Switchable Materials for Smart Windows

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Abstract

This article reviews the basic principles of and recent developments in elec-
trochromic, photochromic, and thermochromic materials for applications
in smart windows. Compared with current static windows, smart windows
can dynamically modulate the transmittance of solar irradiation based on
weather conditions and personal preferences, thus simultaneously improv-
ing building energy efficiency and indoor human comfort. Although some
smart windows are commercially available, their widespread implementation
has not yet been realized. Recent advances in nanostructured materials pro-
vide new opportunities for next-generation smart window technology owing
to their unique structure-property relations. Nanomaterials can provide en-
hanced coloration efficiency, faster switching kinetics, and longer lifetime.
In addition, their compatibility with solution processing enables low-cost
and high-throughput fabrication. This review also discusses the importance
of dual-band modulation of visible and near-infrared (NIR) light, as nearly
50% of solar energy lies in the NIR region. Some latest results show that
solution-processable nanostructured systems can selectively modulate the
NIR light without affecting the visible transmittance, thus reducing energy
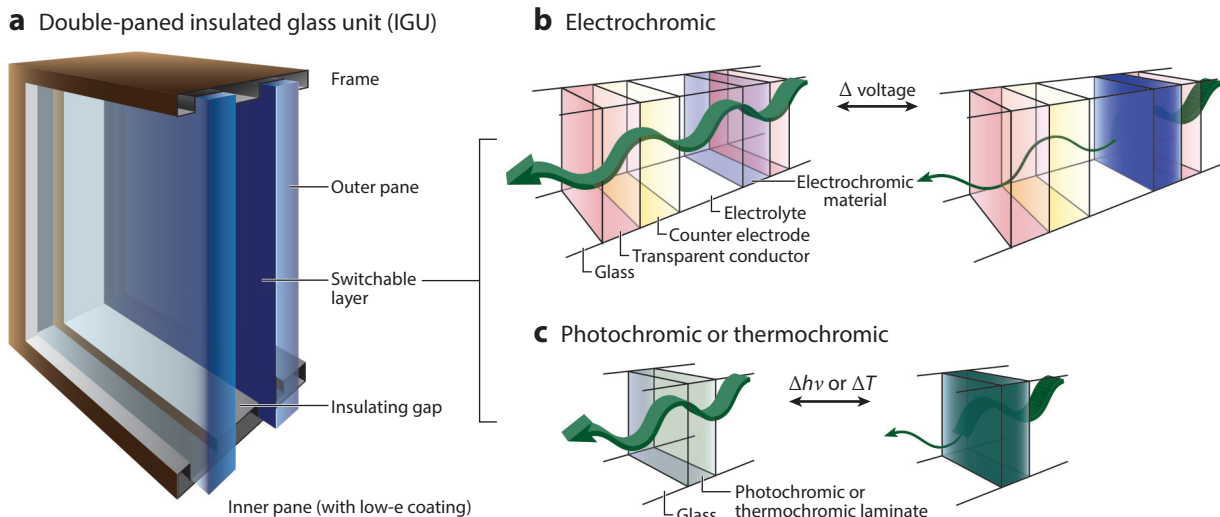consumption by air conditioning, heating, and artificial lighting.

INTRODUCTION

Smart windows dynamically control the transmittance of solar irradiation into buildings by reversibly switching between a transparent state and a blocking state (1). They are emerging as a promising technology to reduce building energy consumption for heating, ventilation, and air conditioning (HVAC), while providing glare reduction, unobstructed views, and natural daylighting (2, 3). HVAC and lighting energy use in buildings currently accounts for ~1.04 TW in the United States, which is approximately 30% of the total US energy demand (4, 5). A large fraction of this energy use is wasted simply because most building fenestration technologies are either not energy efficient or not adaptable to dynamic climates. The most ubiquitous energy-efficient architectures combine glazed double- or triple-paned windows with blinds. Glazed windows incorporate coatings (e.g., thin transparent silver films) to retain or reject solar heat gain but are completely static and cannot respond to changing weather or seasons. Blinds add adaptability and glare control but are expensive to install at $8/ft^2 (more if combined with a building's climate control system) and increase costs associated with artificial interior lighting. Thus, static window technologies are simply not capable of maximizing both energy efficiency and the visual and thermal comfort of a building's occupants.

Herein lies the opportunity for smart windows, as they can tune the transmittance of sunlight to provide variable solar heating and daylight according to changing weather and personal preference (**Figure 1**). Previous simulation studies have shown that smart windows can reduce a building's energy needs by up to 40% relative to static windows (4). Approximately 400 million square feet of windows are installed annually in the United States alone, representing less than 10% of the annual demand globally (6); clearly there is a large potential market for smart windows. There are three main categories of smart windows, which can be categorized by their operating principles: Electrochromic windows change transmittance under applied voltages, whereas photochromic and thermochromic windows respond to environmental stimuli by altering their transmittance with the change of light intensity and temperature, respectively.

Among them, electrochromic windows have attracted the most attention, because they offer dynamic modulation in a broad spectral range, and they can be user controlled to meet personal preferences (**Figure 1b**). However, compared with photochromic and thermochromic windows, they require full device configuration and electric supply, which complicates their design and installation and increases the final installed cost. Photochromic coatings have found applications in transitional eyeglass lenses, but their use in smart windows has been limited, largely because they are not user controlled and their optical switching depends strongly on light intensity (**Figure 1c**). For thermochromic windows (**Figure 1c**), the dynamic range has so far been more limited than electrochromics, and they normally have a limited maximum visible light transmittance. Still, easy integration of photochromic and thermochromic functionality into windows is an advantage for deployment.

An ideal smart window must meet several important criteria. First and foremost, smart windows must meet the same aesthetic requirements as any other window; in their bleached state they must be clear and colorless without visible haze. Similarly, in the dark state they should deliver a neutral color, such as dark gray, without scattering. Moreover, a high optical contrast between the bleached and dark state is desirable. Second, because they provide tunable light and energy transmittance, their dark states must deliver a lower (or at least competitive) solar heat gain coefficient (SHGC) than static windows. SHGC is defined as the fraction of incident solar energy admitted through a window, and low-emissivity static windows normally have a SHGC in the range of 0.2–0.5 (4). Both View Inc. and EControl Glass GmbH have developed electrochromic windows with a SHGC below 0.1 in the dark state. Third, as smart windows typically operate under strong solar

a Double-paned insulated glass unit (IGU)

Frame

Outer pane

Switchable layer

Insulating gap

Inner pane (with low-e coating)

b Electrochromic

Δ voltage

Electrochromic material
Electrolyte
Counter electrode
Transparent conductor
Glass

c Photochromic or thermochromic

Δhv or ΔT

Photochromic or thermochromic laminate
Glass

Figure 1

(*a*) Illustration of a double-paned insulated glass unit. A typical location of the chromogenic layer on the inner surface of the outer pane is denoted. (*b*) Electrochromic smart windows color in response to applied voltage (adapted from Reference 2, published by the Royal Society of Chemistry). (*c*) Photochromic and thermochromic smart windows color in response to light and temperature, respectively.

irradiation and must meet 30-year lifetime requirements, it is important for all device components to have excellent durability (2).

