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Nano-composite based Smart Electrochromic Device with escalated transmittance

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Research Article

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Abstract

Nanocomposites based Electrochromic Membrane Device (EMD) is fabricated by using DC sputtering with differently doped nanomembranes WO_3 doped Ag NW and Li^+, PEO, and $H^+Nb_2O_5$ which undergoes optical and electrochemical characteristics so as to be capabale for smart applications. Highest bleaching transmittance of this device is evaluated to be 96.1% at 549nm and 93.1% at 825nm in the visible and IR spectra. Average colouration transmittance is observed to be 11.1% over visible range and 2.6% over IR range. A comparison with existing devices are also studied and analysed to understand the benefit of the EMD device. Dimming fastness of EMD on 500, 550 and 600nm upon a certain wavelength counted as 105, 111 and 150sec, respectively. Both transmittance modulation and optical density are also computed as 85% and 0.94. Cyclic voltammetry of each film and the whole nanostructured device arrangement is carried out for 50mV/s over +1.5V to 1.5V in the standard environment, which overlayed the understanding of the quantum tunnelling and carrier confinement effects in the device that leads to enhanced device performance. Whole experimentation of EMD stands out as an imperative accomplishment for standard requirements to be fit for future smart applications.

1. Introduction

The contemporary research in nanotechnology persuades interest on developing innumerous applications with possession of all aspects for user controllability, comfortability and energy efficiency, which is the need of today. This advanced technology cultivates adequate attention in modern field of numerous Electrochromic or smart display applications. Electrochromic glass is multifunctional considering energy efficacy, light regulations and durability [1]. Thin films of cathodic and anodic electrochromic (EC) materials with an electrolyte encompasses to form a conventional electrochromic design system. All these nanomembrane are layered between two transparent conductive oxide (TCO) coated glass as substrate. TCO film acts as ion movement medium for both ON and OFF conditions [2,3,4]. A special benefit of Electrochromic Device (ECD) is very low operating potential is needed to switch from nontransparent to transparent state or vice-versa [4].

Many researchers have adopted diverse methods for the growth of different electrochromic material based films. A polymer based Electrochromic device was developed by Vergaz et al. [5] in 2007 where polyethylene terephthalate (PET) covered ITO was treated as substrate on either side of the EC device. The switching voltage of this device varied from 0.5V to 2V. Another ECD comprised of WO_3, NiO and Ta2O5 filmed on ITO glass was fabricated by Wang et al. [6] utilizing two separate processes; (i) DC magnetron sputtering and (ii) cathodic arc plasma. The device developed by sputtering showed enhanced optical characteristics. Subsequently WO_3- Nb2O5 film was developed by Tang et al. [7] using fast alternating bipolar pulse magnetron sputtering. WO_3- Nb2O5 film was treated at different sputtering power and reported highest transmittance of 91% in visible spectra. In 2015 Oukassi et al. [8] fabricated lithium phosphorus oxynitride (LiPON) film by physical vapor deposition technology to use as ion conducting medium in ECD. This inorganic solid state thin film ECD manifested 49% peak bleach transmittance over ± 1.5V. Atak et al. [9] forwarded a concept of developing an ECD filming dry lithiated WO_3 with NiO and Ta2O5 on ITO coated glass substrate. With ± 2V this device exhibited 31.4% optical modulation with a peak bleaching transmittance of ~ 76% in visible region [9].

Innumerous and versatile applications are implemented by engaging all these progressive devices perceived by the researchers of the past decades. But all these devices displayed peak transmittance of ~ 80% on bleaching state and ~ 20% average transmittance in colouration state over visible spectrum therefore not adequate for the purpose of initiating a smart window system. Though these devices remained acceptable for various utilization such as automotive mirror, windows, Dreamliner flights glass as there exists no other alternatives, hence sets room for improvement in technological aspect to meet the obligatory performance requirements [10, 11]. This impression indebted to approach for the fabrication of an Electrochromic Membrane Device (EMD) comprising of two nano-films Li_xWO_3 doped with Ag nanowire and Nb_2O_5 doped with H^+ sandwiched between ITO inlayed glasses. The fabricated and developed device is further characterized for optical and electrochemical properties that is compared with prevailing devices ECD1 (Oukassi et al. [8]) and ECD2 (Atak et al. [9]) significantly to experiment and study the performance of fabricated Electrochromic Membrane Device (EMD) over visible and infrared electromagnetic spectrum.

