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Pre-heating Temperature Effect on Electrochromic Properties of TiO_2 Thin Films

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Abstract

Smart windows represent a promising technology that enables the selective transmission of light and heat, and electrochromism technology is gaining interest in smart window applications. Electrochromic (EC) smart windows are the preferred choice for outdoor applications due to their ability to withstand high temperatures. Particularly, Tungsten Trioxide (WO3) is commonly used as an electrochromic layer in EC devices. Although Titanium Dioxide (TiO2) is a less expensive EC material compatible with optoelectronics applications (including solar cells), it has received little research attention. In the course of this study, the sol-gel spin coating method was utilised to deposit a thin film of TiO2 onto Indium Tin Oxide (ITO). This technique was chosen for its simplicity, affordability, and ease of coating thin films. The pre-heating temperature demonstrated a critical role in sol-gel fabrication, particularly in electrochromic applications. As the impact of the pre-heating temperature remains poorly understood, this study effectively investigated the effect of various pre-heating temperatures on the performance of TiO2-based electrochromic thin films. Moreover, this study effectively analysed the structural, optical, and EC properties of the TiO2 thin films pre-heated at different temperatures.

1. Introduction

In developed nations, the energy consumed by buildings accounts for 30-40 % of total energy consumption, exceeding the combined proportions needed for industry and transportation [1]. Heating, ventilation, and air conditioning systems consume building energy, accounting for 50% of the total energy consumed within buildings. Researchers have recently focused on the promising potential of smart windows in buildings [2]. The significance of smart windows is growing as they play a crucial role in optimising power usage for heating, ventilation, and air conditioning. These windows regulate the amount of sunlight transmitted, effectively reducing the energy needed for heating, ventilation, and air conditioning [3] [4] [5].

One of the most popular technologies used in smart windows is electrochromic technology (EC) [6]. By applying an electrical voltage, this technology employs a thin film of metal oxide, such as tungsten oxide or nickel oxide, to modify its optical characteristics. This process enables the window to transition between opaque and

transparent states depending on the applied voltage. Another technology employed in smart windows is thermochromic [7]. This technology incorporates a thin layer of material that adjusts its tint based on temperature changes. As the temperature rises, the material darkens, while it lightens when the temperature decreases.

When considering the materials utilised in thin film fabrication for electrochromic (EC) applications, tungsten trioxide (WO_3) is commonly employed [8]. Nonetheless, an alternative option exists in the form of titanium dioxide (TiO_2). TiO_2 emerges as a superior alternative to WO_3 for several reasons. Firstly, TiO_2 possesses a faster switching response time, enabling improved control of light transmission in electrochromic applications [9]. Additionally, TiO_2 exhibits superior stability and durability, rendering it highly resistant to degradation and extending the lifespan of electrochromic devices [10]. TiO_2 is also abundant, cost-effective, and environmentally friendly compared to WO_3, which is a less sustainable and more expensive material [11]. These advantages position TiO_2 as a compelling choice for thin film fabrication in electrochromic applications, offering increased efficiency, longevity, and cost-effectiveness.

The successful implementation of TiO_2 electrochromic (EC) applications has the potential to revolutionise the integration of EC smart windows with solar cells. This observation is attributed to the widespread use of TiO_2 in optoelectronic sensor applications. Incorporating TiO_2 into EC devices allows for the seamless combination of light control functionalities with solar energy harvesting capabilities. This integration could lead to innovative smart windows regulating transmitted sunlight and harnessing solar energy for power generation [12].

This paper examined the effect of pre-heating temperature on the optical and structural properties of a sol-gel spin-coated TiO_2 electrochromic thin film for use in smart window applications.

2. Literature Review

The idea of electrochromism, the phenomenon where a material undergoes a reversible change in colour upon application of an electric field, was first suggested in a London patent in 1929. The patent described the molecular I_2 that was studied, forming a bright colour because of chemical oxidation [13]. This discovery laid the foundation for the development of electrochromic devices. Most researchers state that Deb's paper in 1973 described the first EC device, which was a film of WO_3 in an electrolyte.