Insulated glass units (IGUs), shown schematically in **Figure 1*a***, are incorporated into final window products. IGUs commonly consist of two panes of glass separated by an insulating airspace that may be filled by argon gas and sealed at the edge. Switchable chromogenic coatings are normally placed on the interior surface of the outside glass pane, so as to isolate them from harsh environmental conditions and thus extend their lifetime. Placing the chromogenic coating at this surface also provides better heat management, as a low-emissivity coating on the interior pane can reject any black body radiation emitted from the active layer as a result of absorptive heating in its darkened state.

In recent years, chromogenic devices fabricated on flexible substrates [e.g., tin-doped indium oxide- (ITO-)coated polyester films] have attracted a large amount of attention owing to their compatibility with roll-to-roll processes (7). For window applications, flexible devices can be laminated between two flat or curved glass substrates with index-matching glues, so that they can be used in both buildings and automobiles. ChromoGenics AB (1) has demonstrated flexible electrochromic devices based on sputtered WO_3 and NiO films. Flexible devices containing other electrochromic materials, and photochromic and thermochromic materials, have also been reported in the literature (8–14).

This work reviews the fundamental principles and highlights some recent developments for electrochromic, photochromic, and thermochromic materials and their devices. Here we emphasize some of the exciting efforts to introduce nanostructuring and nanomaterials into smart windows, with a particular emphasis on nanostructured electrochromic materials and composites. Smart window materials made from chemically synthesized nanoscale building blocks can be compatible with low-cost solution deposition and low-temperature processing techniques, such as roll-to-roll printing and lamination, which can significantly increase production yield and reduce

manufacturing costs. In addition, the rapid advance of nanomaterial synthesis over the past decade has enabled the control of nanocrystal size, shape, surface chemistry, and composition, which opens new opportunities to take advantage of unique structure-property or composition-property relationships for new chromogenic devices. Finally, we also discuss some of the challenges that both conventional and nanostructured smart window technologies face on the road to large-scale commercialization.

## SWITCHABLE MATERIALS FOR ELECTROCHROMICS

Electrochromic devices must satisfy a few requirements for architectural window applications besides the ones discussed above. First, all device components, including transparent conductors, electrolytes, and charge storage materials, must be highly transparent to visible light, and must also have good refractive index matching at their interfaces to minimize reflections. Second, all the components must be electrochemically stable within the switching voltage range. Finally, practical applications require the use of solid-state electrolytes, such as polymer ion gels or ion-conducting ceramics, as liquid electrolytes can leak, catch fire, or even deform or break the glass owing to gravity, especially for large windows. This section starts with a discussion of three common types of electrochromic devices.

Electrochromic Devices

Type-I devices have electrochromic molecules and a redox agent dispersed in a polymer matrix, which is sandwiched between two transparent conducting oxide (TCO)-coated glass substrates (**Figure 2a**). Under an external bias, the electrochromic molecule and redox agent diffuse to separated electrodes, where the latter is oxidized and provides electrons via the external circuit to reduce the former. This device requires a constant current to maintain coloration, because the reduced electrochromic molecule and the oxidized redox agent freely recombine at open circuit conditions to recover the bleached state. By using viologens and phenlyenediamine as the electrochromic molecules and redox agent, Gentex Corporation has commercialized this type of device for auto-dimming rearview mirrors and smart windows in Boeing 787 aircraft.

Type-II devices contain electrochromic molecules with chelating groups, such as phosphonated viologens, bound to a mesoporous metal oxide film backed by a TCO electrode (**Figure 2b**) (15). The massive surface area of the porous TCO film allows a high loading of electrochromic molecules for deep optical modulation during switching. This device also includes an ion-conducting electrolyte and a counter electrode. Because the electrochromic molecules are surface confined, faster switching rates can be achieved relative to Type-I devices (16, 17). Moreover, coloration can persist for more than 600 s after the voltage is switched off. Some recent developments in this area include the use of 1D TiO_2 or ZnO architectures to further improve the switching speed and coloration efficiency (18, 19).

Type-III devices are based on a thin-film battery-type configuration, in which a layer of electrochromic material (e.g., metal oxide or conjugated polymer) is coated on a TCO working electrode, and a charge storage layer (e.g., Prussian blue, NiO, CeO_2) is coated onto a TCO counter electrode (**Figure 2c**). These two electrodes are joined by a layer serving as an ion-conducting electrolyte and separator. In a typical configuration, the device darkens when electrons and ions are inserted into the working electrode, and it bleaches when the charges are extracted to be stored in the counter electrode. The magnitude of the color change can be controlled directly by the amount of inserted charge. These devices exhibit open circuit memory and can maintain a colored state for an extended period of time. This device configuration is very popular for architectural smart window applications and has been adopted by many companies, including Sage
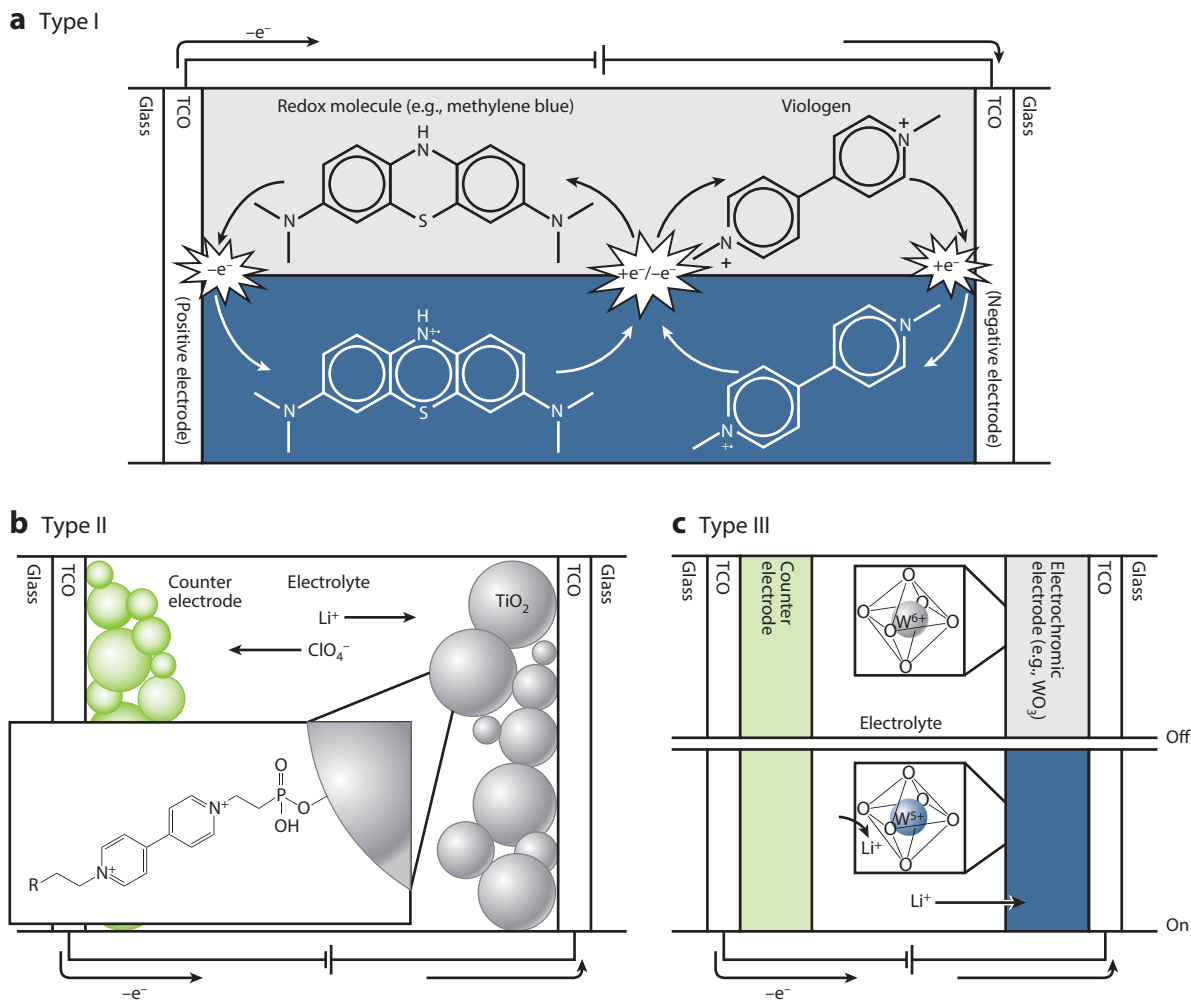
Figure 2

