



Review

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Nanostructured inorganic electrochromic materials for light applications

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Abstract: Electrochromism, an emerging energy conversion technology, has attracted immense interest due to its various applications including bistable displays, optical filters, variable optical attenuators, optical switches, and energy-efficient smart windows. Currently, the major drawback for the development of electrochromism is the slow switching speed, especially in inorganic electrochromic materials. The slow switching speed is mainly attributed to slow reaction kinetics of the dense inorganic electrochromic films. As such, an efficient design of nanostructured electrochromic materials is a key strategy to attain a rapid switching speed for their real-world applications. In this review article, we summarize the classifications of electrochromic materials, including inorganic materials (e.g., transition metal oxides, Prussian blue, and polyoxometalates), organic materials (e.g., polymers, covalent organic frameworks, and viologens), inorganic-organic hybrids, and plasmonic materials. We also discuss the electrochromic properties and synthesis methods for various nanostructured inorganic electrochromic materials depending on structure/morphology engineering, doping techniques, and crystal phase design. Finally, we outline the major challenges to be solved and discuss the outlooks and our perspectives for the development of high-performance nanostructured electrochromic materials.

Keywords: electrochromism; nanostructures; optical materials; plasmonics.

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1 Introduction

Electrochromism is the phenomenon where the optical transmittance or absorbance of a material changes under an applied electric potential [1]. When a voltage is applied to an electrochromic material, the optical properties of the material are altered in a reversible fashion. Owing to the optical switching behavior, electrochromic materials provide great opportunities for a variety of energy-saving and color-tuning applications, including smart windows, multicolor bistable displays, and color-tunable optical elements [2–8].

Generally, electrochromic materials can be either organic or inorganic materials [9]. Among the organic electrochromic materials, organic molecules [10], polymers [11–13], and covalent organic frameworks [14] are widely investigated. These classes of organic electrochromic materials are characterized by their rich color palette, fast response, and ease of fabrication via solution-processing [15]. However, in comparison with the inorganic electrochromic counterparts, the organic electrochromic materials exhibit inferior thermal and chemical stabilities [16, 17], thus limiting their practical use. Recently, inorganic electrochromic materials have emerged at the forefront for real-world applications and potential commercialization. This class of materials offers key advantages, such as long-term durability, wide range of working temperature, and good chemical stability [18–20]. However, despite these advantages, they suffer from the shortcoming of poor switching speed [21, 22]. This is due to the low electrical conductivity of the inorganic material, the high-volume expansion during cycling, and the slow ionic transporting efficiency within the bulk material [23–25]. Reducing the size of the material is regarded to be an efficient strategy to enhance the dynamics of the inorganic material's response and improve its switching dynamics.

In recent years, nanostructured electrochromic materials have been investigated as a means to improve the switching speed because the nanostructured surface provides numerous active sites and shortens the ion's diffusion paths [26]. Moreover, the volume expansion of nanostructured electrochromic materials during the switching process is insignificant as the numerous surface

active sites increase the capacitive contribution during the redox reactions [27]. In other words, the ionic diffusion pathways inside the nanostructured materials are greatly shortened, which, in turn, improve the electrical conductivity [28]. Within this context, a nanostructured electrochromic material is expected to attain a rapid switching speed.

Although many literature reviews focus more on multifunctional electrochromic devices [29–33], a comprehensive review of recent achievements on nanostructured electrochromic materials is still lacking. In this article, we systematically discuss recent progress on designing nanostructured inorganic materials for high-performance electrochromic applications. This article first introduces the general classification of electrochromic materials and the key metrics used in evaluating electrochromic properties. This is followed by in-depth design strategies of nanostructured inorganic electrochromic materials and correlations between the electrochromic properties and synthetic methods for different nanostructured electrochromic materials. Next, the article highlights the challenges that need to be addressed in the future design of photonic devices. Finally, the authors' perspective and outlook to stimulate the development of electrochromic technology are presented.

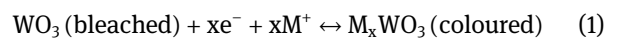
2 Classification of electrochromic materials

As the core component in an electrochromic device, electrochromic materials, having different optical properties, have been utilized for various electrochromic applications. Correspondingly, the electrochromic materials can be classified into a variety of types, including inorganic electrochromic materials, organic electrochromic materials, inorganic-organic hybrids, and plasmonic materials.

2.1 Inorganic electrochromic materials

Inorganic electrochromic materials mainly consist of the oxides of transition metals, which exhibit several different valence states on reduction. Electron delocalization between the mixed-valence states results in different bandgaps of inorganic materials, thus leading to different absorption of the light and inducing distinct color changes of the material [34]. There are two principally different types of electrochromic transition metal oxides which are classified in accordance with the coloration mechanisms: cathodic electrochromic materials, which are colored under guest ion insertion (reduction process); and anodic electrochromic materials, which are colored under guest cation extraction (oxidation process) [33]. The transition metals whose oxides possessing electrochromic properties are shown in the periodic table of elements (Figure 1).

As can be inferred from Figure 1, WO_3 , TiO_2 , Nb_2O_5 , MoO_3 , and Ta_2O_5 exhibit the cathodic coloration effect, which means that these oxides can be tinted via a reduction or cation intercalation [36–41]. These oxides commonly consist of highly distorted MO_6 octahedra crystalline structure [42, 43], where M represents the transition metal atom. The layered structure, formed by the edge- and corner-sharing MO_6 octahedra, facilitates ion transport through the conduits or chains of interstitial sites [44]. Notably, these oxides exhibit similar electronic band structures. Their intrinsically empty *d*-bands become populated on cathodic charge injection, and thus cause a color change through new intraband transitions [45, 46]. Among this class of oxides, WO_3 is the most widely studied cathodic electrochromic material, especially used for electrochromic smart windows platforms. The WO_3 layer is transparent in the oxidation state, whereas it can be tinted to blue as cations injected into the WO_3 structures via the following reaction:



ELECTROCHROMIC OXIDES:

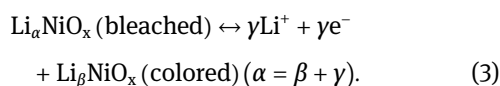
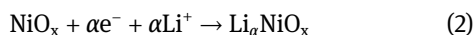
ELECTROCHROMIC OXIDES:																		
H																	He	
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																

Legend: Cathodic coloration (Blue), Anodic coloration (Red)

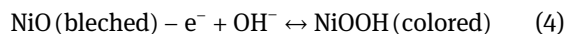
Figure 1: Electrochromic transition metal oxides showing both cathodic and anodic coloration. Reproduced with permission from Ref. [35]. Copyright 2017, Elsevier Ltd.

where M^+ can be either H^+ or an alkali metal ion, such as Li^+ , Na^+ , K^+ , Al^{3+} , or the recently reported Zn^{2+} [3]. Compared with used monovalent ions (e.g., H^+ , Li^+ , K^+ and Na^+), multivalent ions (e.g., Mg^{2+} , Al^{3+} , Zn^{2+}) are expected to provide multiple charges to accelerate the redox reactions for fast electrochromic switching times [47, 48]. Another key advantage of multivalent ions, especially the Zn^{2+} , is their compatibility with aqueous electrolytes, which facilitates the formation of newly developed Zn-based electrochromic devices [2].

On the other hand, the anodic coloration effect is observed in NiO , IrO_2 , Cr_2O_5 , MnO_2 , FeO_2 , and Co_3O_4 [49–55]. Such anodic electrochromic oxides usually serve as a counter electrode which is often used in conjunction with a cathodic electrochromic electrode in a complementary device [56, 57]. The most widely studied anodic electrochromic material is NiO , which is transparent in its reduced state and colors gray in its oxidized state [58]. The schematic reaction of NiO_x cycled in the Li^+ -ion electrolytes can be summarized as follows [59, 60]:



The irreversible reaction (i.e., Eq. 2) refers to an activation process in the initial cycling of NiO_x . The reversible reaction, represented by Eq. (3), indicates the color switching processes accompanying the ion insertion/extraction. The insertion/extraction of OH^- can also lead to the oxidation/reduction of nickel oxide owing to the transformation of nickel ions between Ni^{2+} and Ni^{3+} [61]. This process can be summarized as follows [62]:



In addition to the aforementioned cathodic and anodic electrochromic materials, vanadium oxides (e.g., V_2O_3 , V_3O_7 , and V_2O_5) are considered to be a type of bifunctional electrochromic material. This is due to their multicolor change properties under both anodically and cathodically potentials [63].

Along with the aforementioned transition metal oxides, Prussian blue (PB), represented as $(Fe_4[Fe(CN)_6]_3 \cdot nH_2O)$ and its analogs (e.g., $KFe[Fe(CN)_6]$ and $Na_2Fe[Fe(CN)_6]$) is another important type of inorganic electrochromic material. PB is a type of polynuclear transition metal hexacyanometallates. Similar to the anodic electrochromic transition metal oxides, PB exhibits a blue color in its oxidized state and can be reduced to Prussian white (colorless) via electrochemical redox reactions [64–67].

Recent investigations of PB-based electrochromic devices focused on the Zn-PB electrochromic devices because they show excellent energy retrieval functionalities [68–70]. Here, a Zn anode was used to reduce PB in a K^+ - Zn^{2+} dual-ion electrolyte and the constructed device was capable of self-bleaching via lighting an LED. Kang et al. deposited quasi-cubic PB particles with diameters of ≈ 450 nm on top of a fluorine-doped tin oxide (FTO)-coated glass substrate (Figure 2A) [68]. The Zn-PB electrochromic device achieved a high optical modulation of 84.9% at 633 nm during the voltage variation from 1.9 to 0.5 V (Figure 2B and C). This Zn-PB device also exhibited excellent cycling stability for up to 2000 cycles. Another example of the Zn-PB electrochromic device was recently reported by Li and Elezzabi [69]. Figure 2D and E depict an ideal unit cell of PB with guest ions and the working principle of Zn-PB electrochromic device. The Zn-PB electrochromic device exhibited an optical contrast of 78.6% between coloration/bleaching states (Figure 2F). Moreover, the Zn-PB electrochromic device possessed an open-circuit potential of 1.46 V (Figure 2F, inset) in the fully charged state, thus enabling self-bleaching behavior when lighting an LED. This open-circuit potential arises from the redox potential difference between the Zn foil and the PB electrode, thus providing the driving force that activates the oxidation of Zn and the reduction of the PB film. The built-in voltage allows the device to switch its color from blue to transparent while powering an LED for more than 60 min (Figure 2G). The feature of PB that stands out, in comparison with transition metal oxide-based electrochromic materials, is its fast color response that resulting from the PB's open framework structures [71, 72].

Another class of electrochromic materials that attracts recent attention are based on MXene. MXenes represent a large family of 2D transition metal carbides and nitrides which have been utilized for energy storage and various optoelectronic applications [73]. For example, titanium carbide ($Ti_3C_2T_x$) has been shown to exhibit electrochromic properties cycling in 1 M phosphoric acid polyvinyl alcohol gel electrolyte (H_3PO_4/PVA gel) [74].

