

Article

Enhanced Electrochromic Properties of Nanocrystalline Molybdenum Oxide Films Modified by Dopamine

Dan Zhou ^{1,*}  and Liping Yang ²

¹ Chongqing Key Laboratory of Extraordinary Bond Engineering and Advanced Materials Technology, College of Materials Science and Engineering, Yangtze Normal University, Chongqing 408100, China

² Research Department, Wankai New Materials Co., Ltd., Haining 314415, China

* Correspondence: zhou.dan@yznu.edu.cn; Tel.: +86-023-72791828

Abstract: Molybdenum oxide (MoO₃) electrochromic (EC) materials have not been widely used at present due to relatively poor performance and inadequate research. In order to enhance the EC properties of the MoO₃ to achieve the purpose of practical use, the modified nanocrystalline MoO₃ films were fabricated by a cheap and simple complexation-assisted sol–gel method followed by annealing at 300 °C. In this method, dopamine (DA) is used as a structure-directing agent and the added amount of DA has a great influence on the structure and morphology and, thus, electrochemical and EC properties of the MoO₃ films. Different from the pure MoO₃ polycrystalline film, the film modified with a suitable amount of DA possesses a distinctive nanocrystal-embedded amorphous structure, and, thus, can achieve synergy effects of EC properties through combining the advantages of both amorphous phases and nanocrystalline. Therefore, compared with the pure MoO₃ film, the modified MoO₃ film shows much higher EC properties in terms of optical contrast, coloration efficiency, switching speed, and cycling stability. Moreover, a complementary type EC device with dual active layers (the modified MoO₃ film and polyaniline) was fabricated and tested, and the results demonstrate the potential application of the modified MoO₃ film.

Keywords: electrochromic property; molybdenum oxide; nanocrystalline; film; dopamine; complexation; sol–gel method



Citation: Zhou, D.; Yang, L.

Enhanced Electrochromic Properties of Nanocrystalline Molybdenum Oxide Films Modified by Dopamine. *Coatings* **2023**, *13*, 1292. <https://doi.org/10.3390/coatings13071292>

Academic Editor: Tangirala Venkata Krishna Karthik

Received: 27 June 2023

Revised: 17 July 2023

Accepted: 20 July 2023

Published: 24 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Today's world is experiencing an acute energy shortage due to the fast development of modern society. Reducing energy consumption is one of the major concerns in buildings because buildings account for about 40% of the global primary energy consumption and about 50% of energy in buildings is consumed in cooling, heating and lighting [1,2]. Therefore, it is necessary to develop energy-saving windows to reduce the energy consumption of buildings. Among various energy-saving strategies, electrochromic (EC) smart windows are a very promising technology. The EC window can smartly modulate the heat or light of solar radiation entering the building by changing its optical transmittance, and, thus, is conducive to reducing the energy consumption of air conditioning and artificial lighting and creating comfortable indoor environments.

EC materials are the core component and play an important role for the development of the above-mentioned technologies. EC materials can persistently and reversibly change their color, absorption, transmittance or reflectance induced by a small, applied voltage. Therefore, they can be widely applied to EC smart windows, energy-saving displays, antiglare automobile rear-view mirrors, energy storage systems, wearable devices, military camouflage, and so on. EC materials are considered to be one of the most promising energy-saving materials, in which transition metal oxides have become the focus of research owing to the advantages of their high stability and long lifetime [3–5].

Among the numerous EC materials, tungsten oxide (WO₃) is the most investigated and widely used inorganic material. Molybdenum oxide (MoO₃) is another important and

promising material with electrochemical reaction and EC properties similar to those of WO_3 [5] because molybdenum and tungsten belong to the same group (Group VIB of the Periodic Table of the Elements). Recently, MoO_3 has attracted much attention and has been considered one of the best candidates for EC materials [6] because of its fast response, large optical contrast, high coloration efficiency, low driving voltage, soft color, environmental friendliness, abundant reserves and low cost. Compared with WO_3 , the color state of MoO_3 absorbs light more strongly and more uniformly and is more consistent with the human eye color recognition, which makes MoO_3 of important application value [7].

There are many methods to fabricate MoO_3 thin films on transparent conductive substrates, including evaporation, sputtering, chemical vapor deposition (CVD), etc. [8–11]. The MoO_3 films produced by these methods under high vacuum conditions and using special equipment are costly and it is also difficult to fabricate large-area films, hindering their widespread applications. For the past few years, the fabrication methods underwent a transition from a vacuum-required process to efficient and low-cost wet-chemical methods [12,13], such as the sol–gel method [14]. The sol–gel method attracts extensive attention due to its simplicity and possibility of producing large-area uniform films at low cost. Moreover, it is easy for this method to control the composition, microstructure, crystal size, and porosity of the films by introducing additives into the sols or adjusting various synthesis parameters [15].

However, the research reports on MoO_3 are far less than those on WO_3 because MoO_3 often shows worse EC performance than WO_3 [16]. Currently, the research focus is to prepare MoO_3 films with excellent EC properties, including high optical contrast, switching speed, coloration efficiency and long-term electrochemical cycling stability, which are key performance parameters for EC materials [17].

In order to enhance EC properties of sol–gel derived MoO_3 films, many researchers have explored some improved routes: doping or compositing MoO_3 with other ions or agents, which will produce different composition, morphologies and structures and, thus, affect the corresponding EC performance to different degrees. Dhanasankar et al. [18] prepared the MoO_3 films doped with cerium through the sol–gel dip-coating method and observed the structural and morphological changes of the films. The films with 10 wt.% of cerium exhibit better EC properties, such as higher contrast and better cyclic stability. Undoped and Fe-doped MoO_3 films were obtained by the sol–gel-derived spin-coated method as well [19]. Doping can lead to the transformation of the morphology and structure of the films, which facilitates the ion insertion/extraction and charge transfer reactions. Hybrid porous MoO_3 - WO_3 films were deposited with Pluronic P123 as a template and annealed at 300 °C, which displayed significantly improved electrochromic performance (contrast of 57% at 650 nm and response times are both 25 s) [20]. Cholang et al. prepared $\text{V}_2\text{O}_5/\text{MoO}_3$ thin films by the sol–gel method and dip-coating techniques with a optical modulation of 40% at 633 nm [21]. Although much work has been performed, the EC properties of these pure, doped or composited MoO_3 films are not ideal, such as low contrast, slow response, or poor stability. There is still a key challenge for EC properties of MoO_3 to meet practical requirements.

It is well known that the structure/morphology of EC materials play important roles in determining EC properties. For example, amorphous and crystalline films show quite different EC properties from each other and each of them has its advantages and disadvantages. Amorphous MoO_3 has a loose disordered structure and large specific surface area, which is favorable for quick ion transport, fast switching speed and large optical modulation [15,22,23]. However, amorphous material shows poor cycling stability due to numerous defects and loose structure. In contrast, highly crystalline MoO_3 films are more stable due to their denser and long-range ordered crystalline structure, stronger interatomic bond and lower dissolution rate in electrolytes, whereas their switching kinetics are slower due to relatively low diffusion and intercalation of ions in this dense structure.