(*a*) Depiction of Type-I electrochromic device operation based on methyl viologen and methylene blue (adapted with permission from References 21 and 22, ©2007, Cambridge University Press). (*b*) Operation of a Type-II electrochromic device where phosphonated viologens are bound to TiO_2 surfaces and are reduced/oxidized. (*c*) Operation of a Type-III electrochromic device based on the reduction and oxidation of an inorganic (e.g., WO_3) thin film. Abbreviation: TCO, transparent conducting oxide.

Electrochromics Inc., View Inc., EControl Glass GmbH, and more. In particular, EControl has claimed that their products require less than 1.5 Wh/m² for one complete switching cycle, which takes 15–20 min to complete (20).

Electrochromic Materials

The active material used in an electrochromic device must exhibit a combination of properties that includes the following: (*a*) high coloration efficiency, (*b*) high optical contrast, (*c*) long-term redox and photo stability, and (*d*) fast switching kinetics. Among them, coloration efficiency ($\Delta A/\Delta Q$), defined as the ratio between optical contrast (ΔA, change of absorbance) and consumed charge

density (ΔQ, C/cm^2), is a widely used metric to measure electrochromic performance. This section discusses several types of electrochromic materials that exhibit promising performance.

Metal oxides. Transition metal oxides have long been used in electrochromic devices, where they are almost always the active electrochromic electrode in a Type-III configuration (**Figure 2c**) (7, 23). Reversible color changes in tungsten bronzes have been studied for more than one hundred years (24, 25), and Deb's demonstration of electrochromism in tungsten oxide launched nearly 50 years of ongoing electrochromic research (26, 27). Conventional electrochromic oxides tend to be deposited in thin-film form by physical vapor processes like sputtering, and they typically operate via an electrochemical ion intercalation and redox process. Materials that color upon reduction are referred to as cathodically coloring, whereas those that color upon oxidation are anodically coloring. Although electrochromic devices based on metal oxides are the current state of the art in smart windows, several improvements in cost, durability, and functionality (i.e., spectral control and switching time) still need to be made. Recent advances in nanostructured metal oxides, and the discovery of plasmonic electrochromism in colloidal nanocrystals, are promising signs of progress in this area.

Tungsten oxide, in both crystalline and amorphous form, is easily the most ubiquitous solid-state electrochromic material. Edge- and corner-sharing WO_6 octahedra in WO_3 form periodic structures with open tunnels of interstitial sites, which facilitate ion motion and intercalation. When WO_3 is cathodically charged, intercalated cations (H^+ or Li^+) are compensated by injected electrons, which reduce tungsten cations from W^{6+} to W^{5+} (25). Concurrently, the material changes from a clear, transparent state to dark blue (**Figure 3a**). Although the physical mechanism for coloration is not fully understood, it likely originates from a combination of polaronic absorption at W^{5+} (or W^{4+}) sites and intraband transitions involving the electrons injected into the
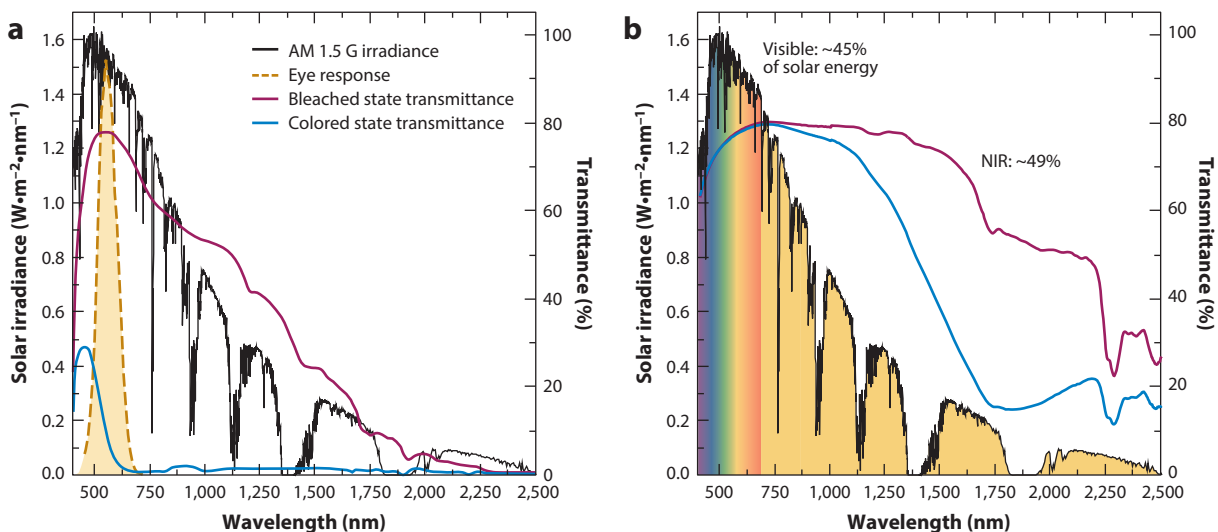
Figure 3

(*a*) Bleached and colored state transmittance curves of a full WO_3-based electrochromic device (Gesimat) compared with the solar irradiance at the earth's surface and the photopic response of the human eye (reproduced from Reference 2, published by the Royal Society of Chemistry; transmittance curves reproduced from Reference 53, ©2009 with permission from Elsevier). (*b*) Bleached and colored state transmittance curves of a full ITO nanocrystal-based electrochromic device constructed in the authors' laboratory compared with the visible and near-infrared (NIR) portions of the solar spectrum.

previously empty WO_3 d band states (1, 28). Intraband transitions dominate the optical response of crystalline WO_3, whereas polaronic absorption is the primary source of color for amorphous WO_3. The other cathodically coloring transition metal oxides, including TiO_2, Nb_2O_5, and MoO_3, also have edge- and corner-sharing MO_6 octahedra and intrinsically empty d bands and color by related mechanisms upon charge injection (23). However, the cathodic metal oxides aside from WO_3 have met with limited success because of low coloration efficiency and poor durability. There are also anodically coloring metal oxides, notably NiO, IrO_2, and V_2O_5 (23, 25, 29). NiO changes from transparent in its reduced state to colored upon oxidation, and it is widely used as a counter electrode that colors in a complementary fashion to WO_3.