2. Theory And Device Fabrication

The performance analysis of Electrochromic systems are relied upon optical transmittance modulation, optical density, memory effect and durability. For a certain range of voltage stepwise transmittance as well as switching time also points significant criteria for the characterization of the devices [12, 13, 14]. The transmittance (%) for the electrochromic device is computed as:

$$(\%)\,T = \frac{m}{m_0} \times 100\%$$

1

where, m_0 is the intensity of light enters and m is intensity of leaving light. The transmittance modulation (δK) is formulated as:

$$\delta K = \delta a - \delta b$$

2

where, δa is the transmittance in bleached state and δb is the colouration state transmittance. The optical density (ΔOD) is calculated as:

$$\Delta OD = \log\frac{a}{b}$$

3

Nanocomposite based Electrochromic Membrane Device (EMD) is hence developed with different nanocomposites deposited on two ITO (Indium tin oxide) filmed glass substrates on either side. The schematic structure of the EMD is presented in Fig. 1. The whole functioning of this device is due to the oxidation and reduction processes that occurs while external voltage is applied. This leads to transportation of carriers within the conduction and valance band of the incorporated materials in the EMD developed here for which the operating condition of the device changes.

Electrochromic Membrane Device (EMD) is fabricated using DC Sputtering process with high resolution that yields reduced impurity and delivers highly uniform film. This device is composed with TCO covered glass on two ends. WO_3 is doped with 0.1wt% of Ag NW and Li^+ treated as anodic EC membrane filmed next to the electrolyte that is Polyethylene Oxide (PEO) whereas cathodic EC film is grown by $H^+Nb_2O_5$ (0.1wt%). These thin films are altogether settled on Indium Tin Oxide (ITO) covered glass on both ends. WO_3 doped with Ag NW and Li + film of 150nm is developed and sputtered at 7.7×10^{-3} torr and 135W sputter power, while the counter EC film of 100nm thick $H^+Nb_2O_5$, deposited at 100W with 6×10^{-3} torr. For both cathode and anode EC film potential is enabled at 10V and 17V, respectively. 100nm thick Polyethylene Oxide (PEO) which acts as TCO, sputtered at 6×10^{-3} torr with a power of 100W at 10V. The addition of AgNW doping in WO_3 instigates in increasing the carrier confinement in the nano-layer and hence succumbs to enhance transportation in the quantum system which is developed in the EMD. Eventually thereafter, circuit arrangement is runned by utilizing conductive tapes and connecting wires and the Electrochromic Membrane Device is thereby manufactured and characterized for optical properties using UV-Visible spectrometer over 300 to 1100nm wavelength. Transmittance as well as switching time and optical density of the Electrochromic device is analyzed and determined with Hitachi U4100 UV- Vis- NIR spectrometer using − 2V to + 2.5V step up voltage. Further electrochemical characterization of the device is investigated applying SECM (Scanning Electro-Chemical Microscopy) system of Ted Pella with model no CHI920D for different external bias from − 1.5V to + 1.5V with platinum auxiliary electrode. The schematic structure and thickness of different nanocomposite films encapsulated in Electrochromic Membrane Device (EMD) are experimentally studied, analyzed and forwarded as shown in Fig. 1 and Table 1 respectively.

