Chapter 9 Electrochromic Smart Windows: An Energy-Efficient Technology

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9.1 Introduction

Sustainable and renewable energies have gain increased attention as people are more aware toward environment protection. While finding alternative energy to replace fossil fuels may be the ultimate solution to keep carbon footprint at minimum, the existing solution available are yet to replace fossil fuel, which is far more cost efficient (Sims et al. [2003\)](#page-17-0). But a different approach such as reducing energy consumption from our daily life can be taken instead to reduce emission of greenhouse gases. One way to achieve this is through implementation of energy-efficient technologies such as "smart windows". Smart window is one of the applications of electrochromic (EC) devices and it stand out to be the most striking and potentially most important application. This is because building with smart windows capable of varying throughput of visible light and solar energy; avoid overheating while achieve good indoor lighting conditions; reduce energy consumption for air conditioning and lighting (Granqvist [1995;](#page-15-0) Gillaspie et al. [2010](#page-15-1)).

Statistical analysis shown that global population had bloom dramatically from just 2.5 billion in 1950 to about 7.9 billion in present year (2019). The number is forecasted to continue growth and level off at a magnitude of nearly eleven billion in around year 2100 (UNDESA [2019](#page-17-1)). Change in qualities of life is happening simultaneously with the explosion of population; countries that are under

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developing have progressed in improving overall living standards of their citizens by providing various amenities. One of dire the consequences is, however, putting strain on the limited resources globally especially on energy, which is derived mainly from unsustainable resources – fossil fuels with ensuing injection of carbon dioxide into air. More carbon dioxides are released into the atmosphere when more energies are demanded; the cycle continues as population growth, causing global warming, sea level rising, and other chain reactions (Houghton et al. [1990](#page-16-0)).

From the total energy production, fossil fuels remained the dominant energy source since industrial era, albeit they are environmentally intensive and contributing to global warming. This situation is not expected to change soon without proper policy interventions and technological improvements. About 30 to 40% of worldwide primary energy has been spent in buildings for heating, cooling, lighting, etc. (Huovila [2007](#page-16-1)). Huge potential for saving tremendous amount of energy in buildings sector, however, a detailed study conducted in USA states that a large fraction of the energy delivered to buildings is wasted because of inefficient building technologies (Richter et al. [2008](#page-16-2)). Energy savings must be made without reducing the standard of living, but by utilizing more efficient technologies to provide the same or better performance.

Windows are the weak links in the buildings' energy system that frequently let in or let out too much energy, then temperature is balanced by energy guzzling of cooling or heating. Windows are very important in both architecture design and connection to outdoor. Without eliminating or making the window apertures smaller, the solution to this conundrum is implementing an energy efficient window. Clearly an energy efficient window must harmonize with nature and make good use of what nature offers in term of light and energy. To further elaborate this, sunlight is an electromagnetic radiation mainly composed of visible and infrared spectrum. An energy efficient "smart window" is capable of providing daylight to the rooms while blocking near-infrared radiation from heating (Kim et al. [2015](#page-16-3)).

Near-infrared (NIR) radiation is accounted for about half of the solar energy that is incident upon a windows but does not contribute to daylighting within a building (Runnerstrom et al. [2014\)](#page-16-4). Smart window can manipulate the amount of transmission of visible and NIR transmission separately so that to save energy from lighting and air conditioning of the buildings. Motivated by the potential for significant energy savings from reduced loads of lighting, cooling and heating, many researches have been conducted in EC smart windows that dynamically control sunlight entering a building (Deb [2008](#page-15-2); Mortimer [2011](#page-16-5)). The focus on improved energy efficiency and the development of advanced buildings drives the majority of current EC research.

In the modern society today, people are get used to the idea of building automation. Robot vacuum, dishwasher, washing machine and much more are already became part of our life. Traditionally, windows are fitted with curtains or blinds to shelter from sunlight (or heat) and provide privacy. The intuitive of energy-saving and automation lead to the development of smart window that can change from clear to dark and vice versa. To realize this, a phenomenon known as electrochromism, where the colour, transparency or other optical property of a material changes when voltage is applied, is integrated into the design of windows. In other words, electrochromism is the basis for operation of smart window that can block or unblock the sunlight with a push of a button.