2.2 Organic materials

Electrochromic characteristics are shown by a wide range of organic materials, including organic molecules [75–77] and conjugated polymers [78–87]. Typically, organic electrochromic materials offer multiple colors under different applied biases, which are highly desired

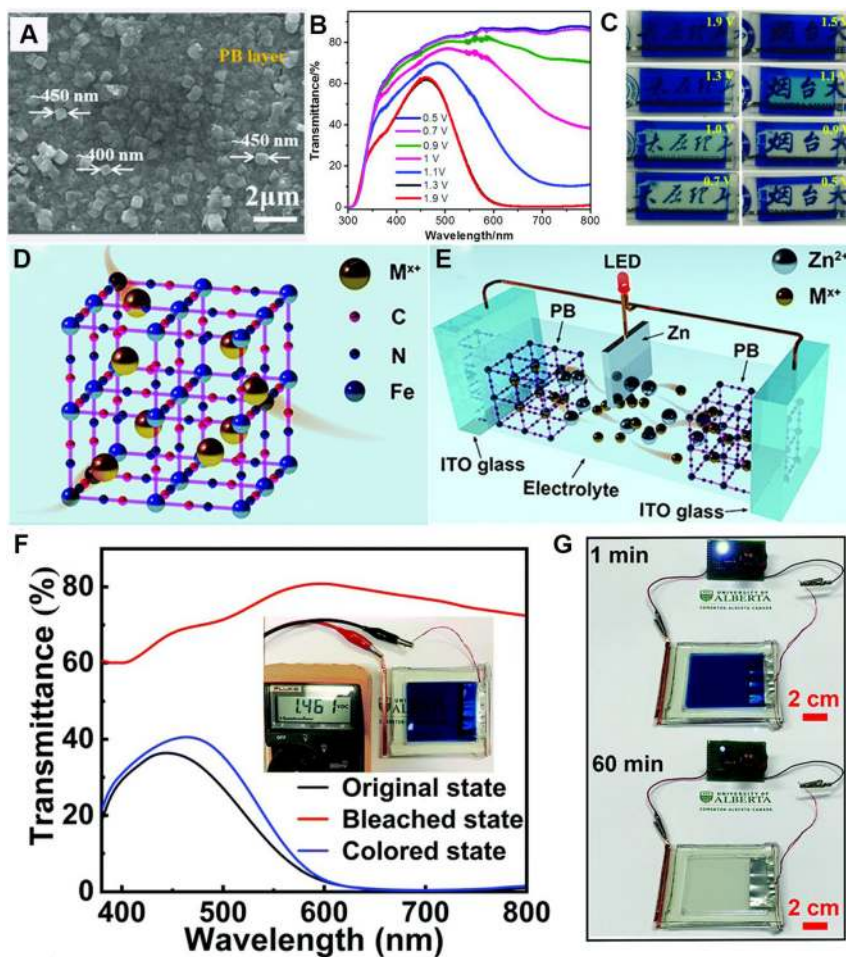


Figure 2: Structure, working principle, and application of Zn-PB electrochromic device. (A) Scanning electron microscope (SEM) image of the PB thin films. (B) Transmittance spectra of the Zn-PB device at different discharge voltages from 0.5 to 1.9 V. (C) Photographs of the Zn-PB electrochromic device at different discharge voltages. (A–C) Reproduced with permission from Ref. [68]. Copyright 2020, Wiley. (D) A schematic diagram of an ideal PB unit cell. M^{x+} represents guest cations (e.g., Li^+ , Zn^{2+} , K^+ , Al^{3+} , Na^+ and the corresponding hydrated ions). (E) A schematic of the working principle of the Zn-PB electrochromic device. (F) Visible-near infrared transmittance spectrum of the Zn-PB electrochromic device under different states. The inset shows the open-circuit voltage (OCV) of the device. (G) Photographs of a 0.5 V LED powered by the Zn-PB electrochromic device along with an obvious self-bleaching phenomenon. (D–G) Reproduced with permission from Ref. [69]. Copyright 2020, Royal Society of Chemistry.

for multicolor displays. Viologens, 1,1'-disubstituted-4,4'-bipyridinium salts, are by far the most intensively investigated small molecule-based electrochromic materials [75]. Viologens exhibit three reversible redox states: a dication (V^{2+}), a radical cation (V^+), and a neutral form (V), thus yielding differently colored species (Figure 3A). The intense color is produced upon reduction of the viologen dication, leading to a strong absorption at its radical cation state. The substitution groups on the nitrogen of the bipyridinium salt mainly control the colors of their reduction states. As illustrated in Figure 3B, an ethyl viologen-based electrochromic device exhibits a blue color in its reduced state and a light yellow color in its oxidized state [77]. The major advantages of viologens as electrochromic materials reside in their high optical contrast, excellent coloration efficiency (CE), ease in molecular design, and the feasibility for large-area assembly. A successful application is their use by Gentex Corporation as a smart window in Boeing 787 aircraft [30].

Some long-chain polymers, such as polypyrroles [78–80], polythiophenes [81–83], and polyanilines [85, 86], are found to possess electrochromic properties by altering the structures of their π -conjugated systems. Polyaniline (PANI) films exhibit reversible multicolors: transparent \leftrightarrow pale yellow \leftrightarrow green \leftrightarrow blue, as the applied potential is varied [88]. As shown in Figure 3C, PANI films can be prepared on flexible indium tin oxide (ITO)/polyethylene terephthalate substrates [86]. The optical transmission spectra of PANI films at different potentials and color states are shown in Figure 3D. The transmittance variation between colorless and blue states can be as high as 49% at 630 nm as the applied potential increased from -0.2 to 1.0 V. Another interesting polymer is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (abbreviated as PEDOT:PSS). PEDOT:PSS is a conductive polymer which exhibits a blue coloration on electrochemical reduction. Figure 3E depicts a series of images of the electrochromic symmetrical displays built from PEDOT:PSS films of various thickness [84]. A clear color gradient was observed with the increase of thickness in reduced (colored) state as

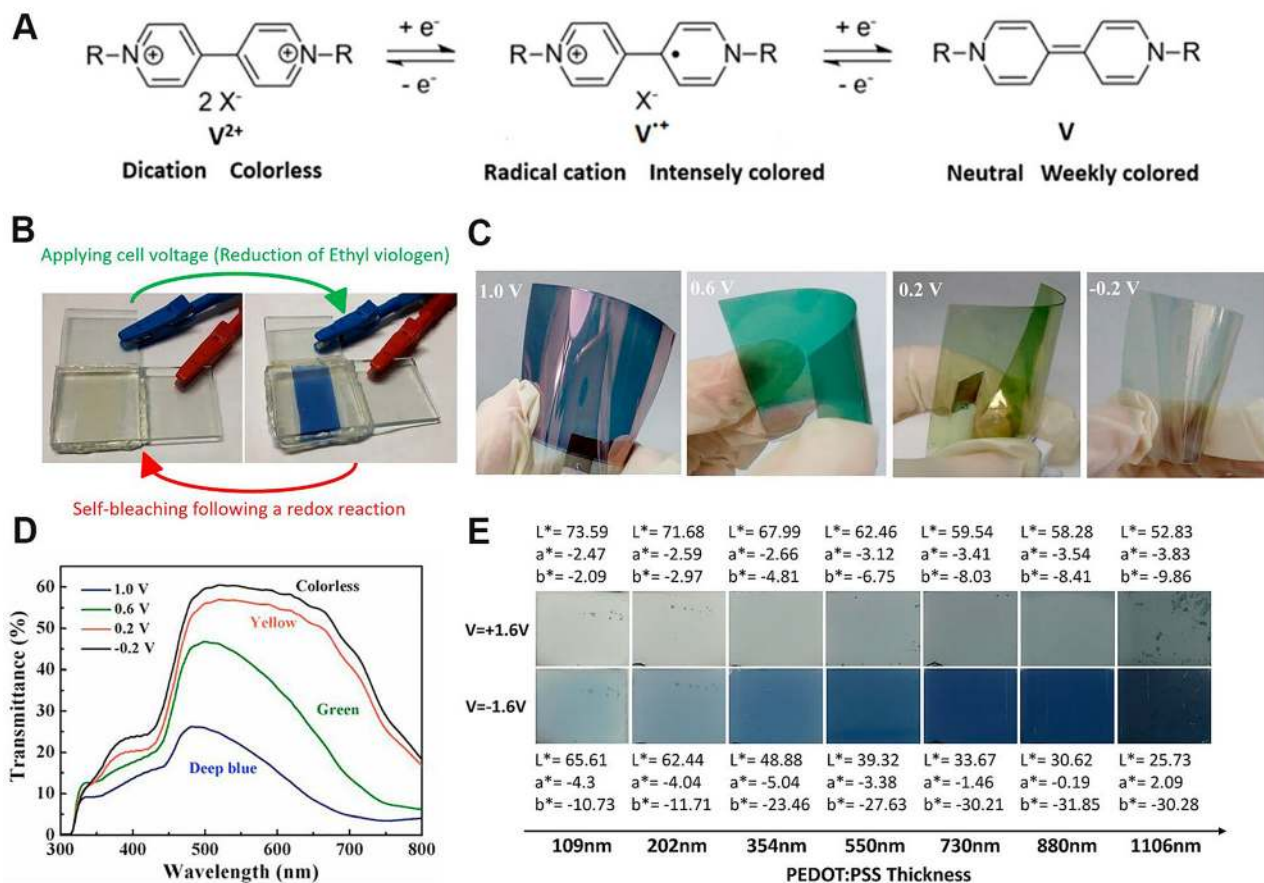


Figure 3: Characterization and demonstration of organic electrochromic materials.

(A) Different redox states of viologen. (B) The photographs of ethyl viologen-based electrochromic device at bleached and colored states. (A–B) Reproduced with permission from Ref. [75]. Copyright 2019, Multidisciplinary Digital Publishing Institute. (C) The photographs of the flexible polyaniline (PANI) film electrode in its colored state at the different potentials. (D) The corresponding optical transmittance spectra of the flexible PANI film electrode at different potentials. (C–D) Reproduced with permission from Ref. [86]. Copyright 2018, Elsevier Ltd. (E) Photographs of the electrochromic symmetrical displays built from PEDOT:PSS films with different thicknesses, showing an oxidized state for a potential of +1.6 V and a reduced (colored) state for a potential of –1.6 V. The corresponding measured CIE $L^*a^*b^*$ parameters are labeled. Reproduced with permission from Ref. [84]. Copyright 2019, Multidisciplinary Digital Publishing Institute.

distinguished by the CIE $L^*a^*b^*$ color space parameters. Clearly, utilizing PEDOT:PSS as a transparent conducting electrode is promising in applications requiring a stretchable electrochromic platform [89, 90].

2.3 Inorganic–organic hybrids

Different electrochromic materials have their respective advantages and disadvantages, thus instead of using a single class of electrochromic materials, organic–inorganic electrochromic hybrids can combine the advantages of each platform, thus offering enhanced electrochromic properties. Considerable efforts have been devoted toward the development of organic–inorganic electrochromic nanocomposites, wherein the assembly of the organic

polymers into an inorganic porous framework is shown to lead to enhanced electrochromic performance and chemical stability [91–93]. For example, the organic polymers PEDOT:PSS can also be introduced into porous nanorod layers of tungsten molybdenum oxide ($W_{0.71}Mo_{0.29}O_3$) [92]. Figure 4A and B schematically illustrate the spray layer-by-layer assembly process used to prepare the $W_{0.71}Mo_{0.29}O_3$ /PEDOT:PSS hybrid electrochromic films. The PEDOT:PSS chains were observed to permeate into the porous nanorod layers of the $W_{0.71}Mo_{0.29}O_3$, forming an interconnected conductive network (Figure 4C and D). The $W_{0.71}Mo_{0.29}O_3$ /PEDOT:PSS hybrid electrochromic films realized an improved electrochromic performance that is superior to both pure PEDOT:PSS and $W_{0.71}Mo_{0.29}O_3$ films. In the organic–inorganic nanocomposites, the interfacial interactions between the organic and the inorganic phases

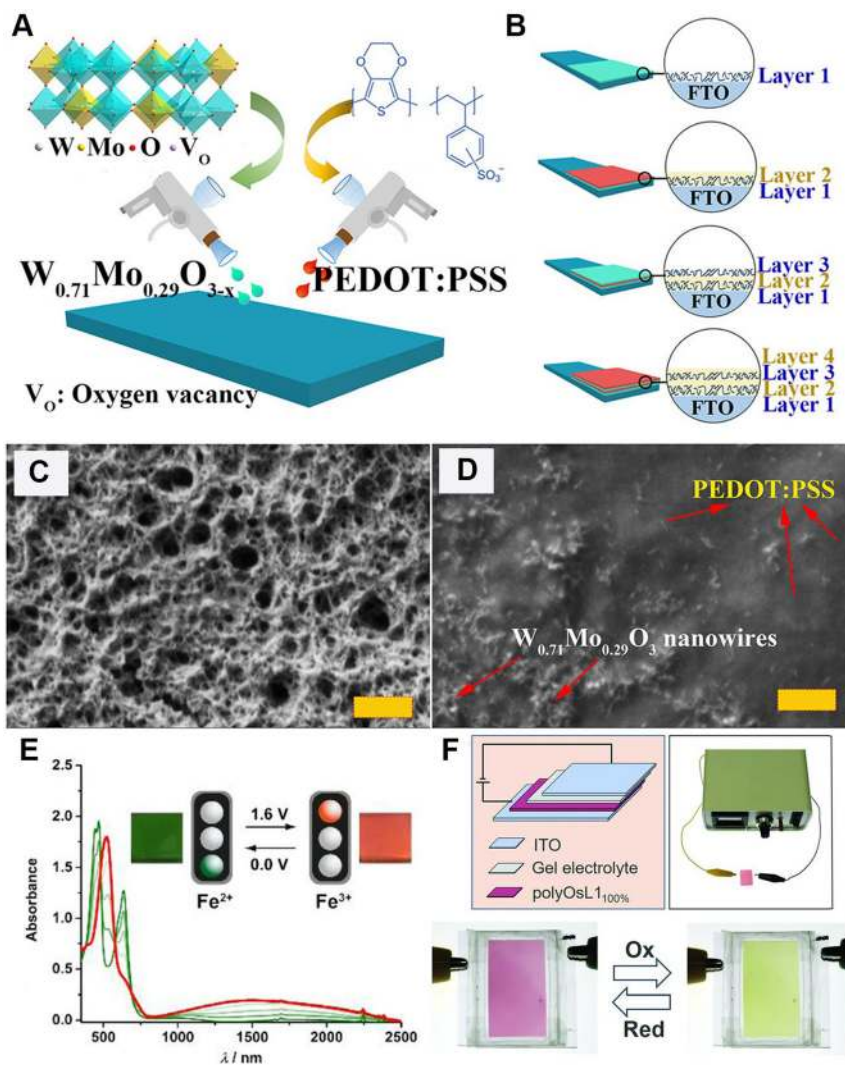


Figure 4: Preparation and characterization of organic-inorganic hybrid films.

