Development and analysis of nanomaterial membrane device

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Abstract. In the contemporary era of research and development, energy efficient gadgets like electrochromic devices (ECD) drag an eye for their functionality and suitability. Modern world of Nanomaterials looks forward to enhance the electrochromic device performance for their unique physical and chemical properties. In this paper, an innovative nanomaterial membrane (NMM) device with ITO coated glass is employed along with WO$_3$, NiO and Li doped NiO is developed, characterized and analyzed for transmittance modulation, optical density and switching time. The transmittance at colouration and bleaching conditions is also compared with an existing ECD of a similar material based device structure. The newly developed NMM device showed a transmittance enhancement reaching a peak of ~88% at bleaching condition in the visible spectrum range. Additionally, optical density and switching time are also investigated and the NMM outshined proving to be extremely beneficial.

1. Introduction
Chromism is the phenomenon of colour change by materials under specific environmental conditions and their optical characteristics like transmittance, absorbance and reflectance change under ambient conditions. Chromism occurs due to the change in electronic state of the molecules in the materials of the device. Hence, this manifestation is induced by various external factors such as electric field, temperature, light intensity, solvent-solutions, etc., which alter electron density of materials [1]. Now on application of external bias to the material or system if the colouration or opacity changes or varies from transparent to dark and vice-versa the phenomenon is known as electrochromism that was developed long back in early 1930s [1] and stands as the most promising variety of chromic effect induced by electric field. Based on this concept the change in optical properties of Electrochromic (EC) materials happen owing to oxidation-reduction (redox) process [2]. One of the prime advantages of electrochromism is that the voltage can be self-controlled so that the variation i.e. change from transparent to dark conditions can be handled individually. Moreover, a low-switching voltage (1 to 5 V) is required for the electrochromic functioning, and varied range of colours viz., blue, grey, brown, etc. are observed and may be considered as per the persons choice of vision [3, 4]. This schematic variation of the electrochromic effect is displayed in figure 1.
Electrochromism occurs in numerous inorganic and organic materials. These materials are currently of considerable interest for newer technological aspects and for the construction of novel EC devices. Today, a large group of materials are available which show the behaviour as observed in Figure 1 and is denotive as a reversible colour change on application of electric field [4-5]. Electrochromic materials are of two types: cathodic EC (coloured due to charge injection (reduction process)), anodic EC (coloured due to charge ejection (oxidation process)). These cathodic and anodic material concepts bring forth the idea of application of bias to form a circuitry device; thereby an electrochromic device can possibly be developed, which institutes as the core focus and motivation of the paper. Cathodic colouration is perceived in WO3, TiO2, Nb2O5, MoO3, and Ta2O5, in which WO3 is the most extensively studied one, which is transparent to translucent in oxidation and deep blue in reduction process [6]. Anodic colouration is found in NiO, Cr2O3, MnO2, FeO2, CoO2 and IrO2 while V2O5 exhibits both anodic and cathodic properties [6]. In transition metal oxides only some of the oxides viz. WO3, TiO2, Nb2O5, NiO and IrO2 are transparent to visible range while other oxides show some absorption in visible range spectrum. Moreover some binary and tertiary mixed oxides [TiO2-V2O5, WO3-Li2O-FeO, WO3-MoO3 and WO3-CeO2] also show electrochromism [4].

Electrochromic devices developed based on the nanomaterials as discussed above can be amalgamated to substitute regular glass windows in residential/commercial buildings or even in Dreamliner based flights to function as electric dimming glass [7-8]. Currently, the regular windows are made of glass and curtains/blinds/shutters are used to block sun light; eliminating such elements is of importance due to its limited functionality/visibility issues. Electrochromic devices (ECDs) are also developed with integrated technology and photovoltaic effects that can be helpful for 20% savings in energy consumption when compared to regular glass transmittance [7]. Through regular glass windows direct sunlight enters the premises during summer months increasing the indoor temperature, while in winter the glass absorb the cold from outside and cool the premises more than desirable. ECDs are useful to maintain comfortable temperature by slashing more power consumption [9-10].