Deb's paper in 1973 described the synthesis and characterisation of a thin film of WO_3 in an electrolyte that exhibited electrochromic properties. The device demonstrated reversible colour changes upon application of a voltage, positioning it as an excellent option for smart glass and displays, among other applications. [14]. In 1978, the description of the reversible electro-insertion of lithium-ion with tungsten trioxide was introduced in a paper by Mohapatra. The study examined the electrochromic behaviour of lithium (Li) with WO_3 and demonstrated that Li-ion could be reversibly inserted into and extracted from WO_3, resulting in colour changes. This discovery was significant as it paved the way for developing EC devices utilising Li-ion as the active material [15]. In 1991, Satoshi Hashimoto and his colleagues used electron beam deposition to make thin films of WO_3 and WO_3-TiO_2. They then compared these two types of films. The research showed that the TiO_2 thin film lasts five times longer than the WO_3 thin film [16]. In 2003, a study by N.N. Dinh *et al.* utilised the sol-gel dipping technique to produce thin films of TiO_2 that exhibited colour-changing properties [17].

In some previous studies, researchers have utilised various methods to deposition and fabricate Titanium dioxide (TiO_2) thin films. For example, Daniela *et al.* employed the thermionic vacuum arc method to deposit TiO_2 thin films on onto various types of transparent conductive oxide (TCO) glass substrates [18]. In another investigation conducted by Cavit *et al.*, co-axial electrospinning was employed to structure non-woven webs of TiO_2 nanofibers loaded with Ag, Au, and CuO nanoparticles [19]. Idris Sorar *et al.* also conducted research in which they prepared TiO_2 films using reactive DC magnetron sputtering [20]. Conversely, these techniques relied on a vacuum-based approach, which rendered them more expensive and intricate.

Several studies have applied sol-gel processes in the fabrication of TiO2 thin films. For instance, Xu Zifang *et al.* conducted a study using the sol-gel method combined with a dip-coating process. Their research incorporated tetrabutyl titanate and glacial acetic acid into the solvent, absolute ethanol. Additionally, they introduced raw materials such as boric acid, deionised water, and nitric acid into the solution [21]. Another group employed the anodic oxidation and sol-gel processes to prepare TiO_2 coatings. While the primary synthesis method was sol-gel processes, they also utilised anodic oxidation to achieve their desired outcomes [22]. Wong *et al.* examined the influence of post-heating on both structural and optical characteristics of TiO_2 thin films. The study revealed a relationship between the annealing temperature and the size of crystalline particles. Higher post-heating temperatures resulted in larger crystalline sizes [23]. Another similar study investigating the impact of annealing temperature using the sol-gel method was conducted by Lukong *et al.*, which exhibited a reduction in the bandgap energy as annealing was increased [24].

This study employed the sol-gel spin coating method to deposit a TiO_2 thin film onto an ITO glass substrate. What distinguished this study from previous literature is its focus on investigating the influence of pre-heating temperature, which has received limited attention so far.

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3. Material and Methodology

The key reagents employed in this experimental procedure were titanium isopropoxide (TTIP), diethanolamine (DEA), and ethanol (C_2H_5OH). TTIP served as the principal precursor, DEA acted as a stabiliser, and C_2H_5OH functioned as the solvent in the formation of TiO_2 gel solution. These constituents were carefully selected to ensure optimal reaction conditions and product quality. The volume ratios of the chemicals in the sol were 3:1:2, indicating that TIP was present in the highest concentration. This relative volume ratio (TIP: DEA:C_2H_5 = 3:1:2) was critical in the reaction pathway. The high concentration of TIP in the sol allowed for precise control over the reaction pathway, resulting in a high-quality product with excellent purity and yield.

The TiO_2 gel solution was deposited onto an ITO glass substrate using the sol-gel spin coating technique. The following step was to preheat the sample at 100 °C for 3 minutes, forming a layer. Three layers were administered for each sample, after which the samples were annealed at 400 °C for 5 min. The ramping up and down durations were 30 minutes each, making the total time 1 hour, 5 minutes.

The structural characteristics of the TiO2 thin films were examined using X-ray diffraction (XRD) spectroscopy. The analysis was conducted using Cu Kα radiation with a wavelength (λ) of 1.5406 Å, and the range of 2θ was set between 20 and 60°. Field emission scanning electron microscopy (FESEM) was used for the examination of surface morphology. Simultaneously, the optical transmittances of the TiO2 thin films were analysed using an ultraviolet-visible (UV-Vis) spectrophotometer. In this study, the researchers employed cyclic voltammetry (CV) and chronoamperometry (CA) techniques to examine the electrochemical (EC) characteristics. Both methodologies used a three-electrode configuration consisting of a titanium dioxide (TiO_2) working electrode, a platinum (Pt) sheet counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode. The electrolytes utilised in the experimental procedures comprised a solution of lithium iodide in polyethylene glycol (PEG) with a concentration of 1 M (PEG: LiI).