(A) Schematic illustration of the spray layer-by-layer assembly process used to prepare the $W_{0.71}Mo_{0.29}O_3$ /PEDOT:PSS hybrid electrochromic films. (B) Schematic illustration of the evolution of the $W_{0.71}Mo_{0.29}O_3$ /PEDOT:PSS hybrid electrochromic films during the initial four cycles. Layers 1 and 3 depict the porous structure of $W_{0.71}Mo_{0.29}O_3$ material, whereas Layers 2 and 4 depict the PEDOT:PSS material. (C) Field emission scanning electron microscope (FESEM) image of the spray-coated pure $W_{0.71}Mo_{0.29}O_3$ films (D) FESEM image of the spray-coated $W_{0.71}Mo_{0.29}O_3$ /PEDOT:PSS hybrid films (A–D) Reproduced with permission from Ref. [92]. Copyright 2018, American Chemical Society. (E) Optical absorbance of FeL2-MEPES at different potentials with the corresponding photographs of the thin films. Reproduced with permission from Ref. [104]. Copyright 2017, American Chemical Society. (F) Schematic illustration of linear Os^{II}-based MEPES electrochromic device. Reproduced with permission from Ref. [105]. Copyright 2018, Wiley.

have a large impact on the properties of the nanocomposites. A good distribution of the introduced materials within the matrix material and their strong interfacial interaction is shown to improve the mechanical and electrochromic properties of structural nanocomposites because of the synergic effect of these materials [94, 95]. A recent study demonstrated a class of hybrid electrochromic materials utilizing polythiophenes and tin-doped indium oxide nanoparticles that enabled the independently modulating visible and near-infrared light [96]. This inorganic–organic hybrid electrochromic film combines polythiophenes to modulate visible light with tin-doped indium oxide nanoparticles that modulate near-infrared light. Therefore, such hybrid materials can be operated in three distinct voltage regimes, each of which uniquely modulates visible and near-infrared light. Besides simple physical contact, the strong interfacial interactions between the organic and inorganic components (e.g., covalent bond, coordination

bond, electrostatic interaction, hydrogen bond, and π – π stacking interaction) are conducive for avoiding structural damage caused by the volume change during the switching process and thus improving the structural stability of the hybrids [97–100]. For example, Yang et al. studied covalently bonded WO_3 /polyvinylimidazole core–shell microspheres [98]. It is found that the chemical and thermal stabilities of covalently bonded WO_3 /polyvinylimidazole are higher than those of pure WO_3 nanoparticles and noncovalently bonded WO_3 /polyvinylimidazole. The covalent bond (~ 100 to 500 kJ mol^{-1}) can supply solid strength for the organic/inorganic electrochromic nanocomposites, leading to enhanced electrochemical and electrochromic performances [97].

Another important example of inorganic–organic hybrids is metallo-supramolecular polyelectrolytes (MEPES). This hybrid electrochromic material is based on the metal-to-ligand charge transfer and the intervalence charge transfer [101–103]. Through altering the metal ion center or

the surrounding organic ligands, MEPE can switch between various colors. As shown in Figure 4E, Kurth et al. reported a reversible redox behavior of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ in FeL2-MEPes device where a color-switching between the red and the green colors was demonstrated [104]. Furthermore, electrochromic performance can be observed in Os^{II} -based MEPes [105]. Figure 4F illustrates an electrochromic device using linear Os^{II} -based MEPes, where a distinct color change from yellow-green to pale-pink was observed on reduction reaction.

2.4 Nanoparticles and nanostructured plasmonic material

Plasmonic devices can experience an unconventional electrochromic process, where the color modulation of the electrochromic device is primarily based on dynamically changing the resonance of plasmonic nanostructures. Nanoparticles plasmonic materials are identified as either colloidal metal nanoparticles, which allow for reversible metal deposition, or highly doped metal oxide nanocrystals that can be electrochemically charged in a capacitive manner due to their extremely small size and high surface area [45]. Light couples to the colloidal plasmonic material via the resonant excitation of free charge carriers as localized surface plasmon resonances (LSPRs). Here, LSPR enables a wide range of spectral tunability by changing the nanocrystal size, altering the host environment, or via doping or injection of charges. When the incident electromagnetic radiation frequency matches the natural resonance frequency of collective electron oscillations in the conduction band (or holes in the valence band) of the nanocrystals (Figure 5A), light absorption and scattering of nanocrystals are notably enhanced. Although the LSPR frequency of nanocrystals is slightly tunable by their shapes, the doping level, and the nanostructure size, the free electron density plays a key role because it determines the starting position, width, and intensity of the LSPR absorption peak [106–108]. Typically, metal-based plasmonic nanostructures exhibit intrinsic free carrier density on an order of 10^{22} cm^{-3} [109], which leads to high energy electronic oscillations resulting in plasmonic resonance frequencies in the visible spectral range. Metal-based electrochromic devices have been demonstrated via reversible electrochemical deposition. Although metals lack the oxidation states necessary for an inherent electrochromism, unconventional electrochromic devices have been demonstrated through the deposition of Ag nanoparticles on an ITO electrode [110–112]. Here, the redox reaction occurs when Ag^+ ions

are reduced at the electrode and thereby agglomerate into elemental metal nanoparticles. Oppositely, an inverse charge can lead to the dissolution of Ag nanoparticles. As such, the deposition and dissolution of Ag nanoparticles are reversible, and thus leading to the reversible optical evolution. Based on the size and shape of the deposited particles, which are strongly dependent on the deposition time, bias voltage, and chemical makeup of the solvent, the resonance frequency can be modulated over a wide range. A recent study by Kobayashi et al. demonstrated a multicolor electrochromic device based on the Ag deposition mechanism [111]. Figure 5B illustrates the morphology of Ag deposited on the ITO particle-modified electrode having a diameter size of 21 nm. With the deposition of Ag on the ITO electrode, the LSPRs of Ag nanoparticles result in displaying multicolors (Figure 5C).

Highly doped metal oxide nanocrystals exhibit charge carrier densities in the range of 10^{20} – 10^{22} cm^{-3} , which leads to pronounced surface plasmon resonances in the near-infrared spectral range. The resonance of free carriers can be modulated through an electrochemical gating process [113]. The change in carrier concentration leads to a shift in the LSPR frequency and a change in absorption, giving rise to plasmonic electrochromism [45]. Even though this plasmonic electrochromism does not lead to a change in the oxidation state of the material, devices based on metal oxide plasmonic nanostructures show reversible optical transmission changes through electrochemical charge modulation. Figure 5D depicts an illustration of the capacitive nature of the plasmonic electrochromic mechanism. The modulation of the electron/hole density is electrochemically controlled by the application of negative and positive potentials to the material. Milliron et al. demonstrated a surface plasmon effect in tin-doped indium oxide (ITO) nanocrystalline film [114]. Figure 5E illustrates a transmission electron microscopy (TEM) image of the ITO nanocrystals having varying sizes of $4.1 \pm 0.6 \text{ nm}$. When different potentials are applied, the surface plasmon resonance peak of the ITO nanocrystalline film (4.1 nm diameter, 16.8% Sn) was shown to be enhanced and shifts to higher energy (Figure 5F).

In addition, conventional electrochromic materials, such as tungsten oxide or polyaniline, can be used to modulate the LSPR frequency of metallic plasmonic nanostructures. Chumanov et al. utilized a WO_3 -sol on an array of Ag nanoparticles to reversibly modulate the resonance frequency of the Ag particles by changing their dielectric surroundings [115]. Recently, several studies have shown the potential of electrochromic modulation of the dielectric environment of metallic nanostructures for a

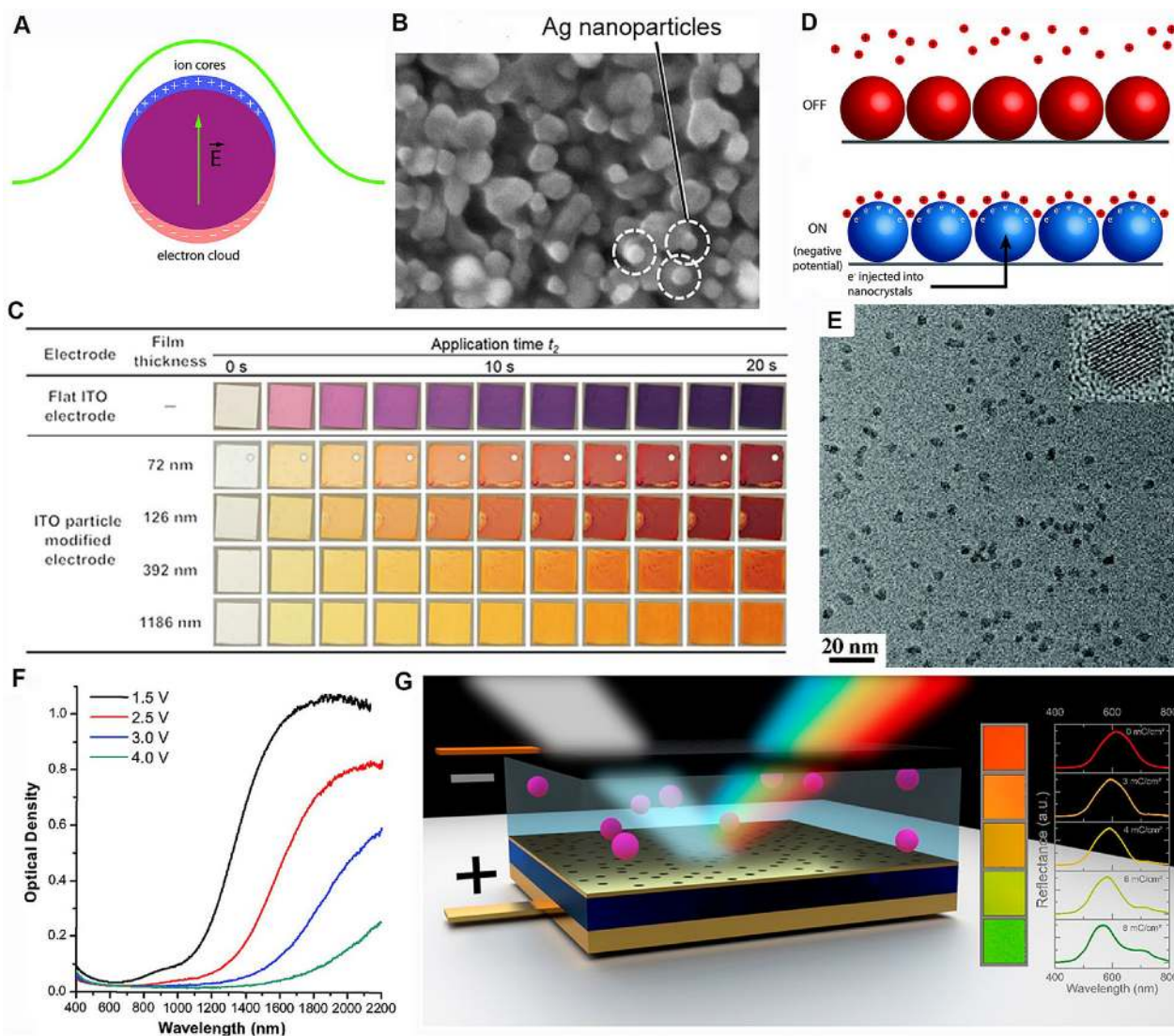


Figure 5: Depiction of plasmonic electrochromic nanocrystals and nanostructures.