Conventionally, EC smart windows are prepared by sputtering of transition metal oxide thin films as the active material (Mortimer [2011;](#page-16-5) Granqvist [2014\)](#page-16-6). Unfortunately, conventional materials suffer significant drawbacks from material degradation associated with repeated ion intercalation, and adopt dark, distinct colours in their tinted states, simultaneously blocking both visible and NIR light (Granqvist [2014](#page-16-6)). For these reasons and also the cost of expenses, conventional electrochromic windows struggled to achieve widespread adoption (Gillaspie et al. [2010\)](#page-15-1). A newly developed and fundamentally different class of EC device based on plasmonic electrochromism is designed to overcome those limitations and ultimately minimize the cost-performance ratio.

One of the unique features of plasmonic electrochromism that standout from conventional electrochromism is the ability to selectively control NIR absorption. Figure [9.1](#page-2-0) shows the plasmonic EC nanocrystal smart window operates at different states; in 'bright' state, the smart window is transparent, allowing both NIR and visible rays to pass through freely; in 'cool' state, the smart window is transparent, allowing visible lights to pass through but blocking NIR rays, providing daylight to the room while keeping away from heat; in 'dark' state, the smart window is translucent that block both NIR and visible rays. Details of spectral selectivity will be further discussed in Sect. [9.4.](#page-11-0) Figure [9.2](#page-3-0) below is the breakdown of various EC windows classes. EC performance is evaluated in terms of coloration efficiency, durability, and switching time, whereby performance of EC window depends on material structure and composition.

Fig. 9.2 Classification of various electrochromic windows

9.2 Fundamentals of Electrochromic Device Operation and Preparation

Figure [9.3](#page-4-0) presents a generic EC device coating with five superimposed layers – an active electrochromic electrode layer, an ion storage layer acts as counter electrode, an ion conductor layer separating the two electrodes, and two transparent conducting layers serve as electrical leads, on a single transparent substrate or positioned between 2 transparent substrates. This EC device structure is referred as thin film electrical battery whose charging state corresponds to a certain level of optical absorption and this is the most common geometry for EC devices (Niklasson and Granqvist [2007;](#page-16-7) Granqvist [2014](#page-16-6)). The working principles of EC devices are similar to electrochemical reaction in battery. Small ions such as protons $(H⁺)$ or lithium ions (Li⁺) are often used as charge carrier in majority of EC devices because of good ion mobility.

During off or bleached state, the cations are residing in the electrolyte and the ion storage layer. When the device is switched on, electric field is generated in between cathode and anode due to potential difference in which driven the cations to migrate from ion storage layer (anode), through the electrolyte, into the electrochromic layer (cathode). Ions insertion and extraction occur during the charge transfer contribute to the variability of the optical transmittance of EC film(s). This is because electrochromic materials are made up from transition metal oxides that consist of multiple oxidation states with different optical properties (Chernova et al. [2009;](#page-15-3) Wang et al. [2010\)](#page-17-2). Transparent conductor layers play an important role here in conducting electricity through external circuit. Indium tin oxide (ITO) is well-known for its superior optical and electrical properties and is commonly used as transparent conductor.

Fig. 9.3 Generic five-layer EC device design. Arrows indicate the movement of ions in an applied electric field (Granqvist [2014\)](#page-16-6)

In previous section, we mentioned that EC device performance is evaluated from material structure and composition which in turn determined by coating technique. Thanks to the emergence of nanotechnology, conventional inorganic EC compounds in nanostructure form opens up possibilities of enhanced properties, such as improved switching times, higher colouration efficiency, and improved stability against electrochemical cycling (Runnerstrom et al. [2014](#page-16-4)). There are numerous numbers of techniques to coat films of EC device. For example, traditional thin film preparation such as physical and chemical vapour deposition, a plethora of chemical methods (chemical bath deposition, sol-gel deposition, spin coating, Langmuir-Blodgett technique, etc.), electrochemical methods (plating, anodization) and others, and sometimes employing nanoparticles as intermediate steps as well as templating. Sputtering from physical vapour deposition is suitable for the EC films preparation because sputtering process is well understood in manufacturing. Hence, suggest that sputtering will likely be the most practical production method for smart windows in foreseeable future (Gillaspie et al. [2010](#page-15-1)). This topic mainly surrounds EC devices based on conventional materials and nanostructured of it.