Therefore, it is highly desirable to design EC materials with a distinctive architecture and an appropriate structure to obtain good comprehensive performance. Several

researchers have tried to synergistically combine the advantages of the amorphous and crystalline structures in a range from several to hundreds of nanometers [24]. In our previous works [25,26], the EC films with WO_3 nanocrystal surrounded by amorphous matrix were prepared by a complexation-assisted sol–gel method using a series of organic small molecules as complexing agents or structure-directing agents. Higher EC properties have been achieved due to the unique structure and morphology of the films.

In this paper, in order to further improve EC properties of the MoO_3 films to achieve the purpose of practical use, a small amount of dopamine (DA) was added into peroxomolybdic acid (PMA) precursor sol to form PMA-DA complex sol. It is widely known that DA containing both catechol and amine functional groups has excellent chelating capability with many types of transition metal ions. Therefore, the DA molecules may act as a structure-directing agent, inhibiting the formation of large MoO_3 particles in the precursor sol and highly stressed polycrystalline structure during annealing. After spin-coating followed by annealing of the PMA-DA complex sol at 300 °C for 2 h, modified unique nanocrystal-embedded amorphous MoO_3 films were generated using a simple and low-cost complexation-assisted sol–gel method for the first time, and show excellent EC properties owing to the synergy effect of amorphous and nanocrystalline phases. The effect of the DA amount on the structure, morphology, electrochemical and EC properties of the resultant modified MoO_3 films were characterized and studied.

2. Materials and Methods

2.1. Materials

Molybdenum powder (99.9%), DA hydrochloride (98%), 30% H_2O_2 , propylene carbonate (PC, 98%), lithium perchlorate (LiClO_4 , 99.9%), aniline (99.5%), dodecylbenzene sulfonic acid (90%), 1-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMIM}^+\text{BF}_4^-$, 98%), ammonium persulfate (98%), xylene (99%), acetone (98%) and isopropanol (99%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Poly(propylene carbonate) (PPC, $M_w = 276,000$) was obtained from Empower Materials Inc. (New Castle, DE, USA). Conducting indium tin oxide-coated glass (ITO/glass, $<7 \Omega/\square$) as a transparent conductor layer and substrate was supplied by Zhuhai Kaivo Optoelectronic Technologies Co. (Zhuhai, China) and cleaned by ultrasonication in a series of solvents including detergent, deionized H_2O , acetone and isopropanol for 10 min each prior to use. Then, a plasma treatment for 5 min was applied to the ITO/glass by using a Plasma Cleaner (Dongxin Hi-Tech Automation Equipment Co., Ltd., Shenzhen, China) with plasma source power of 300 W for further cleaning and improving their hydrophilicity.

2.2. Preparation of the Modified MoO_3 Films

The modified MoO_3 films were prepared according to our previous sol–gel method [25] with slight modification. Under continuous stirring, 33.3 mmol molybdenum powder was dissolved in 100 mL H_2O_2 solution (30%) to form a yellow transparent PMA, which was refluxed at 60 °C for 6 h. After stirring at room temperature for 5 days, 5.6 mmol DA (molar ratio of molybdenum to DA is 6/1) was added into the PMA sol, which was then heated at 60 °C for 10 h to obtain concentrated PMA/DA complex sol. The PMA/DA sol was spin-coated on ITO/glass and dried at 60 °C for 1 h followed by annealing at 300 °C for 2 h to form modified MoO_3 /DA film. The film thickness was controlled at about 200 nm by adjusting the rotating speed of the spinning coater. Moreover, MoO_3 films without DA and with different added amount of DA (molar ratios of molybdenum to DA are 12/1 and 4/1, respectively) at a fixed molybdenum amount (33.3 mmol) were also prepared for comparison under similar conditions. As-prepared films are denoted as MoO_3 -300 °C, MoO_3 /DA(12/1)-300 °C, MoO_3 /DA(6/1)-300 °C, and MoO_3 /DA(4/1)-300 °C, respectively.

For FTIR characterization, MoO_3 and MoO_3 /DA(6/1) xerogels were obtained by drying PMA and PMA/DA(6/1) sols in vacuum oven at 60 °C for 24 h, respectively.

2.3. Structural and Compositional Characterizations

The UV-Vis absorption spectra of the sols were tested on an UV-vis-NIR spectrophotometer (Shimadzu UV-Vis 3600plus, Tokyo, Japan) in the wavelength range of 400–800 nm. FTIR spectra of the samples were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in the transmission mode from 400 to 4000 cm^{-1} . The microstructure and morphology of the films were demonstrated by a field-emission scanning electron microscope (FESEM, ZEISS GeminiSEM 300, Oberkochen, Germany), transmission electron microscope (TEM, JEOL-2100F, Tokyo, Japan) and X-ray diffraction (XRD, Shimadzu XRD-6000) over a 2θ of 10–60° with an X-ray wavelength of 1.542 Å (Cu K α radiation).

2.4. Electrochemical and EC Measurements

The electrochemical properties of the films were checked in a three-electrode electrochemical cell (the films on ITO/glass as working electrodes, Ag/AgCl as a reference electrode, and Pt sheet as a counter electrode, respectively) with 1.0 mol/L LiClO₄ in PC as the electrolyte on an AUTOLAB PGSTAT 302N analyzer (Metrohm Autolab, Utrecht, The Netherlands). Cyclic voltammetry (CV) plots of the films were collected from −1.0 to +1.0 V at a scan rate of 100 mV s^{−1}. The electrochemical impedance spectra (EIS) of the films were obtained under a perturbation voltage of 10 mV with a frequency range of 100 kHz to 10 mHz.

EC properties of the films were tested on a Shimadzu UV-3600 spectrophotometer in combination with an AUTOLAB analyzer. Transmittance spectra from 400 to 800 nm were recorded by applying various potentials and dynamic switching curves at 720 nm ($\lambda_{720 \text{ nm}}$) were measured by applying square-wave potentials (oscillating between +0.8 V and −0.8 V at a regular interval of 50 s). Long-term cycling stability tests were carried out under similar conditions using cycling time of 30 s.

2.5. Fabrication and Characterization of the EC Device

A dual-active-layer complementary EC device with a sandwich configuration of ITO/glass//MoO₃/DA(6/1)-300 °C//electrolyte//Polyaniline//ITO/glass was fabricated and characterized. The PPC electrolyte [27] was prepared by dissolution of LiClO₄, PPC, and BMIM⁺BF₄[−] in PC at mass ratio of LiClO₄/PPC/PC/BMIM⁺BF₄[−] = 0.1/0.7/2.1/2.1. Polyaniline (PANI) was prepared similar to our previous work [28] and spin-coated onto ITO/glass.

Transmittance spectra and dynamic switching curves of the EC device were measured on a UV-Vis spectrophotometer in combination with an AUTOLAB analyzer by applying constant potentials and square-wave potentials (oscillating between +1.2 V and −1.2 V at a time step of 30 s), respectively.