(A) Illustration of a localized surface plasmon in a nanocrystal. Incident electromagnetic radiation displaces the free electron cloud, which then experiences a restoring force exerted by the positively charged ion cores. Reproduced with permission from Ref. [45]. Copyright 2014, Royal Society of Chemistry. (B) Scanning electron microscope (SEM) image of the Ag nanoparticles deposited on the ITO particle-modified electrode. (C) Photographs of the working electrodes with various ITO film thicknesses during the Ag deposition process. (B–C) Reproduced with permission from Ref. [111]. Copyright 2014, American Chemical Society. (D) The mechanism of capacitive electrochromism based on nanocrystal films. In the OFF state, a positive potential is applied to the nanocrystals, no electrons and ions gather at the surface of nanocrystals. In the ON state, a negative potential is applied to the nanocrystals, ions are absorbed to the surface of nanocrystals in order to neutralize the injected electrons. Reproduced with permission from Ref. [45]. Copyright 2014, Royal Society of Chemistry. (E) TEM image of ITO nanocrystals. (F) Potentials-dependent optical density of a film composed of 4.1 nm diameter, 16.8% Sn ITO nanocrystals. (E–F) Reproduced with permission from Ref. [114]. Copyright 2011, American Chemical Society. (G) Schematic of a plasmochromic device based on an electrochromic WO_3 layer and a gold resonator. Reproduced with permission from Ref. [118]. Copyright 2020, American Chemical Society.

full-color generation [116–118]. In general, these devices make use of the inherent change of the refractive index of an electrochromic material during the intercalation and the deintercalation processes. This change is utilized to shift the resonance frequency of plasmonic nanostructures, such as colloids and nanohole arrays. Hopmann and

Elezzabi reported a plasmonic metal-insulator–nanohole cavity based on an electrochromic WO_3 insulator layer. Through intercalation and deintercalation of lithium ions (Li^+) into the WO_3 film, a broad peak resonance wavelength shift of 64 nm was realized, leading to distinct color reflection (Figure 5G) [118].

3 Key metrics for electrochromic materials

An electrochromic material alters its optical and electrical properties in response to an external voltage bias. A high-performance electrochromic material must possess fast color switching, reversible light modulations, high color contrast, low energy consumption, and long-term chemical and thermal stabilities. Key performance metrics are introduced and highlighted below.

3.1 Color and optical contrast

Color is an important aspect in assessing the performance of electrochromic materials as their applications rely on switching between different colors. The colorimetric analysis is usually performed based on the protocols set out by the International Commission on Illumination (CIE). The CIE 1931 xyY color space is widely used to specify color in practice. As shown in Figure 6A, an electrochromic film configured in ultracompact Fabry–Perot nanocavities displays seven distinguished colors [17]. The Fabry–Perot nanocavities utilize partially reflective tungsten metal as the current collector and the reflector layer. As the thickness of the WO_3 thin film changes, various structural colors are generated. These colors cause a remarkable shift of the CIE color coordinates (Figure 6B), forming a circular area with different tints. More interestingly, the Fabry–Perot nanocavity-type electrochromic films exhibit a large variety of multicolor states under different applied potentials (Figure 6C). Although the 163-nm-thick WO_3/W electrode produces a gradual color change from red to green at different biases (Figure 6D), the reflection spectrum displays a drastic shift from 760 to 517 nm in its peak position (Figure 6E).

The intensity difference between the colors is an important factor in determining the quality of the electrochromic coloration process. As such, the optical contrast, referring to the degree of optical change during the switching process (intensity change in transmittance [ΔT %], absorbance [ΔA %] or reflectance [ΔR %]), is another metric used in evaluating the electrochromic material performance. However, when describing the optical contrast of electrochromic materials or devices, it is customary to report this parameter at a single wavelength. This wavelength is selected to be either the wavelength at which a maximum absorbance occurs or the wavelength of maximum human visual sensitivity (i.e., 550 nm) [44]. Figure 6F depicts a WO_3 -based electrochromic device, where a 63% change in transmittance

at 633 nm was achieved at an applied voltage of -2.5 V [22]. The choice of the 633 nm wavelength used to calculate the optical contrast is dictated by the maximum absorbance observed at this wavelength. In general, the optical contrast of a material mainly depends on the thickness of the electrochromic layer [119]. As the film thickness increasing, the transmittance of both the colored and bleached states will decrease. Typically, the maximum optical contrast is reported at an attained intermediate thickness of a few hundred nanometers [120, 121]. The design of nanostructured electrochromic materials is expected to enhance the electrochromic performance (e.g., optical contrast, switching times, CE, and cycling stability) [122–124]. A recent study by Scherer et al. demonstrated that the gyroid-structured vanadium pentoxide films surpass previous inorganic electrochromic materials in all relevant parameters: the switching speed, coloration contrast, and composite CE [125].

3.2 Coloring and bleaching switching times

Switching times, also known as the response times, refer to the times required to switch between the colored/bleached and the bleached/colored states of an electrochromic material or a device. The coloration and bleaching times are defined as the time required for 90% change in the entire optical modulation [126]. As a key parameter when considering the suitability of an electrochromic device for light modulation applications, fast switching between the different color states is highly desirable. Figure 7A illustrates an Al anode-based electrochromic energy storage smart window switching between 4 V (transparent state), 2.2 V (cool state), and 1.6 V (dark state) [4]. The switching times of this device were calculated to be 71 s for bleaching and 19 s for coloration at 633 nm, and 56 s for bleaching and 18 s for coloration at 1200 nm (Figure 7B and C). Generally, the switching times of an electrochromic layer will increase as the film thickness increasing. Thicker films with a fixed porosity would lead to longer ion-transport pathways to insert into the inner active materials, which results in longer switching times [127–129]. The nanostructured electrochromic materials with large surface active area are promising for fast switching times as the active materials are easy to access for guest ions [130, 131]. For example, rapid switching times of 0.5/0.9 s for the coloration and bleaching processes were reported for nanostructured electrochromic materials: core-shell halloysite nanotube (HNT)@inherently conducting polymer nanocomposites [130]. Other Parameters, such as the electrolyte properties, counter electrode material composition, substrate sheet resistance and device size, all have a significant effect on the switching times.

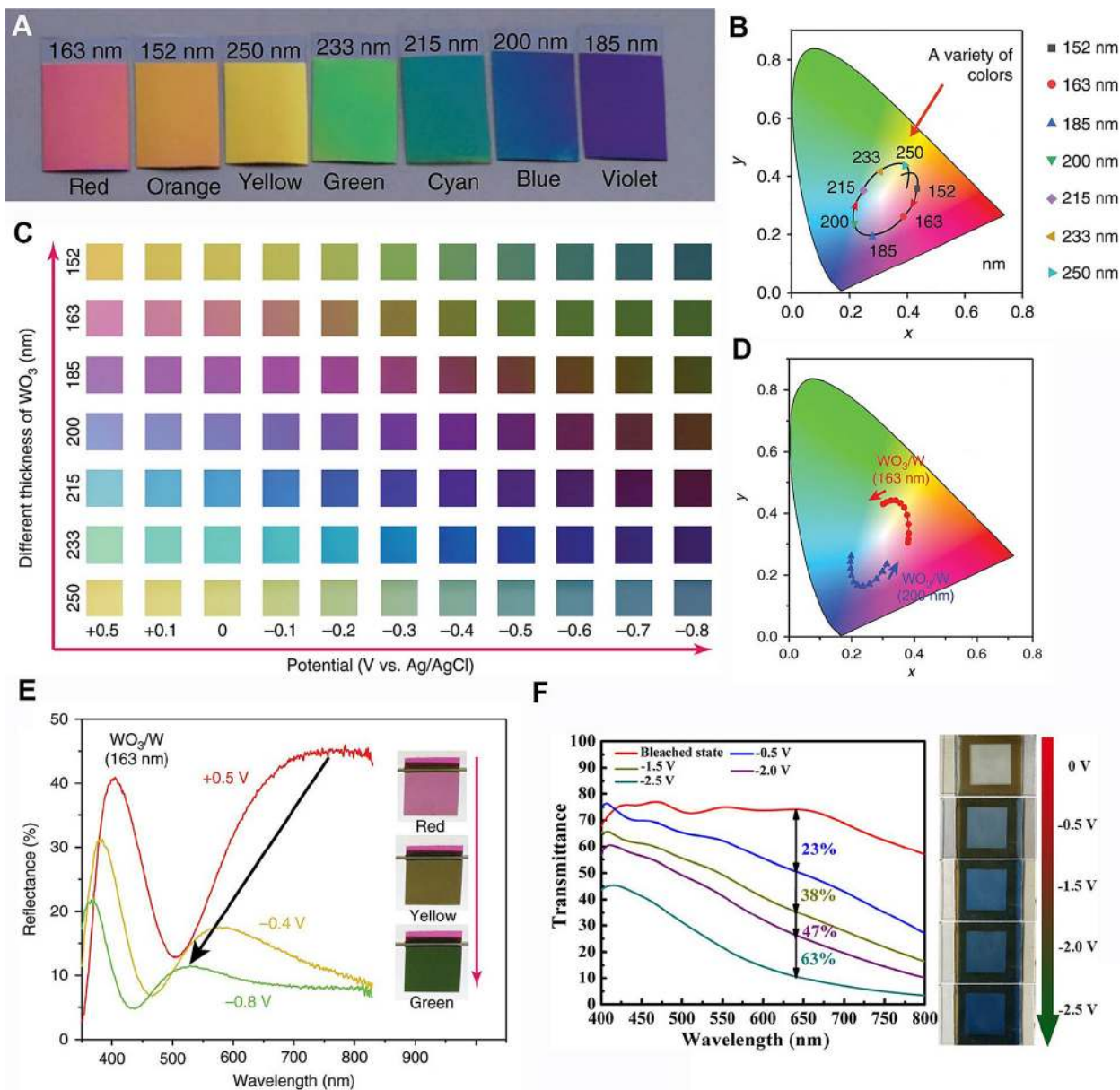


Figure 6: Demonstration of electrochromic materials having different colors and light spectra.

(A) Photographs of the WO_3/W electrodes having different thicknesses of the WO_3 layer. (B) CIE color coordinates of the WO_3/W electrodes having different thicknesses of the WO_3 layer. (C) Color gallery obtained from the WO_3/W electrodes under different voltage biases. (D) CIE color coordinates of the 163/200-nm-thick WO_3/W electrode under different voltage biases. (E) Reflectance spectra and photographs of the 163-nm-thick WO_3/W electrode under different voltage biases. (A–E) Reproduced with permission from Ref. [17]. Copyright 2020, Nature Publishing Group. (F) Transmittance spectra and photographs of $\text{MoO}_{2+x}\text{-WO}_3$ electrochromic device. Reproduced with permission from Ref. [22]. Copyright 2019, American Chemical Society.

3.3 Coloration efficiency

An energy-efficient electrochromic material requires a high optical contrast while consuming fewer charges in the process. In this regard, CE, representing the change in optical density (ΔOD) per unit of charge intercalated into

the electrochromic layer, is proposed to evaluate the energy-related efficiency accordingly,

$$\Delta\text{OD} = \log(T_c/T_b) = \eta Q/A, \quad (4)$$

where η is CE, Q is the charge (C), A is the active area of the electrochromic material (cm^2), T_c and T_b are the

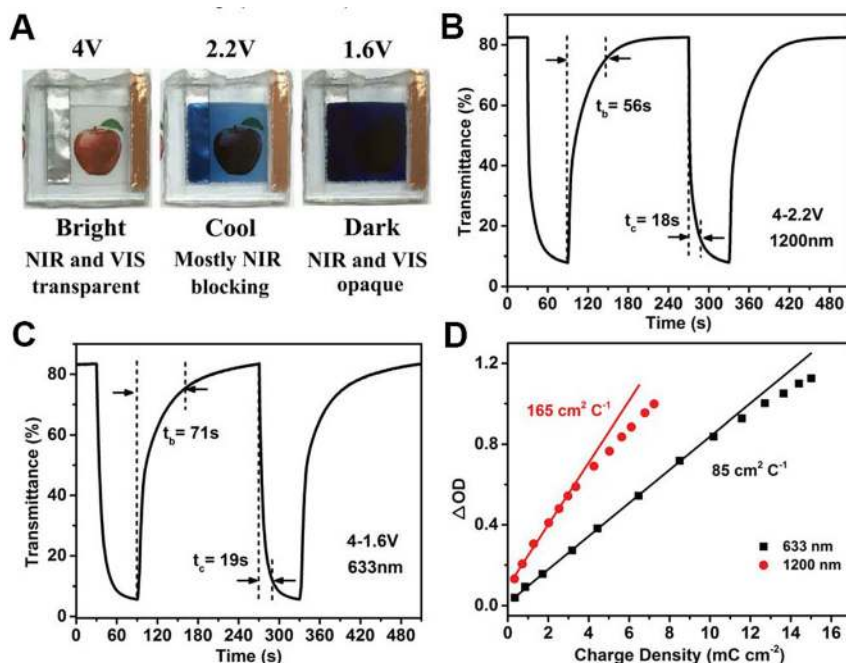


Figure 7: Al anode-based electrochromic energy storage windows.