On the other hand, EC device shown in Fig. [9.1](#page-2-0) utilizes plasmonic nanomaterials which enable it to absorb NIR light at same time allow visible light to pass through. Plasmonic nanoparticles that support localized surface plasmon resonances (LSPR) have been in academic pursuit over the past decade for signal transduction and efficiency in both energy and space, as well as sensitive and specific, through miniaturization to the nanoscale (Pastoriza-Santos et al. [2018](#page-16-8)). Plasmon resonance is the phenomenon of collective oscillations of charge carriers in solids. The excess charge carriers (impurity holes or electrons) in semiconductor plasmonic nanocrystals allow themselves as intense absorption bands in the NIR region of the spectrum. In contrast to metal nanocrystal, the LSPR lies in the visible region of the spectrum and able to absorb light (Litvin et al. [2018\)](#page-16-9). There are two general approaches for the preparation of nanoparticle: (1) colloidal chemistry and (2) epitaxial growth and/or nanoscale patterning through lithography-based technology (Drbohlavova et al. [2009\)](#page-15-4).

9.2.1 Electrochromic Oxides

Perhaps EC films are the most important component inside an EC device. The unique ability to change colour and thus the transmittivity, enable the applications of EC device such as smart windows. All elements that show electrochromism with their respective oxides are transition metals. In principal, EC oxides can be categorised into two kinds, one that referred as "cathodic" that colouring under ion insertion, and the other referred as "anodic" that colouring under ion extraction. Figure [9.4](#page-5-0) indicates the location of transition metals capable of forming oxides of these two particular categories, and interestingly, vanadium oxides are classified as intermediate or "hybrid" which are class of its own (Granqvist [1995](#page-15-0)). From Fig. [9.4](#page-5-0), one can clearly distinguish oxides with cathodic or anodic colouration in transition metal region because electrochromism is closely related to the electronic structure of the oxides. Electrochromism can also be found in binary and ternary mixed oxide and in oxyfluorides. Also, transition metal hexacyanometallates are non-oxide with anodic electrochromism.

Cathodic colouration is found in oxides of Ti, Nb, Mo, Ta, and W, with tungsten oxide (WO_3) being by far the most extensively studied one (Granqvist [2000](#page-15-5)). Take tungsten oxide (WO₃) as example, upon ion injection, WO₃ changes colour from a clear, transparent state to a dark blue, translucent state as tungsten ions are reduced (Granqvist [1995\)](#page-15-0). Protons or cations in the electrolyte compensate the injected electrons through insertion into WO_3 octahedral sites, as shown in Eq. [\(9.1\)](#page-6-0). The injected

1 н Hydrogen 1,008																	$\overline{2}$ He Helium
\mathbf{a} Li Lithium 6.941	Be Beryllium 9.012					Anodic colouration Cathodic colouration							6 с Carbon 12.011	N Nitrogen 14.007	8 о Oxyglen 15.999	F Fluorine 1.8.008	10 Ne Neon 20.180
11 Na Sodium 22 990	12 Mg Magnesium 24.305											13 AI Abeninser 26.982	14 Si Silicon 28.086	15 P Phosphorus	16 s Sulhar 32.066	17 CI Chilorine 35.453	18 Ar Argon 39.948
19 κ Potassium	20 Сa Calcium 40.078	21 Sc Scandium 44.956	22 Τi Titanium 47.88	23 ٧ Vanadium 50.942	24 Сr Chromina 51,996	25 Mn Manganes 54.938	26 Fe Iron 55,933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Сu Copper	30 Ζn Zmc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromane 79,904	36 Κr Mrygiton 84.80
37 Rb Rubidium S4 458	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Ζr Zieconium	Nb Nichium 92.906	42 Mo Mohrbden 95.94	43 Тc Technetius 98.907	44 Ru Ruthenius 101.07	Rh Rhodium 102 906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 $_{\rm Cd}$ Cadmium 112.411	49 In Indiam 114.818	50 Sn $\frac{7n}{118.71}$	51 Sb Antimony 121.760	52 Тe Tellurium 127.6	53 lodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132 905	56 Ba Barkers 137.327	$57 - 71$	72 Hf Hatnium 178.49	73 Ta Tantalum	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium	Ir Indians 192.22	78 Pt Platinum 195.08	79 Au Gold 196,987	80 Hg Mercury 200.56	81 ΤI Thailliam	82 Рb Lead 207.2	83 Bi Brumwith 208.980	84 Po Potonium (208.982)	85 At Astatine 209 987	86 Rn Radon 222.018
87 Fr Francism	88 Ra Radium 226.025	89-103	104 Rf Rutherfordio [261]	105 Db Dubnium [262]	106 Sg 1266	107 Bh Bohrium (264)	108 Hs 1269	109 Mt [268]	110 Ds 1269	111 Rg 12721	112 Cn Dogwenicka [277]	113 Uut unknown	114 FI Flerovius 12891	115 Uup unknown	116 Lv [298]	117 Uus unknown	118 Uuo unknown