3. Results and Discussion

3.1. Preparation and Characterization of the Modified MoO₃ Films

There are both catechol hydroxyl and amino functional groups in DA molecules. The catechol hydroxyl groups have very strong affinity to metals/metal ions [29] and, thus, can preferentially complex Mo on the surface of PMA colloid nanoparticles via the deprotonated O, O' sites [30,31] following the bidentate, monodentate or chelated patterns [32]. The amino groups of DA are mainly present as ammonium salt.

The MoO₃ films modified by DA were prepared through the complexation-assisted sol-gel method. The reaction of molybdenum powder and H₂O₂ for several days forms a transparent yellow sol, whose color change immediately to a deep yellow (insert of Figure 1) when DA is added into the sol. This means the instantaneous formation of a charge transfer complex between PMA colloidal nanoparticles and DA through the complexation, hydrogen bonding or electrostatic interaction. This phenomenon can be characterized using UV-Vis absorption spectra as shown in Figure 1, similar to those observed for DA-WO₃ and DA-TiO₂ complexes [25,26,33,34]. That is, the absorption spectra of the PMA/DA sols

with different DA amounts all show red shift and enhanced intensity compared with that of pure PMA sol.

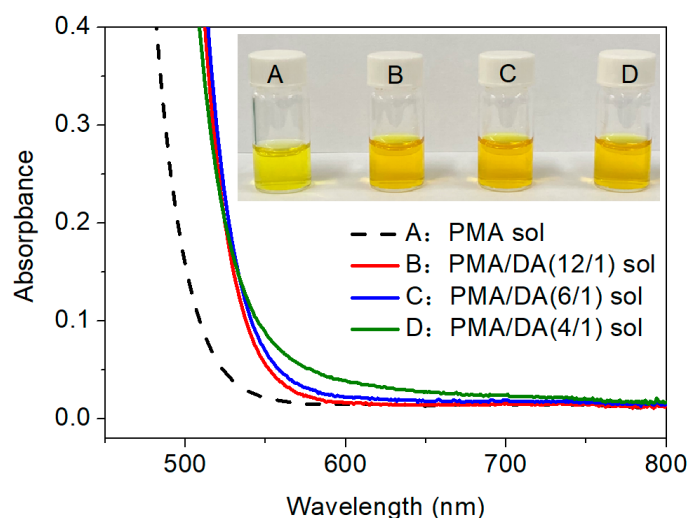


Figure 1. UV-Vis absorption spectra of the PMA and PMA/DA sols. The insert shows the photos of the PMA and PMA/DA sols.

To investigate the interactions between the PMA and DA in the complex sol, the MoO_3 and $\text{MoO}_3/\text{DA}(6/1)$ xerogels were prepared by drying the PMA and PMA/DA(6/1) sols in a vacuum oven at 60°C for 24 h. FTIR spectra of the two xerogels are shown and compared in Figure 2. The absorption bands at around 3450 and 1618 cm^{-1} in Curve b show the hydrated and hydroxylated nature of the pure MoO_3 xerogel, which are attributed to the stretching vibration $\nu(\text{OH})$ and the in-plane bending vibration $\delta(\text{HOH})$ of water molecules [5]. Curve b also displays the characteristic absorption bands at 987 , 898 , 633 cm^{-1} , corresponding to the $\text{Mo}=\text{O}$ stretching vibration, $\text{Mo}-\text{O}-\text{Mo}$ bridging oxygen stretching vibration and $\text{Mo}-\text{O}-\text{Mo}$ stretching vibration, respectively [5]. After the addition of DA to produce $\text{MoO}_3/\text{DA}(6/1)$ xerogel, there are some new bands (Curve c) in addition to those from MoO_3 xerogel, such as several bands at $1000\text{--}1500\text{ cm}^{-1}$ caused by the $\text{C}-\text{C}$, $\text{C}-\text{H}$, $\text{C}-\text{N}$, $\text{N}-\text{H}$, aromatic $\text{C}-\text{C}$ bonds and a broad band at $\sim 3230\text{ cm}^{-1}$ due to the stretching vibration of $\text{N}-\text{H}$ of DA, similar to those of DA (Curve a), indicating the coexistence of molybdenum oxide and DA moieties. Compared with those from the MoO_3 xerogel, the characteristic bands of the MoO_3/DA complex xerogel (Curve c) downshift obviously from 987 cm^{-1} to 974 cm^{-1} for the terminal $\text{W}=\text{O}$ stretching vibration and from 633 cm^{-1} to 628 cm^{-1} for the $\text{Mo}-\text{O}-\text{Mo}$ stretching vibration, due to the complexation interactions between phenolic hydroxyl groups or amino groups (NH_2 or NH_3^+) of DA and Mo or O species of PMA.

After annealing at 300°C , the significant intensity decrease of the bands at $\sim 3450\text{ cm}^{-1}$ and $\sim 1618\text{ cm}^{-1}$ of both the $\text{MoO}_3\text{-}300^\circ\text{C}$ film and $\text{MoO}_3/\text{DA}(6/1)\text{-}300^\circ\text{C}$ film is caused by the loss of absorbed and structural water (Curve d and e). At the same time, for the $\text{MoO}_3\text{-}300^\circ\text{C}$ film (Curve d), the broadening and intensity increase of the characteristic absorption bands at 884 and 653 cm^{-1} attributed to the $\text{Mo}-\text{O}-\text{Mo}$ bridging oxygen stretching vibration and $\text{Mo}-\text{O}-\text{Mo}$ stretching vibration indicate the crystalline structure of MoO_3 . By contrast, the narrower and downshifted bands at 852 and 621 cm^{-1} in Curve e show the dominant structure of $\text{MoO}_3/\text{DA}(6/1)\text{-}300^\circ\text{C}$ is different from the crystalline one of $\text{MoO}_3\text{-}300^\circ\text{C}$. Moreover, the weak bands at $1000\text{--}1500\text{ cm}^{-1}$ attributed to the addition of DA disappear due to the burning of the organic additive after annealing at 300°C for 2 h.

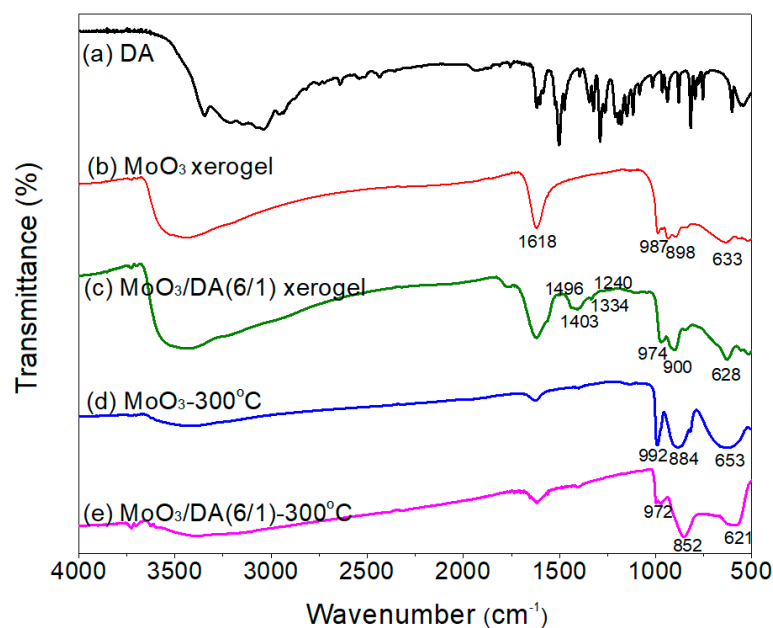


Figure 2. FTIR spectra of (a) DA, (b) MoO₃ xerogel, (c) MoO₃/DA(6/1) xerogel, (d) MoO₃-300 °C film, and (e) MoO₃/DA(6/1)-300 °C film.

