesoscale geometry (NC size, shape) and how they are arranged within the electrochromic layer.[19, 22-23] This not only affects the peak position and width of the LSPR band but also governs the extent of which it can be modulated through electrochromism.[24-26] Correspondingly, a layer of counter electrode is deposited on another piece of a TCO substrate to balance the capacity of working electrode. The counter electrode can either be an ion storage material contributing either minimum optical change or anodically coloring material to complement the cathodically coloring dual-band working electrode. Nonetheless, for final assembly, these two electrodes are then bonded to each other with an electrolyte layer in between and the TCO substrates are connected to external contacts that supply the device with a varied electric potential.

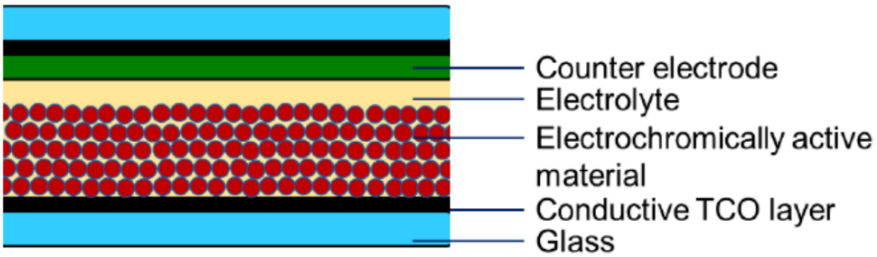

Figure 3: General schematic (not to scale) of an electrochromic device.

Dual-Band Electrochromic Device: Material Selection

Because a polaronic mechanism requires reversible intercalation, materials whose structures include interstitial voids and channels of appropriate size are required to accommodate the intercalating ions. Furthermore, since the charge carriers are localized on the metal centers causing partial reduction of the metal ions, materials with transition metals (having multiple stable oxidation states) as cations or dopants or polymers and organic molecules with conjugated frameworks can be good candidates for polaronic electrochromism. Intercalation of a large amount of counter ions and the presence of high carrier concentration on localized metal centers can bring about a significant amount of lattice strain in the structure. Therefore, stable electrochemical cycling with a polaronic mechanism is more likely in polymorphic materials, possessing multiple

stable structures, or materials with high defect concentration or flexible structures to avoid rapid structural degradation. For the aforementioned reasons, transition metal oxides such as TiO_{2-x}, Nb_2O_{5-x}, and WO_{3-x} and their doped counterparts are candidates for polaronic electrochromism.[11, 27-30]

Plasmonic EC materials, on the other hand, have less stringent structural requirements due to the potential for capacitive charging. Since plasmonic switching is achieved by changes in the population of free carriers, nanomaterials in which high carrier concentration can be achieved either through intrinsic doping or deliberate aliovalent doping are suitable candidates for electrochromism. To most effectively manage the broad spectral range found in sunlight, nanomaterials exhibiting broadband plasmonic absorption are preferred over nanomaterials with narrow plasmonic bands, though heterogeneous plasmonic coupling in nanocrystal films tends to broaden the absorption in any case. It is important to note that even though noble metals have very high free electron density ($>10^{22}$ cm^{-3}) and their nanoparticles exhibit LSPR absorption in the visible region, they are not suitable for capacitive electrochromism because their carrier density is too large to be tuned significantly by applying by a small electric potential. Reversible electrodeposition is instead the preferred strategy for creating EC devices from such materials, as discussed more elsewhere.[31-32] Instead, nanocrystals of doped metal oxides such as ITO, TiO_{2-x}, Nb_2O_{5-x}, and WO_{3-x} possessing low to intermediate carrier concentration (10^{19}-10^{21} cm^{-3}) and LSPR absorption in the near- to mid-infrared region are regularly employed for capacitive plasmonic EC because of their ability to accommodate a wide range of electron concentrations, tuned both during synthesis and post-synthetically.[33-34]

In fact, doped metal oxides can be utilized as both polaronic and plasmonic materials, and added electronic charge can be balanced by ions at the surface or interstitially, depending on the size of the crystal, the potential applied, and the size of the charge compensating ions compared to the interstitial channels. For example, transition metal oxide nanocrystals may support plasmonic electrochromism at potentials far from their redox potential, where ions do not intercalate. At more reducing potential when the redox potential of the transition metal ions is reached, ions will intercalate, which may trigger localization of electrons and instigate a polaronic EC mechanism.[13] In other cases, delocalized electrons may persist even when ions are inserted, depending on the specific interstitial sites occupied.[35,36] A transition from plasmonic to polaronic by varying the potential bias permits spectroscopic control in the visible and NIR regions selectively, leading to a dual-band EC response in a single material.[13, 37] On the other hand, additional control over the absorption of the active layer is possible when dual-band response is achieved by making EC composites containing two different EC component materials, e.g., a metal oxide nanocrystal and a conducting polymer[38-39], two different metal oxides, or two different polymers.[13, 37, 40-43] Beyond the challenges of ensuring chemical compatibility of the constituents and controlling morphology during fabrication of the composite, the choice for the selection of constituents for an EC composite is not always intuitive. For example, the interfacial interaction between amorphous niobium oxide and embedded ITO nanocrystals enhanced the visible, polaronic EC modulation of the Nb_2O_{5-x} about five-fold.[5] _ENREF_35 New polaronic and plasmonic materials are being developed regularly and it might take some time before an optimized combination of constituents and their processing conditions could be developed. Therefore, while it is not mandatory to fabricate the active layer using a single material, it is preferred for the sake of simplicity with an eye toward reliable manufacturability.