In 2015, Wang et al. [11] developed an ECD using WO3 / polymer electrolyte/ NiO materials, where the electrolyte is prepared with and without ferrocene. The highest transmittance is found to be 57.9% in visible range spectrum for the device with ferrocene, while for the device without ferrocene, the highest transmittance is at 42% in visible spectrum. The coloured state and bleached state is characterized at −2.5 V and 1.9 V respectively for the device without ferrocene, and it is observed that for the ECD with ferrocene ΔT is 37.5%, which is 15.5% higher than that of the ECD without ferrocene. Another ECD with ITO coated glass/ TiO2-PEDOT: PSS/ polymer electrolyte/NiO/ ITO Glass is developed by Choi et al. [12] Here the NiO is grown in micro-sized, nano-sized and with ATO (Antimony tin oxide). The ECD with ATO exhibited a highest transmittance in visible spectrum range of 63% at 1.5V. With CeO2 and Nb2O5 as EC layer and counter electrode respectively Llordes et al. [13] augmented ECD performance which showed transmission enhancement of 16%. This device has 79% transmittance at 545 nm at 2 V but in

Figure 1. The schematic view of electrochromic behavioural effect.
bleached state this device has 52% transmittance in visible spectrum range, which is not accommodating for the application purpose, therefore not much convincing performance.

Wang et al. [14] developed an ECD using ITO coated glass with tungsten oxide, tantalum oxide and nickel oxide layers while lithium ion electrolyte is injected in the NiO layer. The device developed with magnetron sputter showed quite good transmittance of ~23% in coloured and ~80% in bleaching conditions respectively for the visible spectrum region [14]. Though this categorization is quite beneficial for the ECD device and is presently being manifested in many applications but, on advancing the technological aspect of ECD development further enhancing the optical transmittance along with the optical density of the ECD is the need of the hour. Thus a material based study of the active region and further research of the ECD device desires a requisite concentration, which was previously not much looked into. Therefore with this motivation, in this work a novel Nanomaterial Membrane (NMM) based Electrochromic Device is developed for the first time with the concept initiated by Wang et al. [14] for an enriched device performance.

2. Theory and Device Structure

2.1. Theory of ECD criterion

The ECDs are analysed based on the quantification of some parameters that are applied for the NMM devices also and these are: transmittance, modulation, colouration efficiency, switching time, memory effect, and cyclic life. So, brief understanding of these NMM device parametric quantifications are laid out.

2.1.1. Transmittance Modulation ($\delta R$). Transmittance modulation is one of the most important electrochromic parameter for electrochromic device operations and is defined as the transmittance change in coloured and bleached state based on

$$\delta R = s - t$$

where $s$ is the bleached state and $t$ is the coloured state. Since, the transmittance modulation depends on the wavelength; the change in the transmittance is measured by the optical transmission spectra of bleached and coloured states respectively as a function of wavelength. Since the transmittance modulation depends on the wavelength, the change in the transmittance is measured by the optical transmission spectra of the bleached (s) and the coloured (t) states as a function of wavelength. Generally, $\delta R$ lies between 70 – 80 %, is particularly used for device applications [15].

2.1.2. Colouration Efficiency (CE). Another measuring factor for ECD is the colouration efficiency (CE) also acknowledged as electrochromic efficiency. The CE is described as considerable magnitude of optical spectrum formed based on the amount of injected/extracted charge at time of operation i.e., the variation in optical density ($\delta f$) per unit of ion density ($\delta c$) per unit electrode area and is given by:

$$CE(\lambda) = \delta f(\lambda) / \delta c$$

where, $\delta f$ is unit optical density and $\delta c$ is unit ion density per unit area of electrode

The optical density depends on the light absorption ability of electrochromic materials. The variation in optical density is measured from optical transmission in bleached (s) and coloured (t) condition of the sample/device and is given as:

$$\delta f(\lambda) = \log \left( \frac{s}{t} \right)$$
The charge density i.e. the charge transferred per unit electrode area is obtained from integration of the corresponding current for total time:

\[ \delta c = I \times t/A \]  

where, \( I \) is current (Amp), \( t \) is total time in second for which current is passed and \( A \) is area electrode (cm²). \( CE \) is positive if colouration is generated cathodically and negative if colouration is generated anodically [15].