X-ray diffraction (XRD) was employed to study the structure and phase variation of the MoO₃ films. The XRD patterns of ITO/glass, MoO₃-300 °C, MoO₃/DA(12/1)-300 °C, MoO₃/DA(6/1)-300 °C, and MoO₃/DA(4/1)-300 °C films deposited on ITO/glass substrates are shown in Figure 3. It was observed that the pure MoO₃ film without DA annealed at 300 °C exhibits several well-defined diffraction peaks (Curve b) corresponding to (020), (110), (040), (021), (111), (060), (210) and (002) planes at $2\theta = 12.8^\circ$, 23.4° , 25.8° , 27.4° , 33.9° , 39.0° , 45.9° and 49.5° , respectively, which are well matched with the standard diffraction data of the orthorhombic phase (α -MoO₃) (JCPDS Card No.05-0508) with a well-crystallized structure. However, after introducing a small amount of DA into the sols, the intensity of the peaks of the MoO₃/DA(12/1)-300 °C film decrease greatly, as shown in Curve c. With a further increase of DA amount, such as for the MoO₃/DA(6/1)-300 °C film, in addition to the peaks corresponding to ITO substrate, there are few characteristic peaks of MoO₃ (Curve d) and a broad hump appears at 2θ of roughly 25° , showing MoO₃ nanocrystals with amorphous background [35]. When the added amount of DA continues to increase, the XRD pattern of MoO₃/DA(4/1)-300 °C film (Curve e) displays no obvious characteristic MoO₃ peak, indicating the amorphous background nature of the MoO₃ film.

The XRD patterns make clear that the transition of the films from crystalline to nanocrystal-embedded amorphous structures with increasing the amount of DA. The broadening, weakening and even disappearance of the diffraction peaks is attributed to low crystallinity, very small size of the nanocrystals in an amorphous matrix and crystal defects caused by organics [34]. This implies that the attachment of DA on the surface of colloidal particles through the complexation hinders the formation of large crystals and interconnected polycrystalline structure, whereas such crystalline morphology would form without DA (for MoO₃-300 °C). Moreover, the hindering effect is more significant with the increase of the DA amount.

Electron microscopy was used to further study the structures and morphologies of the films. The FESEM images of the MoO₃-300 °C, MoO₃/DA(12/1)-300 °C, MoO₃/DA(6/1)-300 °C and MoO₃/DA(4/1)-300 °C films can be seen in Figure 4. The first three films exhibit relatively smooth, uniform and compact surfaces, while there are many particles on the surface of the MoO₃/DA(4/1)-300 °C film with excess DA. The possible reason is that a small amount of DA can effectively stabilize the precursor sol through complexing between DA and the PMA sol, but excess DA, such as molar ratio of molybdenum to DA is 4/1,

will greatly decrease the ζ potential and destroy the stability of the sol, and precipitation is formed during heating. Therefore, many particles on the surface of $\text{MoO}_3/\text{DA}(4/1)\text{-}300^\circ\text{C}$ film can be observed through the FESEM image.

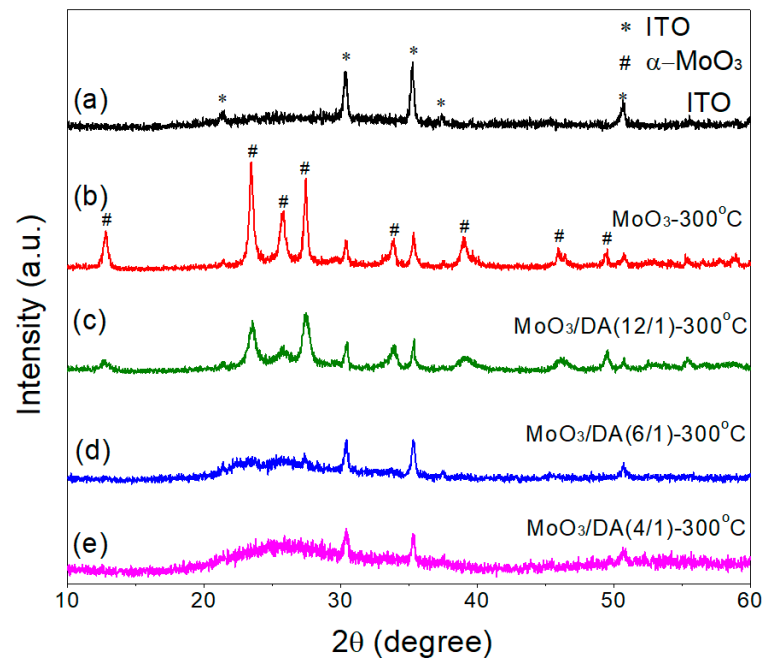


Figure 3. X-ray diffraction (XRD) patterns of (a) ITO/glass, (b) $\text{MoO}_3\text{-}300^\circ\text{C}$, (c) $\text{MoO}_3/\text{DA}(12/1)\text{-}300^\circ\text{C}$, (d) $\text{MoO}_3/\text{DA}(6/1)\text{-}300^\circ\text{C}$, and (e) $\text{MoO}_3/\text{DA}(4/1)\text{-}300^\circ\text{C}$ films.

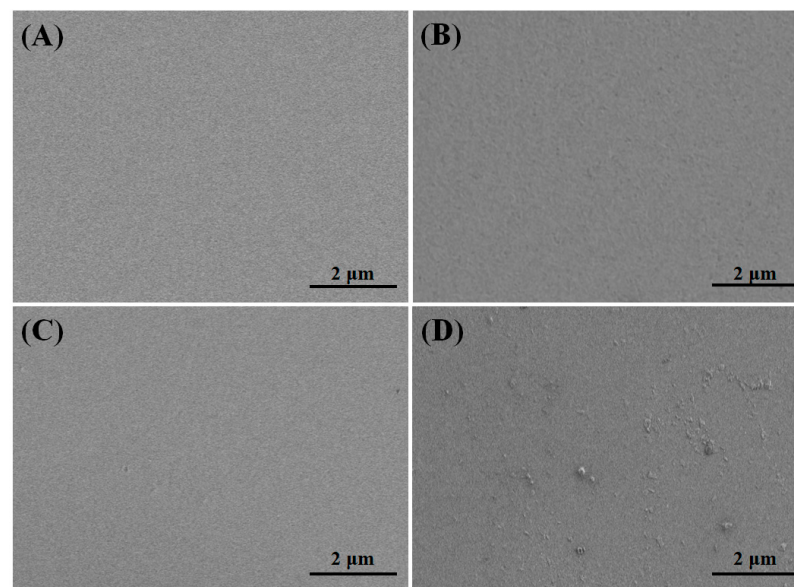


Figure 4. FESEM images showing surface morphology of (A) $\text{MoO}_3\text{-}300^\circ\text{C}$, (B) $\text{MoO}_3/\text{DA}(12/1)\text{-}300^\circ\text{C}$, (C) $\text{MoO}_3/\text{DA}(6/1)\text{-}300^\circ\text{C}$, and (D) $\text{MoO}_3/\text{DA}(4/1)\text{-}300^\circ\text{C}$ films.