In many cases, the electrochromic performance of oxides like WO_3 can be improved through nanostructuring. WO_3 nanocrystals, nanorods, and nanoflakes display enhanced coloration efficiencies, charge capacities, and optical contrast compared with crystalline thin films, with greater enhancement for decreasing particle sizes (30–33). Nanocrystalline WO_3 is an attractive electrochromic material because crystalline WO_3 is much more durable than the amorphous form when protic electrolytes are used (34), and the small length scales for ion diffusion into the nanocrystals enable short switching times that are not possible in dense crystalline WO_3 thin films. Furthermore, electrochromic nanomaterials may be compatible with solution processing methods, which can confer significant benefits for cost and manufacturability. Other cathodically coloring oxides, namely TiO_2 and MoO_3, exhibit similar performance enhancements at the nanoscale (30, 35). Nanostructured versions of the anodically coloring oxides display interesting electrochromic behavior by pseudocapacitive mechanisms, which can be exploited for fast switching and prolonged cycle life by avoiding ion intercalation. Deb and coworkers (36) first discovered pseudocapacitance in electrochromic NiO nanoparticles in 2005. Their NiO nanoparticles, dispersed in a Ta_2O_5 proton-conducting matrix, achieved coloration efficiencies comparable to thin films, but with greater charge capacity and optical modulation that increased with smaller particle sizes. Likewise, gyroidal structures of NiO and V_2O_5, prepared by block copolymer-templated electrodeposition, display pseudocapacitive electrochromism with exceptionally fast switching, deep optical modulation, and high charge capacity (37, 38).

Electrochromic nanomaterials reached another milestone in 2011 when Garcia et al. (39) discovered that capacitive cathodic charge injection into films of colloidal ITO nanocrystals produced an electrochromic effect. Although this work was presaged by the discovery of capacitive charge injection and electrochromism in Ag, Au, antimony-doped SnO_2, and CdSe nanocrystals (2, 40–46), ITO nanocrystals were the first to display deep, tunable modulation over a spectral range relevant for smart windows, along with exceptionally high coloration efficiency and cycle life. Colloidal nanocrystals of doped TCOs, such as ITO (47) and aluminum-doped zinc oxide (AZO) (48), display localized surface plasmon resonance (LSPR), collective oscillations of free carriers that strongly absorb or scatter incident electromagnetic radiation at resonant frequencies (49, 50). The resonance frequency, and consequently the absorption profile, is proportional to the square root of the free carrier concentration (51). Capacitive charge injection is therefore used to dynamically tune the carrier concentration and the LSPR absorption in the nanocrystals, giving rise to a conceptually new electrochromic mechanism (39). The spectral region that can be modulated in a device can be tuned by changing nanocrystal size, material selection, and dopant concentration, though in general LSPR peaks in doped metal oxides fall within the near- to mid-infrared region (2, 52). Because approximately half of solar energy is infrared radiation (**Figure 3**), plasmonic electrochromics are uniquely able to selectively modulate solar heat gain without sacrificing the visible transmittance used for daylighting (**Figure 3***b*). A related simulation has shown that NIR-selective electrochromic devices could potentially save up to 167 TWh/y in US buildings by decreasing HVAC and electric lighting costs (4).

In the past few years, plasmonic electrochromism has also been demonstrated in AZO (54), Nb-doped TiO_2 (55), and oxygen vacancy-doped WO_3 nanocrystal films (56). Plasmonic nanocrystals can also be used as building blocks for advanced electrochromic devices with well-controlled microstructures and/or multiple components that extend device functionality. For example, Llordés et al. (57) used ITO nanocrystals functionalized with polyniobate clusters (POMs) to generate new electrochromic composites. After depositing the POM-capped ITO film, the POMs surrounding the nanocrystal can be condensed into an amorphous NbO_x network, forming a nanocrystal-in-glass composite with unique properties (57, 58). At low cathodic voltages, the LSPR of the ITO phase is modulated for a NIR response, but when the composite is charged further, the NbO_x is reduced to give a polaronic electrochromic response that modulates visible light transmittance. Strikingly, the visible modulation in the composite films was approximately five times greater than for NbO_x films alone, and the durability of the composite was substantially better than homogeneous films of either NbO_x or ITO nanocrystals. This result demonstrated, for the first time, an electrochromic device capable of independently controlling NIR and visible light transmittance. Such a dual-band device has obvious implications for use in smart windows; the bright mode admits both NIR and visible light, the cool mode selectively blocks NIR light, and the dark mode blocks both NIR and visible light. Dual-band functionality gives a smart window the ability to operate in both hot and cold climates and to adapt to various environmental conditions, ultimately reaching performance levels that cannot be achieved by plasmonic or conventional electrochromics (2, 59).

Another noteworthy example used newly developed ligand-stripping techniques and block copolymer-nanocrystal coassembly to create templated mesoporous films of ITO nanocrystals with 60% porosity and controlled wall thickness and pore diameter (60). These mesoporous films had higher coloration efficiency, higher optical contrast, and faster switching times compared with untemplated, randomly close-packed nanocrystal films. Kim et al. (56) used POMs to backfill a templated mesoporous oxygen vacancy-doped WO_3 nanocrystal framework with NbO_x to produce a nanostructured dual-band electrochromic composite (**Figure 4a–d**). WO_{3-x}/NbO_x composites display excellent dual-band modulation (**Figure 4a**); NIR transmittance is controlled by plasmonic absorption in WO_{3-x}, whereas visible transmittance is modulated by polaronic absorption in NbO_x as well as the visible tail of the WO_{3-x} absorption (**Figure 4e**). The inclusion of the glassy NbO_x phase significantly enhanced the bandwidth of visible modulation in the composite relative to WO_{3-x} alone, and furthermore, the combined visible response of both components resulted in a more neutral color (**Figure 4a**). Importantly, the mesoporous architecture and interfacial interaction between WO_{3-x} and NbO_x resulted in rapid switching kinetics, enhanced charge capacity, and good durability.

Besides the nanocrystal-in-glass composites, Nb-doped TiO_2 nanocrystals (55) themselves are particularly interesting because they can support both LSPR-based NIR electrochromism and polaron-based visible electrochromism in one material. Achieving dual-band behavior in a single material has paved the way for new operating modes, i.e., a warm mode that transmits NIR light while blocking visible light (55). These types of nanomaterials and the devices inspired by them are the latest proof-of-concept regarding spectrally selective control over solar transmittance with electrochromic materials.