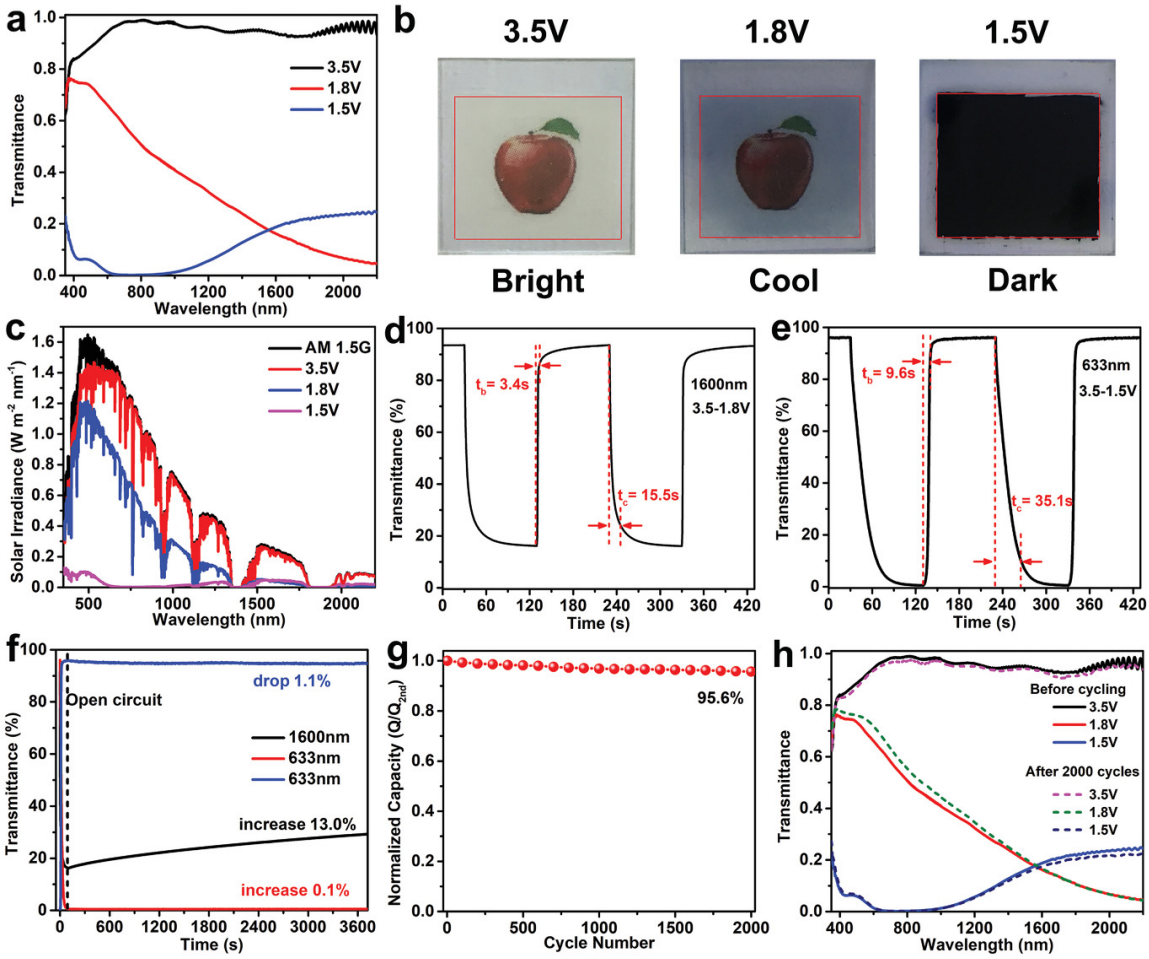

Figure 4: Performance of a dual-band electrochromic film of TiO_{2-x} nanocrystals. (a) Optical transmittance spectra in the voltage range 1.5-3.5 V vs Li/Li^+ showing three different modes of absorption (b) Corresponding digital pictures of bright (3.5 V), cool (1.8 V), and dark (1.5 V) modes (c) AM 1.5G coverage or solar transmittance of different dual-band modes. Determining switching speed for (d) infrared region (1600 nm) and (e) visible region (633 nm) by measuring real time change in transmittance with potential applied (f) Bistability test for different modes in open-circuit condition after charging at respective potentials for 100 s (g) Capacity retention after 2000 cyclic voltammetry cycles between 3.5-1.5 V at 40 mV/s (h) Optical transmittance spectra of different modes after 2000 cyclic voltammetric cycles between 3.5-1.5 V. Reprinted with permission from reference 29. Copyright 2020 Wiley Publishing Group.

Dual-Band Electrochromic Device: Performance

The description of the optical transmittance as exhibiting three modes (bright, cool, and dark) provides a qualitative sense for the performance of a dual-band EC device, but to ascertain the efficiency of a coloration and compare materials and devices, it is helpful to quantify performance through measurable parameters and figures-of-merit. We will now discuss each of these parameters with respect to their significance in governing the overall performance of a dual-band EC device and how EC mechanisms (plasmonic or polaronic) influence the value of each parameter. Employing these concepts, we will compare performance across some examples from

the literature that exemplify which materials perform optimally with respect to individual parameters of interest.

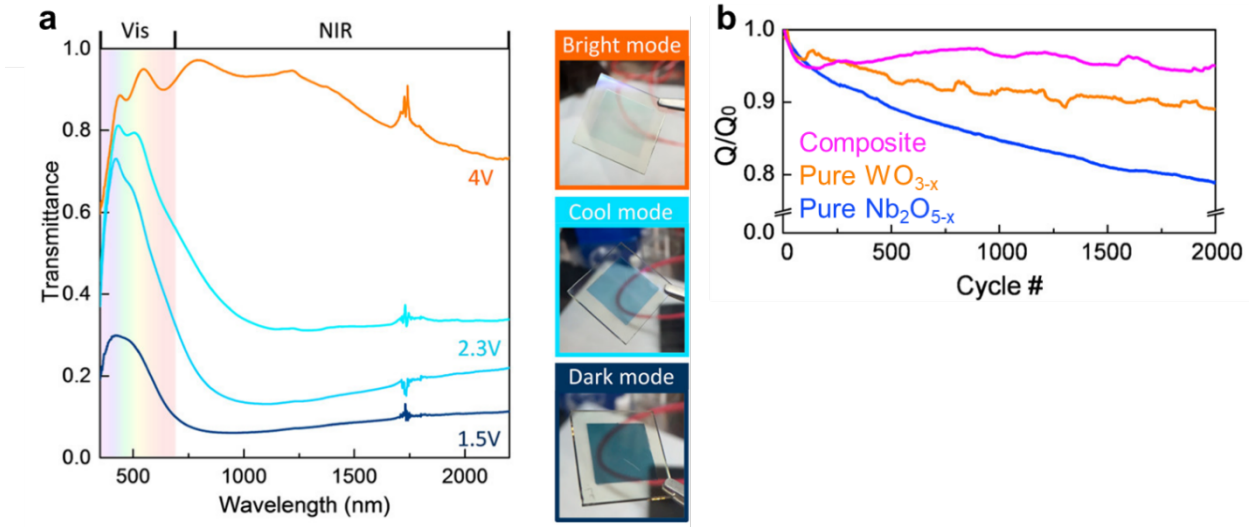

Figure 5: Performance of a dual-band electrochromic film made from a nanocomposite composed of $WO_{2.72}$ nanocrystals and Nb_2O_{5-x} clusters. (a) Optical transmittance spectra in the voltage range 1.5 V-4 V vs Li/Li^+ showing three different modes of absorption and corresponding digital pictures of bright (4 V), cool (2.3 V), and dark (1.5 V) modes. (b) Capacity retention of the nanocomposite after 2000 cyclic voltammetry cycles between 1.5-4 V at 20 mV/s. Reprinted with permission from reference 41. Reference 41 is an open-access article under the author's choice category. Copyright 2015 American Chemical Society.