(A) Photographs of an Al anode-based electrochromic energy storage window at different applied potentials. (B) The dynamic test of the device between 4 and 2.2 V at 1200 nm. (C) The dynamic test of the device between 4 and 1.6 V at 633 nm. (D) Coloration efficiency of the device switching at 633 and 1200 nm. (A–D) Reproduced with permission from Ref. [4]. Copyright 2019, Wiley.

transmittances of electrochromic devices at coloration and bleaching states, respectively. An example of CE value calculation is shown in Figure 7D. Here, the Al anode-based electrochromic energy storage window exhibited CE values of $165 \text{ cm}^2 \text{ C}^{-1}$ at 1200 nm and $85 \text{ cm}^2 \text{ C}^{-1}$ at 633 nm, respectively. The CE will increase as the thickness increasing till a maximum point, then the CE will decrease as the thickness keeps increasing [132, 133]. The maximum CE value is obtained at an intermediate thickness (\sim a few hundred nanometers), which requires rational design and carefully screening several thicknesses of electrochromic films. This phenomenon probably relates to the different ionic/electric resistance of the electrochromic films at various thicknesses [134]. Because the CE is an intrinsic parameter of electrochromic materials and mainly relies on the morphology of the materials [135], the design of nanostructured electrochromic materials having large surface active area is required to achieve high CE values. As reported by Ma et al., the CE value of WO_3 nanoflake films is much higher than the WO_3 nanoparticle/nanorod films [136].

3.4 Cycling stability

Cycling stability is the loss of the optical contrast on electrochemical cycling and is another important parameter used to evaluate the long-term stability of the electrochromic device [137]. For practical applications,

electrochromic materials are expected to exhibit a cycle life of more than 10^5 cycles. However, in laboratory exploration, cycling stability is often reported for a small area of electrochromic film which is not sufficient for real-world applications. Both physical and chemical stabilities are crucial to the cycling stability of an electrochromic thin film. Generally, as the electrochromic film's thickness increasing, the electrochromic film would suffer a poor adhesion to the substrate and thus leading to the significant degradation of the cycle performance due to the peeling of active materials [138]. A strong interfacial interaction between the film and the substrate will certainly enhance the cycling stability [139]. The design of nanostructures is expected to improve both physical and chemical stability of thin films. Nanostructured electrochromic materials can be designed to optimize the contacting area between the film and the substrate and hence providing a strong interfacial adhesion [140]. In addition, the volume expansion of nanostructured electrochromic materials during the switching process is supposed to be significantly eliminated as the numerous surface active sites increase the capacitive contribution during the redox reactions [141]. In other words, nanostructured electrochromic materials possess excellent chemical stability on cycling. Besides the stability of thin films, the cycling stability of an electrochromic device is influenced by several factors, including the electrolyte properties, the counter electrode material, and the device dimensions.

4 Design of nanostructured inorganic electrochromic materials

To develop electrochromic materials having high performance, including the aforementioned metrics for potential real-world applications, a list of recent achievements on the fabrication of promising inorganic electrochromic materials is presented. It is hoped that universal strategies for fabricating nanostructured inorganic electrochromic materials can be realized to advance the future development of the electrochromism.

4.1 Tungsten oxides

The most commonly used cathodic electrochromic materials are based on tungsten oxides (e.g., tungsten oxide, hydrated tungsten oxide, and doped tungsten oxide). Naturally, bulk tungsten oxide exhibits intrinsic oxygen deficiencies [142], making the material appear yellowish. By contrast, in a thin-film configuration, stoichiometric tungsten oxide is transparent and becomes blue on applying a cathodic potential [143]. Tungsten oxide has a nearly cubic structure formed by WO_6 octahedra that share corners [144]. The void space inside the cubes provides the accessibility of numerous interstitial sites where guest ions (e.g., protons or alkali cations) can be inserted. The first study on the electrochromic effect in tungsten trioxide was reported in 1969 [145]. Over the past decades, the most promising application of the WO_3 electrochromic coating is as a switchable glazing for smart windows. The color change in WO_3 electrochromic smart windows offers an important energy-efficient module for designing environmentally friendly buildings by reducing the cost of air conditioning, controlling direct sun illumination, and simultaneously improving the indoor living comfort for the occupants [25].

Recently, nanostructured WO_3 films have been realized for practical applications because of their excellent electrochromic performance. A variety of crystallographic and morphological structures of WO_3 films have been reported to exhibit shorter switching time, higher coloration efficiencies, and higher cycling stabilities compared with their bulk counterparts. The nanostructured WO_3 , including nanoparticles [62, 146], nanowires [147], nanosheets [148], nanofibers [149], and hierarchical structures [150], possess a large interfacial contact area with the electrolyte, short ions diffusion pathway, and good structure stability associated with

the intercalation/deintercalation of guest ions. These advantages of nanostructured WO_3 give rise to highly efficient and stable electrochromic performance. Shan et al. reported the first demonstration of tungsten oxide quantum dots (QDs) for electrochromic applications [151]. As shown in Figure 8A, because the QDs size is very small (~ 1.6 nm), this yielded a fast electron/ion transport during the coloration/bleaching process. Similarly, Yao et al. reported WO_3 QDs with an average diameter of 1.2 nm (Figure 8B) [152]. The cycle stability of WO_3 QDs electrochromic films can reach 20,000 cycles on the intercalation/deintercalation of Al^{3+} . Moreover, larger WO_3 QD nanocrystals and their inks (~ 4 nm in diameter, Figure 8C and D) were investigated by Zhang et al. for inkjet-printed flexible electrochromic devices [146]. The printed tungsten oxide thin films are assembled into a novel Zn-based electrochromic pseudocapacitive device, which exhibits a relatively high capacity (≈ 260 C g^{-1} at 1 A g^{-1}). In addition to the aforementioned QD WO_3 nanocrystalline structures, Zhang et al. reported oxygen-deficient monoclinic tungsten oxide nanowire (m- WO_{3-x} NW) (Figure 8E and F). With efficient Al^{3+} intercalation/deintercalation, the m- WO_{3-x} NWs-based electrochromic device delivered not only efficient and independent control of near-infrared and visible light transmittance but also exhibited high CE [47]. High optical contrast of 93.2%, high CE of 121 $\text{cm}^2 \text{C}^{-1}$, fast switching times of 16/13 s, and good cycling stability (5.5% capacity loss after 2000 cycles) were reported. An interesting form of nanostructured WO_3 films is the hierarchical nest-like $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ film (Figure 8G). Li et al. reported a self-seeded hydrothermal process that eliminates the grain boundaries existing in the nanocrystalline seed layer [153]. This process accelerates electron transport to the FTO glass substrate and promotes electron transfer efficiency. As shown in Figure 8H, the prepared $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ films have an optical contrast of 40.8 and 57.6% after applying voltages of -0.5 and -1.0 V, respectively. The response times of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ films are found to be 26 and 5.5 s under ± 3.0 V bias. Owing to the large active surface area, this self-seeded film also exhibits a high CE value of 126.34 $\text{cm}^2 \text{C}^{-1}$.

Doping WO_3 with other elements has been realized as an efficient method to tune the nanostructures of WO_3 [56]. Li et al. reported that the molybdenum doping of WO_3 significantly reduces the particle size of the WO_3 . The solution-based fabrication process was simple and inexpensive to allow for large-scale fabrication of electrochromic films [126]. Furthermore, a slight increase of the Ni content (from 0 to 2.5%) alters the surface morphology of the WO_3 film (Figure 8I–L) [56]. For the undoped WO_3 film (Figure 8I), the SEM image shows a porous network structure. Whereas by doping the film with only 0.5% Ni, the Ni- WO_3 grows into vertically aligned nanorod array

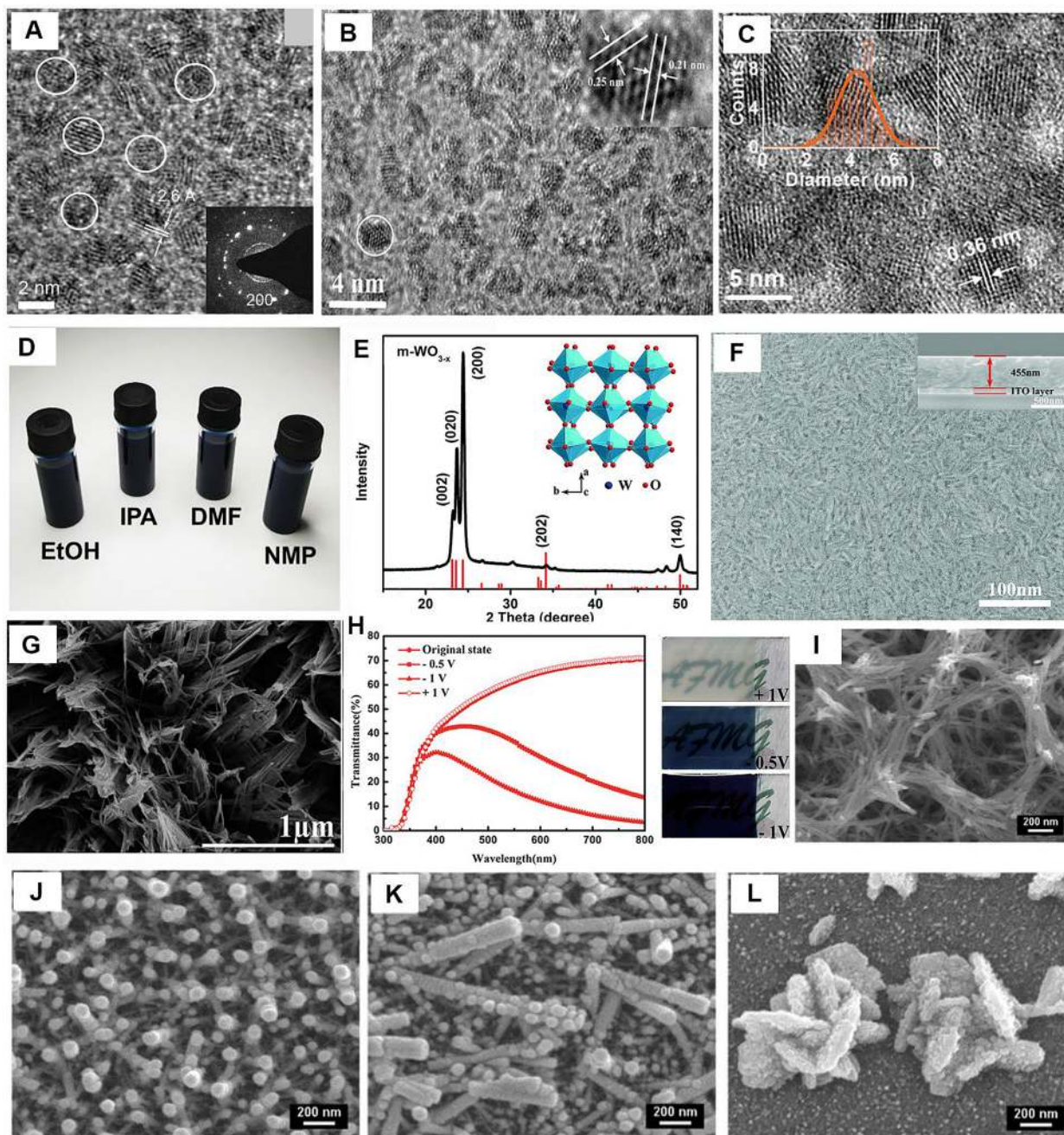


Figure 8: Structure and characterization of WO_3 -based electrochromic films.