2.1.3. Switching Time: Switching time (T) is the requisite time required for transparent to opaque or vice-versa operation of ECDs / NMM devices. Colouration time (t) is the time needed to switch from bleached state to coloured state (90 % - 10 %) and the bleaching time (s) is the time to switch from coloured state to bleached state (10 % - 90 %). Some applications do not require a rapid colour change such as the electrochromic office windows, which requires a very slow response; however, applications such as display devices, require a more rapid response [14-16]. The switching time is influenced by certain factors viz. ionic conductivity of the electrolyte, the applied electric field, device area, and film structure.

2.1.4. Memory Effect: ECD/NMM is either in coloured or opaque state when voltage is applied. Even after removing the voltage, ECD/NMM used to retain its state and this effect is called “open-circuit memory effect”. This is one of the admirable benefits of electrochromic devices for which sometimes ECDs qualify to be named as smart devices. In this state, when the ion self-extract from EC film, due to electrical leakage current or ion diffusion the memory vanishes, this phenomenon is self-bleaching a prominent effect observed efficiently in all organic ECDs. Therefore, the ion conductor plays a crucial role in optical memory effect [15]. The EC memory possibly stays for several days or weeks even without any current however, some EC devices need small refreshing charges to sustain the charged condition due to chemical reactions or short circuits which may change the required colour [14-17].

2.1.5. Cycle-Life: It is calculated on colour-bleach cycles of an ECD before it degrades. The cycle-life is therefore, a measure of the electrochromic durability testing, an immensely sophisticated effect that impose the variability condition of the device. The maximizing of the durability is an important factor of device fabrication and a minimum 10,000 cycles are acceptable [14-15]. ECDs are generally used in window and display applications, deterioration is best gauged by eye vision, and the same illumination that would be employed for normal device operation. However, 50% degradation is often tolerable for display applications [15], but more than that calls for a replacement of the device, thereby ECDs till today have limited life span based applications.

2.2. Device structure and materials
The Nanomaterial Membrane (NMM) device is developed here and the schematic device structure is shown in Figure 2. The device is expected to work as an electric dimming glass based on the concept initiated by Wang et al. [14]. The ECD based NMM device is fabricated with various materials and the thicknesses are as mentioned in the Table I. The fabrication and growth of the device is mostly carried out using the high resolution Turbo Sputter Coater System. Tungsten oxide (WO₃) film is deposited at 5 × 10⁻³ Torr and sputtering power of 100 Watt for a thickness of 150nm, while the NiO film is grown for 150 nm thickness and is deposited under pressure of 5x10⁻³ Torr and 10 watt for 14 sec. The 80 nm thick Ta₂O₅ film is deposited on a NiO/ITO/glass substrate and Li⁺ ions are injected into the NiO film at an applied voltage of 3 V in an electrolyte composed of 0.1M to form LiClO₄ and propylene carbonate (PC) solution. This NMM device was developed in line with structure to the ECD device of Wang et al. [14] where ITO coated glass is used as the substrate followed by tungsten oxide of 170 nm as electrochromic layer. The tantalum oxide of 150nm was deposited on nickel oxide layer which is the counter electrode of thickness 60 nm. An electrolyte having lithium ion is injected in the NiO layer. Though Wang et al. [14] developed the device with two processes, DC magnetron sputtering
and cathodic vacuum arc plasma technology, but here the device grown with sputtered technique is considered to compare with our NMM device here, which is also developed using sputter system. The sputter deposition of EC layer has the advantage in the preparation of high quality and uniform characteristics on large area substrates overcoming the surface roughness, which provided to be highly advantageous in also enhancing the transmittance of the NMM device. The detailed device structure for the NMM device is displayed in Figure 2 while its parametric thicknesses are detailed in Table I.