Other electrochromic materials. Besides the metal oxide materials discussed above, electrochromism can also be found in a wide range of other materials, including small organic and inorganic molecules and conjugated polymers. Compared with metal oxides, most of these materials offer facile processing, synthetic color control, polyelectrochromism, and higher coloration efficiency. However, their photochemical and electrochemical stability can be problematic, as faded optical contrast and yellowing arising from side reactions and redox irreversibility have
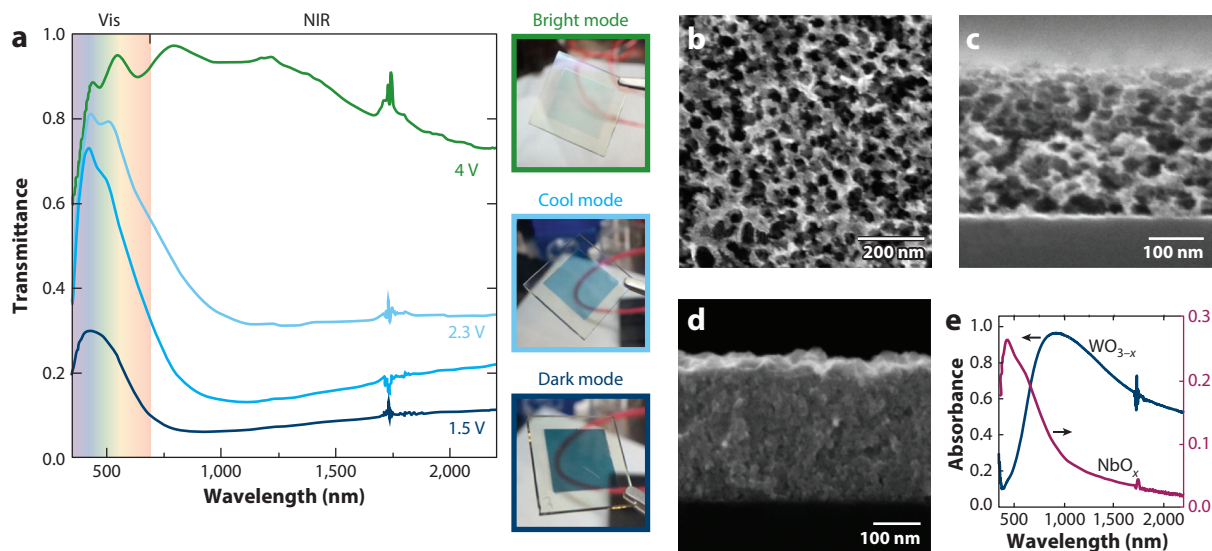
Figure 4

(*a*) Transmittance spectra of a 260-nm-thick WO_{3-x}–NbO_x composite film on ITO-coated glass at different switching potentials (versus Li/Li$^+$ in 0.1 M Li-TFSI/tetraglyme) and the corresponding photographs of the sample. (*b*) Top view micrograph of templated mesoporous WO_{3-x} nanocrystal thin film. (*c*) Cross-section view. (*d*) Cross-section view of WO_{3-x} framework backfilled with NbO_x. (*e*) Absorbance spectra comparing the vis-near-infrared (NIR) absorption of an electrochemically charged WO_{3-x} film to the visible absorption of an electrochemically charged NbO_x film. *a–d* reproduced from Reference 56, ©2015 American Chemical Society.

been reported (61, 62). Moreover, although they normally show strong optical modulation in the visible spectrum, they lack control over NIR insolation and the associated modulation of solar heating. In this section, we discuss some of these electrochromic systems.

Viologens are a class of 4,4′-bipyridine compounds that exhibit reversible redox chemistry between a colorless dication form (V^{2+}) and a deep-blue radical cation ($V^{+\cdot}$) form (61). The well-established substitution chemistry on the two nitrogen atoms in viologens has allowed researchers to tune the color of viologen radical cations; for example, alkyl groups give a deep blue color, whereas 4-cyanophenyl groups induce an intense green color (25). Recent work on viologens and their devices emphasizes the development of novel substitution groups, counter anions, and redox agents to lower the reduction potential and improve switching rate, coloration efficiency, and color neutrality (9, 63, 64). It is worth mentioning that the radical cation ($V^{+\cdot}$) can be further reduced into a yellow neutral form (V^0). However, this reaction does not show good reversibility and thus is not suitable for electrochromic applications (61). This observation suggests that a balance must be established between active oxidation states and electrochemical stability for electrochromic materials.

Transition metal-ligand complexes are another important type of electrochromic molecule, owing to the rich redox activities of metal cations and their ligand complexes (21, 25). Metal polypyridyl complexes, namely [M(bipy)$_3$]$^{2+}$ (M = Fe^{2+}, Ru^{2+}, Os^{2+}; bipy = 2,2′-bipyridine), have a strong visible absorption band owing to metal-to-ligand charge transfer. This absorption is quenched in the M^{3+} redox state (65–67), so a strong electrochromic response can be induced upon oxidation. Metalloporphyrins, especially metallophthalocyanines, have highly delocalized π-conjugated structures whose redox chemistry can be tuned independently of the metal cation in the center to generate polyelectrochromism (25, 68).

Prussian blue (iron hexacyanoferrate, $[Fe^{III}Fe^{II}(CN)_6]^-$) is another widely used electrochromic material consisting of a 3D solid coordination network with an intense blue color arising from intervalence charge transfer between mixed iron oxidation states (68). It is both cathodically and anodically electrochromic, as oxidation gives yellow, $[Fe^{III}Fe^{III}(CN)_6]$, whereas reduction forms colorless Prussian white, $[Fe^{II}Fe^{II}(CN)_6]^{2-}$. Prussian blue and its anodic electrochromism have been used by Gesimat GmbH as a counter electrode to pair with a cathodically coloring WO_3 working electrode (53). This strategy can effectively reduce the material and charge capacity requirements for the device without sacrificing optical contrast.

Electrochromic polymers. Many conjugated polymers, including polythiophenes, polypyrroles, polyanilines, polyfurans, and polycarbazoles, are electrochromic, because electrochemical doping can alter their π-conjugated electronic structures to induce a bandgap change and optical contrast (69, 70). Their electrochromism is synthetically tunable with changes to the monomer type, conjugation length, substitution groups/side chains, stereoregularity, and steric effects. Polythiophenes and polypyrroles are of particular interest owing to their facile chemical and electrochemical synthesis, suitable bandgaps, and low redox potentials. In the past decades, a great amount of effort has been spent on their structural and bandgap engineering by synthesizing thiophene and pyrrole derivatives with different functional groups, with various fused aromatic rings, or with segments that can be polymerized into random, alternating, or block copolymers. Numerous different color changes can be found in the literature; for example, poly(thiophene) can change color from red in the neutral state to blue in the oxidized state, whereas poly(isothianaphthene) exhibits a color change from blue to green upon oxidation (25, 62, 70). Reynolds et al. (71) synthesized a donor-acceptor copolymer electrochrome, consisting of 3,4-bis(2-ethylhexyloxy)thiophene donor and 2,1,3-benzothiadiazole acceptor moieties, which showed a black-to-transmissive color switching, meeting the need for color neutrality that is a highly desirable feature for window applications.

Some polymers, such as poly[3,4-(propylenedioxy)pyrrole] (PProDOP) and poly[3,4-(propylenedioxy)thiophene] (PProDOT), can even have multiple color states based on different doping levels. PProDOP and PProDOT color both cathodically and anodically and can be used as either working or counter electrodes in electrochromic devices to produce new color states. Kang et al. (72) paired PEDOT:PSS and polyaniline electrodes in a device that exhibited an optical modulation of 72% at 580 nm, a switching time of 160 ms, and a color efficiency of 338 cm^2/C, which is approximately four times greater than crystalline WO_3. However, devices based on electrochromic polymers generally lack a clear and highly transparent state, which is important for smart window applications. Also, their electrochemical and photochemical durability upon cycling is generally inferior to those for the inorganic materials, which is often attributed to redox irreversibility (69).