(A) Transmission electron microscopy (TEM) image of tungsten oxide quantum dots (QDs) with average sizes of 1.6 nm. Reproduced with permission from Ref. [151]. Copyright 2014, Wiley. (B) High-resolution TEM image of as-prepared tungsten oxide QDs. Reproduced with permission from Ref. [152]. Copyright 2020, Elsevier. (C) TEM image of WO_{3-x} nanocrystals. Inset shows the nanocrystals diameter statistics. (D) WO_{3-x} inks based on four different solvents. (C–D) Reproduced with permission from Ref. [146]. Copyright 2020, Wiley. (E) XRD patterns and crystal structure (inset) of $m\text{-WO}_{3-x}$ NWs. (F) Surface and cross-sectional (inset) SEM images of $m\text{-WO}_{3-x}$ NW films. (E–F) Reproduced with permission from Ref. [47]. Copyright 2018, Royal Society of Chemistry. (G) Scanning electron microscope (SEM) image of self-seeded grown $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ electrode with less amount of ethylene glycol. (H) Optical transmittance spectra and photographs of the self-seeded grown $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ film measured at different biases. (G–H) Reproduced with permission from Ref. [153]. Copyright 2014, Royal Society of Chemistry. FESEM images of WO_3 films doped with different Ni content: (I) 0%, (J) 0.5%, (K) 1.5% and (L) 2.5%. (I–L) Reproduced with permission from Ref. [56]. Copyright 2016, Royal Society of Chemistry.

structures (Figure 8J). As the doping concentration of Ni is increased to 1.5%, the nanorods become randomly distributed nanorods (Figure 8K). Once the Ni doping content was increased to 2.5%, nanorods disappeared and nanoflowers composed of clusters of nanoplates appear (Figure 8L). For the WO_3 films with 0–1.5% Ni doping, the electrochromic performance is found to be enhanced with the increase of Ni concentration. The optical contrast in both the visible and near-infrared region increases with increasing Ni doping. At a light wavelength of 600 nm, the optical contrast enhanced from 50.9 to 86.0% at 0 and 1.5% Ni concentrations, respectively. Similarly, the CE is also higher at $60.5 \text{ cm}^2 \text{ C}^{-1}$ for 1.5% Ni content compared with $20.8 \text{ cm}^2 \text{ C}^{-1}$ for the undoped WO_3 film. Notably, other doping techniques with different elements, such as Nb [154], Mo [155], Fe [156], and Ti [157], were shown to greatly improve the electrochromic performance of WO_3 films. The most efficient strategy to develop the high-performance electrochromic WO_3 films is the doping method [158], which requires further investigation from the community. To distinguish the electrochromic properties of different nanostructured WO_3 , Table 1 summarizes and compares the key electrochromic metrics.

4.2 Molybdenum oxides

Similar to tungsten oxides, molybdenum oxides (e.g., molybdenum oxide, hydrated molybdenum oxide, and doped molybdenum oxide) are transparent in their oxidized state and become colored gray-blue on reduction. The layered crystalline structure of MoO_3 allows it to exist in a quasi-two-dimensional state [159]. The ion intercalation capabilities, bandgap tunability, and various oxidation states allow MoO_3 to be a promising electrochromic material [160]. Naturally, MoO_3 exists in three phases: orthorhombic $\alpha\text{-MoO}_3$, monoclinic $\beta\text{-MoO}_3$, and hexagonal $h\text{-MoO}_3$ [161]. The orthorhombic $\alpha\text{-MoO}_3$ is the most stable phase of MoO_3 . This phase is constituted by MoO_6 octahedra that share edges and corners. The structure's unique layers parallel to the (010) plane provide open channels for guest ion intercalation (Figure 9A and B). However, molybdenum oxides suffer inferior cycling stability due to the large-volume expansion during the intercalation/deintercalation processes. As such, nanostructured molybdenum oxides in the form of nanoparticles [25], nanobelts [161], and nanosheets [162] have been shown to have improved electrochromic and electrochemical performances. Xie et al. reported on the fabrication of metastable hexagonal

Table 1: Summary of the electrochromic properties of nanostructured WO_3 with different morphologies.

Ref.	Nanostructures	Optical contrast (ΔT)	Switching time (s)	Coloration efficiency ($\text{cm}^2 \text{ C}^{-1}$)	Cycling numbers
Yao et al. [152]	WO_3 Quantum dots	97.8% at 633 nm	Coloration: 4.5 Bleaching: 4	76.8	20,000
Cong et al. [151]	WO_3 Quantum dots	94% at 633 nm	Coloration: 0.9 Bleaching: 1.0	154	50
Zhang et al. [146]	WO_{3-x} nanocrystals	76% at 633 nm	Coloration: 4.5 Bleaching: 3.7	97.7	1000
Zhang et al. [47]	m- WO_{3-x} nanowires	93.2% at 633 nm	Coloration: 16 Bleaching: 13	121	2000
Azam et al. [148]	WO_3 nanosheets	62.6% at 700 nm	Coloration: 10.7 Bleaching: 6.9	–	1000
Adhikari et al. [149]	WO_3 Nanofibers	43% at 550 nm	Coloration: 6.5 Bleaching: 4.0	63.15	500
Li et al. [150]	WO_3 Nanotrees	74.7% at 630 nm	Coloration: 7.3 Bleaching: 2.6	75.35	250
Li et al. [153]	$\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ Nanonests	57.6% at 633 nm	Coloration: 26 Bleaching: 5.5	126.34	1000
Zhou et al. [56]	Ni-doped WO_3 Nanorods	86% at 600 nm	Coloration: 19 Bleaching: 6.2	60.5	5500
Zhan et al. [157]	Ti-doped WO_3 Nanoplates	67.6% at 633 nm	Coloration: ~15 Bleaching: ~5	106.6	3000
Li et al. [126]	$\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_{3-x}$ nanoparticles	42.9% at 633 nm	Coloration: 10 Bleaching: 7.5	36.3	2000
Li et al. [3]	Mo/Ti: WO_3 nanowires	76% at 633 nm	Coloration: 14 Bleaching: ~10	–	100

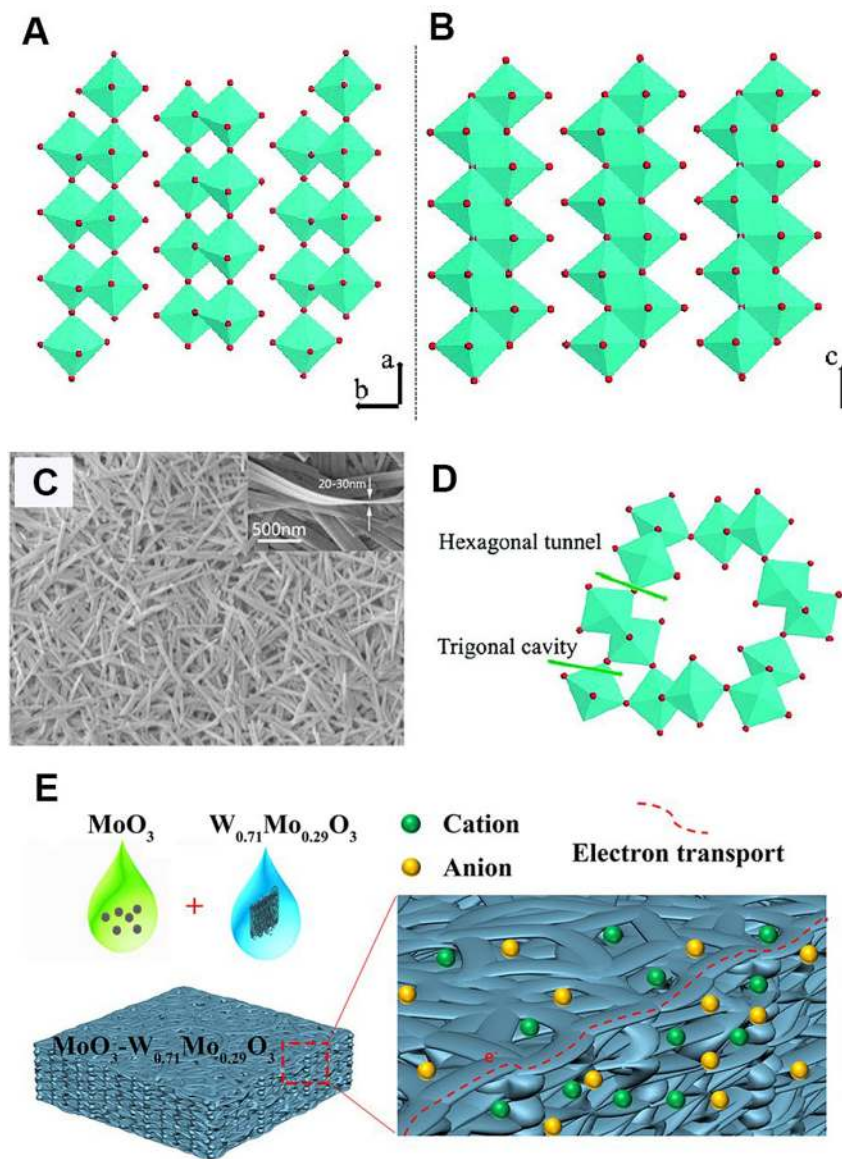


Figure 9: Structure and characterization of MoO_3 -based electrochromic films.

(A–B) Schematic representation of orthorhombic $\alpha\text{-MoO}_3$. (C) SEM image (inset is a cross-section view) of hexagonal MoO_3 nanobelts. (D) Schematic representation of possible intercalation sites in hexagonal MoO_3 . (A–D) Reproduced with permission from Ref. [161]. Copyright 2009, American Chemical Society. (E) Schematic illustration of the matrix effect of the $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$ nanowires. Reproduced with permission from Ref. [25]. Copyright 2018, Elsevier.

MoO_3 nanobelts for electrochromic device applications (Figure 9C) [161]. The open channel structure of the hexagonal MoO_3 nanobelts favors the efficient insertion of the guest ions (Figure 9D). As such, the MoO_3 nanobelt films exhibit a more stable cycling performance than orthorhombic $\alpha\text{-MoO}_3$ films. Moreover, the nanohybridization of molybdenum oxide nanoparticles with tungsten molybdenum oxide nanowires offers an interesting electrochromic material platform as it circumvents many of the issues inherent to MoO_3 (e.g., slow ionic transportation efficiency and volume expansion during cycling) [25]. Through a solution-processed method, MoO_3 nanocrystals were embedded in the nanopores of $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$ nanowire film to form a $\text{MoO}_3\text{-W}_{0.71}\text{Mo}_{0.29}\text{O}_3$ nanocomposite film (Figure 9E). The $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$ nanowires not only serve as a buffer matrix which eliminates the large-volume expansion of

MoO_3 during the intercalation/deintercalation of guest ions, but also provides numerous charge transport pathways to enhance transport kinetics. Notably, the $\text{MoO}_3\text{-W}_{0.71}\text{Mo}_{0.29}\text{O}_3$ nanohybrid films show improved cycling stability compared with the intrinsic MoO_3 films.

4.3 Titanium oxides

Titanium oxides (e.g., titanium oxide, hydrated titanium oxide, and doped titanium oxide) have been recognized as one of the most promising electrode materials for semiconductor electrochemistry [163]. Naturally, bulk titanium oxide exists in three crystalline phases: rutile, anatase, and brookite [164]. Refer to the crystal structure of titanium oxide,

the Ti^{4+} ions are surrounded by six O^{2-} ions creating an $[\text{TiO}_6]$ octahedron, forming large vacant sites to accommodate guest ions. With the intercalation of guest ions, the transmittance of titanium oxide changes from a transparent state to a blue color. However, the electrochromic performance of intrinsic TiO_2 is different from other open structures like WO_3 . A recent report by Tong et al. demonstrated that a TiO_2 mesoporous nanotube film exhibited an optical contrast of 33.5% at 700 nm, which is higher than the bulk TiO_2 films due to the enhanced Li-ion insertion kinetics [165]. Although the optical contrast is enhanced via designing nanotube structures, the electrochromic effect is still lower than other electrochromic materials. This is attributed to the intrinsic moderate electrochromic effect of pure TiO_2 [166]. As such, the aliovalent doping strategy is supposed the most convenient method to attain superior electrochromic effect of TiO_2 -based electrochromic materials [167]. Hence, the focus of titanium oxide research has been shifted toward the synthesis of nanostructured doped- TiO_2 films. Recently, Cao and et al. synthesized Ta-doped TiO_2 nanocrystals [168] (Figure 10A and B). The fabricated Ta-doped TiO_2 thin films showed excellent electrochromic performance in terms of high optical contrast for both the visible and the near-infrared light spectra regions (i.e., 86.3% at 550 nm and 81.4% at 1600 nm). After 2000 cycles, the optical contrasts of Ta-doped TiO_2 thin films

slightly decreased by 1.3 and 6.7% at 550 and 1600 nm, respectively, indicating good electrochemical stability. This Ta-doped TiO_2 nanocrystal represents a promising new electrode material for smart windows applications [169].

