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Optical and Structural Properties of V_2O_5 Electrochromic Thin Films

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***Abstract* — The increase in global temperature has led to a significant surge in energy consumption within the air conditioning industry, resulting in environmental deterioration. Electrochromic (EC) windows have emerged as a promising solution to address these challenges. Vanadium pentoxide (V_2O_5) stands out among all metal oxide materials due to its remarkable EC properties, including substantial Li^+ ion insertion capacity and multicolor capabilities. Despite the potential of V_2O_5, there remains a lack of comprehensive research on the structural and optical properties of V_2O_5 films with varying thicknesses. Therefore, this study aims to investigate the structural and optical properties of V_2O_5 thin films with thicknesses ranging from 46 to 344 nm. By employing the sol-gel spin coating method, V_2O_5 thin films were fabricated and analyzed using X-ray diffraction (XRD) spectroscopy and ultraviolet-visible (UV-Vis) spectrophotometry. The fabricated V_2O_5 thin films with thicknesses of 46-274 nm demonstrated an average film transparency of 83%. XRD analysis further revealed that the V_2O_5 thin films reached their peak crystallinity at a thickness of 344 nm. Moreover, CV analysis revealed that the V_2O_5 device, with a thickness of 274 nm, exhibited a cathodic peak current of -1.63 mA, indicating its excellent ability to facilitate Li^+ ion diffusion. Additionally, CA measurements displayed a high optical modulation of 37.78%. Ultimately, this research contributes to the development of energy-efficient solutions for sustainable environmental practices.**

Keywords—Electrochromic, Sol-gel, V_2O_5, Thin film, Multicolor.

I. INTRODUCTION

The Earth's climate is experiencing rapid and unprecedented changes, primarily due to human activities such as fossil fuel combustion, deforestation, inadequate treatment of wastewater, and industrial processes [1]. These actions have led to the rise in global temperatures and caused a significant surge in energy consumption in the air conditioning industry, hence resulting in energy depletion and environmental deterioration [2]. In Malaysia, buildings utilize 48% of the nation's electricity supply. Among these, commercial buildings consume approximately 38645 gigawatt-hours (GWh), while residential buildings account for 24709 GWh [3]. Therefore, energy-efficient technologies such as electrochromic (EC) windows have emerged as crucial solutions to mitigate the adverse effects of climate change. As compared to conventional windows, EC windows allow users to adjust transparency according to their preference by using low voltage [4], thereby regulating indoor conditions and reducing energy consumption [4]. Given the numerous benefits of EC windows, they can be implemented in construction [5] and automotive industries [6].

In 1953, Thaddeus Kraus introduced the concept of reversible color-bleach characteristics of WO_3, laying the groundwork for future visual display devices [7]. However, Deb's seminal paper, published in 1973, outlining the coloration process of WO_3, is widely recognized as the true origin of EC technology [8]. Since then, extensive research efforts have been dedicated to EC technology, resulting in significant breakthroughs over a few decades. Researchers have explored various metal oxide materials, such as iridium dioxide (IrO_2) [9], tungsten trioxide (WO_3) [10], vanadium oxide (V_2O_5) [11], titanium dioxide (TiO_2) [12], and nickel oxide (NiO) [13] to investigate the EC characteristics. Among these metal oxide materials, V_2O_5 emerges as a promising candidate, not only for energy-saving applications but also for its versatility in multi-color displays.