(a) Optical Contrast and Solar AM 1.5 Coverage

Optical contrast in EC devices can be defined as the difference in transmittance ($\Delta T\%$) at a particular wavelength or range of wavelengths as an EC window switches from one mode to another. Since, a dual-band EC window is concerned with two different regions of the electromagnetic spectrum, two optical contrast values are defined, one for a visible wavelength (or region) and one for an infrared wavelength (or region). For example, in a dual-band EC film made from TiO_{2-x} nanocrystals operating in 3 different modes (Figure 4a,b),[29] we observe that between the bright and the dark mode, the transmittance for the visible (633 nm) and the infrared wavelength (1200 nm) changes by 95.5% and 90.5% (Table 1), respectively, thereby imparting intense blue coloration to the dark mode as compared to a completely transparent bright mode. This high optical contrast for TiO_{2-x} nanocrystals is possible due to a combination of polaronic absorption in the visible region resulting from a phase transformation and plasmonic absorption in the near-infrared region attributed to the presence of oxygen vacancy defects. WO_{3-x} nanowires also show high optical contrast through a combination of polaronic and plasmonic EC[27] (Table 1). Similarly, a nanocomposite made from WO_{3-x} nanocrystals and amorphous Nb_2O_{5-x} utilizes a combination of plasmonic and polaronic mechanisms to achieve a dual-band absorption and exhibit an optical contrast of 93% and 91% in the visible and infrared region respectively (Figure 5a).[41] Optical contrast in itself is independent of the type of mechanism (polaronic or plasmonic) and is determined by the transparency in the bleached state (bright mode) and the strength of the absorption, which is a characteristic of the material and thickness of the EC layer. Therefore, in

principle, a lower optical contrast can be enhanced by increasing the thickness of the electrochromic film.

While having a high optical contrast in the visible and the infrared is beneficial for dual-band EC devices, it is important to evaluate its significance with respect to the solar spectrum being received on the Earth's surface, for which the AM1.5G spectrum serves as a standardized reference.[4] To control solar heat gain dynamically over as wide a range as possible, and improve building energy performance across seasonal weather variations, the optical contrast for modulation of the solar spectrum through the different modes should be maximized. This objective also motivates a preference for broadband absorption over narrow absorption for EC applications, independent of the mechanism of absorption.

The integrated solar transmittance (T_{sol}) is

$$T_{sol} = \frac{\int T(\lambda)\psi(\lambda)d\lambda}{\int \psi(\lambda)d\lambda} \qquad (1)$$

where T(λ) is the transmittance at λ wavelength and $\psi(\lambda)$ is the incident solar intensity in the AM1.5G spectrum. For example, in Figure 4c, TiO_{2-x} nanocrystals modulate the solar transmittance (350-2200 nm) from 93.8% to 53.5% to 4.7% between bright, cool and dark modes respectively. Similarly, for the nanocomposite made from WO_{3-x} nanocrystals and amorphous Nb_2O_{5-x}, the solar transmittance can be modulated from 92% to 54% to 14% between the bright, cool and dark modes respectively (Figure 5a).[41] In fact, within the available literature, we found that the optical contrast reported by Zhang et. al for TiO_{2-x} nanocrystals[29] is one of the highest for a dual-band EC film.

(b) Coloration Efficiency

Coloration efficiency (CE) is a measure of the change in optical density (OD) at a chosen wavelength for every unit of charge density (Q) inserted in or extracted from an EC material. This metric can be utilized for Faradaic processes (ion insertion/extraction) or non-Faradaic processes (ion adsorption), though the relationship between OD and Q may not be linear over the entire range of charging, especially if the EC mechanism changes as charging progresses. Mathematically, it is represented as follows and generally is given in units of cm^2/C:

$$CE = \frac{\Delta OD}{\Delta Q} \qquad (2)$$

Therefore, a high coloration efficiency enables a large optical contrast with a modest amount of charge and a smaller thickness of the active layer, making CE one of the most important material parameters governing the efficiency of a dual-band EC device and the suitability of an EC material for practical devices.[17]

In polaronic materials, optical contrast and CE depend on which crystallographic sites are occupied by the intercalating ions, since these sites influence the nature of the polaronic electronic states formed upon charging.[40] Only intercalation of ions into optically active sites will result in a transmission change and occupation of optically inactive (or weakly active) sites can negatively impact the CE by adding to charge stored without a corresponding increase in ΔOD. For example, Heo et. al. demonstrated that intercalating Li^+, which can access optically inactive triangular interstitials within $WO_{2.72}$ nanorods, results in lower CE than intercalating Na^+ ions, which occupy

only the larger, optically active sites in the crystal structure.[14, 40] In general, WO_{3-x} materials in both bulk and nanocrystalline forms are known to show a high CE for the visible region (Table 1). _ENREF_13

Table 1: Comparison of performance parameters of different materials exhibiting dual-band electrochromism in the literature. We note that in literature, there is no consensus on a standard method for representing switching time for an electrochromic response and thus the numbers cannot be directly compared.

Material	ΔT_{Vis} (%)	ΔT_{NIR} (%)	CE ($cm^2 C^{-1}$)	τ_C/τ_B (s)	Cycle Stability (cycles)	Reference
ITO/NbO_x	~35	~45	30 (500 nm) -	- -	2000 (4% capacity loss)	5
WO_x/NbO_x	93	91	-	-	2000 (5.7% capacity loss)	41
ITO/WO_{3-x}	71.1	58.1	95 (633 nm) 220 (1200 nm)	30/17 (633 nm) 24/5 (1200 nm)	500 (9.5% capacity loss)	42
$W_{18}O_{49}/P_8W_{48}$	62	-	42.3 (500 nm) 287.5 (1060 nm)	26/86 (500 nm) 52/86 (1060 nm)	500 (3% capacity loss)	38
$W_{18}O_{49}/TiO_2$	81.4	91.3	-	1.2/0.9 (633 nm)	20000 (15% capacity loss)	43
Ferrocene/TPBT	66.9	60	101.9 (600 nm) 230.9 (900 nm)	22.0/20.8 (600 nm) 27.4/24.3 (900 nm)	-	44
Nb-doped TiO_2 nanocrystals	72	63	-	105/10 (500 nm)	200	45
Ta-doped TiO_2 nanocrystals	92.4	81.4	33.2 (550 nm) 124.5 (1600 nm)	66.8/6.9 (500 nm) 18.4/1.1 (1600 nm)	2000 (15% capacity loss)	46
WO_{3-x} nanowires	93.2	88.5	121 (633 nm) 254 (1200 nm)	16/13 (633 nm) 8/5 (1200 nm)	2000 (5.5% capacity loss)	27
TiO_{2-x} nanocrystals	95.5	90.5	38.2 (633 nm) 112.7 (1600 nm)	35.1/9.6 (633 nm) 15.5/3.4 (1600 nm)	2000 (4.4% capacity loss)	29
$Nb_{12}O_{29}$ nanoplatelets	71	86	136 (550 nm) 186.4 (1200 nm)	-	500 (32% capacity loss)	30

On the other hand, in plasmonic materials the absorption peak wavelength depends on free carrier density, so ΔOD is not expected to be linear with charge and CE at a given wavelength is generally

dependent on state of charge to some extent. Nonetheless, CE can still be used qualitatively to assess the efficiency of the coloration response and to estimate the thickness of the active layer required to reach target optical contrast. In comparison to polaronic materials, plasmonic materials tend to show a much higher CE since a small amount of charge can bring a significant change in the free carrier density and induce a big change in *OD*.[25-26] Likewise, for materials or composites that exhibit both plasmonic EC (in the infrared) and polaronic EC (in the visible), the CE of infrared region is often higher. Therefore, for the same amount of charge supplied, the plasmonic mechanism is much more efficient than the polaronic mechanism at inducing an optical contrast.