Another dopant of TiO_2 reported by Barawi et al. [36] to enhance the electrochromic performance of TiO_2 is Nb. Four batches of Nb-doped TiO_2 nanocrystals having different doping levels (from 0 to 15% of niobium content) were used to prepare highly transparent mesoporous electrodes. As shown in Figure 10C, the 10% Nb-doped TiO_2 nanocrystals electrode exhibit the best electrochromic performance in both the visible and near-infrared light spectral regions. A dual-band (i.e., capable of independent control of visible light and near-infrared transmittance) electrochromic device was constructed using a 10% Nb-doped TiO_2 nanocrystals electrode. This dual-band electrochromic device is capable of independent control of visible light and near-infrared transmittance, showing a 67% optical contrast at 2000 nm (Figure 10D).

4.4 Vanadium oxides

By virtue of their multicolor behaviors, vanadium oxides are regarded as the most favorable inorganic materials for

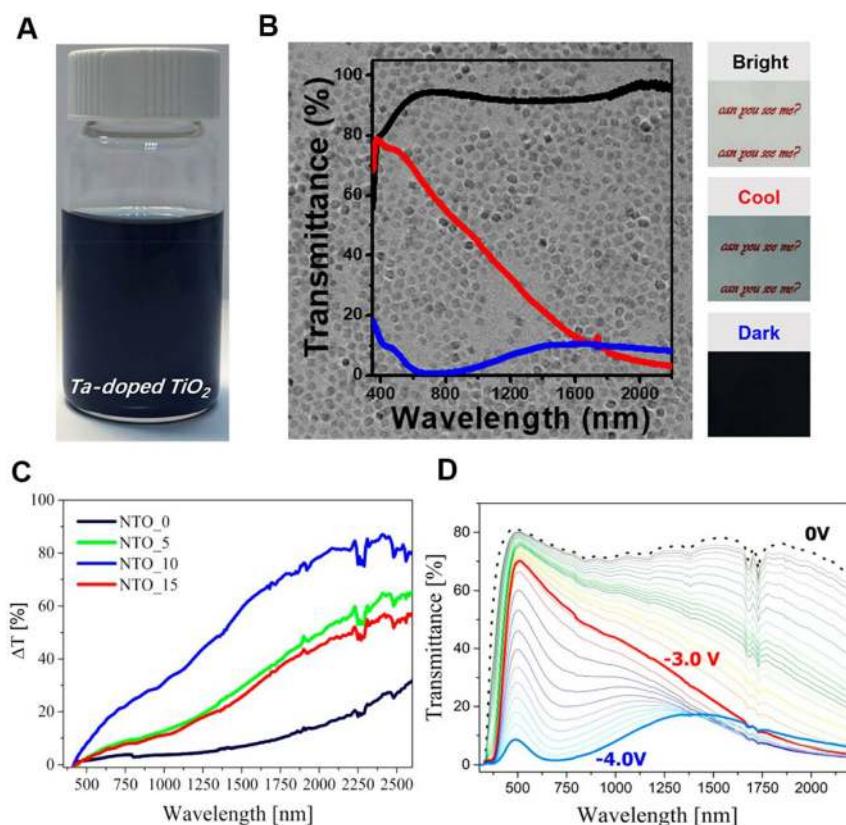


Figure 10: Structure and characterization of TiO_2 -based electrochromic films. (A) Photograph of Ta-doped TiO_2 nanocrystals dispersion in tetrachloroethylene. (B) Transmittance and corresponding photographs of Ta-doped TiO_2 thin films electrode at different states. (A–B) Reproduced with permission from Ref. [168]. Copyright 2018, American Chemical Society. (C) Spectral variation of the optical transmittance at -1.6 V for four batches of Nb-doped TiO_2 nanocrystal films with different doping levels (from 0 to 15% of niobium content). (D) Transmittance spectra of a device embodying 10% Nb-doped TiO_2 nanocrystals electrode at different bias potentials. Reproduced with permission from Ref. [36]. Copyright 2017, American Chemical Society.

electrochromic displays [125, 170, 171]. Vanadium cation exists in V^{2+} , V^{3+} , V^{4+} , and V^{5+} states in vanadium compounds, thus inducing the associated multicolor characteristics. While VO_2 is known to be a thermochromic material [172], V_2O_3 [173], V_3O_7 [174], and V_2O_5 [175] are found to have attractive electrochromic properties. The most widely investigated vanadium oxide is V_2O_5 . With the intercalation/deintercalation of guest ions, this oxide offers reversible three-color states (i.e., yellow \rightleftharpoons green \rightleftharpoons blue) [23]. However, owing to their low electrical conductivity, significant volume expansion during cycling, and the slow reaction kinetics of bulk, intrinsic unstructured vanadium oxides have not been widely used in electrochromic devices [24]. In recent years, nanostructured vanadium oxides have been studied to mediate these drawbacks because the nanostructures shorten the diffusion paths of ions and provide abundant active sites on the surface. Steiner et al. demonstrated a self-supporting double-gyroid (DG) structure of V_2O_5 (Figure 11A) [171]. The DG nanostructured V_2O_5 possessed a highly ordered structure having 11 nm wide struts and a high specific surface-to-bulk volume ratio of $161.4 \mu\text{m}^{-1}$, leading to a fast and efficient lithium-ion intercalation/extraction process. The assembled electrochromic supercapacitor based on two opposite DG nanostructured V_2O_5 electrodes is shown in Figure 11B, and its three-color displays (i.e., yellow, green, and blue) are presented in Figure 11C.

Extending the color palette for electrochromic devices is one of the major technological challenges in the field [5]. In 2020, Zhang et al. reported a transparent multicolor display enabled by Zn-based electrochromic devices [16]. The authors developed a method for synthesizing $\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$ (SVO) nanorods as an electrochromic material. The hydrated sodium ions, inserted between the V_3O_8 layers, act as pillars to stabilize the layered structure (Figure 11D). The SVO film exhibits a reversible multicolor switch (orange \rightleftharpoons yellow \rightleftharpoons green) during Zn^{2+} insertion and extraction. The presence of sodium in SVO induces the orange color. A Zn-SVO device was assembled via sandwiching a Zn frame anode and a gel electrolyte (polyvinyl alcohol– ZnSO_4) between two SVO electrodes (Figure 11E). Through the combination of two SVO electrode segments, the color overlay effect broadened the resultant color palettes of the Zn-SVO display. Figure 11F illustrates the color overlay effect obtained by superimposing the orange, yellow, and green colors. Because the two SVO electrode segments can be colored and bleached independently, the Zn-SVO device can display six colors (i.e., orange, amber, yellow, brown, chartreuse, and green) (Figure 11G).

4.5 Nickel oxides

As typical anodic electrochromic materials, serving as complementary material to tungsten oxides when assembling a device, nickel oxides (e.g., nickel oxide, hydrated nickel oxide, and doped nickel oxide) are known for their high coloration efficiency and optical contrast [59]. In contrast to the cathodic electrochromic materials such as WO_3 , the colored state of NiO is caused by electrochemical oxidation, with anion insertion (OH^-) or cation extraction (Li^+) [58]. On the other hand, the NiO films become bleached by electrochemical reduction. The NiO film exhibits a reversible color change that switches between brown color and transparent state [176]. Similar to other intrinsic oxide electrochromic materials, critical issues, such as slow switching speed, low color contrast, and poor cycle durability of NiO limit its practical utility in electrochromic devices [177, 178]. Enhanced electrochromic performances of NiO thin films have been recently achieved through nanostructured NiO films. Boo et al. reported a nanoporous NiO thin film fabricated by chemical bath deposition [55]. The nanoporous NiO thin films having high porosity showed excellent electrochromic properties, with a transmittance change of 77% at 550 nm and a coloration efficiency of $99.5 \text{ cm}^2 \text{ C}^{-1}$. Liou et al. described the growth of NiO nanorods via hot-filament metal-oxide vapor deposition where large-area arrays of one-dimensional NiO nanorods were grown on a conducting ITO film [179]. The NiO nanorod films showed excellent electrochromic performance, including high optical transmittance difference (60%), large diffusion coefficient ($\sim 6.33 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$), and very fast coloration and bleaching times (1.55 and 1.22 s).

An interesting platform of nanostructured NiO thin films is the one prepared by inkjet printing of NiO nanoparticles [181]. Inkjet printing is a low-cost and efficient technology for patterning and deposition of multilayered nanostructured materials on various substrates. The printed NiO film, with nine printed layers, exhibited an optical contrast of 64.2% at 550 nm and a coloration efficiency of $136.7 \text{ cm}^2 \text{ C}^{-1}$. Moreover, by doping NiO with other elements, such as Cu [182], Al [176], and Co [180], the material electrochromic performance was greatly enhanced. As shown in Figure 12A–F, with an increase in Co doping (from 0 to 3%), the thickness of the formed NiO film becomes thin and the pore diameter of the nanoflakes decreases [180]. However, nanoflake-shaped NiO films cannot form when the amount of Co doping reaches 3%. This suggests that an optimum Co doping concentration is required for electrochromic applications. In this regard, the 1% Co-doped NiO nanoflake array film exhibited an outstanding optical

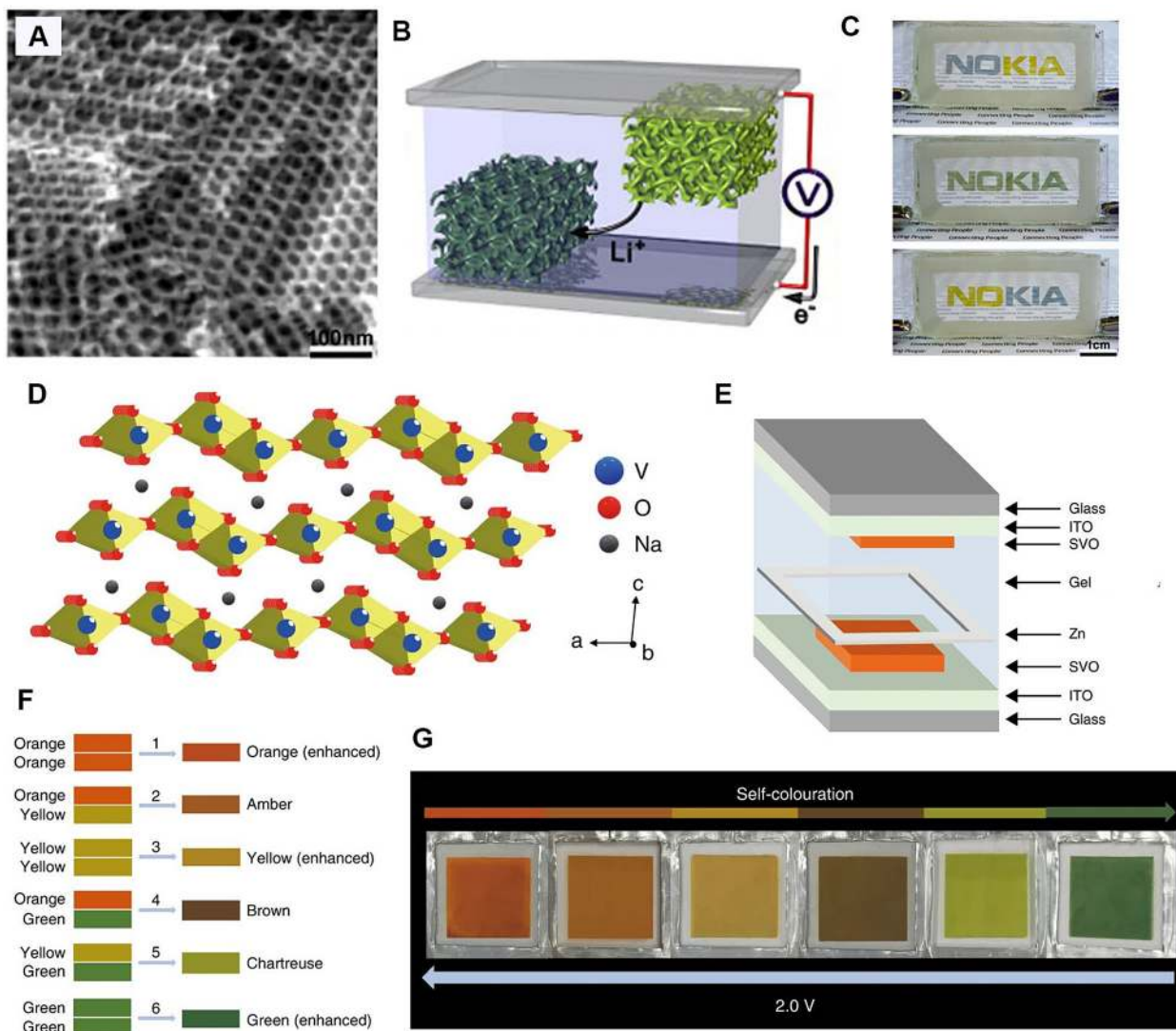


Figure 11: Structure and characterization of vanadium oxide-based electrochromic displays.