Metal-organic frameworks (MOFs) are a class of porous materials constructed from metal-based nodes and organic linkers. Their high permanent porosity and nanostructured pores provide channels for fast ion transport, making them attractive candidates for electrochemical applications. Kung et al. (73) reported that 1D MOF thin films consisting of Zr nodes and modified pyrene linkers showed reversible color change from yellow to blue upon oxidation. As Zr^{4+} nodes are redox inactive, the electrochromism arises from the oxidation of the pyrene linker to a radical cation form. This MOF achieved a good coloration efficiency of 204 cm^2/C at 587 nm. Recently, Wade et al. (74) synthesized Zn-pyrazolate MOFs containing redox-active naphthalene diimide linkers, which exhibited two sequential redox reactions at different reduction potentials. Hence, the MOF thin film showed polyelectrochromic behavior in the spectroelectrochemical characterization. Zhang et al. (75) recently reported the independent redox activity on metal nodes and ligand

sites, whose electrochromism, however, was not studied. Future studies will surely explore how different electrochromic states can be obtained by selectively manipulating the redox chemistry of the metal nodes and ligands.

## SWITCHABLE MATERIALS FOR PHOTOCHROMICS

Introduction

Photochromic materials change color when exposed to certain wavelengths of light. Based on the types of materials and coloration mechanisms, the reverse process can be driven by different stimuli. Unlike electrochromics, photochromic devices do not require an external power supply or full cell configuration, thus potentially allowing simple fabrication and installation. Photochromic coatings are generally made by embedding active materials into host matrices, such as polymers or ceramics, and they have already found applications in transitional lenses and after-market window tints for buildings and automobiles. A good photochromic material should have a high photocoloration contrast, fast and reversible switching, and acceptable photochemical stability. This section reviews some important types of photochromic materials.

Photochromic Molecules and Polymers

In organic systems, photochromism is characterized by a photo-induced transformation between two chemical isomers that have different absorption spectra. Chemical bond rearrangement during the transformation leads to structural and electronic changes of the molecules. Molecules, including azobenzene, spiropyran, furylfulgide, and diarylethene, and their polymers can be photoswitched between two different color states (76). For instance, under UV irradiation, spiropyran isomerizes, changing color from clear to dark blue. As the photo-induced coloration is energetically uphill, the colored spiropyran is not thermally stable, and it spontaneously bleaches back to colorless after removing UV light. Spiropyran-based photochromism is widely used for transitional lenses. The more recently investigated diarylethene family can switch from colorless to red under UV exposure via a structural transformation from an open-ring to a closed-ring isomer with extended conjugation (**Figure 5a,b**). Compared with spiropyran, diarylethene has a thermally stable colored state, which cannot be bleached in the dark at room temperature. However, bleaching can be driven by visible light exposure or elevated temperatures. Thus, this feature is particularly useful for applications in optical memories and data storage (76). Recent effort in this area has been focused on obtaining different color states by introducing suitable functional groups that can either increase or decrease the conjugation length, and thus tune the HOMO-LUMO gap of the molecules (77). Irie et al. (10) reported that the diarylethenes can have a switching time on a picosecond scale and a durability over 10,000 cycles. Reviews that focus primarily on organic photochromic systems can be found elsewhere (10, 78–80).

Metal Oxides

Many electrochromic transition metal oxides, including MoO_3, WO_3, V_2O_5, Nb_2O_5, ZnO, and TiO_2, can also exhibit photochromism via proton-coupled electron transfer (81–84), which leads to the formation of reduced and colored metal oxides, such as a deep blue color for reduced WO_3. Bleaching occurs when the colored oxides are exposed to air or electrochemically oxidized. Some groups have used this effect to store or regenerate charge for WO_3-based electrochromic devices (85). The Mayer and Gamelin groups have also observed similar effects for TiO_2 and ZnO
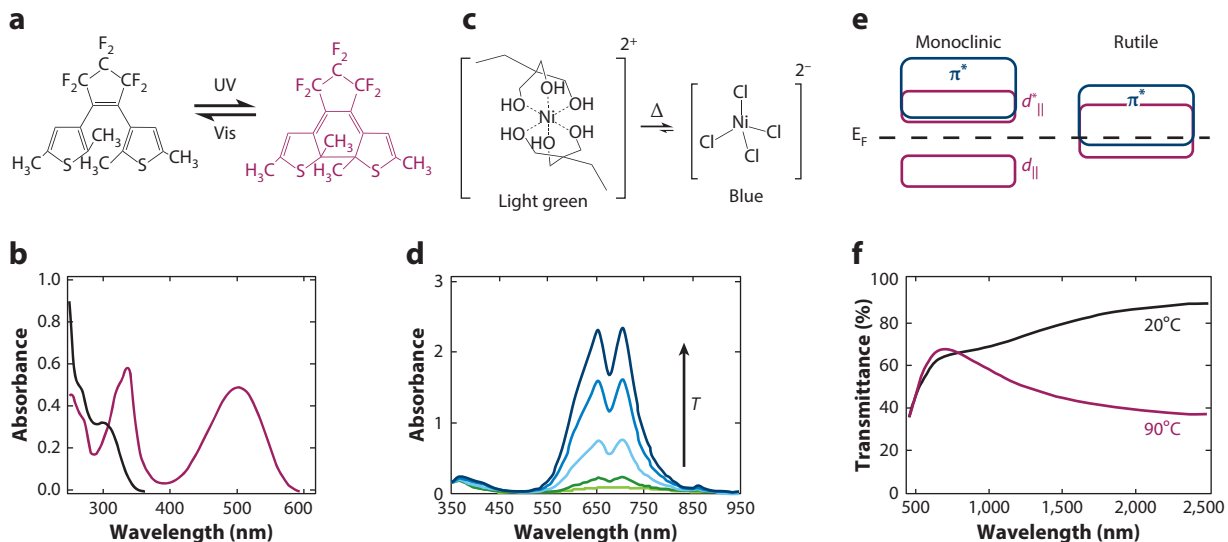
Figure 5

(*a*) Photo-induced structural transformation between two diarylethene isomers. (*b*) Absorption spectra of these two isomers. (*a,b*) Reprinted with permission from Reference 10. (*c*) Ligand-exchange thermochromism of Ni^{2+} complexes with TMOLP and chlorine ligands. (*d*) Increasing absorption with temperature as more Ni^{2+} is coordinated by chlorine (adapted from Reference 97). (*e*) Schematic illustration of electronic structure changes in the temperature-driven metal-to-insulator transition (MIT) for VO_2 (reprinted with permission from Reference 96, ©2014 American Chemical Society). (*f*) Transmittance spectra for a VO_2 film were recorded at two temperatures, one lying below and the other one above the MIT temperature (adapted with permission from Reference 98, ©2010 American Chemical Society).

nanocrystals after exposure to UV light (81, 86). In addition, a photoelectrochromic cell can be fabricated by combining a photovoltaic film (e.g., dye-sensitized TiO_2) and an electrochromic film (e.g., WO_3) (87–89). Under illumination, the photovoltaic film converts absorbed photons into electrons and holes. The former are injected into the electrochromic film and induce coloration, whereas the latter oxidize the redox shuttle in the electrolyte. Although this system can be potentially self-powered, the use of dye-sensitized electrodes lowers the transmittance of the clear state owing to the dye's absorption, which is not ideal for window applications.

Polyoxometalates (POMs), which are nanoscale transition metal oxo clusters, can in some cases accept and release electrons without major structural changes, and these charges can induce obvious color changes (90). Their photochromism has been described as an oxygen-to-metal electron transfer process, which leads to photo-reduced metal centers and a new absorption band arising from intervalence charge transfer. Based on this principle, Liu et al. (91) showed that thin films of anionic tungstate POMs embedded in cationic polyelectrolyte layers could display reversible photochromic and electrochromic properties under optical and electrochemical stimuli, respectively. Reversible photochromic switching has also been observed for molybdate and vanadate POMs (92, 93). Lately, hybrid inorganic/organic photochromic composites, consisting of POM clusters and organic functional molecules, have attracted much attention because of their potential synergy in producing new properties (92). Dessapt et al. (94) reported that hybrid composites containing anionic molybdate POMs and cationic spiropyrans exhibited a new low-energy intermolecular charge-transfer transition, which allowed drastic improvement

of the photochromic contrast. Other photochromic materials, including metal halides, metal cyanides, and metal-ligand complexes, have been reviewed elsewhere (92).