4. Results

4.1 Structural Properties

Fig. 1 illustrates the thickness of the thin film for each sample set at various pre-heating levels. The data obtained under the specified experimental conditions indicated a correlation between the pre-heating temperature and the thickness of the TiO_2 film. The samples subjected to pre-heating temperatures of 100°C, 200°C, 300°C, and 400°C exhibited average thicknesses of 220 nm, 300 nm, 350 nm, and 370 nm, respectively. These findings demonstrated that augmenting the pre-heating temperature correlated with a corresponding raise in the thickness of the TiO_2 film. Interestingly, a previous study by the authors fabricated TiO_2 thin films using a default pre-heating temperature of 100°C [25]. The study investigated the number of layer effects of electrochromic performance, which revealed that the thickness was almost similar for all the samples. Although the result was attributed to the incomplete pre-heating process in the study, this study resolved this issue by increasing the pre-heating temperature.

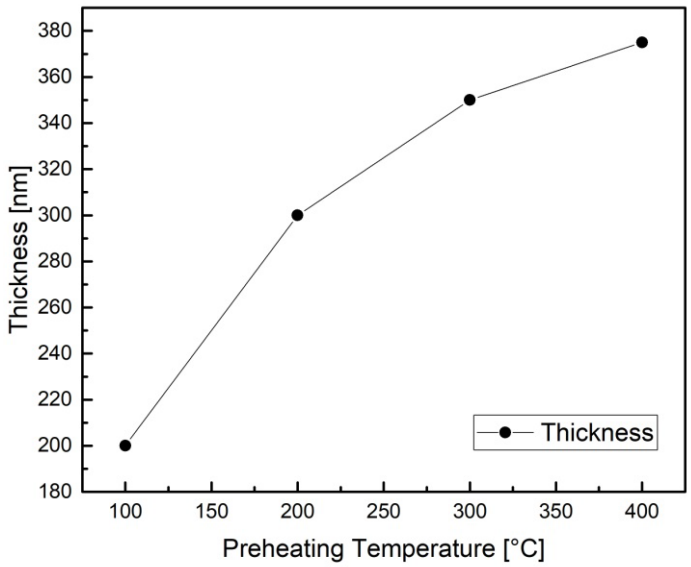

Fig. 1 *Thickness for different pre-heating temperatures*

Fig. 2 demonstrates the X-ray diffraction (XRD) pattern of the TiO_2 films formed at various pre-heating temperatures. The XRD peaks at 25.37° and 48.11° consistently appeared in all samples, confirming the presence of TiO2 material in the anatase phase. The presence of the peak at an angle of 54.27° was initially detected at a temperature of 200°C and subsequently at a temperature of 400°C. In addition, the peak observed at 37.52 was consistently observed across all pre-heating temperatures, except for the temperature of 400°C. The increase of the pre-heating temperature from 100°C to 200°C led to a distinct crystalline anatase peak at 54.27°. There were three crystalline structures for TiO_2: rutile, brookite, and anatase. Thus, anatase could accommodate more ions mainly due to its large internal surface area [26], which was a favourable factor in this study.

The Debye-Scherer formula can be employed to determine the crystalline size:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle. The TiO_2 thin films pre-heated at 100°C, 200°C, 300°C, and 400°C showed an average crystalline size of 35.54 nm, 19.04 nm, 14.62 nm, and 10.83 nm, respectively.