To further elaborate, vanadium oxide (Vox) comprises multiple oxidation states (V^{2+} to V^{5+}), resulting in the formation of inorganic compounds such as vanadium monoxide (VO), vanadium dioxide (VO_2), vanadium sesquioxide (V_2O_3), and vanadium pentoxide (V_2O_5) [14]. Among these oxidation states, V_2O_5 stands out as the most stable phase [14]. The fundamental unit of the V_2O_5 structure consists of the distorted VO_6 octahedron, which comprises six oxygen atoms arranged around a central vanadium atom [15]. These VO_6 octahedra form a continuous layer by sharing edges and corners, thereby establishing bonds between adjacent layers [15]. Thus, this structural layer endows V_2O_5 with substantial lithium (Li^+) ion insertion capacity, making it exceptionally suitable for EC applications. Moreover, V_2O_5 is unique among metal oxides in its ability to display both anodic and cathodic coloration electrochromism, which contributes to its multicolor capabilities. In terms of V_2O_5 thin films fabrication, various techniques such as spray pyrolysis deposition [16], sol-gel spin coating [17], hydrothermal synthesis [18], and chemical vapor deposition [19] have been employed by previous researchers. The sol-gel process is noteworthy among these methods due to its low cost and simplicity [20].

The EC performance of metal oxide thin films is greatly dependable on both the fabrication process and film thickness. For instance, Park *et al.* reported that V_2O_5 thin films with a thickness of 500 nm, fabricated using the radio frequency (RF) sputtering method, exhibited excellent discharge capacity and cyclic stability [21]. Additionally, Atak *et al.* mentioned that NiO film, 480 nm in thickness and fabricated using the RF magnetron sputtering technique, exhibited high coloration efficiency and optical contrast [22]. These examples show that the effect of thin film thickness is worth studying. To date, there has been a lack of comprehensive research on the structural and optical properties of V_2O_5 films with varying thicknesses fabricated using the sol-gel spin coating technique. Additionally, numerous studies examining the EC properties of V_2O_5 had primarily concentrated on the thin film level, neglecting the importance of transforming them into device forms suitable for practical applications.

Therefore, in this study, V_2O_5 thin films with varying thicknesses were fabricated on ITO glass substrates using the sol-gel spin coating method to investigate their structural and optical properties. The film thicknesses for various layers were measured at 46, 122, 274, 309, and 344 nm, respectively. Furthermore, to verify the functionality of the V_2O_5 thin film, a randomly selected sample was transformed into a device to analyze its EC characteristics.

The V_2O_5 thin film examined in this study shows potential across various areas. Firstly, it serves as a counter electrode in complementary EC devices, enhancing coloration efficiency and optical modulation through its ion storage capability [23]. Additionally, V_2O_5 thin films are utilized as an EC material for energy-efficient smart windows due to their low operating voltage and high transparency [24]. Moreover, V_2O_5 thin films are utilize for aesthetic purposes, such as multicolor displays and colorful window designs [25]. Recent research has even integrated V_2O_5 thin films into energy storage devices [15], allowing users to visually monitor stored energy levels by observing color changes, which offers insights into energy usage patterns.

II. Methodology

The chemicals employed in this study were of analytical grade. The ingredients used in the V_2O_5 sol-gel fabrication process include vanadium (IV) powder (V_2O_5) as the precursor and hydrogen peroxide (H_2O_2) as an oxidizing agent, both procured from Sigma-Aldrich, Rockville, MD, USA.

The V_2O_5 sol-gel process is illustrated in Fig. 1. Initiating the V_2O_5 sol-gel process, V_2O_5 powder was added into a conical flask containing 15% H_2O_2. The mixture was promptly heated to 70°C and stirred vigorously to yield a dark orange solution. Following an exothermic reaction, the orange solution was consistently heated at 70°C and stirred continuously, resulting in the formation of a viscous dark red solution. The resulting V_2O_5 sol-gel was kept in a glass vial and was aged for 24 h. Before the deposition of V_2O_5 sol-gel, ITO glass substrates were ultrasonically cleaned in isopropanol and acetone for 15 mins each.

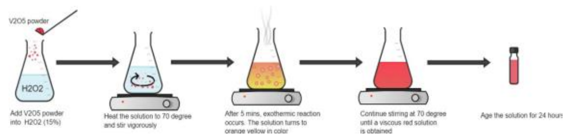

Fig. 1. Fabrication process of V_2O_5 sol-gel.

