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Thin Film Coatings For Electrochromic Applications – A Comparative Review

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Abstract:
This paper delves into the exploration of optical properties and phenomena observed in everyday materials and environments. It focuses specifically on their applications in a significant area: electrochromic thin films for electrochromic devices (ECDs). By conducting an extensive review of existing literature, the paper establishes crucial formulas and criteria for assessing material performance in both these applications. Furthermore, it carefully evaluates three different synthesis methods for electrochromic coatings to determine the most effective approach. WO_3 is experimentally synthesised through electrodeposition method and characterised to provide a practical aspect and understanding for the study of electrochromism.

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I. Background Information

It is essential to define and review basic optical properties through a thorough secondary literature review. Optical (from opticus "of sight or seeing," in mediaeval Latin) refers to the manner in which matter interacts with light. Optical properties consist of a large range of features, including but not limited to: refractive index, dispersion, scattering, dichroism, photosensitivity, reflectivity, transmittance and absorption. This section will discuss a few of the relevant properties for the study of electrochromic coatings in detail.

Absorbance and Transmittance

Spectrophotometry refers to a quantitative measure of the manner in which electromagnetic radiation (particularly infrared radiation, visible light and ultraviolet radiation) interacts with a sample. This includes two important, interconnected measurements: absorbance and transmittance.[1]

Absorbance (A), also termed as optical density, refers to the quantitative amount of radiation that the sample can take in or absorb. It is a unitless quantity, but measured in absorbance units (referred to as AU).[2] Absorption of light occurs when the natural frequency of the incident light wave is the same as that of the vibrational frequency of the electrons in the material, thus causing a conversion of the energy in the light wave to vibrational energy in the material. This will cause the light that exits the material (transmitted light) to be attenuated. Transmittance is a property in spectrophotometry, which is a ratio of the transmitted light to the incident light.

Given the molar concentration of a sample is uniform throughout:

The absorbance can be given by the following relation[3]: $A = \varepsilon c l$
Where:
A is the absorbance is unitless, often reported in AU
ε is the wavelength-dependent molar absorptivity/attenuation coefficient of the material in $Lmol^{-1}cm^{-1}$
l is the length of the solution light passes through in cm
c is the concentration of the material in mol L^{-1}

The transmittance can be given by the following equation:

[1] Hughes, Harold K. "Beer's Law and the Optimum Transmittance in Absorption Measurements." *Applied Optics* 2, no. 9 (1963): 937. https://doi.org/10.1364/ao.2.000937.
[2] Info note 804: UV-VIS nomenclature and Units - NanopartzTM. Accessed July 10, 2023. https://www.nanopartz.com/PDFs/Info%20Notes/IN804%20UV-VIS%20Nomenclature%20and%20Units.pdf.
[3] Swinehart, D. F. "The Beer-Lambert Law." *Journal of Chemical Education* 39, no. 7 (1962): 333. https://doi.org/10.1021/ed039p333.

$$T\% = \frac{I}{I_o}$$

Where:
T% is the transmittance expressed as a percentage
I is the intensity of transmitted light
I_o is the intensity of incident light
Transmittance can also be calculated through the ratio of the transmitted radiant flux to incident radiant flux.

The absorbance and transmittance can be related by the Beer-Lambert Law, also referred to as the Bouguer-Lambert law.[4] This states:

$$log_{10}\frac{I_o}{I} = \varepsilon\, l\, c$$

Thus, it follows that[5]:

A = $log_{10}\frac{I_o}{I}$

A = $log_{10}\frac{1}{T}$

A = $log_{10}\frac{100}{T\%}$
A = $2 - log_{10}(T\%)$

This can be graphically described as follows:

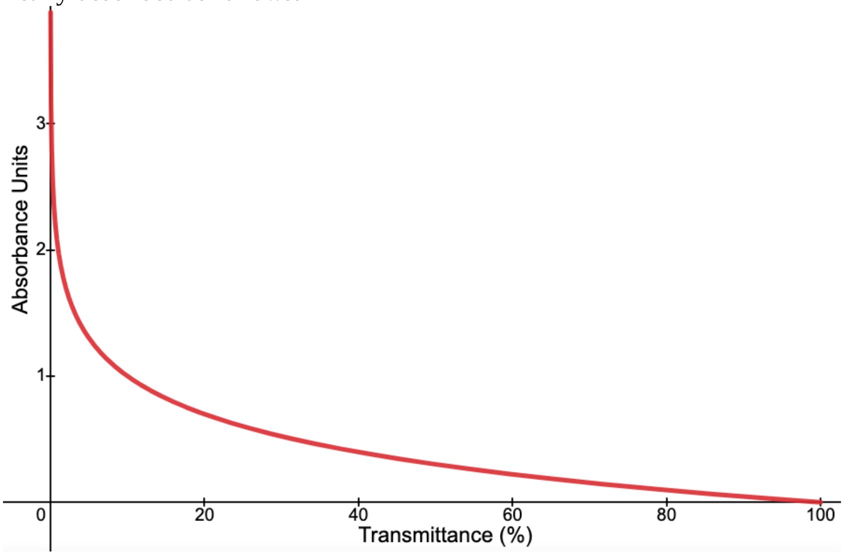


Figure 1.1 - % of Light Transmitted per Absorbance Unit

[4] The bouguer-beer-lambert law: Shining light on the obscure. Accessed June 7, 2023. https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cphc.202000464.
[5] "Theory of Absorbance ." Turner Designs. Accessed June 20, 2023. http://docs.turnerdesigns.com/t2/doc/appnotes/S-0075.pdf.