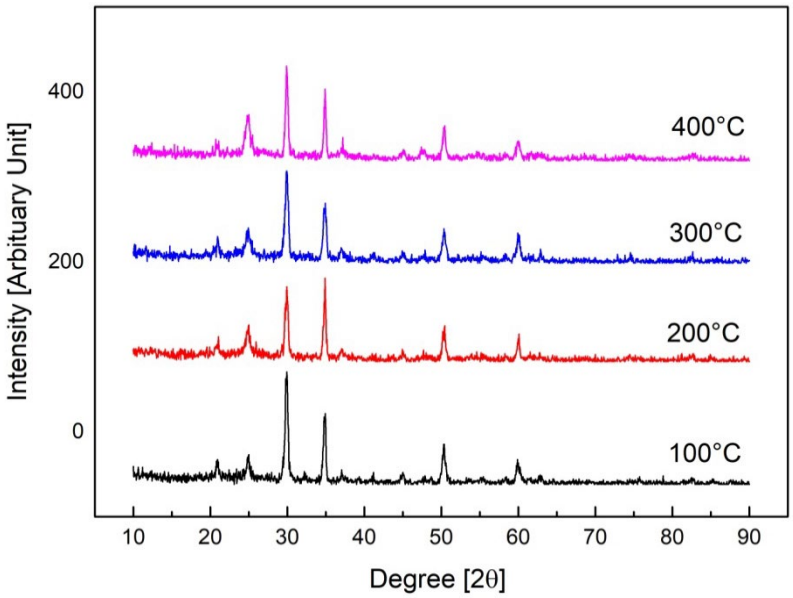

Fig. 2 *XRD pattern of the TiO_2 films formed at various pre-heating temperatures*

Fig. 3 depicts the FESEM images of the TiO_2 films formed at various pre-heating temperatures. The FESEM images clearly illustrated that the TiO_2 film consisted of fine nanoparticles. The images exhibited a dense and uniform film devoid of any pinholes. Thus, these observations remained consistent across all pre-heating temperatures.

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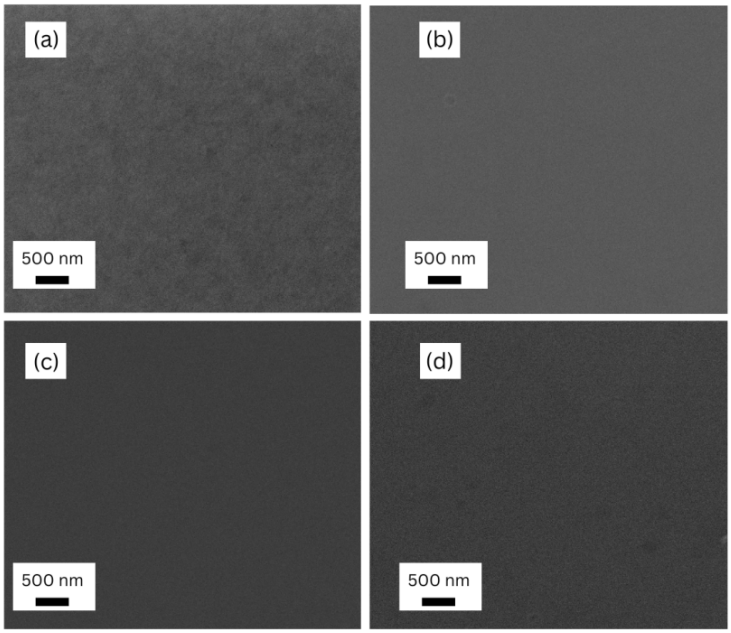

Fig. 3 *FESEM images for TiO_2 thin film preheated at (a) 100°C; (b) 200°C; (c) 300°C; (d) 400°C*

4.2 Optical Properties

Fig. 4 reveals the transmittance spectra of the TiO2 thin film in its original state. Higher pre-heating temperatures were associated with a rise in transmittance for the TiO2 thin film. TiO_2 films subjected to pre-heating temperatures ranging from 100°C to 200°C displayed an optical transmittance of 78%. Once the pre-heating temperature reached 300°C, the TiO_2 thin films exhibited a significant increase in film transparency, reaching approximately 98%. Nevertheless, once the pre-heating temperature was elevated to 400°C, the transparency of the TiO_2 thin film decreased to 91%. The variation in transparency was attributed to differences in crystallinity and particle size, where the lower transparency at a pre-heating temperature of 100°C and 200°C could be due to the bigger crystalline size of the TiO_2 film. As the pre-heating temperature increased to 300°C, the TiO_2 film particle size decreased, increasing transparency to its highest value of 98%. After attaining a pre-heating temperature of 400°C, the decrease in film transparency to 91% was attributed to the disappearance of the peak at 37.52°. Comparable findings were documented by Qiang Min *et al.*, who studied the effect of pre-heating temperature on ZnO thin films prepared using the sol-gel spin coating technique [27].

It is worth noting that the increase in pre-heating temperature accelerated the evaporation process, leading to faster removal of solvents, water, and any residuals. As a result, the transparency of the TiO_2 thin film increases [28].