Fig. 9.4 Location of transition metal oxides in periodic table that are anodic (red) or cathodic (blue) colouration

electrons occupy the previously empty d band, giving rise to new electronic transitions. In crystalline WO₃, the added electrons occupy delocalized states, whereas in amorphous WO_3 electrons are localized at metal sites, resulting in polaronic absorption that can be described as an electronic charge-transfer transition between adjacent metal sites with different valency (Runnerstrom et al. [2014](#page-16-4)).

$$
\left[\text{WO}_3 + \text{H}^+ + \text{e} \right]_{\text{bleach}} \rightleftharpoons \left[\text{HWO}_3 \right]_{\text{coloured}} \tag{9.1}
$$

Anodic colouration is found in oxides of Cr, Mn, Fe, Co, Ni, Rh, and Ir, with nickel oxide and iridium oxide being the ones investigated in most detail (Granqvist [1995\)](#page-15-0). Anodic colouration mechanism is in reverse manner compared to cathodic colouration. Take nickel oxide (NiO) as example, the electrochromic reaction can proceed via the exchange of H+ and OH− depending on the nature of the films as well on the electrolyte (Wen et al. [2014\)](#page-17-3). The situation become more complicated when the films evolve during electrochemical cycling (Estrada et al. [1988](#page-15-6); Ren et al. [2013\)](#page-16-10). The electrochromic effect in NiO involves several phases and is pointed at the general applicability of the Bode reaction scheme (Wen et al. [2014\)](#page-17-3); specifically the reactions in alkali electrolyte associate with $Ni(OH)$ ₂ and NiOOH as shown in Eq. [\(9.2\)](#page-6-1) in a simplified manner (Avendaño et al. [2005;](#page-15-7) Avendaño et al. [2009](#page-15-8)).

$$
\left[\text{Ni(OH)}_{2}\right]_{\text{bleach}} \rightleftharpoons \left[\text{NiOOH} + \text{H}^{+} + \text{e}\right]_{\text{coloured}} \tag{9.2}
$$

Both cathodic oxide and anodic oxide are usually employed in a typical smart window with two respective EC films; one can adjust the optical transmittance and achieve better colour neutrality than with one single EC film (Granqvist [2014\)](#page-16-6). Take combination of tungsten oxide and nickel oxide as illustrated in Eqs. [\(9.1](#page-6-0)) and ([9.2](#page-6-1)) for example, applying voltage in one direction between these two EC films will transport the ions from one to another makes both of these films coloured, while reversing the potential polarity makes both of the films bleached by return to their original properties. When there is no move of charges, the EC device shows memory effect by retaining the current state (coloured or bleached respectively). The terminology "rocking chair" has been used describe operation in smart windows as well as rechargeable battery applications (Goldner et al. [1993](#page-15-9)).

$$
CE(\lambda) = \frac{\Delta OD}{Q} = \frac{\log \left[T_{\text{bleached}}(\lambda) / T_{\text{coloured}}(\lambda) \right]}{Q}
$$
(9.3)

Furthermore, performance of each individual EC materials and devices is merited by colouration efficiency (CE) given in Eq. [\(9.3\)](#page-6-2) (Gillaspie et al. [2010;](#page-15-1) Thakur et al. [2012](#page-17-4)), where *Q* is the electronic charge injected into the EC material per unit area, T_{bleached} is the transmittance in the bleached state, and T_{coloured} is the transmittance in the coloured state. The CE therefore gives the change in optical density (OD) achieved by the injection of unit charge over unit area. In general, materials

with higher CEs will have better durability and faster switching times, since less charge is required to produce a given optical response (Gillaspie et al. [2010](#page-15-1)).