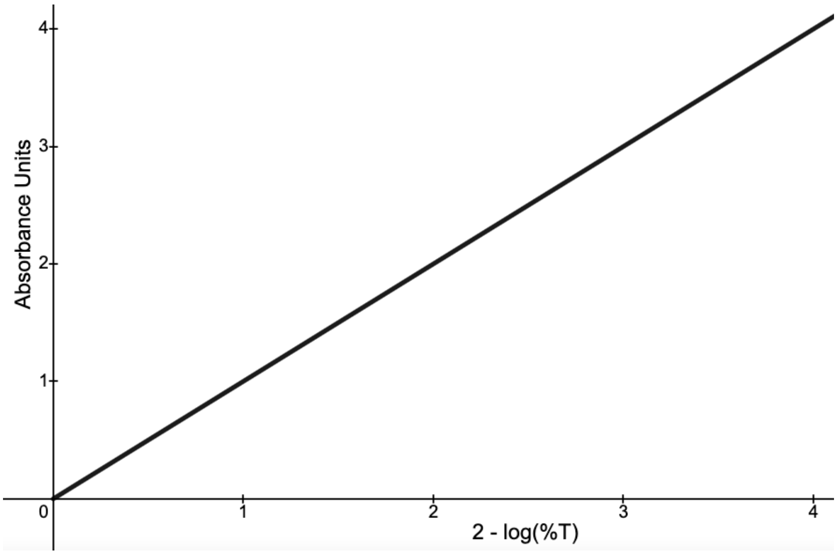


Figure 1.2 - Relationship between Absorbance and Transmittance (T)

These properties can be measured through a spectrophotometer. The study of transmittance and absorbance is highly relevant to this study since the concept of electrochromism revolves around ensuring the largest difference in transmission between the two states of the electrochromic material. Further, with respect to anti-glare coatings on lenses, caution must be exerted to ensure the material coated does not decrease the transmittance of light, but instead increase it through decreasing the amount of light lost to reflection.

Thin Film Synthesis Methods

A thin film is a layer of a particular material that ranges from a few nanometers to a few micrometres in width.[6] It has a multitude of applications in our daily lives, such as in photovoltaic cells, camera lenses, and display screens.[7]

Using a thin film deposit is the manner to coat glass for electrochromic coatings. With respect to synthesising thin films for these applications, there are a variety of approaches that one can take.[8] In this section, I will refer to three common methods:

Sol-gel Method

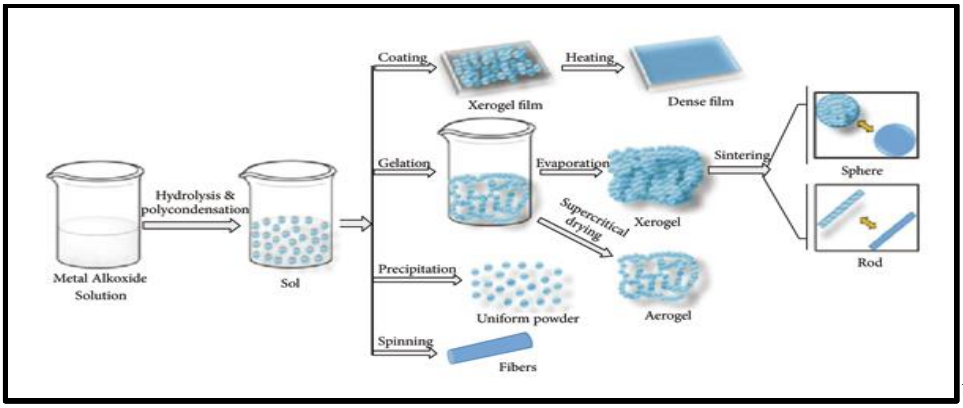
The sol-gel synthesis method is a commonly used method for the synthesis and application of nanomaterial thin films.[9] There are several processes under the sol-gel method, displayed in the flowchart below:

[6] "Thin Films." Thin Films - an overview | ScienceDirect Topics. Accessed June 20, 2023. https://www.sciencedirect.com/topics/materials-science/thin-films.

[7] Acosta, Edwin. "Thin Films/Properties and Applications." *Thin Films*, 2021. https://doi.org/10.5772/intechopen.95527.

[8] Baig, Nadeem, Irshad Kammakakam, and Wail Falath. "Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges." *Materials Advances* 2, no. 6 (2021): 1821–71. https://doi.org/10.1039/d0ma00807a.

[9] "Sol Gel Process." Sol Gel Process - an overview | ScienceDirect Topics. Accessed June 22, 2023. https://www.sciencedirect.com/topics/chemistry/sol-gel-process.



[10]

Fig 1.3 - The sol-gel method for synthesis of nanomaterials.

The most common sol-gel process for coating for electrochromism works as follows:

First the desired material is dissolved in a solvent such as water or alcohol, and heated slightly and stirred to obtain the precursor solution (normally a metal alkoxide solution). Next, polymerisation and hydrolysis or alcoholysis of the solution takes place to create a colloidal suspension mixture referred to as the 'sol.'[11] Next, this is coated onto the substrate; this coating can be done in various ways, including the spin or dip coating. Following this, the process of gelation is performed, where the solvent is evaporated in a controlled manner in order to lead to the formation of a coating.[12] Finally, the coated substrate undergoes a heat treatment where the layer of coating is made uniform.

Sputtering Method

This is a physical vapour deposition (PVD) process widely used in industry for thin film coatings with a nanomaterial. This process involves the bombardment of a target material with high energy ions, resulting in the ejection of molecules or atoms from the target material, and causing them to deposit as a thin film on a substrate.[13] There are several different types of sputtering, including DC diode sputtering, radio frequency sputtering, and magnetron sputtering.

The method for a basic sputtering set-up is displayed in the picture below:

[10] Bokov, Dmitry, Abduladheem Turki Jalil, Supat Chupradit, Wanich Suksatan, Mohammad Javed Ansari, Iman H. Shewael, Gabdrakhman H. Valiev, and Ehsan Kianfar. "Nanomaterial by Sol-Gel Method: Synthesis and Application." *Advances in Materials Science and Engineering* 2021 (2021): 1–21. https://doi.org/10.1155/2021/5102014.

[11] Fernández-Hernán, Juan Pablo, Belén Torres, Antonio Julio López, and Joaquín Rams. "The Role of the Sol-Gel Synthesis Process in the Biomedical Field and Its Use to Enhance the Performance of Bioabsorbable Magnesium Implants." *Gels* 8, no. 7 (2022): 426. https://doi.org/10.3390/gels8070426.

[12] Bokov, Dmitry, Abduladheem Turki Jalil, Supat Chupradit, Wanich Suksatan, Mohammad Javed Ansari, Iman H. Shewael, Gabdrakhman H. Valiev, and Ehsan Kianfar. "Nanomaterial by Sol-Gel Method: Synthesis and Application." *Advances in Materials Science and Engineering* 2021 (2021): 1–21. https://doi.org/10.1155/2021/5102014.

[13] "Ion Beam Sputtering." Ion Beam Sputtering - an overview | ScienceDirect Topics. Accessed July 19, 2023. https://www.sciencedirect.com/topics/chemistry/ion-beam-sputtering.