Table 1: Thickness of different nanocomposites film

Nanocomposites	**Thickness(nm)**
ITO coated Glass	–
WO_3 doped Ag NW and Li^+	150
PEO	100
$H^+ Nb_2O_5$	100

3. Results And Discussion

The constructed nanocomposite based Electrochromic Membrane Device (EMD) is examined for optical and electrochemical properties. The prevailing devices namely ECD1 (Oukassi et al. [8]) and ECD2 (Atak et al. [9]) are also compared with the EMD for discussing all the accumulated outcomes. Oukassi et al. [8] has fabricated the electrochromic device composed of TCO/ V_2O_5/ LiPON/ LixWO_3/ TCO whereas Atak et al. [9] developed the device with ITO/ NiO/ Ta_2O_5/ dry lithiated WO_3/ ITO composition. All the electrochromic devices operate at very low voltages. At higher voltage the device shows bleaching state due to ion intercalation while at lower voltage the device is opaque due to intervention of charge carrier blockages [15, 16, 17].

EMD is circuited through + 2.5V to -2V for the optical characterization. Bleaching transmittance of the existing devices as well as EMD is experimentally acquired and displayed in Fig. 2 (a). Peak bleaching transmittance of ECD1 (Oukassi et al. [8]) and ECD2 (Atak et al. [9]) are observed to be ~ 49% and ~ 76%, respectively, in the visible domain. The constructed EMD delivers 96.1% peak transmittance at 549nm and 93.1% at 825nm. Positive external voltage intrudes extended intercalation of Li + and H + from both the electrochromic films resulting in quantum tunnelling in the three dimensional nanostructures. This tunnel through the quantum potential barrier system inspires dissociated ion movements for balancing charge between the electrodes imposing transparent state in the electrochromic device [18, 19]. At + 2.5V, the EMD appears to have transmittance range of 86.8% – 91.9% over visible spectrum and 92.6% – 59.9% over the IR spectra.

At lower voltage EMD exhibits opaque condition as featuring in Fig. 2 (b). Since there is no external field no alignment is there in the electronic state of the molecules and therefore any recombination of the carriers will not happen in the colouration state [19, 20]. Whie the literature devices ECD1 (Oukassi et al. [8]) and ECD2 (Atak et al. [9]) state the average colouration transmittance over visible light are ~ 14% and ~ 26% respectively whereas colouration transmittance range of EMD approach 17.1% – 5.6% in visible range and 4.1% – 1.1% in the IR range. The average colouration transmittance of EMD is calculated as 11.1% over visible range and 2.6% over IR range.

A distinctive difference of bleaching (a) and colouration (b) transmittance over visible wavelength spectrum is presented in Fig. 3 comparing the EMD fabricated here with the existing devices ECD1[8] and ECD2[9]. At higher external bias electrons transits from HOMO of the anode to LUMO of the cathode causing a clear state run by quantum tunnelling as the electrochromic layer based system inherits an interband quantum super-lattice structure concept with the nano-molecular structure owing to Coulomb Diamonds composed with tri-filmed system. This transportation of carrier is for quantum tunnelling phenomenon where ions move through the degenerate semiconductor layers to the conduction band [20, 21]. At positive bias the EMD resolves 96.1% peak transmittance while at negative bias average transmittance is availed at 11.1%, which is significantly enhanced in comparison with ECD1 (Oukassi et al. [8]) and ECD2 (Atak et al. [9]) mainly due to the influx of AgNW doping in the WO_3 that speedyfies the quantum tunnelling in the nanosystem device.

In both Fig. 2(a) and (b), EMD appears to hold improved functionality in both bleach and colour condition. In comparison with the existing devices ECD1 and ECD2, an increment in peak bleaching transmittance is witnessed to be ~ 20%, while for average colouration a performance improvement of ~ 3% in visible light is acquired. Both transmittance modulation and optical density for the EMD are thereby computed with equations (2) and (3) and are enlisted in Table 2. Enhanced transmittance modulation and optical density of the EMD in comparison to ECD1 and ECD2 is invariably tabulated as ~ 25% and 0.40 in nominal condition. Keeping together all the outcomes of transmittance and further derivatives, it is unveiled that Electrochromic Membrane Device (EMD) with added quantum tunnelling due to incubated AgNW doping hits the mark with efficacious accomplishments.