(c) Switching Speed and Bistability

While optical contrast between modes is essential and determines the achievable energy performance, it is also important that the switching between different modes is not too sluggish. Slow switching can limit the potential applications and compromise the experience of users. In traditional EC devices, switching speed is simply a descriptor for the time required to go a bleached mode to a colored mode and vice-versa. In dual-band EC devices, we define bleaching time (τ_B) and coloration time (τ_C) for each spectral region, visible and infrared, even though the terms "colored" and "bleached" do not have literal meaning for infrared transmittance. Although the infrared transmittance and associated switching speed are not visible to users, some degree of visible tint often accompanies infrared blocking in the cool mode and switching very slowly would also compromise energy performance. Just as traditional EC devices, switching speed of a dual-band EC device may be limited by the switching kinetics of the active EC materials, which will be discussed in detail later in context of polaronic and plasmonic mechanisms. The switching speed of an EC device can also depend on electrolyte concentration, which influences the diffusion of ions in bulk electrolyte and the rate to charge the pores at the nanocrystal-electrolyte interface,[47] and the sheet resistance of the transparent conducting substrates, especially when scaling up the working area of the device to large commercial building windows.[48]

Since polaronic materials switch between different modes by redox reactions involving ion intercalation/deintercalation, their switching speed could be constrained by the diffusion speed of the inserted ions and the distance they travel within the material. To evaluate this as a kinetic limitation, we consider the one-dimensional diffusion in a characteristic time (t) at a characteristic distance (l), where $l = \sqrt{Dt}$ and D is the diffusion coefficient. When the characteristic distance is sufficiently small, as in small nanocrystals, and $l << \sqrt{Dt}$, diffusion is not rate limiting over time, t .[37, 49] In this situation, other device parameters may more dominant in determining the overall switching speed. On the contrary, the diffusion of ions can often be the dominating factor in switching kinetics for larger particles and bulk films of polaronic materials. For materials that exhibit low D, switching times can extend unacceptably to hours for films thick enough to provide strong optical contrast. Although the short diffusion paths are a key advantage for nanocrystals as EC materials, it is still important to critically evaluate the diffusion of ions within the EC nanocrystals by considering their particle size and diffusion coefficient. When diffusion of ions is a kinetic bottleneck, switching of polaronic EC materials can be slow since a large number of ions must move through the crystalline lattice (Figure 4e and Table 1). To increase the switching speed, the quantity of intercalated ions required for switching should be decreased. Engineering materials with higher CE achieves this goal while using small multivalent ions such as Al^{3+} instead of monovalent ions such as H^+ and Li^+ offers a complementary strategy. In this case, the same amount of charge requires only $1/3^{rd}$ equivalent of Al^{3+} ions to be intercalated, potentially decreasing the

switching time. Unfortunately, small multivalent cations also have high charge-to-radius ratio which increases their electrostatic interactions with the host lattice and tends to decrease their diffusivity. Nonetheless, in some materials such as WO_{3-x} nanowires reported by Zhang et. al.,[27] the diffusion constants for Li^+ and Al^{3+} are similar and hence employing Al^{3+} ions does significantly improve the switching speed for the dual-band EC switching.

Dual-band EC materials that operating on a plasmonic mechanism, common for the infrared region, are expected to have a faster switching speed than those operating on a polaronic mechanism. Hence, for most EC materials, bleaching and coloration times for infrared wavelengths are much lower than those for visible wavelengths (Figure 4d and Table 1).

Once the EC device is set to a particular mode by applying a specific electric potential, it is desirable to maintain that transmittance state (for infrared and visible light) without the need for an additional applied charge. Known as bistability or optical memory effect, this steadiness avoids consuming energy to maintain coloration or driving electrochemical side reactions that can degrade device performance over time. In general, ion intercalation, especially in polaronic EC materials, results in better bistability since it is difficult to extract the inserted ions without applying any potential bias. By contrast, capacitive charging (in plasmonic EC materials) is easier to reverse since the ions are only adsorbed on the surface. Figure 4f shows the bistability of different modes of a dual-band EC film made from TiO_{2-x} nanocrystals, where even after 6 hours in open-circuit condition, the film continues to exhibit a similar transmittance in the visible region, but has lost 13% of transmittance in the infrared region due to the difference in bistability between polaronic and plasmonic charging mechanisms.

(d) Cycling Stability

For a continued operation, a dual-band EC device needs to maintain its charge capacity and optical contrast over a long period of time. To stress test an EC material device, it can be cycled continuously for a large number of cycles, monitoring the capacity and optical contrast at each cycle or after some number of cycles. For materials that operate on a polaronic mechanism, ions are intercalated and deintercalated repeatedly, potentially straining the EC material and causing mechanical breakdown over time. Even though the size of ion travelling into the voids and channels is usually much smaller than the size of the channel, repeated intercalation and deintercalation can lead to structural disintegration of the material, e.g. through change of the crystal structure and introduction of secondary phases.[13, 50-52] Degradation of the electrolyte at the electrode-electrolyte interface[40, 53] and irreversible trapping of ions in smaller insertion sites[54-56] can also cause fading performance. Microscopically, the film morphology and stability could be changed significantly due to irreversible ion trapping along with volume expansion, all of which eventually leads to degradation of the films.[57] With time, these contribute to a loss in capacity of the dual-band EC device and the device may remain irreversibly tinted or fail to darken sufficiently when charged (Figure 4g,h).[17] In contrast, capacitive charging materials are much more tolerant towards repeated charging and discharging of the device and do not lose much capacity even after extensive cycling. However, since all dual-band EC devices developed thus far include a polaronic component, their capacity may be substantially reduced after a few hundred cycles (Table 1). Among those reported, the composite of ITO with NbO_x glass made by Llordes et al.[5] and a nanocomposite of $WO_{2.72}$ nanocrystals with amorphous Nb_2O_{5-x}[41] showed the best capacity retention after 2000 cycles (Figure 5b). However, for application as smart windows in buildings,

EC devices should withstand at least 50,000 cycles, as well as strenuous thermal cycling, without much degradation.