The spin coating method was employed to deposit V_2O_5 sol-gel onto the ITO glass substrates, with a rotation speed of 3000 rpm. The process was repeated to achieve multiple layers with thicknesses of 46 to 344 nm. Following this, the thin films were annealed at 200 °C. Moving on, the assembly of the V_2O_5 EC device follows this order: ITO/ V_2O_5 thin film/$LiClO_4$-PC gel electrolyte/ITO, as shown in Fig. 2. The device was then sealed using UV resin to prevent leakage of the gel electrolyte. Further details on the recipe for the EC device could be found in our prior research [20]. The structural and optical characteristics of V_2O_5 thin films were analyzed through X-ray diffraction (XRD) spectroscopy and ultraviolet-visible (UV-Vis) spectrophotometry, respectively. Meanwhile, the EC properties were examined using cyclic voltammetry (CV) and chronoamperometry (CA).

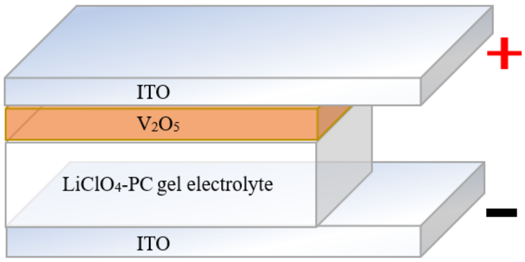

Fig. 2. V_2O_5 electrochromic device.

III. Results

A. Optical Properties

Figure 3(a) depicts the average film transmittance of V_2O_5 thin films with different thicknesses over the visible wavelength range (300 to 900 nm). The results indicated that the thin film with thicknesses of 46, 122, and 274 nm demonstrated high transparency levels, averaging around 83%. In contrast, thin films with thicknesses of 309 and 344 nm exhibited average film transmittance of 75% and 70%, respectively. The reduction in transparency with increasing film thickness was attributed to the increasing surface light scattering and hence reduced the amount of light passing through the film [26]. Moreover, with increasing thickness, there was a red shift in the absorption edge which was consistent with those reported in the literature [27, 28].

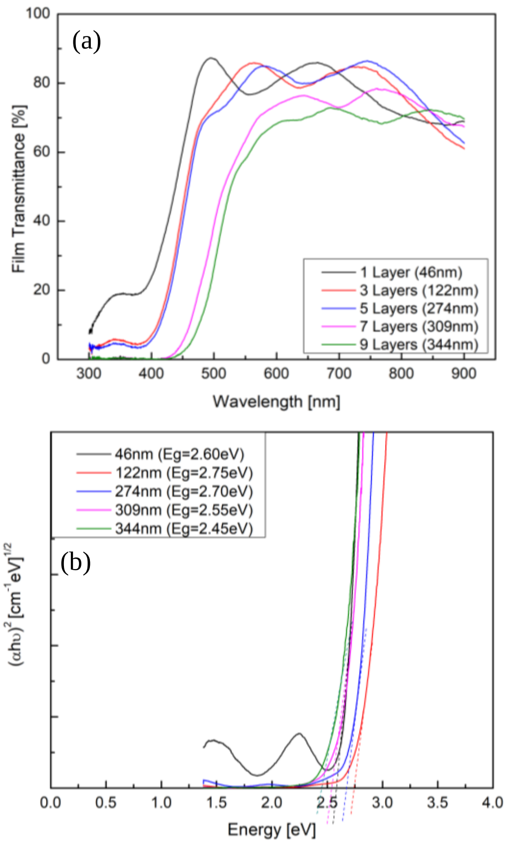

Fig. 3. (a) Film transmittance (b) Optical bandgap of V_2O_5 thin films with various thicknesses.

Interestingly, Liang *et al.* suggested that this red shift was due to a reduction in the optical band gap at thicker films [28]. Consequently, lower-energy photons are absorbed, causing the light to shift towards longer wavelengths [28]. To validate the concept, the optical bandgap of the V_2O_5 thin films was calculated using their absorbance. In Fig. 3(b), the results revealed a decreasing bandgap from 2.75 eV at 122 nm to 2.45 eV at 344 nm. Moreover, the oscillation pattern depicted in Fig. 3(a), known as the interference fringe, is a result of the incident light bouncing back and forth between the glass substrates, air, and thin films [27].