Table 2: Transmittance parameter variations of the EMD comparing with ECD1 and ECD2

Device Name	Bleaching Transmittance (%)	Colouration Transmittance (%)	Transmittance Modulation (%)	Optical Density	Minimum Increment in optical density
ECD1 (Oukassi et al [8])	49	14	35	0.54	0.40
ECD2 (Atak et al [9])	76	26	60	0.47	
EMD (present work)	96.1	11.1	85	0.94	

The redox reaction responsible for bleaching and colouration condition is stated as:

$WO_3 + x\ Li + + x\ Ag + + x\ e- \rightarrow Ag/Li_xWO_3$ (i)

$H^+\ Nb_2O_5 \rightarrow Nb_2O_5 + H^+ + e^-$ (ii)

Furthermore another significant criteria that is switching time of nanocomposite based EMD is experimented for 500, 550 and 600nm. The rapidity depicts the fastness of transmittance change from dark to clear condition and vice versa. Faster switching time over a certain transmittance range is preferable for better potential of an electrochromic device. Switching time of EMD is presented in Fig. 4. Time calculation for all three visible wavelength are enlisted in Table 3 where it is seen that EMD acquire fastness of 105, 111 and 150sec over 500, 550 and 600nm respectively making the electrochromic device clear to dark or reversible state.

Electrochemical analysis of the nanocomposite based EMD is investigated for ± 1.5V with 50mV/s scan rate in 1M Ferrocene of 98% purity. Cyclic voltammetry analysis is carried out which signifies that the redox response for both bleaching and colouration condition takes place within the nano-membranes of the electrochemical cell [22, 23, 24]. This initiates the quantum tunnelling process due to carrier transportation in the EMD. Therefore, the CV of the cathodic EC, anodic EC and for the whole nanosystem electrochromic device are plotted in Fig. 5 at 300 and 400K. As disclosed in Fig. 5 higher temperature provokes higher charge movement through forced tunnelling in the nanosystem device exerting rapid electrochemical changes across the cell [25,26, 27]. At cathodic scan (+ 1.5V to -1.5V) when the electrochromic device experiences colouration condition all the charge carriers continuously intercalate from the electrolyte to the film in the degenrate LUMO level by tunnelling. At anodic scan (-1.5V to + 1.5V) due to deintercalation of ions, bleaching electrochromism occurs in the system [28, 29]. Since EMD experiences both oxidation and reduction $W^{6+} \leftrightarrow W^{5+}$ simultaneously current density reduces for charge confinement effect [30].

Figure 5 reveals that the current density rises with increase in temperature as a large number of electrons migrate in the nano membranes due to heat accumulation. Since, both the EC films with PEO electrolyte in between settled on two ITO covered glass current density apparently contracts on voltage application owing to carrier confinement effect arising by coagulation of the nano-membrane layers in the novel EMD [31, 32].

Table 3: Switching time computation of EMD in visible wavelength

Wavelength (nm)	Transmittance (%)	Switching Time (sec)
500	45↔85	125↔20
550	45↔85	138↔27
600	45↔85	190↔40

The acquisition of current density from the CV measurements as well as colouration and bleaching transmittance in both visible and infrared spectra for the EMD device is challenging as it estimates the standardization of Nanostructured EMD applications in electric dimming effect. Therefore, from various observations in aspect of optical and electrochemical properties of developed EMD manifest to overtop the prevailing devices conquering the necessary standard in smart and progressive applications required in modern era.