Dual-Band Electrochromic Device: Challenges and Opportunities

A primary challenge that remains with dual-band EC devices is the contribution of the counter electrodes to achieve better control over the solar transmittance. In commercialized EC windows that dynamically control mostly visible light, the counter electrode usually darkens in sync with the active EC material, thus contributing towards modulation of the transmittance. However, no similar demonstration has been reported for amplifying infrared control using the counter electrode optical response. In fact, even systematic studies on using the conventional counter electrode materials to complement the modulation of dual-band EC materials coated on the working electrode are still not well investigated. Therefore, considerable amount of attention is deserved to develop counter electrodes with functionality in both the visible and infrared region. Moreover, while current commercial electrochromic devices have employed TCOs that are transparent to the visible region but become less transparent in the solar infrared (such as highly doped ITO), for dual-band electrochromic devices to become a commercial reality, highly conductive TCOs that have broadband transparency across both the visible and the near-infrared region are required. High mobility TCOs such as Ce-doped In_2O_3[58-59] and Ti-doped In_2O_3[60-62] _ENREF_55 are excellent candidates for dual-band EC window application, as are metal mesh or nanowire transparent conductors.[63-64]

Another challenge associated with dual-band EC devices is realization of more than 3 modes of operation to selectively modulate the visible and the infrared transmittance. For example: dual-band EC devices could be designed to operate in a fourth mode which we like to define as the "warm mode" where the visible transmittance is blocked while most of the infrared transmittance is allowed to pass through, which inverts the effect of the "cool" mode. This mode would be useful for operation of dual-band EC devices in cold weather where the user desires to benefit from some solar heating while controlling glare or ensuring privacy. There are some examples in the literature[65] where the existence of this "warm" mode has been demonstrated by sandwiching polymer dispersed liquid crystals in between thin films of doped metal oxides[66] and, by capacitively charging the lithiated phase of TiO_2 nanocrystals,[13] however, the visible transmittance is still fairly high in these cases and more improvement is required to give user the comfort of privacy. One unexplored approach to produce a warm mode would be to creatively combine the EC absorption characteristics of materials reported in the literature either in composite EC films or by leveraging the additive filtering effects from the cathodic EC film and the counter electrode.

To improve the aesthetic appeal of dual-band EC devices, better control is needed over the color of the tint imparted while switching between different modes. While conventional EC devices typically show a single hue that becomes progressively darker, dual-band EC devices have the ability to operate in a cool mode with a minimum absorption at the edge of visible region, often resulting in blue hue, and progressive reduction to the dark mode further leads to stronger absorption in the visible region and a dark blue/brown/black hue, depending on the polaronic absorption spectra of the materials.[37, 41] Switching between different operating voltages of dual-band EC devices offers a wide range of visible transmittance between the cool and dark mode for energy management and also a tunable presentation of colors for aesthetic requirements based on the combination of mechanisms contributing to optical absorption. When dual-band coloration is achieved by compositing two or more EC materials with absorption in different solar regions,

selection of these materials is constrained by the need for them to switch at distinctively different potentials to achieve sequential blocking of different spectral regions, and the fabrication of composite films brings additional engineering difficulty. Nonetheless, the component selection and mixing ratio offer some flexibility to meet aesthetic objectives.

Another unmet opportunity is the possibility of plasmonic EC in the visible region, potentially enabling a fully capacitive device operation. Throughout the discussion, we highlighted the advantages of capacitive charging and plasmonic EC mechanisms. While materials like nanocrystalline tungsten oxides are dominantly plasmonic and can efficiently absorb both the NIR and longer (red) wavelengths in the visible region, so far only classical metal nanoparticles exhibit plasmonic absorption in the blue region of the visible spectrum. The high carrier density changes required to modulate optical absorption of these materials even modestly undercuts the practical outlook of an all-plasmonic dual-band EC device. Intriguingly, nanocrystals of ReO_3 show a plasmon band in the blue region of the visible spectrum[67] but their spectroelectrochemical response was not immediately promising for EC device applications. Further investigation of other transition metal oxides and their doped counterparts or ultra-small noble metal nanoparticles could help achieve an all plasmonic dual-band EC device in the future that might exceed the performance of devices reported to date.

One can also potentially increase the usefulness of EC devices by adding to their functionality. While EC devices are generally concerned with regulating the absorption of the incident solar spectrum, they can also allow a dynamic control over the thermal emissivity by modulating the emitted spectrum especially in the atmospheric window of 3-5 μm and 8-13 μm which is not absorbed by the Earth's atmosphere.[68-70] These different modes of thermal mid-infrared control could be activated in tandem with the absorption modulation through an electric potential. While conventional visible light EC devices made from WO_{3-x} have been extensively studied for this purpose, such investigation on materials constituting dual-band EC devices (that offer more modes of operation and hence more room for thermal management control) is quite rare in literature.

Conclusion:

In conclusion, this perspective describes the characteristics of dual-band EC materials and devices and the motivating purpose for their development in saving energy and improving experiences for users. Most of the dual-band EC materials reported thus far employ a combination of a polaronic EC mechanism (involving carrier localization) and a plasmonic mechanism (involving delocalized carriers) and often undergo Faradic or capacitive charging at different applied potentials. These electrochemical and optical mechanisms significantly impact the achievable performance parameters in the overall device. Polaronic EC mechanisms involve ion intercalation, which can result in long switching times (especially for larger crystal sizes or low diffusivities), low coloration efficiency, and limited cycling stability. Plasmonic EC, especially when activated by capacitive charging, tends to realize fast switching times, high coloration efficiency, and improved cycling stability. To provide a significant push to the field of dual-band electrochromism, the scientific progress in this area needs to revolve around two key areas: 1) development of counter electrodes that work in tandem with the active electrochromic layer and contribute towards the realization of different modes of absorption, 2) investigation of new non-noble metal plasmonic systems that could absorb the high energy edge of the visible spectrum so that an all plasmonic dual band electrochromic device could be made. Although dual-band EC devices based entirely on capacitive plasmonic EC are conceptually appealing, no such material has yet been

demonstrated that can modulate across the visible spectrum, especially in the blue region. Additional innovation in the active materials, including compositing and nanocrystal development, may improve color neutrality and make an efficient "warm" mode possible. At the device level, performance can also be improved by deliberate electrolyte selection, with ion intercalation sites, diffusivities, and reactivity at the active material interface in mind or by adding another functionality such as dynamic control over the thermal mid-infrared radiation.