![Figure 2. Schematic structure of Nanomaterial Membrane (NMM) Device](image)

**Table 1.** Materials used with their thickness

| Materials         | Thickness (nm) |
|-------------------|----------------|
| Glass coated ITO  | --             |
| WO₃               | 150            |
| Ta₂O₅             | 150            |
| NiO               | 80             |

3. Results and Discussion

On incorporating a thin film of electrochromic material into a circuit, colour-switchable electrochemical cell is formed. The material of the cell is deposited at one electrode, which is combined with a counter-electrode. Alternately, the electrochromic material can be dissolved in an electrolyte solution between the electrodes. In response to a small electrical voltage (typically around 1 volt to 2 volt), electrochromic materials will change in its coloration, thereby evoke or bleach their colour state. The electricity induces in the material a process of either reduction (gain of electrons) or oxidation (loss of electrons), this happens with the variation occurring due to transport of carriers within the conduction and valence band in the material based device. The colour of the device changes from dark and gradually it becomes light blue. This implies that the Li⁺ ions diffuse into the NiO layer spontaneously on application of bias. Ideally when the applied voltage is −5 V, the device is opaque, it becomes transparent when the voltage is changed to 5V. The chemical reactions maintained in the device are as follows
Cathodically, \[
\text{WO}_3 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{WO}_3
\]
(Transparent)\(\rightarrow\)(Coloured)

Anodically, \[
\text{LiNiO} \rightarrow \text{NiO} + \text{Li}^+ + e^- \]
(Transparent)\(\rightarrow\)(Coloured)

The NMM device is characterized and analyzed for the study of optical transmittance and optical density in comparison to the existing ECD device of Wang et al. [14] to understand the functionality of the device. Figure 3 displays the colouration state graph for the newly developed NMM device that showed the transmittance range varying between 19.7 – 9.2 % in the visible spectrum region while 8.9 – 8 % in the IR region. This is observed to be quite comparable to the existing ECD that showed the transmittance range to be 18.2 – 13.4 % in visible spectrum and 13.5 – 7.94 % in the IR spectrum. From Figure 3, it is visibly pragmatic that in the IR range of the colouration state of device operation the NMM device have enhanced performance with low transmittance percentage leading to have a higher opacity. While for the visible spectrum range of the coloration state, the NMM device is observed to provide a healthy completion in transmittance with a wide transmittance range throughout the wavelength in comparison to the ECD device which is highly beneficial for variety applications. Thereby the NMM device under operation evidently warrants an enhanced amount of transmittance percentage as perceived in Figure 3 performance in the colouration state.

![Figure 3](image)

**Figure 3.** Colouration state of the Nanomaterial Membrane Device being compared to the ECD (Wang et al. [14]) showing enhanced transmittance performance.

The NMM device is also characterized for observing transmittance for the bleached state as is exhibited in Figure 4 which is compared with the optical transmittance of the existing ECD. The transmittance range for ECD varies from 52.5 – 77 % in visible spectrum range and 78.8 – 32.8% in IR region [14] while NMM device demonstrates transmittance of 58.7 – 80.6 % in visible range 80.8
− 31.5 % in the IR region for bleached state condition. The IR spectrum transmittance range is almost edging alike for both the devices as detected in Figure 4. But, in the visible wavelength range the NMM device completely outshines the ECD for optical transmittance percentage under bleached condition with a reinforcement of ~ 3–5 % while also the NMM device is observed to peak in optical transmittance with 88.9% at 675 nm. Therefore, it is evidently demonstrated and validated from Figure 3 and Figure 4 that NMM has augmented transmittance from violet to red light wavelength range which inducts that at a particular wavelength there are very few bonds to absorb the colour in that sample.

Figure 4. Bleached state of ECD (Wang et al. [14]) compared to the Nanomaterial Membrane Device, which showed enriched performance.