The TEM image (Figure 5A) of $\text{MoO}_3\text{-}300^\circ\text{C}$ displays a polycrystalline structure with clear lattice fringes, and the lattice spacing of 0.35 nm belongs to the (040) plane of $\alpha\text{-MoO}_3$ [36]. After the addition of DA, the modified films show different structure from the pure MoO_3 film, that is to say, there are many MoO_3 nanocrystals dispersed in an amorphous MoO_3 matrix (Figure 5B–D). When DA amount is low, the $\text{MoO}_3/\text{DA}(12/1)\text{-}300^\circ\text{C}$ film shows relatively large and heterogeneous nanocrystals with estimated sizes of about 8–15 nm according to the TEM image and a small amount of amorphous matrix due to insuf-

ficient DA complex agent, and clear fringes can be observed for each individual nanocrystal (Figure 5B). When the DA amount is appropriately increased, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film (Figure 5C) displays more uniform and finer MoO_3 nanocrystals with size of about 7 nm separated from each other and surrounded by an amorphous MoO_3 matrix. This is because the suitable amount of DA can effectively complex with the colloidal nanoparticles, constrain the size of colloidal particles and destroy the structure order of particles. When there is a further increase of the DA amount, excess DA causes the sol to be unstable and precipitate, and there is a certain amount of carbonaceous residue of DA remaining after annealing at 300 °C, leading to a decrease in not only crystallization but also the grain size of MoO_3 nanoparticles, as can be seen in Figure 5D. The TEM results are consistent with those obtained from FTIR and XRD discussed above.

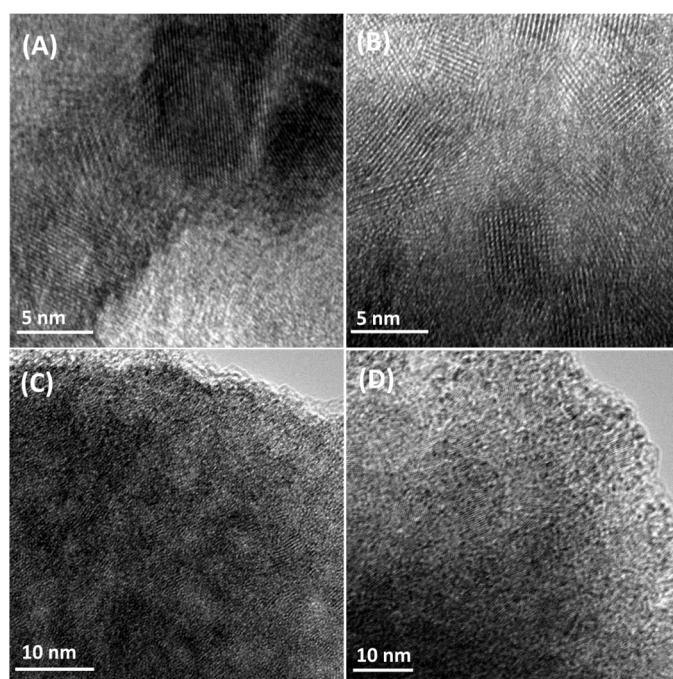


Figure 5. TEM images of (A) MoO_3 -300 °C, (B) $\text{MoO}_3/\text{DA}(12/1)$ -300 °C, (C) $\text{MoO}_3/\text{DA}(6/1)$ -300 °C, and (D) $\text{MoO}_3/\text{DA}(4/1)$ -300 °C films.

3.2. Electrochemical Properties of the Modified MoO_3 Films

Cyclic voltammetry (CV) curves can reflect the electrochemical properties of the films during ion insertion/extraction process. As shown in Figure 6A, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C and $\text{MoO}_3/\text{DA}(12/1)$ -300 °C films, especially the former, exhibit significantly higher current density and integral area than the pure MoO_3 -300 °C film, which reveals that the nanocrystal-embedded amorphous structure possesses more active mass and higher ion/electron storage capacity during the electrochemical reaction [37], more ions and electrons involved at the interface between the film and electrolyte, and, thus, foreseeably better EC performances. The $\text{MoO}_3/\text{DA}(4/1)$ -300 °C film shows the lowest current density in all the films, probably because the carbonaceous residue of DA reduces the active mass of this film. Moreover, the onset potentials of the cathodic current density for the modified MoO_3 film are obviously more positive than that for the pure MoO_3 -300 °C film, indicating that the Li^+ ions start inserting much earlier at lower applied voltage and faster charge transfer kinetics [38] in the modified MoO_3 films than in the pure MoO_3 -300 °C film.

Electrochemical impedance spectroscopy (EIS) was also applied to further study the electrochemical behaviors of the modified MoO_3 films, providing information on the charge transfer and ion diffusion. Nyquist plots of the MoO_3 -300 °C and $\text{MoO}_3/\text{DA}(6/1)$ -300 °C films can be seen in Figure 6B, approximately consisting of a depressed arc at high frequencies and a inclined line at low frequencies [39]. Compared with the MoO_3 -300 °C,

the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film shows lower series and charge transfer resistance and higher Li^+ ion diffusion rate for ion insertion/extraction into/from the film [40,41]. This is because the nanocrystal-embedded amorphous phase structure is more beneficial to both Li^+ ion diffusion and charge transfer than the compact polycrystalline structure. Therefore, it is inferred that the modified films show improved EC properties.

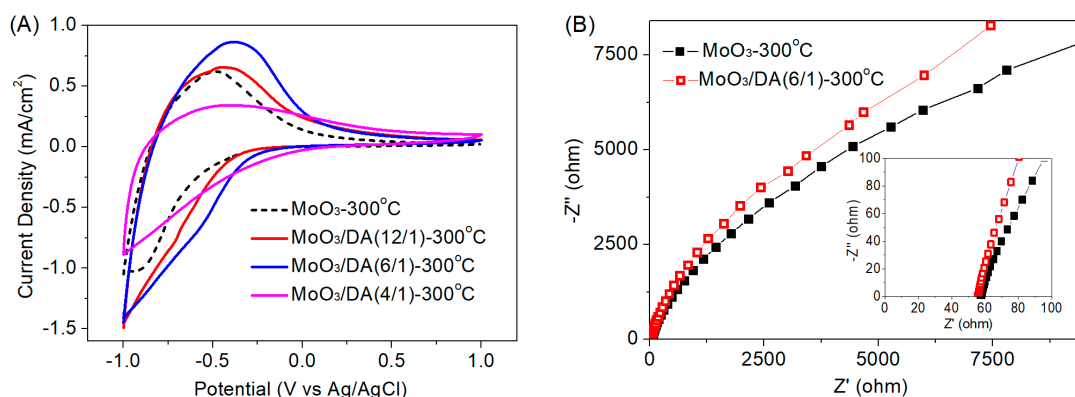


Figure 6. (A) CV curves of MoO_3 -300 °C, $\text{MoO}_3/\text{DA}(12/1)$ -300 °C, $\text{MoO}_3/\text{DA}(6/1)$ -300 °C, and $\text{MoO}_3/\text{DA}(4/1)$ -300 °C films at a scan rate of 100 mV s^{-1} and (B) Nyquist plots of MoO_3 -300 °C and $\text{MoO}_3/\text{DA}(6/1)$ -300 °C films using a perturbation amplitude of 10 mV at the potential of 0 V with a frequency range from 100 kHz to 10 mHz.