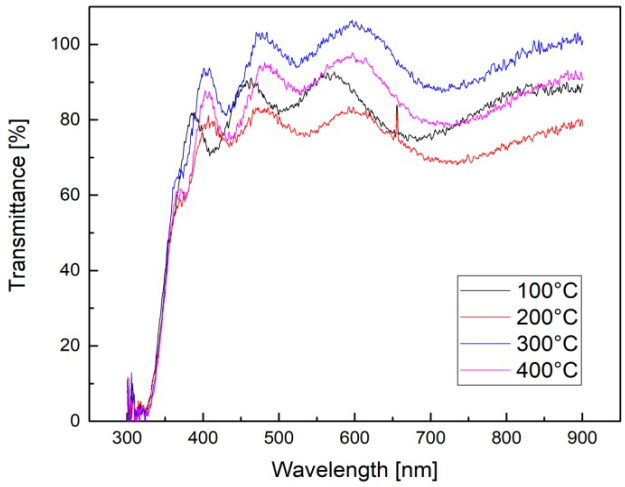

Fig. 4 *FESEM original transmittance spectrum of the TiO_2 thin films at different pre-heating temperatures*

4.3 Electrochromic Properties

Fig. 5 illustrates the cyclic voltammetry for the different pre-heating temperatures. Cyclic voltammetry (CV) was utilised to analyse the immediate response observed during the reduction (cathodic) and oxidation (anodic) potential scans. From Fig. 5, the anodic peak current for the TiO_2 thin film pre-heated at 100°C, 200°C, 300°C, and 400°C was 1.25 mA, 1.49 mA, 1.29 mA, and 0.79 mA, respectively. The results indicated an increase in the anodic peak current with a rising pre-heating temperature up to 200°C, followed by an overall decrease in the anodic peak current when the pre-heating temperature exceeded 200°C. The lowest recorded anodic peak value of 0.79 mA was observed at a pre-heating temperature of 400°C.

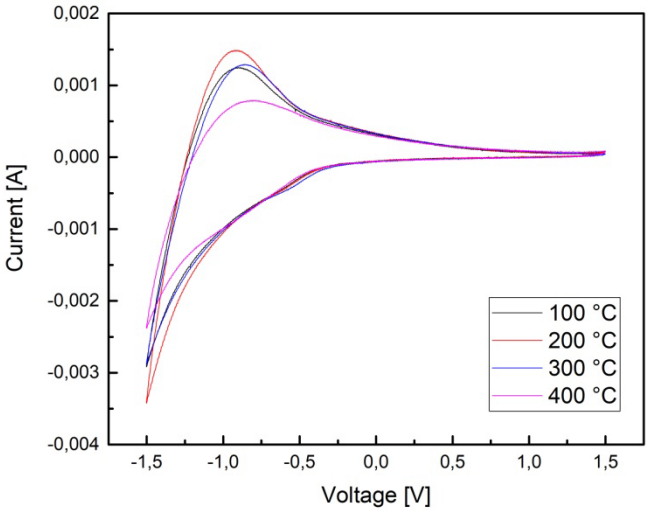

Fig. 5 *Cyclic voltammetry for different pre-heating temperatures*

The cathodic peak current exhibited a similar pattern to the anodic peak current, with the 200°C preheated sample showing the highest cathodic peak current of 3.42 mA and the 400°C pre-heated sample demonstrating the lowest cathodic peak current of 2.37 mA. The pre-heated samples at 100°C and 300°C exhibited cathodic peak currents of 2.92 mA and 2.88 mA, respectively.

The reason behind the highest recorded anodic and cathodic peak current at a pre-heating temperature of 200°C was attributed to the appearance of anatase crystalline peak 54.27° at this specific temperature. The lowest peak current was recorded at 400 °C pre-heating temperature, corresponding to the disappearance of the 37.52° anatase crystalline peak. According to a study conducted by Nur Dalilah *et al.*, which investigated the TiO_2 crystalline phases deposited via dip and spin coating using the sol-gel technique, heat treatment at 200°C and 300°C resulted in the formation of a single brookite TiO_2 thin film. In contrast, samples subjected to heat treatment at 400°C and 500°C resulted in a more amorphous TiO_2 thin film [29]. Other findings have also portrayed a similar change in the crystalline state of the deposited TiO_2 with increasing heat treatment temperatures from 200°C and above [30] [31].