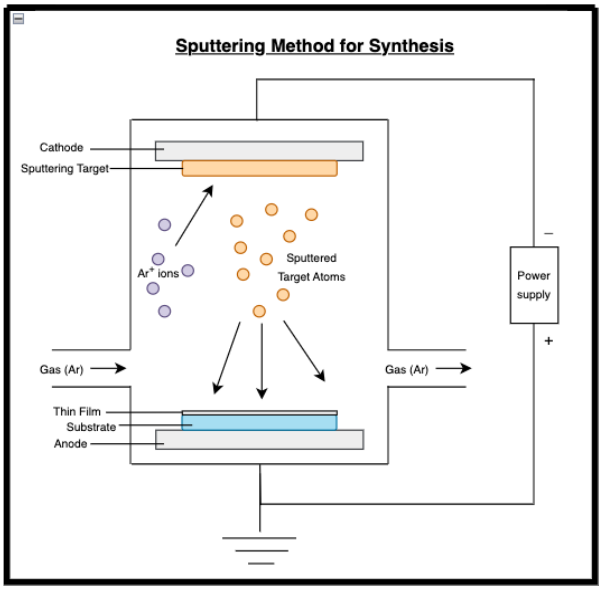


Fig 1.4 - The basic sputtering process for synthesis of nanomaterials.

The basic idea behind sputtering is as follows:

A vacuum chamber is created, which contains a target material (to be deposited) and a substrate (to be coated). A low pressure, often inert, gas is filled in the vacuum chamber. Subsequently, the gas atoms are ionised through applying a high voltage in the chamber, which creates an electric field. This causes the argon atoms to be accelerated, subsequently giving them kinetic energy. These atoms with high energy collide with the surface of the target material, transferring their energy, causing the atoms or molecules to gain sufficient energy to overcome the intermolecular forces of attraction in the target material.[14] This leads to the ejection of atoms or molecules from the target material. This ejection is referred to as sputtering. The sputtered atoms or molecules move freely within the vacuum chamber, and may undergo a change in trajectory or energy due to collisions with gas atoms or ions present. Some sputtered atoms or molecules travel towards the surface of the cleaned substrate, where they deposit and contribute to the growth of the film.[15] However not all the sputtered species reach the substrate, as some may be lost through collisions or diffusion in the chamber. To maximise deposition rate and ensure control over the film's thickness and properties, it is essential to optimise the process parameters, such as gas pressure, sputtering power, and target-substrate distance.

Electrodeposition

The method of electrodeposition for thin film synthesis, also referred to as electrochemical deposition, is another well-known technique for the synthesis of nanoparticles. This method enables us to obtain desired nanoparticles with a high purity, and also allows us to easily control the particle size by adjusting the current density. For this method, the precursor solution is first filtered to act as the electrolyte, and placed in a container. Two electrodes are set up in the same container: the cathode (negative electrode) is the substrate that needs to be coated, and the anode (positive electrode) is made of the same material as the one to be deposited and acts as the reference electrode.[16] In this way, the anode serves as a source of metal ions which function to replenish the electrolyte. This setup is completed through the provision of a direct current (DC) power supply, with the negative terminal attached to the cathode and the positive terminal attached to the anode. This setup is displayed in the diagram below:

[14] Wilczopolska, Magdalena, Katarzyna Nowakowska-Langier, Sebastian Okrasa, Lukasz Skowronski, Roman Minikayev, Grzegorz W. Strzelecki, Rafal Chodun, and Krzysztof Zdunek. "Synthesis of Copper Nitride Layers by the Pulsed Magnetron Sputtering Method Carried out under Various Operating Conditions." *Materials* 14, no. 10 (2021): 2694. https://doi.org/10.3390/ma14102694.

[15] Larson, Bridget. Deposition of Nanoparticles or Thin Films via Magnetron SputteringTowards Graphene Surface Functionalization and Device Fabrication . Accessed June 19, 2023. https://core.ac.uk/download/237136072.pdf.

[16] Florea, R M, and I Carcea. "Sustainable Anti-Corrosive Protection Technologies for Metal Products by Electrodeposition of Hea Layers." *IOP Conference Series: Materials Science and Engineering* 591, no. 1 (2019): 012014. https://doi.org/10.1088/1757-899x/591/1/012014.

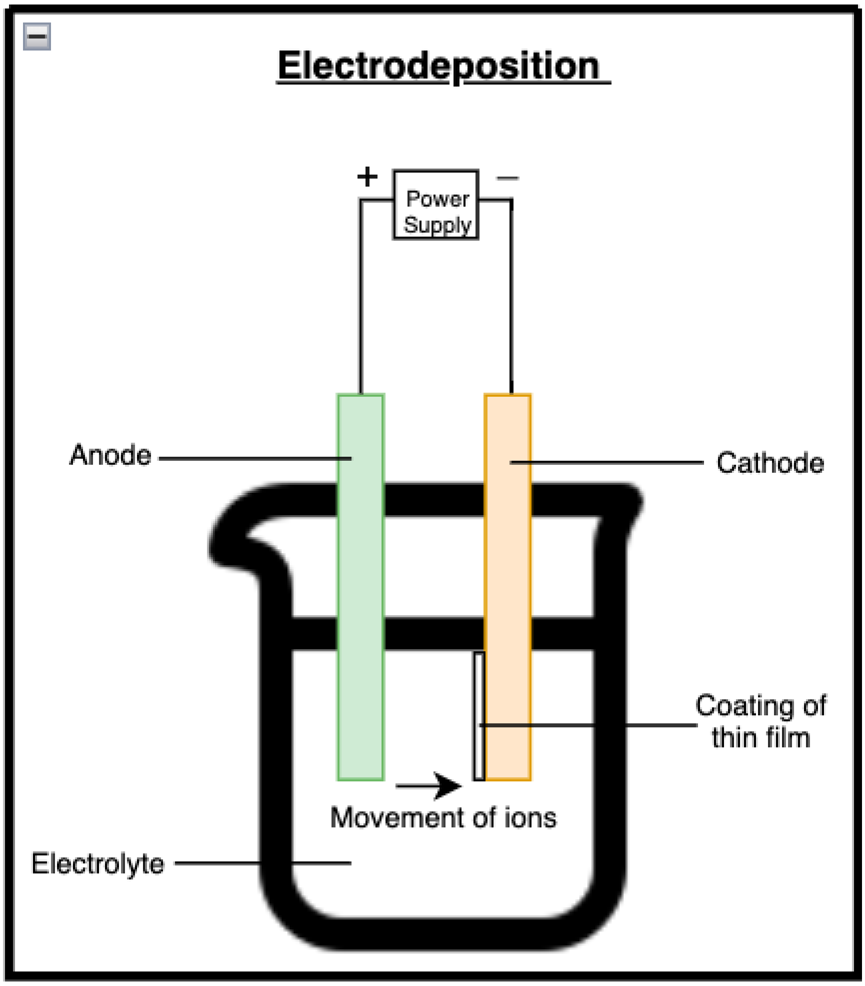


Fig 1.7 - The method of electrodeposition for synthesis of nanomaterials.