3.3. EC Properties of the Modified MoO_3 Films

EC properties of the pure MoO_3 -300 °C and the modified MoO_3 films were studied and compared. UV-vis transmittance spectra of the pure MoO_3 -300 °C and $\text{MoO}_3/\text{DA}(6/1)$ -300 °C films under different applied potentials from -0.8 to $+0.8$ V and dynamic switching curves of all the films can be seen in Figure 7A–C and the results obtained from Figure 7C are listed in Table 1. Optical contrast (transmittance modulation), ΔT , is defined as the difference in the transmittance between the bleached and the colored states at a specific wavelength and a high optical contrast means that the EC film has an excellent ability for regulating solar radiation. The $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film exhibits much higher ΔT (71%) than pure MoO_3 -300 °C film (51%). This is because the nanocrystal-embedded amorphous structure of the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film can provide more electrochemical active sites and easier access of more intercalated Li^+ ions and electrons than the compact polycrystalline structure of the MoO_3 -300 °C film [17,42], in agreement with the results on the electrochemical properties as shown in Figure 6.

Response times, namely the bleaching and coloration times, are defined as the times required achieving 90% of the transmittance contrast between bleached and colored states. The MoO_3 -300 °C film shows relatively long switching times, the bleaching time is 14 s and the coloration time is 8 s, while the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film has much faster dynamic response, that is, the bleaching and coloration times are 5 s and 6 s, respectively. The switching times depend on the ion diffusion coefficient and the length of diffusion path [43]. In the highly crystalline MoO_3 -300 °C film, ion movement is obstructed by the dense structure, which leads to a long response time. However, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film has a larger amorphous region, which can serve as ion transport channels to shorten diffusion length and increase the diffusion rate of Li^+ ions, benefiting fast ion insertion and extraction [12].

Coloration efficiency (CE) is the change in optical density per unit charge inserted into the EC films at a specific wavelength. Compared with the MoO_3 -300 °C film, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film presents much higher CE (88 vs. $65 \text{ cm}^2 \text{ C}^{-1}$), which can be attributed to its more efficient Li^+ ion diffusion and charge transfer caused by the nanocrystal-embedded amorphous structure. A high CE value of an EC material indicates that a small amount of charge (low energy) can achieve a large optical contrast, leading to

better energy-saving capability for EC films. This is a crucial parameter for practical EC devices, since low charge insertion/extraction enhances the long-term cycling stability [44].

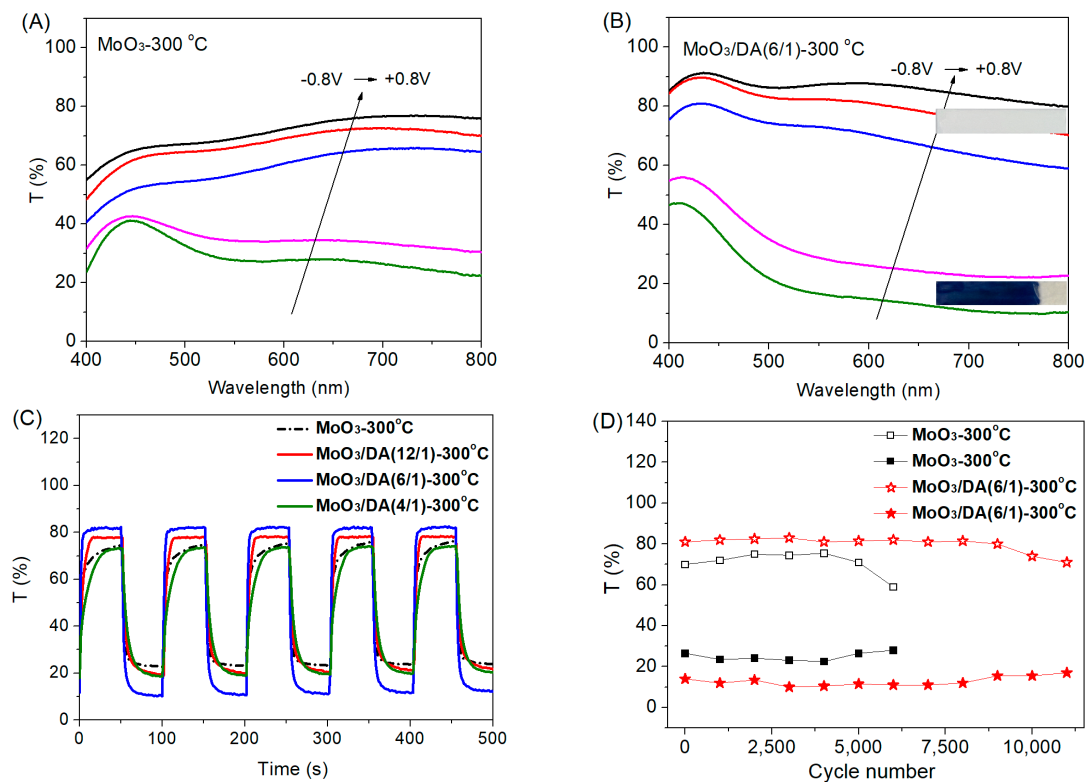


Figure 7. UV-vis transmittance spectra of (A) pure MoO₃-300 °C and (B) MoO₃/DA(6/1)-300 °C at different potentials, the inset showing the photos of the bleached and colored MoO₃/DA(6/1)-300 °C film on ITO glass, (C) switching curve comparison between MoO₃-300 °C, MoO₃/DA(12/1)-300 °C, MoO₃/DA(6/1)-300 °C and MoO₃/DA(4/1)-300 °C at $\lambda_{720\text{ nm}}$ (−0.8 V/+0.8 V, 100 s/cycle), and (D) Cycling stability of MoO₃-300 °C and MoO₃/DA(6/1)-300 °C films at $\lambda_{720\text{ nm}}$ (−0.8 V/+0.8 V, 30 s/cycle).

Table 1. EC properties of the MoO₃-300 °C, MoO₃/DA(12/1)-300 °C, MoO₃/DA(6/1)-300 °C, MoO₃/DA(4/1)-300 °C films, and dual active layer device containing MoO₃/DA(6/1)-300 °C film at $\lambda_{720\text{ nm}}$.