9.2.2 Ion Conductor

At the central of the EC device resides the ion conductor layer which is the key component for ions transportation between cathode and anode during EC reaction. To ensure proper operation of the device, the ion conductivity of electrolyte should be larger than 10⁻⁴ S/cm (Granqvist [1995\)](#page-15-0). Other requirement of electrolyte is high thermal and UV stability on top of not cause any degradations toward EC layers (Marszalek et al. [2012\)](#page-16-11). Ion conductor can be generalized into two – liquid and solid electrolyte. Figure [9.5](#page-7-0) shows the schematic diagram EC devices with different type of electrolytes.

Transparent liquid electrolytes and ion-containing thin oxide films were used in early studies on EC and later the interest has switched toward polymer (solid) electrolyte mainly following the development of electrical battery technology (Granqvist [2014\)](#page-16-6). Undoubtedly, the main advantages of liquid electrolyte are easy to synthesize, high ion conductivity (response time) and good stability (cycle life) (Girotto and Paoli [1999](#page-15-10)), which make it the popular candidate over the years when researching EC device. Regardless, efforts in sealing to prevent the potential of leakage and evaporation are the biggest flaws of liquid electrolyte as ion conductor in application like smart window. But the problems can be overcome by opting solid electrolyte, and it opens up the doors to all plastic and flexible EC devices too. Ionic charge transports as well as the diffusing species that enter the EC layers via electrolyte are the only major drawback in comparison to liquid electrolyte.

Fig. 9.5 The electrochromic device with (**a**) liquid and (**b**) solid electrolyte (Marszalek et al. [2012\)](#page-16-11)

9.2.3 Transparent Conductive Oxide

Transparent conductive oxides (TCO) are semiconductors such as tin doped indium oxide, In₂O₃: Sn (ITO), fluorine doped tin oxide, SnO₂: F (FTO) and antimony doped tin oxide, $SnO₂$: Sb (ATO). They are known with high optical transparency in the visible region, good electrical conductivity, and high infrared reflectivity (Chuang [2010\)](#page-15-11). These characteristics are found particularly useful as transparent thin-film conductors in applications like flat panel displays and solar cells, transparent heaters, heat mirrors, optoelectronic devices, and smart windows.

TCO materials suitable for transparent conductor thin films should have a carrier concentration on the order of 10^{20} – 10^{21} cm⁻³ and band-gap energy above approximately 3 eV, that is, degenerated n-type or p-type semiconductors. Furthermore, TCO thin films that are in practical use as transparent conductors are polycrystalline or amorphous and exhibit a resistivity on the order of $10^{-3} \Omega$ cm or less and an average transmittance above 80% in the visible range (Minami [2013\)](#page-16-12). ITO is wellknown in excellent optical and electrical properties. It is a highly degenerated n-type and wide band gap (e.g., 3.5–4.3 eV) semiconductor (Kim et al. [1999\)](#page-16-13). Due to its relatively low electrical resistivity and high visible transmittance, this material has been used extensively as transparent conductors. ITO thin films can be obtained readily through various growth techniques including sputtering, evaporation, chemical vapor deposition, and sol-gel (Chuang [2010](#page-15-11)).

TCO thin films on glass substrate are located at outermost layer of smart windows as shown in Fig. [9.3](#page-4-0). The excellent electrical and optical properties of TCO allow conduction of electricity between the transparent conductors without hinder transparency of a window. When voltage is applied to the transparent conductors, ions are transferred between the ion storage film and the EC film through the ion conductor layer at the centre. Depend on the voltage polarity, the electrons are then extracted from or injected into the transparent conductors that alter the optical absorption of the EC films. The original state can be easily restored by reversing the voltage.

9.3 Characterization of Electrochromic Materials

There are many different techniques to choose to deposit EC metal oxide thin films. EC thin films prepared by DC magnetron sputtering are specifically chosen in this work to elaborate various characterizations of EC materials. As mentioned earlier, sputtering is well understood in manufacturing. On top of that, sputtering has good reproducibility, good substrate adherence and the possibility of depositing many different types of materials with a variety of different compositions, layers, structures and stoichiometry. The general idea of sputtering is that a target (source) of certain raw material is bombarded by accelerating ions (typically $Ar⁺$) impart a high kinetic energy to the expelled source atoms. These atoms transit through the discharge and condense onto the substrate, thus providing the film growth. Then, a series of analyses on thickness, morphology, optic, etc. to identify the microstructure and composition of deposited thin films.