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References:

1. Azens, A.; Granqvist, C., Electrochromic Smart Windows: Energy Efficiency and Device Aspects. *J. Solid State Electrochem.* **2003**, *7*, 64-68.
2. Granqvist, C. G., 20 - Electrochromic Glazing for Energy Efficient Buildings. In Nanotechnology in Eco-Efficient Construction (Second Edition), Pacheco-Torgal, F.; Diamanti, M. V.; Nazari, A.; Granqvist, C. G.; Pruna, A.; Amirkhanian, S., Eds. Woodhead Publishing: **2019**; 467-501.
3. https://www.alliedmarketresearch.com/electrochromic-glass-market
4. Gueymard, C. A., The Sun's Total and Spectral Irradiance for Solar Energy Applications and Solar Radiation Models. *Sol. Energy* **2004**, *76*, 423-453.
5. Llordés, A.; Garcia, G.; Gazquez, J.; Milliron, D. J., Tunable Near-Infrared and Visible-Light Transmittance in Nanocrystal-in-Glass Composites. *Nature* **2013**, *500*, 323-326.
6. Aste, N.; Compostella, J.; Mazzon, M., Comparative Energy and Economic Performance Analysis of an Electrochromic Window and Automated External Venetian Blind. *Energy Procedia* **2012**, *30*, 404-413.
7. DeForest, N.; Shehabi, A.; O'Donnell, J.; Garcia, G.; Greenblatt, J.; Lee, E. S.; Selkowitz, S.; Milliron, D. J., United States Energy and CO_2 Savings Potential from Deployment of Near-Infrared Electrochromic Window Glazings. *Build. Environ.* **2015**, *89*, 107-117.
8. Piccolo, A.; Marino, C.; Nucara, A.; Pietrafesa, M., Energy Performance of an Electrochromic Switchable Glazing: Experimental and Computational Assessments. *Energy Build.* **2018**, *165*, 390-398.
9. Tällberg, R.; Jelle, B. P.; Loonen, R.; Gao, T.; Hamdy, M., Comparison of the Energy Saving Potential of Adaptive and Controllable Smart Windows: A State-of-the-Art Review and Simulation Studies of Thermochromic, Photochromic and Electrochromic Technologies. *Sol. Energy Mater. Sol. Cells* **2019**, *200*, 109828.
10. Runnerstrom, E. L.; Llordés, A.; Lounis, S. D.; Milliron, D. J., Nanostructured Electrochromic Smart Windows: Traditional Materials and NIR-Selective Plasmonic Nanocrystals. *Chem. Commun.* **2014**, *50*, 10555-10572.
11. Granqvist, C. G., Oxide Electrochromics: An Introduction to Devices and Materials. *Sol. Energy Mater. Sol. Cells* **2012**, *99*, 1-13.

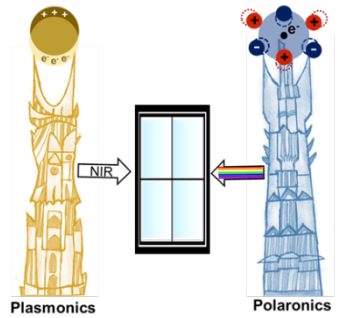
12. Granqvist, C. G., Chapter 2 - Bulk Crystalline Tungsten Oxide. In Handbook of Inorganic Electrochromic Materials, Granqvist, C. G., Ed. Elsevier Science B.V.: Amsterdam, **1995**; 19-27.
13. Dahlman, C. J.; Tan, Y.; Marcus, M. A.; Milliron, D. J., Spectroelectrochemical Signatures of Capacitive Charging and Ion Insertion in Doped Anatase Titania Nanocrystals. *J. Am. Chem. Soc.* **2015**, *137*, 9160-9166.
14. Heo, S.; Cho, S. H.; Dahlman, C. J.; Agrawal, A.; Milliron, D. J., Influence of Crystalline and Shape Anisotropy on Electrochromic Modulation in Doped Semiconductor Nanocrystals. *ACS Energy Lett.* **2020**, *5*, 2662-2670.
15. Somani, P. R.; Radhakrishnan, S., Electrochromic Materials and Devices: Present and Future. *Mater. Chem. Phys.* **2003**, *77*, 117-133.
16. Dahlman, C. J.; Heo, S.; Zhang, Y.; Reimnitz, L. C.; He, D.; Tang, M.; Milliron, D. J., Dynamics of Lithium Insertion in Electrochromic Titanium Dioxide Nanocrystal Ensembles. *J. Am. Chem. Soc.* **2021**, *143*, 8278-8294.
17. Niklasson, G. A.; Granqvist, C. G., Electrochromics for Smart Windows: Thin Films of Tungsten Oxide and Nickel Oxide, and Devices Based on These. *J. Mater. Chem.* **2007**, *17*, 127-156.
18. Lu, H.-C.; Zydlewski, B. Z.; Tandon, B.; Shubert-Zuleta, S. A.; Milliron, D. J. Understanding the Role of Charge Storage Mechanisms in the Electrochromic Switching Kinetics of Metal Oxide Nanocrystals. ChemRxiv 2022, doi:10.26434/chemrxiv-2022-hsf4p.
19. Agrawal, A.; Johns, R. W.; Milliron, D. J., Control of Localized Surface Plasmon Resonances in Metal Oxide Nanocrystals. *Ann. Mater. Res.* **2017**, *47*, 1-31.
20. Triana, C. A.; Granqvist, C. G.; Niklasson, G. A., Electrochromism and Small-Polaron Hopping in Oxygen Deficient and Lithium Intercalated Amorphous Tungsten Oxide Films. *J. Appl. Phys.* **2015**, *118*, 024901.
21. Jain, P. K.; Lee, K. S.; El-Sayed, I. H.; El-Sayed, M. A., Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applications in Biological Imaging and Biomedicine. *J. Phys. Chem. B* **2006**, *110*, 7238-7248.
22. Staller, C. M.; Gibbs, S. L.; Saez Cabezas, C. A.; Milliron, D. J., Quantitative Analysis of Extinction Coefficients of Tin-Doped Indium Oxide Nanocrystal Ensembles. *Nano Lett.* **2019**, *19*, 8149-8154.
23. Gibbs, S. L.; Dean, C.; Saad, J.; Tandon, B.; Staller, C. M.; Agrawal, A.; Milliron, D. J., Dual-Mode Infrared Absorption by Segregating Dopants within Plasmonic Semiconductor Nanocrystals. *Nano Lett.* **2020**, *20*, 7498-7505.
24. Tandon, B.; Shubert-Zuleta, S. A.; Milliron, D. J., Investigating the Role of Surface Depletion in Governing Electron-Transfer Events in Colloidal Plasmonic Nanocrystals. *Chem. Mater.* **2022**, *34*, 777-788.
25. Tandon, B.; Agrawal, A.; Heo, S.; Milliron, D. J., Competition between Depletion Effects and Coupling in the Plasmon Modulation of Doped Metal Oxide Nanocrystals. *Nano Lett.* **2019**, *19*, 2012-2019.
26. Zandi, O.; Agrawal, A.; Shearer, A. B.; Reimnitz, L. C.; Dahlman, C. J.; Staller, C. M.; Milliron, D. J., Impacts of Surface Depletion on the Plasmonic Properties of Doped Semiconductor Nanocrystals. *Nat. Mater.* **2018**, *17*, 710-717.
27. Zhang, S.; Cao, S.; Zhang, T.; Fisher, A.; Lee, J. Y., Al^{3+} Intercalation/De-Intercalation-Enabled Dual-Band Electrochromic Smart Windows with a High Optical Modulation, Quick Response and Long Cycle Life. *Energy Environ. Sci.* **2018**, *11*, 2884-2892.