Here, the electrode to be coated is the electrode connected to the negative terminal (cathode). As the power is supplied, reduction takes place at the substrate (cathode), as ions in solution gain electrons and form a deposit on the substrate. Alternatively, at the anode, oxidation occurs in order to replace the ions in solution lost through reduction. In this manner, a coating is formed on the substrate.[17] The substrate with the deposited metal film is carefully removed from the electrolyte, rinsed, and often subjected to post-treatment processes such as annealing, cleaning, or drying. It is essential to keep several parameters carefully controlled for successful deposition including the current density, electrolyte composition, temperature, and pH.[18]

II. Electrochromism

Chromism refers to a reversible change that could occur in the optical properties of a compound. Electrochromism, then, refers to a process where the opacity or colour of a material can be changed in response to an electric field or current. This phenomenon has several applications, in the case of smart windows, to control the transmittance of light through a window, or in display screens. Typically, electrochromic devices (ECDs) have two states: a coloured state, and a bleached state. To evaluate the performance of electrochromic materials, we can calculate several parameters. These include the optical density, optical contrast, coloration efficiency, lifetime, switching time, and hysteresis.

Optical density (OD) is a dimensionless quantity that is inversely proportional to the transmittance of light (a phenomenon discussed in section 1.2). Thus, the higher the optical density the lower the intensity of light

[17] Al-Bat'hi, Souad A. M. "Electrodeposition of Nanostructure Materials." IntechOpen, December 2, 2015. https://www.intechopen.com/chapters/49413.

[18] Sobha Jayakrishnan, D. "Electrodeposition: The Versatile Technique for Nanomaterials." *Corrosion Protection and Control Using Nanomaterials*, 2012, 86–125. https://doi.org/10.1533/9780857095800.1.86.

transmitted. The optimal ECD will have a high change in optical density between the coloured and bleached states (a higher ΔOD).

Optical contrast (OC), in terms of evaluating ECDs, can be quantified as the ratio of ΔOD to the initial OD. A higher OC value implies a larger difference in the transmittance of the two states of the ECD.

In simple words, colouration efficiency (CE) refers to the ability of an ECD to convert electric charge into a change in colour. This can be mathematically expressed as the change in OD per unit charge. A high CE value provides a basis for the high effectiveness and efficiency of the ECD.

Life-time is a self-explanatory parameter, and refers to the total operating time of the ECD before it experiences a significant degradation in its performance.

Switching-time is a feature specific to ECDs, and delineates the amount of time taken for an ECD to switch between states (that is, from a bleached state to a coloured state, and vice versa). For most applications, a low switching time is optimal.

Hysteresis, also referred to as the memory effect delayed or residual change in OD when the electrical stimulus is changed. Minimising this effect is essential to develop well-performing ECDs.

A classic basic layered ECD consists of five layers as displayed below.

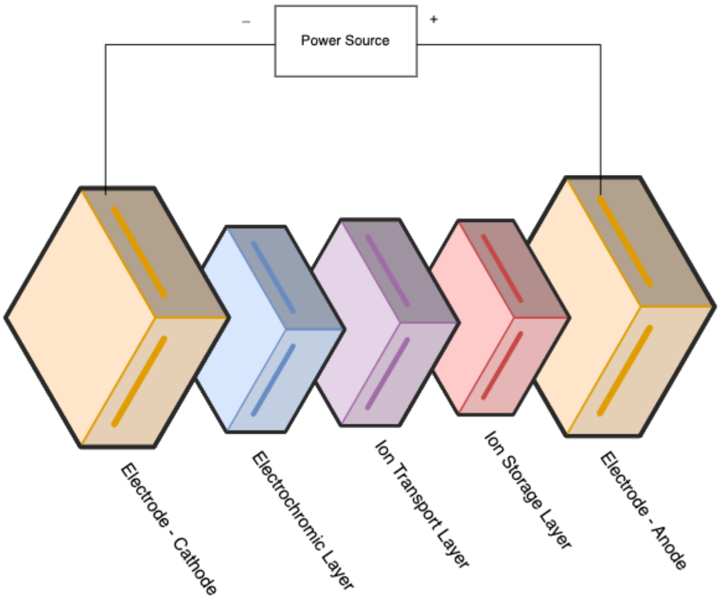


Fig 2.1 - A layered structure of a basic ECD design

In operation, this device functions by creating an electric field or applying an electric current between the two electrode layers. This causes the ions to migrate across the electrochromic layer. As a result, the electrochromic materials in the electrochromic layer undergo reversible redox reactions, leading to a change in their optical properties.[19] In this paper, the 'electrochromic layer' is the one that will be thoroughly explored in a novel manner through considering the thickness and methods of preparation of the electrochromic materials.

Examples of electrochromic materials primarily include transition metal oxides such as tungsten oxide (WO3), molybdenum oxide (MoO3), and nickel oxide (NiO).[20] Other materials that exhibit electrochromic materials include some conducting polymers and organic dyes. Indisputably, however, the most widely studied electrochromic material is WO_3. This is because of several important optical properties.[21] WO_3 is an n-type

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19 Sobha Jayakrishnan, D. "Electrodeposition: The Versatile Technique for Nanomaterials." *Corrosion Protection and Control Using Nanomaterials*, 2012, 86–125. https://doi.org/10.1533/9780857095800.1.86.

20 Somani, Prakash R., and S. Radhakrishnan. "Electrochromic Materials and Devices: Present and Future." *Materials Chemistry and Physics* 77, no. 1 (2003): 117–33. https://doi.org/10.1016/s0254-0584(01)00575-2.