9.3.1 Physical Characterization

9.3.1.1 Film Thickness by Profilometry

Deposited EC thin films from sputtering are usually measured by contact surface profilometry. The surface profilometer measures the thickness by moving a diamond tip over the step between uncoated and coated sample areas. Multiple measurements from different positions along the step are always taken and averaged.

9.3.1.2 Crystal Structure by X-Ray Diffraction

In a crystalline structure the atoms form regularly repeating atomic planes separated by a certain distance, *d*, which varies with the material. If *d* is shorter than the X-ray wavelength λ , the X-rays are diffracted by the uniform atomic planes and an interference pattern is seen, as described by Bragg's law,

$$
m\lambda = 2\text{dsin},\tag{9.4}
$$

Where m is an integer and θ is the diffraction angle, i.e. the angle between the incident X-ray beam and the atomic plane. A spectrum with constructive inferences is obtained from scanning the diffracted beam. The peak distribution is directly related to the atomic distances. Hence, information about structure, phase composition and orientation of planes can be obtained by comparing the spectra with the database from JCDPS-International Centre for Diffraction Data (ICDD).

Non-crystalline materials with no long-range order, i.e. amorphous materials, do not show any diffraction peaks and cannot be examined by XRD. Polycrystalline materials are composed of many different crystalline grains of varying size and orientation. The size of the grains determines whether they will be detected. Crystalline samples show very distinct narrow peaks whereas the peaks from polycrystalline samples are broader. The width of the peak depends on the size of the grains, and the grain size, *D*, can be calculated by Scherrer's formula (Cullity and Stock [2001](#page-15-12)):

$$
D = \frac{k\lambda}{2\cos\theta} \tag{9.5}
$$

Where *k* is the shape factor, λ is the wavelength of X-ray, β is the full width at half maximum of the X-ray diffraction peak, and *θ* is the diffraction angle. Figure [9.6](#page-10-0)

Fig. 9.7 SEM images of NiO thin film. (**a**) and (**b**) are top view at different magnifications, and (**c**) cross-sectional view of the film on an ITO-coated glass substrate (Wen et al. [2014](#page-17-3))

shows an example of an XRD spectrum for polycrystalline NiO measured from Siemens D5000 diffractometer.

9.3.1.3 Surface and Cross-Sectional Morphology by Scanning Electron Microscopy

The scanning electron microscope (SEM) which uses electrons that are reflected or knocked off the near-surface region of a sample to create an image. Various signals are giving off when the electrons interact with the atoms on the surface of sample that contain information about the surface topography and composition of the sam-ple. Figure [9.7](#page-10-1) shows SEM image of $a \sim 500$ nm thick NiO film deposited on ITOcoated glass substrate. One can deduce that the film featured triangular morphology with linear extents of ≤ 40 nm as shown in panel (a) and (b). The cross-sectional image in panel (c) indicates a columnar nanostructure of the deposited NiO film.

9.3.2 Electrochemical and Optical Characterization

Cyclic voltammetry (CV) test and optical transmittance measurement are usually conducted together to evaluate the CE in Eq. [\(9.3\)](#page-6-2). Figure [9.8](#page-11-1) displays an example of cyclic voltammograms of NiO-based films in KOH electrolyte for the first 15 cycles. Broad oxidation and reduction features are observed, which deduce that some minor evolution takes place during the initial cycles, but the properties are stabilized after a few cycles. Figure [9.9](#page-12-0) presents in situ optical transmittance during the CV test as obtained in Fig. [9.8](#page-11-1). Information obtained from these two graphical data enable the calculation of CE for this NiO films. The CE was evaluated and found to be 44 ± 2 cm²/C at wavelength of 550 nm (Wen et al. [2014\)](#page-17-3).