4. Conclusion

Nanocomposites based Electrochromic Membrane Device (EMD) fabricated by DC sputtering in high resolution encapsulated with varied nanomembrane of WO_3 doped Ag NW and Li^+, PEO, and $H^+Nb_2O_5$. The whole device is analyzed in both visible and infrared electromagnetic spectrum over the applied biases of + 2.5V to -2V. The Smart Nanomembrane Electrochromic device is thereafter characterized for optical and electrochemical properties using UV-Visible spectrometer and scanning electrochemical microscopy. A maximum bleaching transmittance of 96.1% at 549nm while transmittance modulation and optical density are evaluated to be 85% and 0.94, respectively, enpowering the enhancement of the device fabricated here, which signifies that the device undergoes quantum tunnelling through the HOMO-LUMO quantum well barrier molecular nanomemberane system. Electric dimming rapidness is also observed for the EMD and is calculated as 105, 111 and 150sec over 500, 550 and 600nm, respectively, proving the doping of Ag NW with Li + is highly efficient for the transportation of carriers across the system. Electrochemical properties of each film and the whole arrangement are carried out for 50mV/s over + 1.5V to 1.5V in the standard environment. All the analysis evidenced that the EMD is appropriate for modern high tech practical smart applications with efficiency and comfortability.

Declarations

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Availability of data and material: There is no affiliations or involvement in other organization or entity with financial or non-financial interest in this research or material data.

Code availability: The authors have no software application or custom code in the manuscript.

Relevance Summary: The authors summarize distinct contributions

1. Fabrication and characterization of Electrochromic Membrane Device (EMD) comprising of ITO coated glass substrate, WO_3 doped with Ag NW and Li^+ as electrochromic film (150nm), PEO (Poly-ethylene-oxide) as electrolyte (100nm) and H^+ doped Nb_2O_5 as counter electrode (100nm).

2. 25sec faster switching for electric dimming of EMD is an admirable accomplishment for smart application.

3. CV measurement on ENM Nanosystem for first time revealed current density contraction when scanned at 50mV/s scan rate over ±1.5V.

4. Maximum bleaching transmittance at 96.1% and an average colouration transmittance at 11.1% in visible spectrum for novel EMD device attained; with ~8% enhancement supersedes existing devices is a supreme achievement contributing to advancement of the state-of-the-art technology.

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Author’s Contributions

S.T. has carried out the experimental work, characterization and data analysis as well as composed the manuscript. R.S.D. has conceptualized and supervised the work and contributed to manuscript development and corrections.