The area under the CV curve reveals the charge storage capacity of the TiO_2 thin film. A higher area under the CV curve is proportional to a greater charge storage capacity, indicating better performance for EC-related devices [32]. The diffusion coefficient, D, for Li^+ ions can be calculated using the Randles-Sevcik equation [33]:

$$i_p = 2.72 \times 10^5 \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C_0 \times v^{\frac{1}{2}} \quad (2)$$

where i_p is the cathodic peak current, n is the number of electrons, D is the diffusion coefficient, C_0 signifies the electrolyte's active ion concentration, whereas v stands for the scan rate. The diffusion coefficients of the TiO_2 thin films in various pre-heating temperatures are summarised in Table 1. Observation of the diffusion coefficient at varied temperatures shows the highest anodic and cathodic diffusivity of 3×10^{-16} cm^2/s and 1.58×10^{-15} cm^2/s, respectively, occurred at a pre-heating temperature of 200 °C. The lowest diffusion coefficients of 8.48×10^{-17} cm^2/s and 7.65×10^{-16} cm^2/s were recorded at a pre-heating temperature of 400 °C. At a pre-heating temperature of 400°C, the diffusion coefficients were the lowest compared to the other samples due to blocked ion insertion sites [34]. In a study conducted by M. Anji Reddy *et al.* on the effect of crystalline size on lithium insertion into

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brookite TiO_2, smaller particles have a higher number of inserted/extracted Li ions. The study also demonstrated that increasing the heat treatment temperature resulted in larger crystalline particles [35].

Table 1 *Diffusion coefficient for TiO_2 thin films at different pre-heating temperatures*

Pre-heating Temperature (°C)	Anodic Diffusion Coefficient (cm^2/s)	Cathodic Diffusion Coefficient (cm^2/s)
100	2.11×10^{-16}	1.15×10^{-15}
200	3.00×10^{-16}	1.58×10^{-15}
300	2.25×10^{-16}	1.12×10^{-15}
400	8.48×10^{-17}	7.65×10^{-16}

Another important characteristic of EC devices was the colouring and bleaching transmittance. High-performance EC devices require high transparency in the bleaching state and high colouration in the coloured state. The transmittance modulation (ΔT) of an electrochromic material is determined by its optical contrast, which was expressed as the difference between the bleached state (T_b) and the coloured state (T_c):

$$\Delta T = T_b - \mathrm{T_c} \tag{3}$$

An alternative method for measuring the color shift between the bleached and colored states the alteration in optical density (ΔOD). The natural logarithm of the ratio of the bleached state transmittance expresses this (T_b) to the coloured state transmittance (T_c) [36]:

$$\Delta OD = \ln(\frac{T_b}{\mathrm{T_c}}) \tag{4}$$

CA measurements were performed on TiO_2 thin films preheated from 100°C to 400°C by applying a voltage between -1.5V and 1.5V. This process was done to investigate the transmittance in the bleached and coloured states at 633 nm while simultaneously recording the switching characteristics of the opaque and transparent states. The summarised data obtained from these measurements are presented in Table 2. The optical transparency profiles of the TiO_2 thin films are shown in Fig. 6, illustrating the variations in their respective coloured and bleached states across a wavelength range of 300 nm to 1000 nm.

The TiO_2 thin film preheated at 100°C exhibited an optical transmittance of 80% and 71% in the transparent and opaque states, respectively. Increasing the temperature to 200°C decreased the transmittance for the bleached and coloured states, with values of 77% and 66%, respectively. At pre-heating heat levels of 300°C and 400°C, the TiO_2 thin films exhibited a transparent state with a transmittance of 78% for both temperatures and a coloured state with transmittance values of 90% and 91%, respectively.