The optical density and transmittance modulation for both (NMM and ECD) the devices are also evaluated. The ECD of Wang et al. [14] witnessed the optical density and transmittance modulation to be 0.67 and 63 % respectively. But in the present work the Nano-material Membrane (NMM) Device superseded the ECD device for both the transmittance modulation (TM) and optical density (OD), which are detected and calculated to be 68 % and of 0.72 respectively, and are tabulated in Table 2. The TM and OD enhancements among the two devices are also deliberated and listed in Table 2 and the huge augmentation is unmistakably cherished by the novel NMM device in comparison to the existing ECD, thereby provide an upper hand to the NMM device.

An analysis of fast switching time of the colored and bleached state speed is also investigated experimentally and a comparison between the existing ECD and NMM device is revealed in Figure 5. The colored and bleached switching time are displayed as the optical transmittance that is varied between 88% and 36% at the wavelength for the ECD and NMM devices. The NMM device characteristics are done at three different visible wavelength ranges (500 nm, 550 nm, 600 nm) and is
compared with the ECD at 550nm (which was highest transmittance for Wang et al.[14]). But as observed from Figure 5, the NMM device provided a similar transmittance at wavelength of 500 nm while it completely outperformed the ECD at both wavelengths of 550 nm and 600 nm. Therefore, the Nanomaterial Membrane Device showed lower switching time with higher transmittance value at the visible range, indicating that the NMM device is highly enriched in the comparison to the existing ECD. The switching time data for both the devices are showed in Table 3 and the enhancement percentage is also listed.

Table 2. Transmittance modulation and optical density

| Device                      | Fabrication Process                      | Bleached State Transmittance | Colored state Transmittance | Transmittance Modulation (TM) | Optical Density (OD) | Enhancement (NMM) |
|-----------------------------|------------------------------------------|------------------------------|------------------------------|-------------------------------|---------------------|-------------------|
| Electrochromic Device       | DC magnetron sputtering                  | 81%                          | 17%                          | 63%                           | 0.67                | 5%                |
| Nano-material Membrane Device | sputter coater with high resolution coating | 84.1%                        | 16.1%                        | 68%                           | 0.72                | 0.05              |

Figure 5. Switching time graph for Electrochromic Device (Wang et al. [14]) and Nanomaterial Membrane Device at visible light wavelength
Table 3. Switching time of the devices

| Devices                  | Fabrication Process                      | Wavelength (nm) | Switching Transmittance (%) | Switching Time (sec) | Enhancement (NMM) |
|--------------------------|------------------------------------------|-----------------|----------------------------|----------------------|-------------------|
| Electrochromic Device    | DC magnetron sputtering                   | 550             | 40 ↔ 80                    | 230 ↔ 38             |                   |
| Nano-material Membrane   | sputter coater with high resolution coating | 500             | 40 ↔ 80                    | 20 ↔ 170             | 25 sec            |
| Device                   |                                          | 550             | 40 ↔ 80                    | 30 ↔ 190             |                   |
|                          |                                          | 600             | 40 ↔ 80                    | 50 ↔ 230             |                   |

Transmittance modulation, optical density and switching time for the ECD and NMM Devices are evaluated. The transmittance modulation is found to increase by 5% and optical density is 0.05. Switching time has been reduced to 25 sec in the visible spectrum range. Strong optical absorption is therefore realized using a thin electrochromic layer, while simultaneously achieving a fast switching time due to correspondingly small charge-propagation distance. Therefore compared to the ECD device, the NMM device is observed to have acquired improved performance in all respect and can thereby be a standalone device that has the capability to replace the existing ECD and become the NMM device of future.