21 Rydosz, A., K. Dyndał, K. Kollbek, W. Andrysiewicz, M. Sitarz, and K. Marszałek. "Structure and Optical Properties of the WO3 Thin Films Deposited by the Glad Magnetron Sputtering Technique." *Vacuum* 177 (2020): 109378. https://doi.org/10.1016/j.vacuum.2020.109378.

semiconductor. It's band gap ranges from approximately 2.6 eV to 3.3 eV[22] based on its structure. When a voltage is applied to a WO3 thin film, it undergoes redox reactions that cause the material to intercalate or de-intercalate ions. This process alters the electronic structure of WO3, leading to changes in its optical properties and resulting in coloration or bleaching. Furthermore, other properties of WO_3 must be kept in mind while designing ECDs. For example, it has an abbe's number in the range of 10-20 (depending on its conditions), which indicates higher dispersion, which can lead to more pronounced colour separation. While designing ECDs, it is essential the properties of material used are kept in mind.

Comparison of effectiveness of ECDs based on method of preparation of WO_3

Although there are a variety of synthesis methods, 3 common ones for this application are discussed above: sol-gel, sputtering and electrodeposition. Several studies have been conducted on their individual outputs, however very few delve into evaluating whether different methods yield different outputs, and which one to employ for which purpose. Thus, I will systematically use data to provide a comprehensive overview of the synthesis method to obtain optimal optical properties of the electrochromic material.

Table 3: Evaluation of the methods for synthesis of WO_3

Method	Sol-gel Deposition	Sputtering	Electrodeposition
Advantages of the method	The thickness of the film can be carefully controlled.[23] Similarly, the particle size can be controlled and varied from approximately 10 nm to 100 nm.[24] There is a large temperature range that can be used (around 200°C - 600°C).[25] This process is easily scalable, and thus can be used for industrial purposes.[26]	This method allows for a good adhesion of synthesised nanomaterial to substrate. Uniformity of the thin film coating is easy to achieve with this method.[27] The substrate temperature is kept low, (even though the target temperature is high). This means there is no structural harm done to the substrate. Sputtering usually yields films with a high purity, however this is based on the specific sputtering process.	This method is cost-effective and requires a comparatively low capital investment. Electrodeposition allows for control over the properties of the deposit formed due to easy control over the applied potential (voltage) and current density. [28] This method is applicable at room temperatures, no high temperatures are required for synthesis. This method allows for conformal coatings (coatings that adapt to the shape of the substrate).
Disadvantages of the method	Even a small concentration of impurities would disrupt the synthesis and result in problems with the	This process tends to have a lower deposition rate than others since all the sputtered atoms or molecules will deposit	A poor distribution (where the nanomaterial layer is not

[22] Johansson, Malin B., Burkhard Zietz, Gunnar A. Niklasson, and Lars Österlund. "Optical Properties of Nanocrystalline WO3 and WO3-X Thin Films Prepared by DC Magnetron Sputtering." *Journal of Applied Physics* 115, no. 21 (2014). https://doi.org/10.1063/1.4880162.
[23] THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI FASCICLE IX. METALLURGY AND MATERIALS SCIENCE No. 1 - 2020, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2020.1.08
[24] MODAN, Ecaterina Magdalena, and Adriana Gabriela PLĂIAȘU. "Advantages and Disadvantages of Chemical Methods in the Elaboration of Nanomaterials." *The Annals of "Dunarea de Jos" University of Galati. Fascicle IX, Metallurgy and Materials Science* 43, no. 1 (2020): 53–60. https://doi.org/10.35219/mms.2020.1.08.
[25] ibid
[26] Paul, Ralph. Sol-gel method : Overcoming the limitations in nanoparticle synthesis, March 31, 2023. https://www.rroij.com/open-access/solgel-method--overcoming-the-limitations-in-nanoparticle-synthesis.pdf.
[27] Doolittle, Alan. "Lecture 1 Introduction to Microelectronic Technologies ." Georgia Tech. Accessed June 20, 2023. https://alan.ece.gatech.edu/ECE6450/Lectures/ECE6450L1-Introduction%20Chap%201%20and%202.pdf
[28] Al-Bat'hi, Souad A.M. "Electrodeposition of Nanostructure Materials." *Electroplating of Nanostructures*, 2015. https://doi.org/10.5772/61389.

	synthesis. There is often a large cost associated with the precursors, especially alkoxides.[29] There are a large number of variables which affect thickness of the film and size of the nanoparticles, all of which have to be carefully controlled for optimal yield. (eg: concentration of precursor) This process is often time-intensive since it has various steps, and can take up to several days to complete. This method makes it difficult to produce porous films.[30] Here, heat-intensive annealing is required.	on the substrate. (on average, this is less than 300nm/min).[31] This method could require high setup costs, and have a low efficiency since energy is used for target heating. High pressures (1-100 mtorr) are required and could be hazardous or energy-intensive. The bombardment of target atoms could lead to substrate damage.[32] The basic process of sputtering has low scalability as compared to other methods.[33] However, scalable modifications to this basic process are being developed. For this process, heat-intensive annealing is required.	homogeneous) may occur.[34] The coating layer could consist of differing particle sizes The scalability of this method may be unfeasible Although low temperatures are required as mentioned above, the annealing process is heat-intensive.
Advantages in the resulting WO3 nanostructure	Using this method, the refractive index of the synthesised WO_3 film can be controlled with a change in temperature conditions.[35]	Sputtering, especially magnetron sputtering, provides a WO_3 sample that is highly transparent in its bleached state. [36] Optimal CE can reach up to 49.2 cm2/C [37]	It is easy to vary or control the rate of deposition. For example, rates varying from 1.7 × 1014 at./cm^{2}s to 4 × 1015 at./cm^{2}s can be obtained. Generally, the layer thickness is around 50nm, which is ideal for most applications.
Disadvantages in the resulting	It often leads to the formation of large particles unless a microfluidic connector is used.[38]	Sharp Changes in coloration efficiency of synthesised np based on wavelength and	Varying the potential used (high) and electrodeposition for a longer duration of time

[29] Raut, Bimal. "Sol Gel Method: Synthesis of Nanoparticles." Chemistry Notes, January 28, 2023. https://chemistnotes.com/nanochemistry/sol-gel-method-synthesis-of-nanoparticles-easy-explanation/#Advantages_of_Sol_Gel_Method.