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Figures

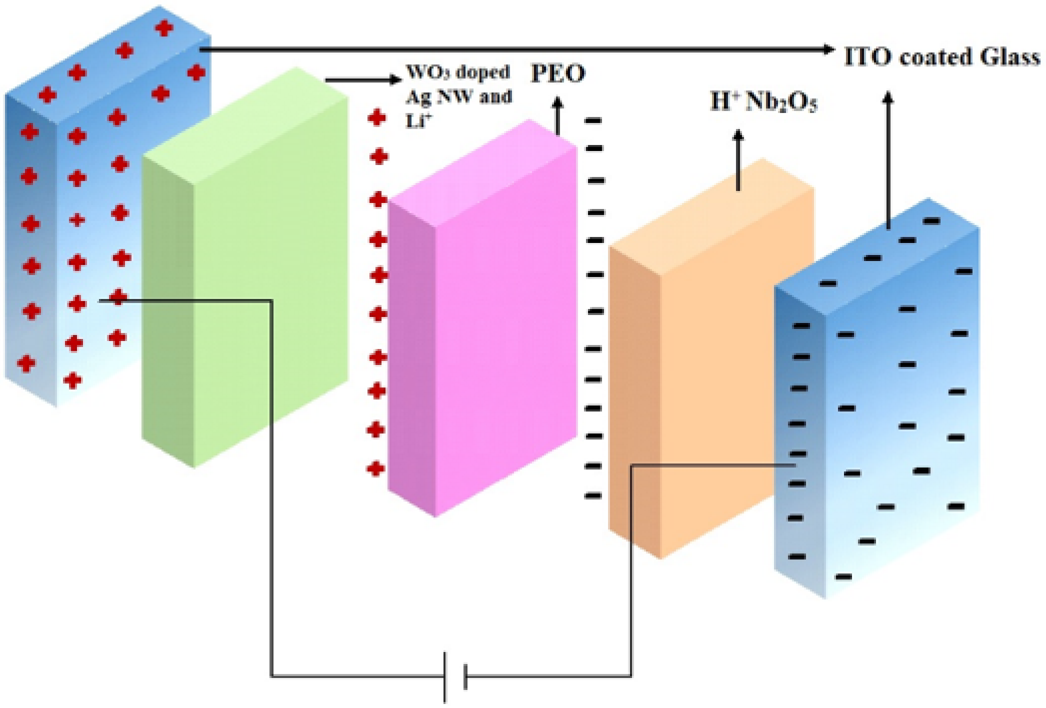
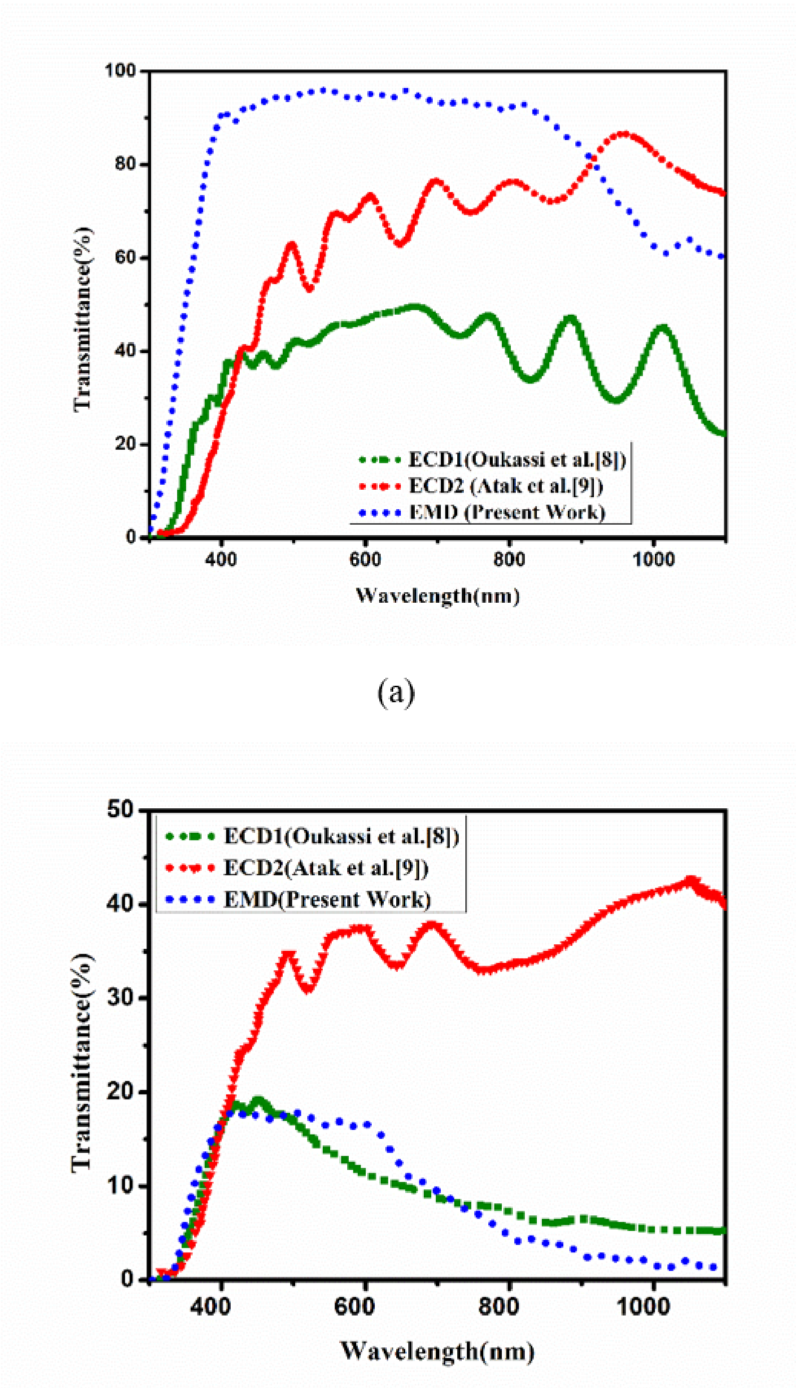