(A) Scanning electron microscope (SEM) of a mesoporous V_2O_5 double-gyroid film on an FTO substrate (B) Schematic illustration of the electrochromic supercapacitor design based on two laterally offset double-gyroid structured electrodes. (C) Photographs of an electrochromic supercapacitor device displaying color change on charge and discharge. The letters “NO” form the double-gyroid structured top electrode and “KIA” form the bottom electrode. (A–C) Reproduced with permission from Ref. [171]. Copyright 2012, American Chemical Society. (D) Crystal structure of the SVO nanorods. (E) Schematic illustration of the Zn–SVO electrochromic display. (F) Schematic illustration of the color overlay effect via the combination of orange, yellow, and green colors. (G) Digital photographs of the Zn–SVO display showing six colors obtained through the color overlay effect. Reproduced with permission from Ref. [16]. Copyright 2020, Nature Publishing Group.

contrast of 88.3% at 550 nm. Most recently, Liang et al. developed a self-templating method to build up metal-organic framework-derived hierarchical-porous carbon-embedded nickel oxide nanoparticle (NiO@C) films for high-performance electrochromism [62]. Figure 12G illustrates the preparation procedures of the hierarchical-porous NiO@C electrodes. As a result, the hierarchical-porous NiO@C electrodes with both good ion diffusion and electrical conductivity were achieved. This electrode showed a fast switching speed (0.46/0.25 s for coloring/

bleaching), high coloration efficiency ($113.5 \text{ cm}^2 \text{ C}^{-1}$), and excellent cycling stability (90.1% after 20,000 cycles).

4.6 Cobalt oxides

Cobalt oxide normally exists in three different polymorphs: CoO, Co_3O_4 , and Co_2O_3 [183]. Among them, the crystalline Co_3O_4 phase has been widely studied because of its thermodynamic stability and electrochemical properties [184].

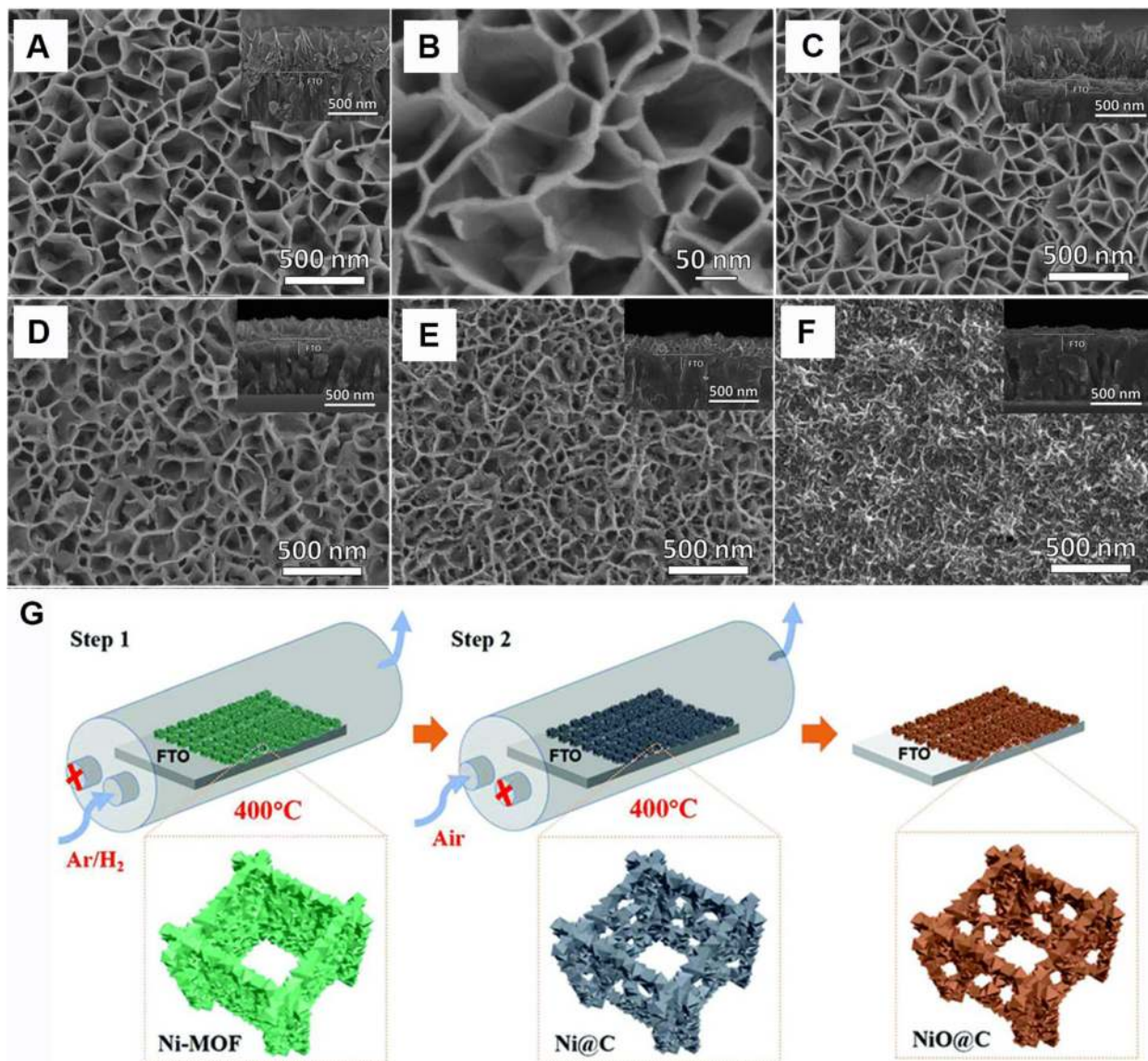


Figure 12: Characterization of NiO-based electrochromic films.

Scanning electron microscope (SEM) images of the films: (A and B) undoped NiO, (C) NiO-Co 0.3%, (D) NiO-Co 0.5%, (E) NiO-Co 1%, and (F) NiO-Co 3% (cross-sectional view is presented in the inset). Reproduced with permission from Ref. [180]. Copyright 2014, Royal Society of Chemistry. (G) Preparation procedures of the hierarchical-porous NiO@C electrode. Reproduced with permission from Ref. [62]. Copyright 2019, Royal Society of Chemistry.

Co₃O₄ exhibits a reversible color change between a yellow-brown and dark brown under potential cycling [185]. Similar to other metal oxides suffering the large-volume expansion during the coloration and bleaching processes, Co₃O₄ suffers from structural decomposition, poor stability, and cation kinetics. To minimize such shortcomings, several reports described the growth of nanostructured Co₃O₄ thin films for electrochromic applications. Xia et al. demonstrated a facile method for synthesizing ordered bowl-like Co₃O₄ arrays [186]. The as-prepared Co₃O₄ films had a hierarchical porous structure (Figure 13A) when

annealed at 200 °C, and it exhibits reversible color switchings between dark gray and pale yellow (Figure 13B). The coloration efficiency was calculated to be 29 cm² C⁻¹ at 633 nm, with an optical contrast of up to 33%. Notably, owing to the microporous structures, the bowl-like Co₃O₄ arrays are found to have good electrochemical stability.

The aforementioned strategies for developing nanostructured inorganic electrochromic materials are mainly focused on the solution process techniques. This nanofabrication process has several advantages, such as low-cost, ease of designing nanostructures, and fast switching

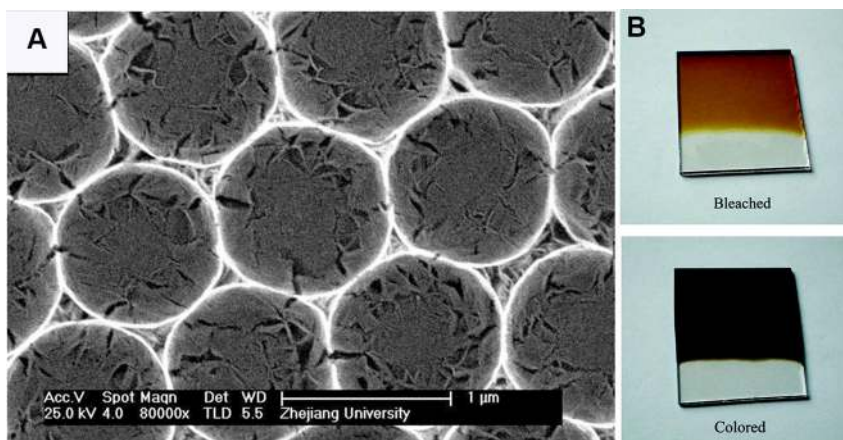


Figure 13: Characterization of Co₃O₄-based electrochromic films. (A) Scanning electron microscope (SEM) images of the Co₃O₄ film annealed at 200 °C for 1 h. (B) Photographs of the Co₃O₄ electrode with a size of 1.5 × 1.5 cm² in the colored and bleached states. Reproduced with permission from Ref. [186]. Copyright 2010, American Chemical Society.

times which allow the fabrication of electrochromic material having kinetics compared to the vacuum deposition methods. To further enhance their electrochemical stability, future research needs to be focused on the interface engineering of the solution-processed nanostructured films, via strengthening the adhesion between the nanostructural electrochromic layers and the substrates. Notwithstanding, there is still a need for innovative designs of high-performance nanostructural inorganic electrochromic films to make the electrochromic device more practical for light control applications.

5 Outlook and future challenges

This review summarizes the recent progress of nanostructured inorganic electrochromic materials, which we hope to be helpful to those scientists who have recently entered this field. The classification of common electrochromic materials is outlined as inorganic, organic, inorganic–organic hybrids, and plasmonic materials. The evaluation metrics for electrochromic materials, including color and optical contrast, coloration efficiency, switching time, and cycling stability are discussed. Electrochromic properties and synthetic methods for different nanostructured electrochromic materials are evaluated based on structure/morphology engineering, doping techniques, and crystal phase designs. Although the field of nanostructured inorganic electrochromic materials has witnessed rapid development and remarkable achievements, there are still some major challenges that hinder the high performance of electrochromic materials and their real-world applications: 1. Most of the electrochromic performance tests were conducted based on a single electrode but not a device. However, there are enormous differences between a single electrode and a device in terms of electrochromic performance. Because a device is required for

practical use, future research of electrochromism should be more focused on the assembly of an electrochromic device, especially large area devices as the size exerts a significant effect on both the switching times and color uniformity. 2. The practical use of electrochromic materials requires long-term durability favoring innovative designs of robust nanostructured inorganic electrochromic layers. As such, a better understanding of the interface engineering between the electrochromic layers and the substrates is critical to promote performance and to enhance stability. 3. The multifunctional electrochromic devices (e.g., electrochromic supercapacitors [5, 85], electrochromic batteries [2, 3], and electrochromic fibers [187, 188]) are poised for future development of novel electrochromic devices. Exploring nanostructured material functionalities will provide additional avenues for multifunctional electrochromic devices.

Such key issues illustrate the importance of understanding electrochromic materials on the nanoscale and processing compatibility of electrochromic devices on a large scale. With the recent achievement regarding the designs of nanostructured inorganic electrochromic materials, future efforts should demonstrate the electrochromic devices to meet real-world applications, such as durable smart windows, multicolor inorganic displays, and color-tunable optical devices.

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