B. Structural Properties

Figure 4 depicts the crystalline nature of the V_2O_5 thin films across various thicknesses as determined by XRD analysis. The detected peaks corresponded to the Miller indices (1 0 1), (1 1 0), and (0 0 2) confirming the presence of orthorhombic V_2O_5 peaks (ICDD no. 01-089-0612).

The observation revealed that V_2O_5 thin films with thicknesses of 122 nm and below exhibited no visible peaks, indicating an amorphous nature. At a thickness of 274 nm, slight crystallinity was evidenced by small peaks appearing at 22° and 26°. Beyond 274 nm, the peak corresponding to (1 0 1) became intense and narrow, whereas the intensity of the peak corresponding to (1 1 0) remained low and broad. The predominance of the peak corresponding to (1 0 1) implies that the crystallization orientation of V_2O_5 mainly grew along the (1 0 1) axis. Additionally, the observation suggested that thin films with greater thickness exhibited higher crystallinity. Giraldi *et al.* reported that as the thickness of the thin film increased, the crystallinity increased owing to the growth in crystallite size [29]. Similarly, Kwong *et al.* revealed that the improved crystallinity was due to the relief of stress at the interface between the substrate and the thin film [30]. Interestingly, at a thickness of 344 nm, a new orthorhombic V_2O_5 peak, corresponding to the Miller indices (0 0 2) at 43° was observed.

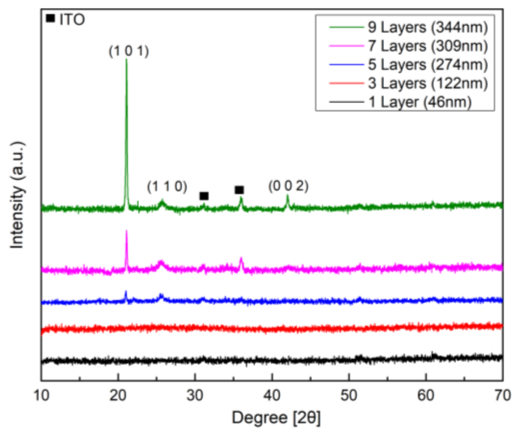

Fig. 4. XRD measurement of V_2O_5 thin films with various thicknesses.

C. Electrochromic Properties

Cyclic voltammetry (CV) measurement was conducted on a V_2O_5 device with a thickness of 274 nm, aiming to explore its redox process for practical applications. Additionally, chronoamperometry (CA) was employed to further investigate the optical modulation of the V_2O_5 devices. Fig. 5(a) depicts the CV curve (initial cycle), wherein the potential was swept from -2 to 2 V at a scan rate of 0.1 V/s. Similar voltage settings had been applied for CA measurement. The CV result revealed that the V_2O_5 device exhibited a notable cathodic peak current of -1.63 mA in its first cycle, indicating its exceptional ability to facilitate Li^+ ion diffusion. Additionally, the excellent EC performance of the V_2O_5 device was further confirmed by the CA measurements. Before ion insertion, the V_2O_5 device exhibited an original transmittance of 67.58%. However, during ion insertion, its transmittance reduced to 29.8%, indicating a significant optical modulation of 37.78%, as depicted in Fig. 5(b).