EC Films or Device	ΔT (%)	CE (cm ² C ^{−1})	Bleaching Time (s)	Coloration Time (s)
MoO ₃ -300 °C Film	51	65	14	8
MoO ₃ /DA(12/1)-300 °C Film	59	74	8	9
MoO ₃ /DA(6/1)-300 °C Film	71	88	5	6
MoO ₃ /DA(4/1)-300 °C Film	54	69	19	15
Dual Active Layer Device	63	148	4	3

Cycling stability is also an important indicator to evaluate the practicability of an EC material. Figure 7D shows the cycling stability of the MoO₃-300 °C and MoO₃/DA(6/1)-300 °C films using short cycle time of 30 s for saving time. Therefore, the initial contrasts in Figure 7D are lower than those in Figure 7C. However, it is important to notice that both the contrast and response speeds slightly increase with cycling test because after fast and repetitive insertion/extraction of Li⁺ ions there are more diffusion paths for Li⁺ ions, more active sites for the EC reaction and more electrolytes absorbed in the films [3,22,25,45]. The MoO₃-300 °C film maintains relatively stable up to 5000 cycles due to its crystalline structure. However, the contrast shows a marked fall after 5000 cycles. Compared with

the MoO_3 -300 °C film, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film exhibits much higher stability up to 9000 cycles. This is because the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film possesses a distinctive nanocrystal-embedded amorphous structure. On the one hand, the amorphous phase in the film serves as a buffer layer to accommodate the volume change caused by ion insertion/extraction without causing bond breakage and protects the film from mechanical destruction. On the other hand, nanometer-sized amorphous and crystalline regions are uniformly distributed in the film, which decreases stress concentration and inhibits erosion due to high local stress [26]. Therefore, the modified $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film can easily withstand repetitive insertion and extraction of Li^+ ions and shows excellent cycle stability.

According to the characterization results obtained from UV-Vis, XRD, FTIR, SEM and TEM, it is obvious that the DA amount has a great influence on the structure and morphology of the modified MoO_3 films through complexation of DA and PMA sol to inhibit the formation of large MoO_3 particles in the precursor sol and polycrystalline structure during annealing. It is well known that the change of structure and morphology will lead to the change of various properties, such as electrochemical properties as mentioned above. Therefore, the effects of DA amount on EC properties of the MoO_3 films were also studied. When the DA amount is low, as shown in Figure 7C and Table 1, the $\text{MoO}_3/\text{DA}(12/1)$ -300 °C film with relatively large and heterogeneous nanocrystals and a small amount of amorphous regions shows higher contrast and CE and faster bleaching time than the crystalline MoO_3 -300 °C film. When the Mo/DA is 6/1, it can be concluded that the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film shows higher EC properties than not only the pure film but also the other modified films, indicating Mo/DA of 6/1 is the optimum added amount. That is, of all the pure and the modified MoO_3 films, the $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film displays the highest optical contrast, CE and switching speed because its uniform and fine nanocrystal-embedded amorphous structure can make good use of the advantages of the amorphous and nanocrystalline phases. When the DA amount is excessive, the $\text{MoO}_3/\text{DA}(4/1)$ -300 °C film still contains carbonaceous residue of DA after annealing at 300 °C, blocking ion transport, and, therefore, exhibits slower switching speed than other films.

3.4. EC Properties of the Device with the Modified MoO_3 Film as an Active Layer

In order to demonstrate and expand the practical application of the modified MoO_3 film, a complementary EC device of dual active layers with configuration of ITO glass// $\text{MoO}_3/\text{DA}(6/1)$ -300 °C//PPC electrolyte//PANI//ITO glass was fabricated. As shown in Figure 8 and Table 1, this device shows excellent EC properties, such as high contrast (63%), CE ($148 \text{ cm}^2 \text{ C}^{-1}$) and switching speed (bleaching time of 4 s and coloration time of 3 s), verifying that the modified $\text{MoO}_3/\text{DA}(6/1)$ -300 °C film has great potential for practical application in smart windows or other EC devices.

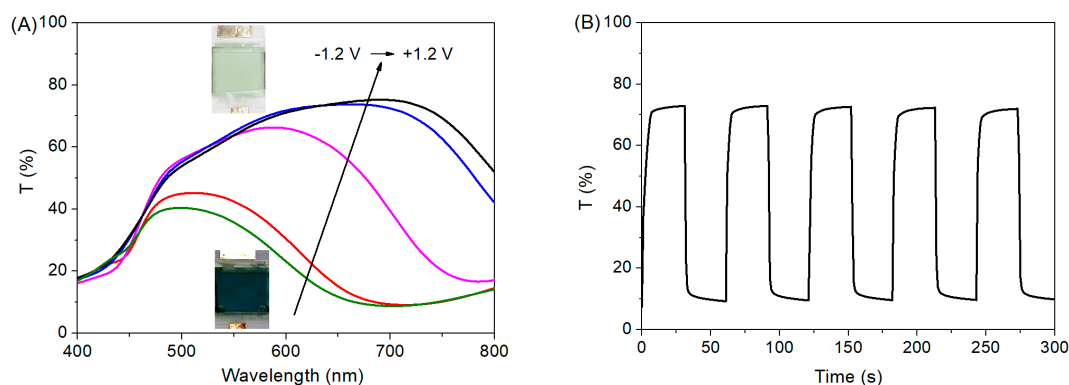


Figure 8. (A) UV-vis transmittance spectra of the dual active layer device containing $\text{MoO}_3/\text{DA}(6/1)$ -300 °C and PANI films at different potentials, the inset showing the photos of the bleached and colored device, and (B) switching curve of the dual active layer device containing $\text{MoO}_3/\text{DA}(6/1)$ -300 °C and PANI films at $\lambda_{720 \text{ nm}}$ (-1.2 V/+1.2 V, 60 s/cycle).

4. Conclusions

In conclusion, the modified nanocrystalline MoO₃ films have been prepared through a simple and low-cost complexation-assisted sol–gel method using DA as a structure-directing agent. DA containing both catechol and amine functional groups can complex with the PMA colloidal particles, inhibit the formation of large MoO₃ particles in the precursor sol and highly stressed polycrystalline structure during annealing and form unique nanocrystals embedded in an amorphous matrix after annealing at 300 °C. The DA amount has a great influence on the structure and morphology and, thus, electrochemical and EC properties of the MoO₃ films. Compared with the pure MoO₃ film, the MoO₃/DA(6/1)-300 °C film with appropriate DA amount possesses significantly enhanced EC properties, such as higher optical contrast, coloration efficiency, switching speed and cycling stability because the uniform and fine nanocrystal-embedded amorphous structure can adequately combine the advantages of the amorphous and nanocrystalline phases. Moreover, the dual-active-layer EC device with the MoO₃/DA(6/1)-300 °C film as the cathodically coloring layer shows high optical contrast, coloration efficiency and switching speed. These demonstrate that the complexation-assisted sol–gel method using DA as a structure-directing agent is a promising wet-chemical route to prepare low-cost modified MoO₃ film and MoO₃-based EC device with excellent EC properties.

At present, MoO₃ EC materials have not been widely used. In the future, however, this research work could be further improved and then used to enrich the research directions and potential application fields of MoO₃, such as EC smart windows, electrocatalytic devices, field emission devices, batteries, supercapacitors, energy storage devices, sensors and so on.