9.4 Spectral Selective Nano Structured Thin Films

Plasmonic electrochromism is the current approach to isolate visible and infrared radiations from solar spectrum via modulated LSPR. Research team led by Milliron is spearheading in this field with notable publications (Garcia et al. [2013](#page-15-13); Llordés

Fig. 9.8 Cyclic voltammograms for a \sim 500 nm thick NiO film in 1 M KOH; the voltage sweep rate was 10 mV/s and arrows indicate sweep direction (Wen et al. [2014](#page-17-3))

Fig. 9.9 (a) Spectra transmittance of a \sim 500 nm thick NiO film in 1 M KOH. Inserted images refer to NiO in fully bleached and coloured states respectively, and (**b**) corresponding optical transmittance modulation at wavelength of 550 nm (Wen et al. [2014](#page-17-3))

et al. [2013](#page-16-14); Runnerstrom et al. [2014](#page-16-4)). Figure [9.10](#page-13-0) schematically illustrates this concept with two types of nanostructure designs of the EC thin films. As shown in Fig. [9.10](#page-13-0) a, the nanocomposite electrolyte consists of polymer hosts and transparent conducting nanoparticles such as ITO, aluminium-doped zin oxide (AZO), and lanthanum hexaboride $(LaB₆)$ (Bayrak Pehlivan et al. [2012](#page-15-14)). Electrochemical changes

Fig. 9.10 (**a**) Structure of nanocomposite electrolyte with nanoparticles, and (**b**) ITO nanocrystal- NbO_x film (deposited ion a conducting glass substrate) as the working electrode in an EC structure (J. (Jialiang) Wang and Shi [2017\)](#page-17-6)

under different electrical potential, which alter the LSPR absorption level and in turn the electron density. This alteration enables modulation of solar infrared absorption with minor effects on the visible region. In Fig. [9.10](#page-13-0) b, development of the electrode based on deposition of ITO nanocrystals on niobium oxide (NbO_x) glass presents another approach (Llordés et al. [2013;](#page-16-14) Kim et al. [2015](#page-16-3)). Both ITO nanocrystals and NbO_y glass matrix exhibit distinctly different spectral EC responses, therefore each may independently yield modulation in the NIR (ITO nanocrystals) and visible region (NbO_x) (Llordés et al. [2013\)](#page-16-14).

9.5 Other Implementation of Electrochromic Thin Films

In this work, we mainly talked about electrochromic oxides incorporate in smart windows and their sole purpose in filtering lights. However, researchers have come up with creative ideas by integrating electrochromism with other usability, such as energy storage (Yang et al. [2016\)](#page-17-5). Moreover, the demand of bezel-less phone screen has pushed the smartphone manufacturers in developing new technology to hide the front cameras and sensors beneath the display, without compromising the display quality nor the camera capability (Byford [2019;](#page-15-15) Gartenberg [2019\)](#page-15-16). Figure [9.11](#page-14-0) showcase the working principle of under-display camera technology by Xiaomi. Judging from the illustration, we can conclude that it is a variant of EC devices because of the cathode and anode layers. The cameras and sensors beneath the display stay hidden until the user activates the front-facing camera as shown in the demo (Porter [2019\)](#page-16-15).

Nonetheless, it is important to note that other than electrochromism, alternative materials that exhibit photochromism or thermochromism can also be used to

Fig. 9.11 (**a**) Normal display when front camera is inactive, and (**b**) Transparent display when front camera is active from "transparent display-in-a-display" for under-display camera technology by Xiaomi Corp (Gartenberg [2019](#page-15-16))

fabricate smart windows. For example, perovskites are materials made of mix elements with a particular crystalline structure and they can be made into solar cells. By changing the perovskites' elemental components, their optical properties such as transparency can be altered. Researchers have successfully created modified perovskite solar window that combine all these features (Wheeler et al. [2017;](#page-17-7) Lin et al. [2018\)](#page-16-16). For example, a lead-based perovskite solar window that switched from transparent to opaque when the temperature hit 60 \degree C while converting solar energy to electricity at the same time (Wheeler et al. [2017](#page-17-7)).

9.6 Conclusion

Electrochromism is one of the "green" nanotechnologies which are of large current interest (Smith and Granqvist [2011\)](#page-17-8). The potential of saving energy from building sector by replacing conventional glass windows with EC smart windows is unmeasurable. This is the greatest importance for combating global warming as discussed in the beginning of this chapter. Smart windows also increased the aesthetics and comforts of modern buildings. Although tremendous research works have put into smart windows, the applicability is still far from large scale implementation. The major impediments for the installation of large-area EC windows remain fabrication cost and extended lifetime. One purposed solution is development of flexible EC devices that offer "retrofit installation" on existing glass windows to reduce overall cost. Finally, further researches on this field are necessary to realize this technology into every building and bring the concept of energy-efficient smart windows closer.

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