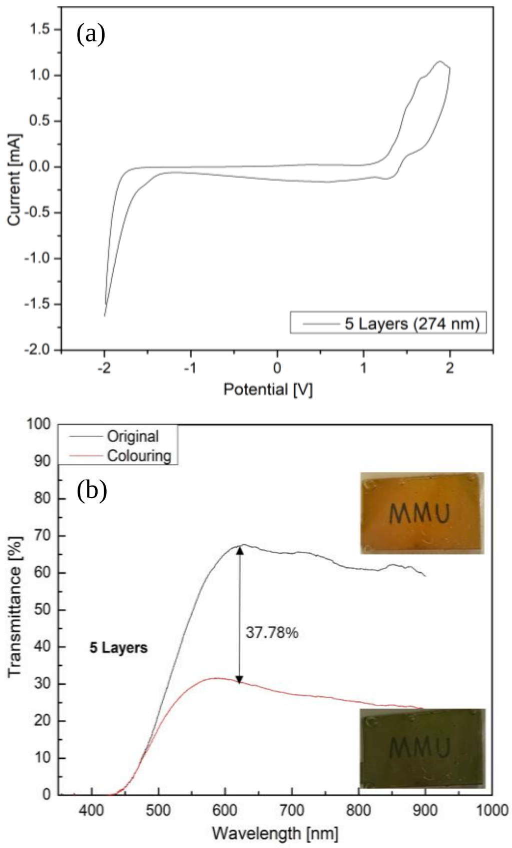

Fig. 5. (a) CV measurements and (b) optical modulation of V_2O_5 thin films with a thickness of 274 nm.

Besides, the observation revealed that the CV curve exhibited two cathodic (at 1.5 V and -2 V) and anodic peaks (at 1.7 V and 2 V), indicating a two-step EC process. This observation was consistent with those previously reported in the literature [24, 31]. During the reduction process, the V^{5+} ions were initially reduced to a mixture of V^{5+} and V^{4+}, causing the V_2O_5 device to transition from its original orange color to a greenish-yellow color. Subsequently, as the V^{5+} ions were completely reduced to V^{4+}, the V_2O_5 device changed to a deep blue color. Conversely, during the oxidation process, the thin film transitioned back from blue to greenish-yellow and finally regained its original orange color as the V^{4+} ion lost electrons. To note, the CV and CA measurements in this study were performed for only one cycle to demonstrate the functionality of the V_2O_5 device. Further investigation into stability testing will be conducted in future studies.

IV. CONCLUSION

This research successfully fabricated V_2O_5 thin films of different thicknesses (46 to 344 nm) using sol-gel spin coating methods. V_2O_5 thin films with thicknesses of 46, 122, and 274 nm exhibited a high average film transparency of 83%. Besides, XRD examination indicated that thicker films showed higher levels of crystallinity. Additionally, CV analysis demonstrated that the V_2O_5 device with a thickness of 274 nm displayed a cathodic peak current of -1.63 mA, highlighting its excellent capability to facilitate Li^+ ion diffusion. Meanwhile, CA measurement indicated a substantial optical modulation of 37.78%. These findings underscored the importance of varying thickness in influencing the structural and optical properties of V_2O_5 thin films, thus indicating their potential applications in diverse fields such as smart windows and aesthetic electronic devices.

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REFERENCES

[1] P. S. Hansamali, E. C. Y. Yang and S. Zakaria, “A Short Review: Photocatalysis As An Alternative Method for POME Treatment,” *J. Eng. Technol. and Appl. Phys.*, vol. 6, no. 1, pp. 32–39, 2024.

[2] S. Bilgen, “Structure and Environmental Impact of Global Energy Consumption,” *Renew. and Sustain. Ener. Rev.*, vol. 38, pp. 890-902, 2014.

[3] J. S. Hassan, R. M. Zin, M. Z. A. Majid, S. Balubaid and M. R. Hainin, “Building Energy Consumption in Malaysia: An Overview,” *J. Teknol.*, vol. 70, no. 7, pp. 1-6, 2014.

[4] Y. Xu, C. Yan, S. Yan, H. Liu, Y. Pan, F. Zhu and Y. Jiang, “A Multi-objective Optimization Method Based on An Adaptive Meta-Model for Classroom Design with Smart Electrochromic Windows,” *Energy*, vol. 243, pp. 122777, 2022.

[5] A. Cannavale, U. Ayr, F. Fiorito and F. Martellotta, “Smart Electrochromic Windows to Enhance Building Energy Efficiency and Visual Comfort,” *Energies*, vol. 13, no. 6, pp. 1449, 2020.