4. Conclusion
A Nanomaterial membrane (NMM) device employing materials in the thickness of nano regime is developed here based on the concept of electrochromic device. The newly developed NMM device is characterized and analysed here and is compared with an existing ECD of thicker material configuration. The NMM device is fabricated by sputter deposition and is found to possess significant enrichment in transmittance modulation and optical density by 5% and 0.05 respectively in the visible spectrum range. While also in the visible wavelength range the NMM device completely outshined the ECD for optical transmittance percentage under bleached condition with a reinforcement of ~6 – 5% reaching a peak in optical transmittance with 88% at ~650nm. The switching times for the devices are also inspected for ECD and NMM device and the NMM demonstrated distinct advancement by 25 sec in visible range. As a whole NMM device is clearly observed to have achieved an excellent optical attribution in all aspects, therefore, the new NMM device hoists the capability for replacing other device in the range and be the future smart efficient device.

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5. References
[1] Deb S K 1969 A novel electrophotographic system Applied Optics Vol. 8 192-5
[2] Granqvist C G 2014 Electrochromics for smart windows: oxide-based thin films and devices Thin Solid Films 564 1–38
[3] Granqvist C G, Green S, Niklasson G A, Mlyuka N R, Kramér V S and Georén P 2010 Advances in chromogenic materials and devices Thin Solid Films 518 3046–53
[4] Phuriwat J, Simona B, Md N. Al Sawalta Lek, Sikong Vo-Van T 2017 Electrochromic properties of sol–gel prepared hybrid transition metal oxides – a short review Journal of Science: Advanced Materials and Devices Volume 2 Issue 3 286-300
[5] Kwok W S, Su-Xi Wang, Debbie Xiang Y S and Jianwei X 2019 Viologen-based electrochromic materials: from small molecules, polymers and composites to their application Polymers 11(11) 1839
[6] Granqvist C G 2000 Electrochromic tungsten oxide films: review of progress 1993-1998 Solar Energy Materials & Solar Cells 60 201-62
[7] Dhar R S, Elezzabi A and Md Al-Hussein 2016 Smart window technologies: electrochromics and nanocellulose thin film membranes and devices SDRP Journal of Nanotechnology & Material Science volume 1 Issue 1 1-14
[8] Jaime W, Berzelius J J 2000 A Guide to the Perplexed Chemist, Chem. Educator 5, 343 343-350
[9] Knittlmayer C, Muffler H F, Ch.-H. Fischer and W Weppner 2016 Investigation of electrochromic tungsten trioxide thin films prepared by the ILGAR method Ionics 12 127–130
[10] Alexander K, Gesimat G H 2008 On the discovery and history of prussian blue Bull. Hist. Chem volume 33 Number 2 61-67
[11] Wang J Y, Wang M C and Jan D J 2015 A flexible quasi-solid-state electrochromic device with polymeric electrolyte and wo3/nio complementary system Journal of Materials Science and Chemical Engineering 3 136-141
[12] Choi D, Lee M, Kim H, Chu W S, Chun D M, Ahn S H and Lee C S 2018 Investigation of dry-deposited ion storage layers using various oxide particles to enhance electrochromic performance, Solar Energy Materials and Solar Cells 174 599–606
[13] Llordès A, Wang Y, Martinez F A, Xiao P, Lee T, Poulain A, Zandi O, Camila A. Cabezas S, Henkelman G and Milliron J D 2016 Linear topology in amorphous metal oxide electrochromic networks obtained via low-temperature solution processing Nature Materials vol 15 1267-75
[14] Wang M C, Chen Y C, MH H, Y C Li, J Y Wang, Jin-Yu W, Wen-Fa T, and Der-Jun J 2016 The improvement of all-solid-state electrochromic devices fabricated with the reactive sputter and cathodic arc technology AIP Advances 6 115009 1-6
[15] Madhavi V, Kumar P J, Kondaia P, Hussain O M and Uthanna S 2014 Effect of molybdenum doping on the electrochromic properties of tungsten oxide thin films by RF magnetron sputtering Ionics 20 1737–45
[16] Mortimer R J 2017 Spectroelectrochemistry, methods and instrumentation, Encyclopedia of Spectroscopy and Spectrometry 1 172–7
[17] Rougier A, Danine A, Faure C and Buffière S 2015 Electrochromism: from oxide thin films to devices Proceedings of SPIE - The International Society for Optical Engineering 9364 1-11