Compared with electrochromics, photochromic materials have not received much attention for use in smart windows, because they heavily rely on light intensity and cannot be user controlled (10). However, it is possible to overcome these drawbacks by using materials that have both electrochromic and photochromic behaviors, which have been observed for a variety of materials, as discussed above. Switch Materials has developed a hybrid photochromic/electrochromic film containing diarylethenes that automatically darkens when exposed to sunlight and bleaches under an applied voltage (95). This strategy opens a new avenue for using multifunctional chromogenic materials for enhanced window performance.

SWITCHABLE MATERIALS FOR THERMOCHROMICS

Introduction

Thermochromic smart windows operate in response to temperature-based stimuli, typically switching between a clear state at low temperatures and a darkened state at high temperatures. Most thermochromic materials achieve coloration by undergoing a reversible phase transition or chemical reaction that is initiated by heating above a well-defined critical temperature. A central research objective for thermochromic materials is to control the critical temperature through doping, nanostructuring, or other processing, with the goal of bringing the transition temperature close to room temperature. Secondary objectives include increasing durability and cycle life and enhancing the optical contrast between bright and dark states to maximize the modulation of solar energy.

Like photochromic devices, thermochromic smart windows cannot be user controlled. However, because thermochromic materials are self-contained, they also do not require a full-cell configuration, external wiring, or other building integration. Here we highlight the key categories of thermochromic materials: inorganic solids, polymers and small organic molecules, and coordination complexes. We also discuss some of the interesting syntheses and applications of thermochromic materials with regard to nanostructuring, composites, and devices.

Thermochromic Inorganic Solids

As reviewed by Day (99, 100), many materials based on transition metals are thermochromic owing to changes in accessible d-d transitions with a shifting Fermi level, lattice expansion, and temperature-dependent electron-phonon coupling. The ideas pioneered in the early days of thermochromic research, such as manipulating composition to tune the temperature of an abrupt phase transition, guide contemporary studies of thermochromic materials. Many of the lower oxides of vanadium, titanium, iron, and niobium have optical properties appropriate for use in windows and are thermochromic owing to first-order phase transitions (101). Vanadium dioxide (VO_2) is the most well-studied thermochromic inorganic solid and undergoes an insulator-to-metal transition (MIT) at 68°C, where it transforms from the low-temperature semiconducting (insulating) monoclinic phase to the high-temperature metallic tetragonal rutile phase (**Figure 5e**) (102). Although the exact physical mechanism responsible for the MIT is still being debated, it is clear that the structural phase transition is closely tied to an electronic transition involving correlation between electrons occupying levels derived from the vanadium 3d orbitals (96, 103, 104). Although VO_2 is an extremely popular switchable material to study for applications like optoelectronic switches and phase-change memory, it is also particularly useful for a spectrally selective smart

window, as the insulating phase is transparent, whereas the metallic phase strongly reflects IR light (**Figure 5f**) (102, 105).

In addition to the huge volume of research that attempts to understand the physical basis for the MIT in VO_2, researchers are working to solve the three main drawbacks obstructing VO_2's use in smart windows by (*a*) bringing the transition temperature closer to room temperature, (*b*) increasing the visible transparency, and (*c*) maximizing the overall modulation of solar transmittance (105). Lowering the transition temperature is usually achieved by doping VO_2 with supervalent metals such as Nb^{5+} and W^{6+}. Such dopants increase the VO_2 lattice parameter and likely inject electrons into the vanadium *d* band; both effects reduce the MIT temperature, and 2% tungsten-doped VO_2 has a transition temperature near 25°C (106). Several strategies exist to increase the visible transmittance of VO_2, including doping with Mg^{2+} to increase the bandgap (107) or using high–refractive index materials to engineer multilayer stacks (e.g., $TiO_2 | VO_2 | TiO_2$) that transmit more visible light (102).

Thermochromic Polymers and Small Molecules

Many polymeric and molecular systems exhibit thermochromism, which can be activated by processes like thermally driven reversible reactions or temperature-dependent structural rearrangements. In the first case, reversible charge transfer, bond rearrangements, or stereoisomerism in a thermochromic (macro)molecule changes its absorption spectrum and causes a color change. In the second, mesoscale structural changes in a liquid crystal or photonic crystal change the scattering properties of the device and cause it to become reflective, cloudy, or opaque.

Many of the photochromic molecules discussed above, namely spiropyrans, spirooxazines, Schiff bases, and bianthrylidenes, also display thermochromic properties. For example, bis-spiropyrans in a solvent undergo sequential ring openings at 60°C and 70°C to change from colorless to red to blue (108). Schiff bases in planar form change from yellow to orange/red based on the thermal equilibrium between the two tautomeric forms of the molecule, and thermally accessible folded and twisted stereoisomers of bianthrylidenes are yellow and green, respectively (108, 109). These types of dyes can be incorporated into hydrogels or other polymeric matrices to form composites suitable for use in smart windows (110, 111).

Many conjugated polymers, such as polythiophenes, polyacetylenes, and polysilanes, exhibit a color change owing to structural changes within polymer chains upon heating (112). At low temperatures, these polymers are planar and form well-ordered stacked sheets with high degrees of conjugation through π-π interactions, whereas at higher temperatures, individual polymer chains become twisted, and the ordering is lost with a concomitant decrease in electron conjugation length and blue shifting absorption (108, 112). Polythiophenes, for example, are red-violet at room temperature and yellow at higher temperature (108). The transition temperature of conjugated polymers is easily tuned by adding substituting groups along the backbone, which modify the steric and inter/intrachain forces that dictate polymer conformation and assembly (112). This subsection provides only a very brief overview of thermochromism in organic systems. Several comprehensive reviews exist that cover thermochromic materials and mechanisms in small molecules and polymers in greater detail (101, 113, 114).

Thermochromic metal ligand complexes change color as their coordination environment changes with temperature. This effect relies on shifting thermal equilibrium between a transition metal cation and multiple ligands or solvent molecules with different coordination numbers or geometries, where the lower-coordinate complex is typically more intensely colored and favored at higher temperature (100, 108). Thermochromic transition metal complexes are typically based on Ni^{2+}, Co^{2+}, Cu^{2+}, and Fe^{2+} chelates (115). In the low-temperature, low-absorbance

regime, the metal cation is coordinated by polydentate ligands, such as diketonates, diamines, polyols, or thioethers, to give high coordination numbers and stable chelate rings (97). In the high-temperature and strongly colored regime, the cation is coordinated by monodentate X-type anionic ligands, such as halides, cyanides, and azides, and/or monodentate L-type ligands binding through lone pairs on oxygen, nitrogen, or sulfur (97). Based on the specific ligands, solvent effects, and other considerations of coordination chemistry, this equilibrium can be tuned so that the ligand exchange and color change occur over a desired temperature range. One embodiment of this idea is based on a nickel (II) bis(trimethylopropane) [$Ni(TMOLP)_2^{2+}$] complex (**Figure 5c,d**) in thermal equilibrium with the tetrachloronickelate (II) ($NiCl_4^{2-}$) complex (97). The TMOLP ligand is tridentate, and so the first complex is six-coordinate and a light green color, whereas the monodentate chlorine ligands give the $NiCl_4^{2-}$ complex fourfold coordination and a blue color (97). Interestingly, thermochromics based on ligand exchange reactions do not have a well-defined switching temperature, but rather gradually reduce their transmittance as the temperature increases and the thermal equilibrium shifts. More detailed descriptions of coordination chemistry and thermochromism of these complexes can be found throughout the literature (97, 108, 115–117).