28. Cao, S.; Zhang, S.; Zhang, T.; Yao, Q.; Lee, J. Y., A Visible Light-near-Infrared Dual-Band Smart Window with Internal Energy Storage. *Joule* **2019**, *3*, 1152-1162.
29. Zhang, S.; Cao, S.; Zhang, T.; Lee, J. Y., Plasmonic Oxygen-Deficient TiO_{2-X} Nanocrystals for Dual-Band Electrochromic Smart Windows with Efficient Energy Recycling. *Adv. Mater.* **2020**, *32*, 2004686.
30. Cai, L., et al., Spectrally Selective Nanocomposite Textile for Outdoor Personal Cooling. *Adv. Mater.* **2018**, *30*, 1802152.
31. Tao, X.; Liu, D.; Yu, J.; Cheng, H., Reversible Metal Electrodeposition Devices: An Emerging Approach to Effective Light Modulation and Thermal Management. *Adv. Opt. Mater.* **2021**, *9*, 2001847.
32. Barile, C. J.; Slotcavage, D. J.; Hou, J.; Strand, M. T.; Hernandez, T. S.; McGehee, M. D., Dynamic Windows with Neutral Color, High Contrast, and Excellent Durability Using Reversible Metal Electrodeposition. *Joule* **2017**, *1*, 133-145.
33. Willets, K. A.; Duyne, R. P. V., Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Ann. Rev. Phys. Chem.* **2007**, *58*, 267-297.
34. Agrawal, A.; Cho, S. H.; Zandi, O.; Ghosh, S.; Johns, R. W.; Milliron, D. J., Localized Surface Plasmon Resonance in Semiconductor Nanocrystals. *Chem. Rev.* **2018**, *118*, 3121-3207.
35. Lu, H.-C.; Katyal, N.; Henkelman, G.; Milliron, D. J., Controlling the Shape Anisotropy of Monoclinic $Nb_{12}O_{29}$ Nanocrystals Enables Tunable Electrochromic Spectral Range. *J. Am. Chem. Soc.* **2021**, *143*, 15745-15755.
36. Zydlewski B, Lu H-C, Celio H, Milliron D. Site-Selective Ion Intercalation Controls Spectral Response in Electrochromic Hexagonal Tungsten Oxide Nanocrystals. ChemRxiv 2022, doi:10.26434/chemrxiv-2022-dbplk.
37. Lu, H.-C.; Ghosh, S.; Katyal, N.; Lakhanpal, V. S.; Gearba-Dolocan, I. R.; Henkelman, G.; Milliron, D. J., Synthesis and Dual-Mode Electrochromism of Anisotropic Monoclinic $Nb_{12}O_{29}$ Colloidal Nanoplatelets. *ACS Nano* **2020**, *14*, 10068-10082.
38. Gu, H.; Guo, C.; Zhang, S.; Bi, L.; Li, T.; Sun, T.; Liu, S., Highly Efficient, near-Infrared and Visible Light Modulated Electrochromic Devices Based on Polyoxometalates and $W_{18}O_{49}$ Nanowires. *ACS Nano* **2018**, *12*, 559-567.
39. Tarver, J. D.; Sezen-Edmonds, M.; Yoo, J. E.; Loo, Y.-L., 5.01 - Organic Electronic Devices with Water-Dispersible Conducting Polymers. In Comprehensive Nanoscience and Nanotechnology (Second Edition), Andrews, D. L.; Lipson, R. H.; Nann, T., Eds. Academic Press: Oxford, **2019**; 1-34.
40. Heo, S.; Dahlman, C. J.; Staller, C. M.; Jiang, T.; Dolocan, A.; Korgel, B. A.; Milliron, D. J., Enhanced Coloration Efficiency of Electrochromic Tungsten Oxide Nanorods by Site Selective Occupation of Sodium Ions. *Nano Lett.* **2020**, *20*, 2072-2079.
41. Kim, J.; Ong, G. K.; Wang, Y.; LeBlanc, G.; Williams, T. E.; Mattox, T. M.; Helms, B. A.; Milliron, D. J., Nanocomposite Architecture for Rapid, Spectrally-Selective Electrochromic Modulation of Solar Transmittance. *Nano Lett.* **2015**, *15*, 5574-5579.
42. Zhang, S.; Li, Y.; Zhang, T.; Cao, S.; Yao, Q.; Lin, H.; Ye, H.; Fisher, A.; Lee, J. Y., Dual-Band Electrochromic Devices with a Transparent Conductive Capacitive Charge-Balancing Anode. *ACS Appl. Mater. Interfaces* **2019**, *11*, 48062-48070.
43. Huang, Y., et al., 3d Pine-Needle-Like $W_{18}O_{49}/TiO_2$ Heterostructures as Dual-Band Electrochromic Materials with Ultrafast Response and Excellent Stability. *Adv. Opt. Mater.* **2022**, *10*, 2102399.