Figure 1

Schematic structure of Nanocomposites based EMD



(a)

(b)

Figure 2

(a) Bleaching transmittance and (b) Colouration transmittance of EMD comparing with ECD1 and ECD2

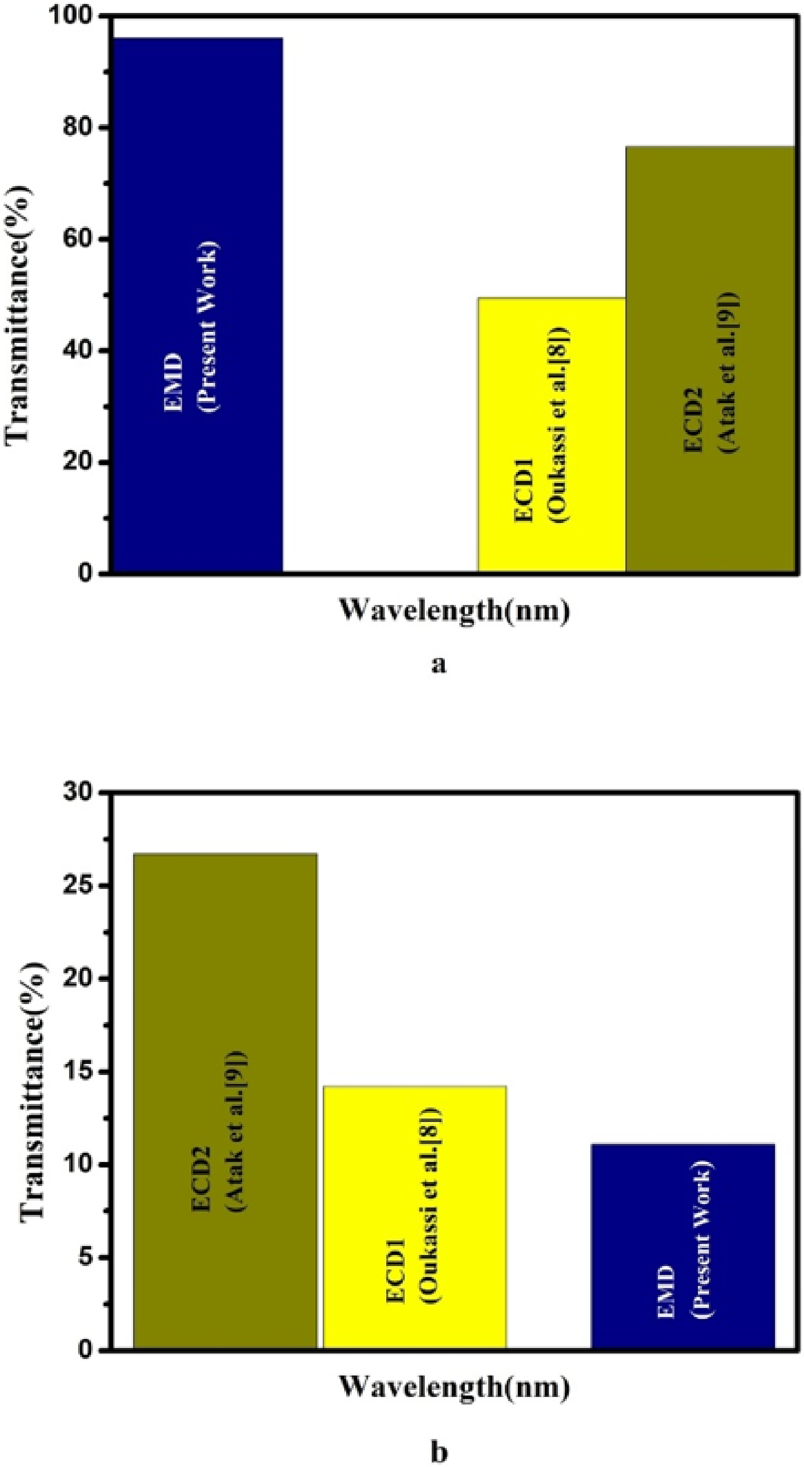