[6] N. I. Jaksic and C. Salahifar, “A Feasibility Study of Electrochromic Windows in Vehicles,” *Solar Ener. Mater. and Solar Cells*, vol. 79, no. 4, pp. 409-423, 2003.

[7] R. Mortimer, “Switching Colors with Electricity,” *American Scientist*, vol. 101, no. 1, pp. 1-38, 2013.

[8] B. Wen-Cheun Au, K. Y. Chan and D. Knipp, “Effect of Film Thickness on Electrochromic Performance of Sol-Gel Deposited Tungsten Oxide (WO_3),” *Opt. Mater.*, vol. 94, pp. 387-392, 2019.

[9] T. F. Ko, P. W. Chen, K. M. Li, H. T. Young, C. Te Chang and S. C. Hsu, “High-performance Complementary Electrochromic Device Based on Iridium Oxide As A Counter Electrode,” *Materials*, vol. 14, no. 7, pp. 1591, 2021.

[10] Y. Yao, Q. Zhao, W. Wei, Z. Chen, Y. Zhu, P. Zhang, Z. Zhang and Y. Gao, “WO_3 Quantum-dots Electrochromism,” *Nano Ener.*, vol. 68, pp. 104350, 2020.

[11] W. Zhao, J. Wang, B. Tam, P. Pei, F. Li, A. Xie and W. Cheng, “Macroporous Vanadium Oxide Ion Storage Films Enable Fast

Switching Speed and High Cycling Stability of Electrochromic Devices," *ACS Appl. Mater. Interfaces*, vol. 14, no. 26, pp. 30021–30028, 2022.

[12] L. Zhao, Z. Cai, X. Wang, W. Liao, S. Huang, L. Ye, J. Fang, C. Wu, H. Qiu and L. Miao, "Constructed TiO_2/WO_3 Heterojunction with Strengthened Nano-Trees Structure for Highly Stable Electrochromic Energy Storage Device," *J. Adv. Ceramics*, vol. 12, no. 3, pp. 634-648, 2023.

[13] Y. Abe, Y. Kadowaki, M. Kawamura, K. H. Kim and T. Kiba, "Two-color Electrochromic Devices Using A Tungsten Oxide and Nickel Oxide Double Layer," *Jpn. J. Appl. Phys.*, vol. 62, no. 1, pp. 015502, 2023.

[14] D. T. Cestarolli, E. M. Guerra, D. T. Cestarolli and E. M. Guerra, "Vanadium Pentoxide (V_2O_5): Their Obtaining Methods and Wide Applications," *Transition Metal Compounds – Synthes., Propert., and Appl.*, IntechOpen, pp. 96860, 2021.

[15] Q. Fu, H. Zhao, A. Sarapulova and S. Dsoke, "V_2O_5 As A Versatile Electrode Material for Postlithium Energy Storage Systems," *Appl. Res.*, vol. 2, no. 3, p. e202200070, 2023.

[16] M. Mousavi, A. Kompany, N. Shahtahmasebi and M. M. Bagheri-Mohagheghi, "Characterization and Electrochromic Properties of Vanadium Oxide Thin Films Prepared via Spray Pyrolysis," *Modern Phys. Lett. B*, vol. 27, no. 21, pp. 1350152,2013.

[17] D. P. Partlow, S. R. Gurkovich, K. C. Radford and L. J. Denes, "Switchable Vanadium Oxide Films By A Sol-gel Process," *J. Appl. Phys.*, vol. 70, no. 1, pp. 443-452, 1991.

[18] J. Livage, "Hydrothermal Synthesis of Nanostructured Vanadium Oxides," *Materials*, vol. 3, no. 8, pp. 4175-4195, 2010.

[19] N. Arya, D. Verma and V. Balakrishnan, "Fabrication of Vertically Aligned CNT- Vanadium Oxide Hybrid Architecture with Enhanced Compressibility and Supercapacitor Performance," *Nanotechnology*, vol. 34, no. 11, pp. 115401, 2023.