44. Wu, N.; Ma, L.; Zhao, S.; Xiao, D., Novel Triazine-Centered Viologen Analogues for Dual-Band Electrochromic Devices. *Sol. Energy Mater. Sol. Cells* **2019**, *195*, 114-121.
45. Barawi, M.; De Trizio, L.; Giannuzzi, R.; Veramonti, G.; Manna, L.; Manca, M., Dual Band Electrochromic Devices Based on Nb-Doped TiO_2 Nanocrystalline Electrodes. *ACS Nano* **2017**, *11*, 3576-3584.
46. Cao, S.; Zhang, S.; Zhang, T.; Lee, J. Y., Fluoride-Assisted Synthesis of Plasmonic Colloidal Ta-Doped TiO_2 Nanocrystals for Near-Infrared and Visible-Light Selective Electrochromic Modulation. *Chem. Mater.* **2018**, *30*, 4838-4846.
47. Appiah, W. A.; Dzakpasu, C. B.; Lee, H.; Lee, H.; Lee, Y. M., Effect of Electrolyte Concentration on Electrochromic Performance of Sputtered Tungsten Oxide Film: Experiments and Simulation. *Electrochimica Acta* **2021**, *369*, 137699.
48. Costentin, C.; Savéant, J.-M., Electrochemical Capacitive Charging in Porous Materials. Discriminating between Ohmic Potential Drop and Counterion Diffusion. *ACS Appl. Energy Mater.* **2019**, *2*, 4981-4986.
49. Gogotsi, Y.; Penner, R. M., Energy Storage in Nanomaterials – Capacitive, Pseudocapacitive, or Battery-Like? *ACS Nano* **2018**, *12*, 2081-2083.
50. Huang, S. Y.; Kavan, L.; Exnar, I.; Grätzel, M., Rocking Chair Lithium Battery Based on Nanocrystalline TiO_2 (Anatase). *J. Electrochem. Soc.* **1995**, *142*, L142-L144.
51. Van de Krol, R.; Goossens, A.; Meulenkamp, E. A., In Situ X-Ray Diffraction of Lithium Intercalation in Nanostructured and Thin Film Anatase TiO_2. *J. Electrochem. Soc.* **1999**, *146*, 3150-3154.
52. Bouessay, I.; Rougier, A.; Poizot, P.; Moscovici, J.; Michalowicz, A.; Tarascon, J. M., Electrochromic Degradation in Nickel Oxide Thin Film: A Self-Discharge and Dissolution Phenomenon. *Electrochimica Acta* **2005**, *50*, 3737-3745.
53. Han, X.; Liu, Y.; Jia, Z.; Chen, Y.-C.; Wan, J.; Weadock, N.; Gaskell, K. J.; Li, T.; Hu, L., Atomic-Layer-Deposition Oxide Nanoglue for Sodium Ion Batteries. *Nano Lett.* **2014**, *14*, 139-147.
54. Balaji, S.; Djaoued, Y.; Albert, A.-S.; Ferguson, R. Z.; Brüning, R., Hexagonal Tungsten Oxide Based Electrochromic Devices: Spectroscopic Evidence for the Li-ion Occupancy of Four-Coordinated Square Windows. *Chem. Mater.* **2009**, *21*, 1381-1389.
55. Wen, R.-T.; Granqvist, C. G.; Niklasson, G. A., Eliminating Degradation and Uncovering Ion-Trapping Dynamics in Electrochromic WO_3 Thin Films. *Nat. Mater.* **2015**, *14*, 996-1001.
56. Soto, F. A.; Ma, Y.; Martinez de la Hoz, J. M.; Seminario, J. M.; Balbuena, P. B., Formation and Growth Mechanisms of Solid-Electrolyte Interphase Layers in Rechargeable Batteries. *Chem. Mater.* **2015**, *27*, 7990-8000.
57. Hu, A.; Jiang, Z.; Kuai, C.; McGuigan, S.; Nordlund, D.; Liu, Y.; Lin, F., Uncovering Phase Transformation, Morphological Evolution, and Nanoscale Color Heterogeneity in Tungsten Oxide Electrochromic Materials. *J. Mater. Chem. A* **2020**, *8*, 20000-20010.
58. Kim, B. H.; Staller, C. M.; Cho, S. H.; Heo, S.; Garrison, C. E.; Kim, J.; Milliron, D. J., High Mobility in Nanocrystal-Based Transparent Conducting Oxide Thin Films. *ACS Nano* **2018**, *12*, 3200-3208.
59. Runnerstrom, E. L.; Bergerud, A.; Agrawal, A.; Johns, R. W.; Dahlman, C. J.; Singh, A.; Selbach, S. M.; Milliron, D. J., Defect Engineering in Plasmonic Metal Oxide Nanocrystals. *Nano Lett.* **2016**, *16*, 3390-3398.

60. Tandon, B.; Ghosh, S.; Milliron, D. J., Dopant Selection Strategy for High-Quality Factor Localized Surface Plasmon Resonance from Doped Metal Oxide Nanocrystals. *Chem. Mater.* **2019**, *31*, 7752-7760.
61. Tandon, B.; Gibbs, S. L.; Zydlewski, B. Z.; Milliron, D. J., Quantitative Analysis of Plasmonic Metal Oxide Nanocrystal Ensembles Reveals the Influence of Dopant Selection on Intrinsic Optoelectronic Properties. *Chem. Mater.* **2021**, *33*, 6955-6964.
62. Fang, H.; Hegde, M.; Yin, P.; Radovanovic, P. V., Tuning Plasmon Resonance of In_2O_3 Nanocrystals Throughout the Mid-Infrared Region by Competition between Electron Activation and Trapping. *Chem. Mater.* **2017**, *29*, 4970-4979.
63. Rao, K. D. M.; Gupta, R.; Kulkarni, G. U., Fabrication of Large Area, High-Performance, Transparent Conducting Electrodes Using a Spontaneously Formed Crackle Network as Template. *Adv. Mater. Interfaces* **2014**, *1*, 1400090.
64. Han, Y.; Lin, J.; Liu, Y.; Fu, H.; Ma, Y.; Jin, P.; Tan, J., Crackle Template Based Metallic Mesh with Highly Homogeneous Light Transmission for High-Performance Transparent Emi Shielding. *Sci. Rep.* **2016**, *6*, 25601.
65. Barawi, M.; Veramonti, G.; Epifani, M.; Giannuzzi, R.; Sibillano, T.; Giannini, C.; Rougier, A.; Manca, M., A Dual Band Electrochromic Device Switchable across Four Distinct Optical Modes. *J. Mater. Chem. A* **2018**, *6*, 10201-10205.
66. Sang, J., et al., Smart Windows with a VO_2 Thin Film as a Conductive Layer for Efficient and Independent Dual-Band Modulation. *ACS Appl. Electron. Mater.* **2021**, *3*, 4882-4890.
67. Ghosh, S.; Lu, H.-C.; Cho, S. H.; Maruvada, T.; Price, M. C.; Milliron, D. J., Colloidal ReO_3 Nanocrystals: Extra Re d-Electron Instigating a Plasmonic Response. *J. Am. Chem. Soc.* **2019**, *141*, 16331-16343.
68. Gong, H.; Li, W.; Fu, G.; Zhang, Q.; Liu, J.; Jin, Y.; Wang, H., Recent Progress and Advances in Electrochromic Devices Exhibiting Infrared Modulation. *J. Mater. Chem. A* **2022**, *10*, 6269-6290.
69. Niu, J.; Wang, Y.; Zou, X.; Tan, Y.; Jia, C.; Weng, X.; Deng, L., Infrared Electrochromic Materials, Devices and Applications. *Appl. Mater. Today* **2021**, *24*, 101073.
70. Wei, H.; Gu, J.; Ren, F.; Zhang, L.; Xu, G.; Wang, B.; Song, S.; Zhao, J.; Dou, S.; Li, Y., Smart Materials for Dynamic Thermal Radiation Regulation. *Small* **2021**, *17*, 2100446.

TOC Graphic


NIR
Plasmonics
Polaronics
Two Towers of Dual-Band EC Window