Figure 3

Transmittance difference of EMD with ECD1 and ECD2 at (a) bleaching state and (b) colouration state

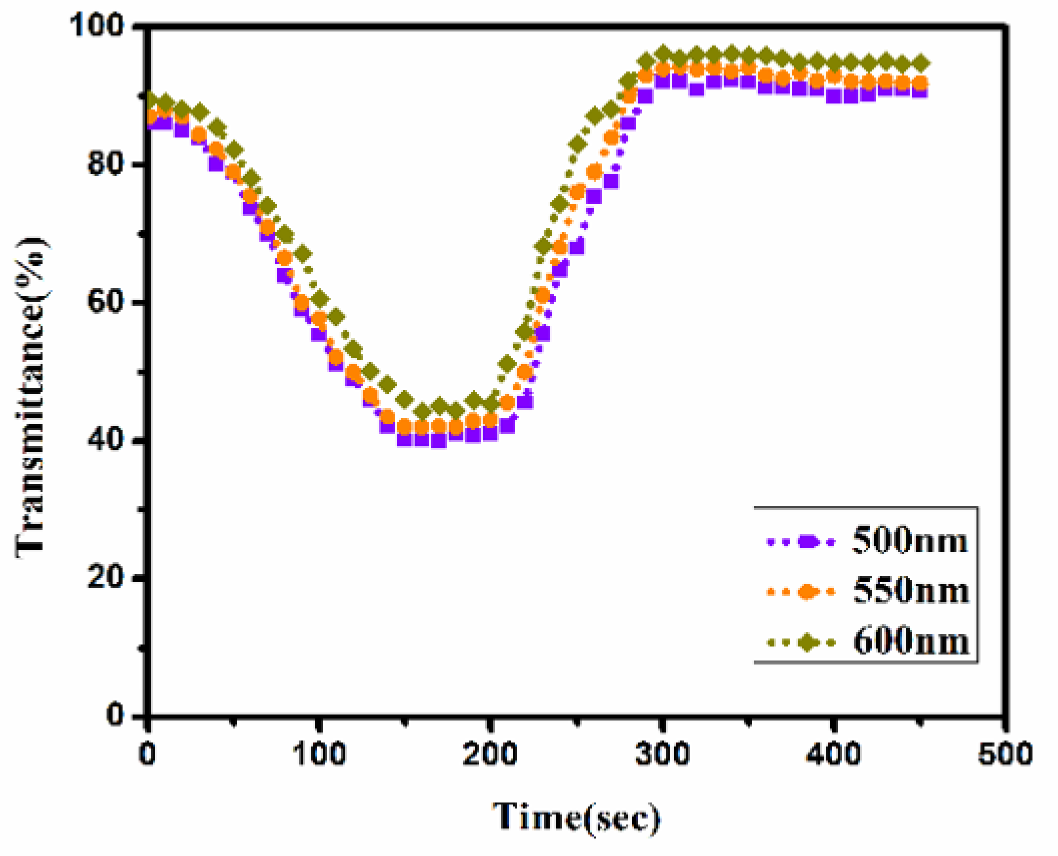


Figure 4

Switching time of EMD in 500, 550 and 600nm