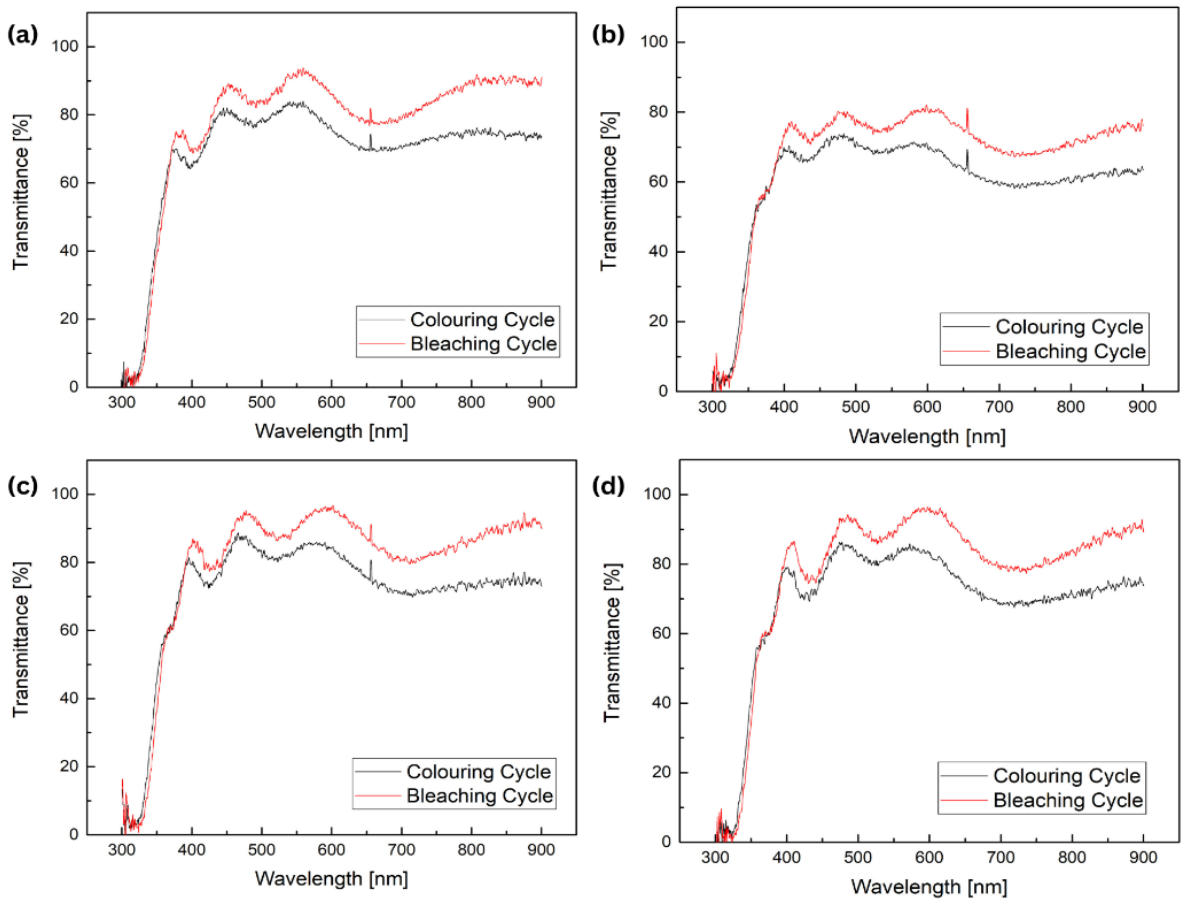

Fig. 6 *The transmittance spectra of the colouring and bleaching cycles for TiO_2 thin films preheated at: (a) 100°C ; (b) 200°C ; (c) 300°C ; (d) 400°C*

Examining the calculated optical modulation in Fig. 7 reveals a gradual increase with higher pre-heating temperatures. The figure demonstrates that the TiO_2 thin film samples exhibited optical modulations of 9%, 11%, 12%, and 13% for the samples preheated at 100°C, 200°C, 300°C, and 400°C, respectively.

The optical density of the samples preheated at 100°C and 200°C can be depicted as 0.05 and 0.067, respectively, showing a relatively small increase. On the other hand, the samples subjected to preheating at 300°C and 400°C demonstrated an optical modulation of 0.061 and 0.068, respectively, indicating no significant relative increase. Therefore, we can conclude that the samples preheated above 200°C have optical modulations within the same range.

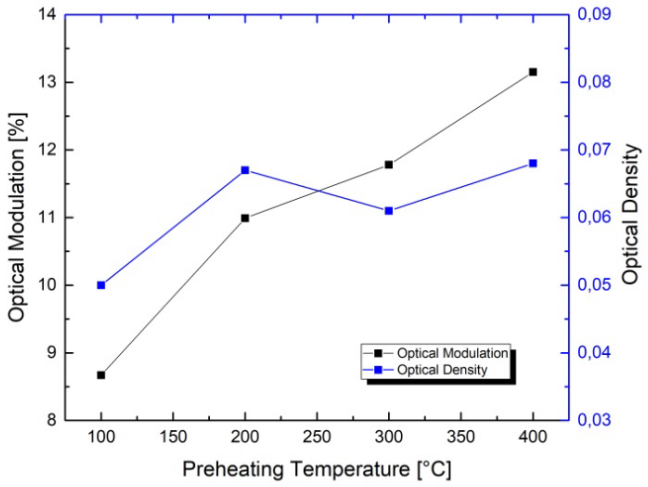

Fig. 7 *The Optical modulation and density of various TiO_2 thin films preheated at different temperatures*