For window applications, the thermochromic complexes, ligands, and solvent can be dispersed in a polymer gel matrix, or moieties on the polymer itself can participate in the ligand exchange reaction. The entire composite can then be laminated between two pieces of glass to be used as a thermochromic windowpane. Pleotint is a successful smart window company based in the United States that uses thermochromic metal coordination complexes in its Suntuitive® product, a switchable laminate that can be integrated into IGUs. Smart windows manufactured with this technology modulate transmitted visible light from 60% in the bright state to approximately 5% in the darkened state with SHGCs as low as 0.11, limiting direct insolation throughout the day while allowing diffuse sunlight to enter through the cooler sides of a building not facing the sun (118).

Novel Synthesis, Processing, and Nanostructures

In addition to studying the fundamental science responsible for thermochromism, researchers are also applying new processing techniques to thermochromic devices to enhance their performance, realize the benefits associated with solution and polymer processing, and in some cases achieve new functionality. Polymer/solution processing and nanostructuring are two of the most exciting advances in thermochromic material processing. Whereas oxide thin films for thermochromics have traditionally been deposited using vapor-phase methods (e.g., sputtering), VO_2 films can now be fabricated with solution-based processes like sol-gel and polymer-assisted deposition (98, 101, 119). These techniques confer the benefits of solution processing, including decreased deposition costs, high throughput, and compatibility with complex substrate shapes, and they can further be used to generate films with unique and useful properties, like porosity. Solution processing and polymer blending are also very frequently used to create thermochromic devices from organic molecules or metal coordination complexes (97, 108), which facilitates integration of multiple chromogenic technologies into one device and the fabrication of complex structures like photonic crystals (114).

Nanostructured thermochromic materials are also under widespread investigation and may provide enhanced thermochromic performance or even entirely new types of thermochromic devices. Granqvist and coworkers (120) have used effective medium theory calculations to predict that VO_2 nanoparticles dispersed in dielectric media will display both enhanced visible transmittance and deeper thermochromic contrast. Nanostructuring may also fundamentally influence the

phase transition in VO_2; gold nanoparticles famously have depressed melting points as a result of the surface energy associated with their high surface area–to-volume ratio (121). Surface energy effects may induce phase transformations at lower (or higher) temperatures in nanocrystals of VO_2 and other thermochromic oxides. Finally, just as in electrochromics, nanocrystals that display LSPR have enabled entirely new types of thermochromic devices (113, 114). Although plasmonic nanocrystals (113) and quantum dots (122) can be made thermochromic via several mechanisms, one of the most promising techniques is to use a polymer matrix to thermally control interparticle distances. Reversible thermal expansion of a polymer matrix or gel containing plasmonic particles increases the distance between particles, leading to reduced coupling and a blue shift in the plasmonic response of the composite (114). The optical features and temperature response of the composite can easily be tuned by changing nanocrystal composition, size, and shape and the thermal properties of the polymer matrix. Based on our own interests in plasmonic-based chromophores, we are excited to see how this field progresses.

CONCLUSION AND OUTLOOK

In many ways, switchable smart windows and the materials that underlie them are a mature technology. Electrochromic, photochromic, and thermochromic materials have been known and studied for decades, often with architectural applications in mind. Several established and start-up companies, some decades old, including View, Sage, Gesimat, Gentex, ChromoGenics, EControl Glass, Pleotint, Ravenbrick, Switch Materials, Heliotrope, and Kinestral, are researching, manufacturing, and selling smart windows based on all three material strategies.

And yet smart windows have not achieved significant market penetration owing to a confluence of factors. Perhaps the most significant is cost: Smart windows are sold at a premium of $40 or more per square foot incremental cost compared with high-performance static windows but would become cost competitive in a broad range of markets only at approximately $20 premium per square foot. Indeed, the simple fact that smart windows are perceived as expensive architectural elements, along with a lack of awareness regarding durability or performance, may be limiting their adoption (123). Other end user–related considerations, such as switching time, installation complexity, and the color tone of the darkened state, surely contribute to the decision of whether or not to install smart windows (124). For an architect to select, for example, a tungsten oxide–based electrochromic window over a static low-e IGU in the construction of a new building, the smart window must meet price and performance considerations and be able to confer economic benefits through direct energy savings and enabling the use of smaller and cheaper HVAC systems to minimize cooling costs (125). However, smart windows also must switch deeply and quickly enough to mitigate glare to prevent user discomfort (126). Otherwise, additional expenses associated with installing blinds will be incurred, and building users typically do not raise and lower blinds efficiently in response to changing weather and lighting conditions, limiting the effectiveness of smart windows and increasing artificial lighting costs (127). Likewise, architects and building occupants alike can be put off by non-neutral window colors like vibrant blue or even slight yellow hues.

To be a successful technology, smart windows still need to make improvements in cost-to-performance ratio through lower-cost manufacturing processes and new functionalities or operating modes. As discussed earlier, recent developments in nanotechnology open new avenues for integrating multiple functional materials into composites and novel form factors via solution processing. In addition, several important scientific issues must be addressed in order to make significant breakthroughs in material performance. For instance, a deeper understanding of nano- and microstructure-property relationships for chromogenic materials is required to improve color neutrality, switching rate, bleached/colored state contrast, and durability. For electrochromic

windows in particular, knowledge about charge transport kinetics and chemical reactions at electrode-electrolyte interfaces is still lacking. These challenges demand more thorough theoretical and experimental investigations on materials and device engineering. Nonetheless, based on the recent advances in electrochromic, photochromic, and thermochromic materials that we have described in this review, it appears that smart window technology may finally be approaching the point of addressing these problems and achieving broader market adoption.

As a parting note, we invite the reader to consider the many recent publications using modeling and direct field testing to examine how smart window performance impacts energy use and the environment (4, 125, 127–130). Many of these studies have identified critical performance targets for chromogenic devices to reduce energy use; for example, increasing the switching speed of smart windows can confer increased energy savings, and the most effective modulation ranges and optical characteristics may be independent of climate, which would indicate that performance targets are universal (125). Another interesting field study of thermochromic windows found that efforts to reduce their transition temperature might be misplaced, as the researchers found that, based on the outdoor air temperature and incident solar radiation, a transition temperature of 60°C was appropriate (130). Likewise, a study of the energy and environmental impacts of NIR-selective electrochromic devices found that although they provided energy savings of 167 TWh/year compared with existing building stock, that savings drops to only 8 TWh/year compared with high-performance static windows combined with lighting controls (4). This underlines how important it is for electrochromic windows to achieve better performance and cost competitiveness if they are to ever enjoy widespread adoption. As academic research and technological development in this field progress, researchers and companies should leverage these advances to inform their materials and device research, performance targets, and product design.

DISCLOSURE STATEMENT

ACKNOWLEDGMENTS

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