[30] Lokhande, Prasad Eknath, Umesh S. Chavan, and Abhishek Pandey. "Materials and Fabrication Methods for Electrochemical Supercapacitors: Overview." *Electrochemical Energy Reviews* 3, no. 1 (2019): 155–86. https://doi.org/10.1007/s41918-019-00057-z.

[31] Muralidharan, Govindarajan, Dane F Wilson, Michael L Santella, and David Eugene Holcomb. *Cladding alloys for fluoride salt compatibility final report*, 2011. https://doi.org/10.2172/1006466.

[32] Targets, Author SAM Sputter. "Sputter Coating Advantages and Disadvantages." SAM Sputter Targets, June 15, 2022. http://www.sputtering-targets.net/blog/sputter-coating-advantages-vs-disadvantages/.

[33] Novinrooz, Abdoljavad, Masoomeh Sharbatdaran, and Hassan Noorkojouri. "Structural and Optical Properties of WO3 Electrochromic Layers Prepared by the Sol-Gel Method." *Open Physics* 3, no. 3 (2005). https://doi.org/10.2478/bf02475650.

[34] "Electrochemical Deposition." Electrochemical Deposition - an overview | ScienceDirect Topics. Accessed June 20, 2023. https://www.sciencedirect.com/topics/engineering/electrochemical-deposition.

[35] ibid

[36] Washizu, E. "Optical and Electrochromic Properties of RF Reactively Sputtered WO3 Films." Solid State Ionics 165, no. 1–4 (2003): 175–80. https://doi.org/10.1016/j.ssi.2003.08.030.

[37] Xia, Zhu-jie, Hong-li Wang, Yi-fan Su, Peng Tang, Ming-jiang Dai, Huai-jun Lin, Zhi-guo Zhang, and Qian Shi. "Enhanced Electrochromic Properties by Improvement of Crystallinity for Sputtered WO3 Film." *Coatings* 10, no. 6 (2020): 577. https://doi.org/10.3390/coatings10060577.

[38] Boateng, Emmanuel, Sapanbir S. Thind, Shuai Chen, and Aicheng Chen. "Synthesis and Electrochemical Studies of WO3 Based Nanomaterials for Environmental, Energy and Gas Sensing

WO3 nanostructure	There is a narrow range of temperatures which yield the optimal WO_3 properties. For example, at 500ºC, the electrochromic properties degrade as the transparency of the bleached state goes down to 30% from around 80% at 250ºC.[39]	temperature used [40] Changing the temperature results in thin film changes from amorphous to monoclinic phase crystal [41]state. It must be carefully controlled based on the requirements.	could cause the film to be broken.[42]

Note - there are several modifications to techniques that have been introduced in recent years such as hybrid sol-gel methods, reactive sputtering, and pulse electrodeposition; however, this table discusses only the basic methods themselves.

In summary, the selection of the most suitable method for WO_3 synthesis depends on the specific needs and requirements of the application. Sol-gel deposition offers precise control over film thickness and particle size, while sputtering provides high purity films with good adhesion and uniformity. Electrodeposition allows for control over deposit properties and conformal coatings. However, each method has its disadvantages, such as the complexity of controlling variables in sol-gel deposition, heat-intensive annealing in sputtering and electrodeposition, and challenges in scalability. Considering these factors, the choice should be made based on the desired film properties, scalability needs, cost considerations, and available resources.

Comparison of optical properties of WO3 films of different thickness

Another important factor influencing the optical properties of the electrochromic material and thus the ECD is the thickness of the film. With reference to several secondary studies, it is evident that the absorption, diffraction and redox peaks are unaffected by the thickness of the film. Furthermore, the structure of different thicknesses also tends to be similar (monoclinic or amorphous). However, a slight variation occurs in the transmittance of the coloured and bleached states based on film thickness - at a particular wavelength as the film width increases, the OC increases and then decreases, forming an inverted parabola shaped graph. For instance, in a particular experiment[43] conducted by Yingpeng Zhen, Bjørn Petter Jelle, and Tao Gao, 4 films of WO_3 with varying thickness (36 nm, 72 nm, 108 nm and 180 nm) were tested for transmission with a wavelength of 50 nm in their bleached and coloured state. Initially, the difference in transmission increased from 16% at 36 nm to 41% at 72 nm to 66% at 108 nm, but then it showed a sharp decrease - only 21% at 180 nm, with a bleached state transmittance of only 29%. This indicates the importance of identifying the optimal film thickness for electrochromic material, and displays that to a certain extent, a thicker film would contribute to a more effective electrochromic material. However, past the optimal point, the performance would deteriorate.

A practical trial: WO3 Tungsten trioxide

In order to provide a practical aspect to this study, the synthesis of WO_3 through the electrodeposition method was undertaken.

Applications." *Electrochemical Science Advances* 2, no. 5 (2021). https://doi.org/10.1002/elsa.202100146.

[39] Novinrooz, Abdoljavad, Masoomeh Sharbatdaran, and Hassan Noorkojouri. "Structural and Optical Properties of WO3 Electrochromic Layers Prepared by the Sol-Gel Method." *Open Physics* 3, no. 3 (2005). https://doi.org/10.2478/bf02475650.

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Cleaning process

Before the synthesis, it is essential to clean the apparatus thoroughly, with a specific emphasis on the beakers used and the two electrodes for electrodeposition. This comprehensive cleaning process allows us to obtain synthesised nanoparticles of the highest purity.

Cleaning of beakers, funnel and magnetic stirrer:
These are first washed with tap water, rinsed with acetone, rinsed with dilute HCl and then finally washed thoroughly with double distilled water.

Cleaning of reference electrode (stainless steel):
A stainless-steel sheet is first to a required size (1 cm by 4 cm). Subsequently, its surface is smoothed through the use of rough flint paper. Next, it is rinsed with dilute HCl, cleaned with acetone and washed with double distilled water. Finally, the substrate is stood in a beaker with double distilled water, which is placed in an ultrasonic cleaner for a duration of 15 minutes.

Cleaning of electrode for film deposition (conductive glass):
The glass is washed with tap water, rinsed with dilute HCl, cleaned with acetone and finally washed with double distilled water. It is also placed in an ultrasonic cleaner for a duration of 15 minutes to further rid any impurities.