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One of the important aspects of an electrochromic device is its switching characteristics, defined as the bleaching time (T_b)and the colouration time (T_c). The duration required for an electrochromic device to reach 90% of its full optical contrast is called the response time [36]. The colouration and bleaching times are depicted in Table 2. The TiO_2 thin film deposited at the 300°C mark presents the fastest switching characteristics with a colouring time of 9.5 s and a bleaching time of 3.8 s. Factors such as diffusion coefficients, diffusion distance to the active sites, and the rate of charge transfer between the TiO_2 film and the electrolyte can impact the switching characteristics of the TiO_2 thin film [37]. Observing the samples' response time, regardless of their pre-heating temperature, reveals that the colouring response duration was faster than its corresponding bleaching response duration. This observation is attributed to the conductive state of the TiO_2 in the colouring cycle compared to the insulating state of the thin film in the bleaching cycle [38].

Colouration efficiency (CE) is another key component that defines the electrochromic performance of a thin film in electrochromic applications. CE is defined as follows:

$$CE = \frac{\Delta OD}{Q_{in}} = \frac{\log(\frac{T_b}{T_c})}{Q_{in}} \tag{4}$$

where Q_{in} is the intercalated charge. The calculated colouration efficiency (CE) values are revealed in Table 2. The TiO_2 thin film preheated at 100 °C presented the lowest CE value of 0.35 cm^2/C. At the 200°C mark, the TiO_2 thin film exhibited a higher colouration efficiency of 0.63 cm^2/C. The samples pre-heated at 300°C and 400 °C demonstrated relatively similar CE values of 0.54 cm^2/C and 0.56 cm^2/C. Increasing pre-heating temperature indicates a small increase in the CE values. Higher colouration efficiency was achieved when the pre-heating temperature was 200 °C and above.

Table 2 *Switching time and colouration efficiency of TiO_2 thin films pre-heated at different temperatures*

Pre-heating Temperature (°C)	Bleaching Time (s)	Colouring Time (s)	Colouration Efficiency (cm^2/C)
100	5.1	11.3	0.35
200	4	12.2	0.63
300	3.8	9.5	0.54
400	4.4	11.4	0.56

5. Conclusion

This study investigated the impact of pre-heating temperature on the structural, optical, and electrochromic properties of sol-gel fabricated TiO_2 thin films. The results revealed that increasing the pre-heating temperature increased the thickness of the TiO_2 thin films. Moreover, higher pre-heating temperatures accelerated the evaporation process, resulting in the removal of solvents, water, and residuals, thereby enhancing the overall optical transmittance and transparency of the TiO_2 thin film. The FESEM images exhibited uniform and dense TiO_2 films without any pinholes. The highest peak currents and diffusion coefficients were observed at a pre-heating temperature of 200°C. This outcome was attributed to the change in crystalline size corresponding to the difference in the pre-heating temperature. The highest optical modulation was also recorded at a pre-heating temperature of 400°C. Interestingly, all the samples exhibited similar response times for switching. The TiO_2 thin film preheated at 300°C demonstrated the fastest switching characteristics. Furthermore, increasing the pre-heating temperature showed an overall improvement in colouring efficiency, with the highest colouration efficiency value observed at a pre-heating temperature of 200°C. These findings shed light on the significance of pre-heating temperature in controlling the structural, optical, and electrochromic properties of TiO_2 thin films fabricated via the sol-gel route.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Kah-Yoong Chan;* ***data collection:*** *Cheikh Zakaria Eldjilali, Ming-Yue Tan, Abdelrahman Hamed Ebrahem Abdelhamed;* ***analysis and interpretation of results:*** *Cheikh Zakaria Eldjilali, Kah-Yoong Chan, Gregory Soon How Thien, Pei-Ling Low, Yew-Keong Sin, Chu-Liang Lee, Wai-Leong Pang;* ***draft manuscript preparation:*** *Cheikh Zakaria Eldjilali. Kah-Yoong Chan. All authors reviewed the results and approved the final version of the manuscript*

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