[20] K. Y. Chan, B. W. C. Au, M. Z. Sahdan, A. S. I. Chong and D. Knipp, "Realisation of Solid-State Electrochromic Devices Based on Gel Electrolyte," *F1000Res.*, vol. 11, pp. 1-13, 2022.

[21] Y. J. Park, K. S. Ryu, K. M. Kim, N. G. Park, M. G. Kang and S. H. Chang, "Electrochemical Properties of Vanadium Oxide Thin Film Deposited by R.F. Sputtering," *Solid State Ion.*, vol. 154–155, pp. 229-235, 2002.

[22] G. Atak and Ö. D. Coşkun, "Effects of Anodic Layer Thickness on Overall Performance of All-Solid-State Electrochromic Device," *Solid State Ion.*, vol. 341, pp. 115045, 2019.

[23] D. S. Dalavi, A. K. Bhosale, R. S. Desai and P. S. Patil, "Energy Efficient Electrochromic Smart Windows Based on Highly Stable CeO_2-V_2O_5 Optically Passive Counter Electrode," in *Mater. Today: Proc.*, vol. 43(4), pp. 2702-2706, 2021.

[24] M. B. Sahana, C. Sudakar, C. Thapa, G. Lawes, V. M. Naik, R. J. Baird, G. W. Auner, R. Naik and K. R. Padmanabhan, "Electrochemical Properties of V_2O_5 Thin Films Deposited by Spin Coating," *Mater. Sci. and Eng.: B*, vol. 143, no. 1–3, pp. 42-50, 2007.

[25] J. Kim, K. H. Lee, S. Lee, S. Park, H. Chen, S. K. Kim, S. Yim, W. Song, S. S. Lee, D. H. Yoon, S. Jeon and K. An, "Minimized Optical Scattering of MXene-derived 2D V_2O_5 Nanosheet-based Electrochromic Device with High Multicolor Contrast and Accuracy," *Chem. Eng. J.*, vol. 453, pp. 139973, 2023.

[26] A. Abudula, F. Gao, T. Liu, Y. Zhang, M. Song, N. Li, S. Liu and P. Tuersun, "Effect of Ag Film Thickness on The Morphology and Light Scattering Properties of Ag Nanoparticles," *Nanosci. and Nanotechnol. Lett.*, vol. 6, no. 5, pp. 392-397, 2014.

[27] M. A. Zubair, M. T. Chowdhury, M. S. Bashar, M. A. Sami and M. F. Islam, "Thickness Dependent Correlation Between Structural and Optical Properties of Textured CdSe Thin Film," *AIP Adv.*, vol. 9, no. 4, pp. 045123, 2019.

[28] G. X. Liang, P. Fan, X. M. Cai, D. P. Zhang and Z. H. Zheng, "The Influence of Film Thickness on The Transparency and Conductivity of Al-doped ZnO Thin Films Fabricated by Ion-Beam Sputtering," *J. Electron. Mater.*, vol. 40, no. 3, pp. 267–273, 2011.

[29] T. R. Giraldi, M. T. Escote, M. I. B. Bernardi, V. Bouquet, E. R. Leite, E. Longo and J. A. Varela, "Effect of Thickness on The Electrical and Optical Properties of Sb Doped SnO_2 (ATO) Thin Films," *J. Electroceramics*, vol. 13, pp. 159–165, 2004.

[30] W. L. Kwong, H. Qiu, A. Nakaruk, P. Koshy and C. C. Sorrell, "Photoelectrochemical Properties of WO_3 Thin Films Prepared by Electrodeposition," *Ener. Proced.*, vol. 34, pp. 617-626, 2013.

[31] M. Benmoussa, A. Outzourhit, R. Jourdani, A. Bennouna, and E. L. Ameziane, "Structural, Optical and Electrochromic Properties of Sol-gel V_2O_5 Thin Films," *Active and Passive Electron. Componen.*, vol. 26, no. 4, pp. 245–256, 2003.