Preparation of the Precursor Solution

To create the precursor solution, Tungstic Acid (H_2WO_4) with a molar weight of 249.87 was utilised. In order to calculate the mass of H_2WO_4 required for the preparation of a 0.3M solution with 25 ml of water, the following formula is used:

$$mass\ (g) = \frac{molar\ weight \times molarity \times volume}{1000}$$

$$mass\ (g) = \frac{249.87 \times 0.3 \times 25}{1000} = 1.874025 \text{ g}$$

Thus, the mass of tungstic acid required to be dissolved in 25 ml of water to obtain a 0.3M solution is approximately 1.87g.

The specified volume of water is measured using a measuring cylinder, and the required mass is weighed using a weighing balance. These are added to a beaker, and stirred at an RPM of 280 using a magnetic stirrer for approximately 15 minutes. During the stirring process, the pH of the solution was controlled to remain constant at 12 through the addition of ammonium hydroxide. A colour change of the solution could be observed from yellow to cream. Finally, the solution was filtered to provide a colourless precursor solution.

Fig 2.2 - 0.3M tungstic acid solution.

Fig 2.3 - Stirring while adding ammonium hydroxide

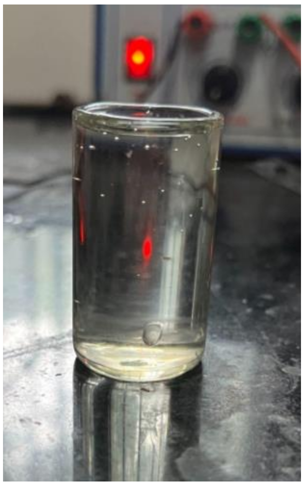
Fig 2.4 - Filtered precursor solution

Electrodeposition

The electrodeposition set-up was as follows:

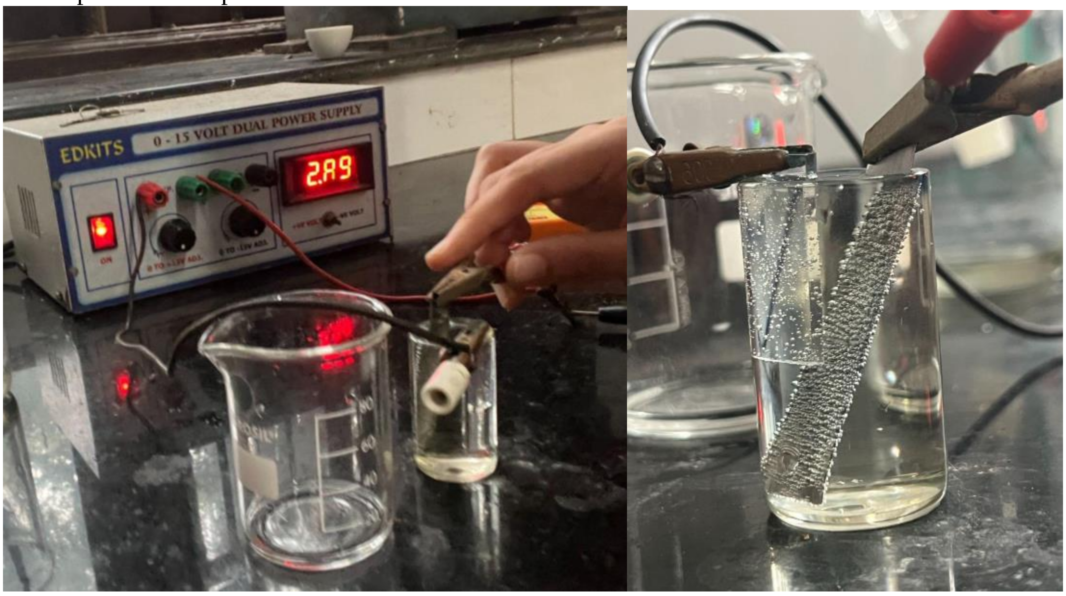

Fig 2.5 and 2.6 - Electrodeposition set up

The filtered precursor solution was added to a small container as an electrolyte, where both the electrodes (conductive glass and stainless steel) were placed in the correct orientation. The cleaned glass substrate was connected to the anode such that its conductive surface faced the steel substrate. Deposition of WO_3 would occur on this substrate. The stainless-steel electrode was connected to the cathode, to act as the reference electrode. The power supply was increased to a value ranging from 2.6-2.9 volts. An ammeter attached to the circuit displayed the current, to ensure it was flowing. After 15 minutes, the glass substrate was removed. It was coated with a fine, transparent layer of WO_3 nanoparticles. The substrate was dried at room temperature for 15 minutes.

Characterization

While there are many methods for characterisation such as fourier transform infrared spectroscopy (FTIR) or X-ray diffraction (XRD), in order to view the colour change, electrochemical analysis through cyclic voltammetry was performed. In order to do this, a new electrolyte solution was created: A sulfuric acid solution of 0.5M through the addition of 7ml of H_2SO_4 to 30 ml of water.

A 3-electrode system was utilised to analyse the electrochemical characteristics of the synthesised WO_3. This setup featured a reference electrode and a working electrode as cathode, the synthesised substrate as the anode. The system was connected to the electrochemical analyser, which was then connected to a computer that provided the data results. This process of cyclic voltammetry displayed a reversible redox reaction as the oxidation and reduction caused the WO_3 to change states between its bleached and coloured state.

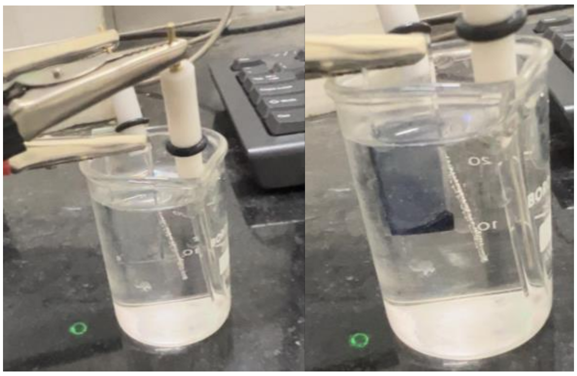

Fig 2.7 and 2.8 - change in state of WO_3 film from bleached to coloured during cyclic voltammetry

First, in order to ensure that the WO_3 film did display electrochromic properties, one cycle was tested, to obtain the following result:

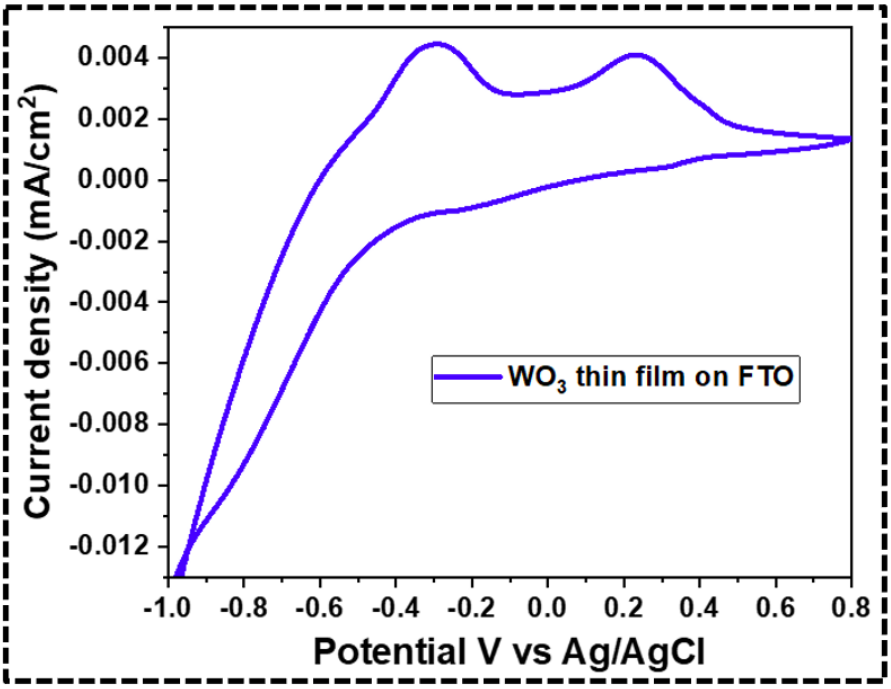

Fig 2.9 - Cyclic voltammetry curve (Current Density vs Potential) for 1 cycle

As can be observed, the two peaks indicate the redox reactions that take place. Colouration occurred as the potential returned to negative values, while decolorization occurred towards positive values. This trial helped verify that the synthesised WO_3 film was in fact an electrochromic material and could be used for ECD applications.

In order to further test the efficacy of the WO_3 thin film synthesised, 20 cycles were conducted.

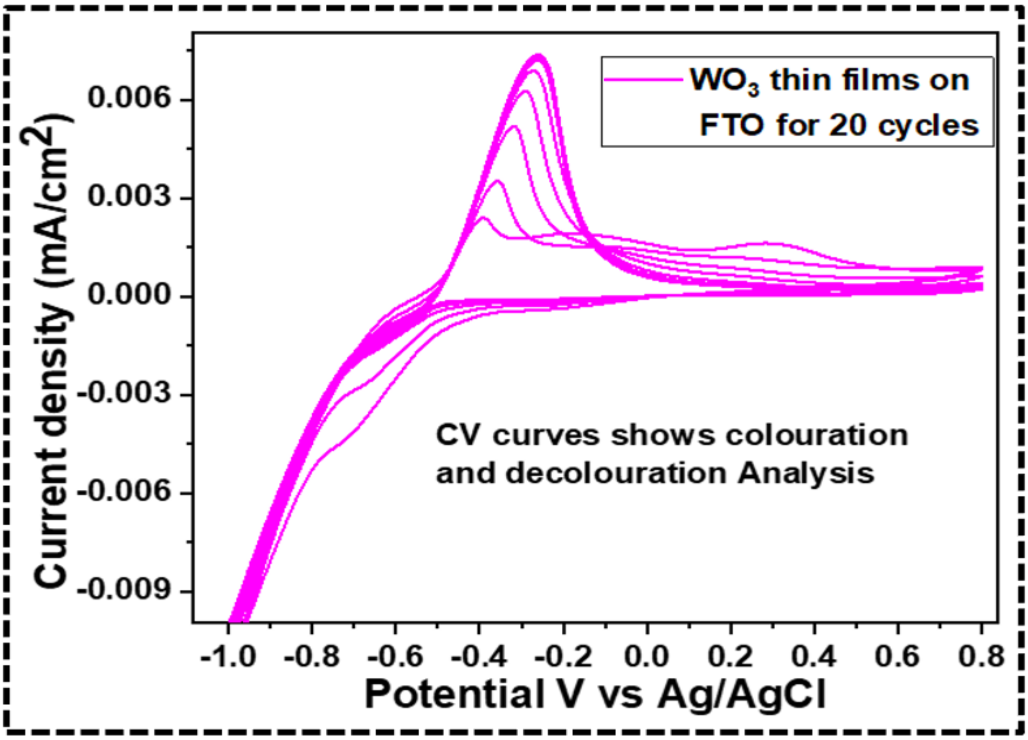

Fig 2.10 - Cyclic voltammetry curve (Current Density vs Potential) for 20 cycles

As displayed, the coloration and decolouration of the WO_3 sample took place for all 20 cycles, however decreasing in magnitude each time (as seen by the lowering peaks of the graph. This indicates that although the colour change from bleached to coloured occurs over a duration of time (20 cycles), steps must be taken to ensure the difference in transmission between the two states does not decrease over time.

Potential applications of ECDs and uses in the future

Currently, the primary use of ECDs is for smart windows: glass that is able to act in accordance to weather conditions to block sunlight or heat, as well as provide a degree of privacy. However, ECDs are extremely versatile devices which can be used in various spheres of our lives in the future.[44] For instance, they are increasingly being used in the automotive industry, where they can enhance the visibility of the driver through adjusting transmission in response to changing light conditions. Other potential applications include information displays and wearable technology such as smartwatches,[45] where the electrochromic material could be used to provide increased readability for the user based on the lighting conditions. The fashion and design industry could also be benefitted through the integration of ECD technology to create dynamic visual effects in clothing.[46] An extremely significant future application is the use of ECDs in smart eyewear such as sunglasses or prescription glasses for responding to varying light conditions through varying transmission levels.[47]

III. Summary and Conclusion

This paper explores the optical properties relevant to electrochromic materials within ECDs. It focuses on a specific case study of WO3, investigating synthesis methods, conducting experimental synthesis, and characterising it through cyclic voltammetry for practical insights. In conclusion, this paper provides valuable insights into ECDs through offering a comprehensive analysis of WO3 synthesis and characterization. The findings contribute to our understanding of enhancing optical performance and furthering applications in these fields. Continued research and development in electrochromic materials holds significant promise for future advancements in optical technology and related applications.

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