Author Contributions: Conceptualization, D.Z.; methodology, D.Z. and L.Y.; validation, D.Z. and L.Y.; preparation, D.Z.; characterization, D.Z. and L.Y.; writing-original draft preparation, D.Z.; writing-review and editing, L.Y.; supervision, D.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Chongqing Research Program of Basic Research and Frontier Technology (grant number cstc2019jcyj-msxmX0510), the Major Project of Science and Technology Research Program of Chongqing Education Commission of China (grant number KJZD-M202301403), and the Research Project of Yangtze Normal University (grant number 2017KYQD39).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are available from the corresponding author.

Acknowledgments: The authors would like to thank Qihuang Deng for the XRD characterization.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Huang, Y.; Wang, B.; Chen, F.; Han, Y.; Zhang, W.; Wu, X.; Li, R.; Jiang, Q.; Jia, X.; Zhang, R. Electrochromic materials based on ions insertion and extraction. *Adv. Opt. Mater.* **2021**, *10*, 2101783. [[CrossRef](#)]
2. Zhang, S.; Peng, Y.; Zhao, J.; Fan, Z.; Ding, B.; Lee, J.Y.; Zhang, X.; Xuan, Y. Amorphous and porous tungsten oxide films for fast-switching dual-band electrochromic smart windows. *Adv. Opt. Mater.* **2022**, *11*, 2202115. [[CrossRef](#)]
3. Wu, C.-L.; Wang, C.-K.; Lin, C.-K.; Wang, S.-C.; Huang, J.-L. Electrochromic properties of nanostructured tungsten oxide films prepared by surfactant-assisted sol-gel process. *Surf. Coat. Technol.* **2013**, *231*, 403–407. [[CrossRef](#)]
4. Kim, J.; Lee, K.H.; Lee, S.; Park, S.; Chen, H.; Kim, S.K.; Yim, S.; Song, W.; Lee, S.S.; Yoon, D.H.; et al. Minimized optical scattering of MXene-derived 2D V₂O₅ nanosheet-based electrochromic device with high multicolor contrast and accuracy. *Chem. Eng. J.* **2023**, *453*, 139973. [[CrossRef](#)]
5. Hsu, S.-C.; Chao, S.-H.; Wu, N.-J.; Huang, J.-H.; Kang, J.-L.; Weng, H.C.; Liu, T.-Y. Facile synthesis of hybrid WO₃/MoOx electrochromic films for application in complementary electrochromic devices. *J. Alloys Compd.* **2023**, *945*, 169256. [[CrossRef](#)]
6. Duan, Y.; Wang, C.; Hao, J.; Jiao, Y.; Xu, Y.; Wang, J. Electrochromic performance and capacitor performance of α -MoO₃ nanorods fabricated by a one-step procedure. *Coatings* **2021**, *11*, 783. [[CrossRef](#)]
7. Wang, J.; Hou, L.; Ma, D. Molybdenum oxide electrochromic materials and devices. *J. Inorg. Mater.* **2021**, *36*, 461–470. [[CrossRef](#)]

8. Sivakumar, R.; Gopalakrishnan, R.; Jayachandran, M.; Sanjeeviraja, C. Characterization on electron beam evaporated α -MoO₃ thin films by the influence of substrate temperature. *Curr. Appl. Phys.* **2007**, *7*, 51–59. [\[CrossRef\]](#)
9. Mohamed, S.H.; Kappertz, O.; Ngaruiya, J.M.; Leervad Pedersen, T.P.; Drese, R.; Wuttig, M. Correlation between structure, stress and optical properties in direct current sputtered molybdenum oxide films. *Thin Solid Film.* **2003**, *429*, 135–143. [\[CrossRef\]](#)
10. Gesheva, K.; Szekeres, A.; Ivanova, T. Optical properties of chemical vapor deposited thin films of molybdenum and tungsten based metal oxides. *Sol. Energy Mater. Sol. Cells* **2003**, *76*, 563–576. [\[CrossRef\]](#)
11. Ivanova, T.; Gesheva, K.A.; Popkirov, G.; Ganchev, M.; Tzvetkova, E. Electrochromic properties of atmospheric CVD MoO₃ and MoO₃–WO₃ films and their application in electrochromic devices. *Mater. Sci. Eng. B* **2005**, *119*, 232–239. [\[CrossRef\]](#)
12. Lin, F.; Cheng, J.; Engtrakul, C.; Dillon, A.C.; Nordlund, D.; Moore, R.G.; Weng, T.-C.; Williams, S.K.R.; Richards, R.M. In situ crystallization of high performing WO₃-based electrochromic materials and the importance for durability and switching kinetics. *J. Mater. Chem.* **2012**, *22*, 16817–16823. [\[CrossRef\]](#)
13. Wei, C.-C.; Wu, T.-H.; Huang, J.-W.; Young, B.-L.; Jian, W.-B.; Lin, Y.-L.; Chen, J.-T.; Hsu, C.-S.; Ma, Y.-R.; Tsukagoshi, K. Nanoparticulate films of WO₃ and MoO₃ composites for enhancing UV light electrochromic transmittance variation and energy storage applications. *Electrochim. Acta* **2023**, *442*, 141897. [\[CrossRef\]](#)
14. Lin, S.-Y.; Wang, C.-M.; Kao, K.-S.; Chen, Y.-C.; Liu, C.-C. Electrochromic properties of MoO₃ thin films derived by a sol–gel process. *J. Sol-Gel Sci. Technol.* **2009**, *53*, 51–58. [\[CrossRef\]](#)
15. Taylor, D.J.; Cronin, J.P.; Allard, L.F.; Birnie, D.P. Microstructure of laser-fired, sol-gel-derived tungsten oxide films. *Chem. Mater.* **1996**, *8*, 1396–1401. [\[CrossRef\]](#)
16. Novak, T.G.; Kim, J.; Tiwari, A.P.; Kim, J.; Lee, S.; Lee, J.; Jeon, S. 2D MoO₃ nanosheets synthesized by exfoliation and oxidation of MoS₂ for high contrast and fast response time electrochromic devices. *ACS Sustain. Chem. Eng.* **2020**, *8*, 11276–11282. [\[CrossRef\]](#)
17. Ou, J.Z.; Balendhran, S.; Field, M.R.; McCulloch, D.G.; Zoolfakar, A.S.; Rani, R.A.; Zhuiykov, S.; O'Mullane, A.P.; Kalantar-zadeh, K. The anodized crystalline WO₃ nanoporous network with enhanced electrochromic properties. *Nanoscale* **2012**, *4*, 5980–5988. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Dhanasankar, M.; Purushothaman, K.K.; Muralidharan, G. Enhanced electrochromism in cerium doped molybdenum oxide thin films. *Mater. Res. Bull.* **2010**, *45*, 1969–1972. [\[CrossRef\]](#)
19. Layegh, M.; Ghodsi, F.E.; Hadipour, H. Experimental and theoretical study of Fe doping as a modifying factor in electrochemical behavior of mixed-phase molybdenum oxide thin films. *Appl. Phys. A* **2019**, *126*, 14. [\[CrossRef\]](#)
20. Jittiporn, P.; Sikong, L.; Kooptarnond, K.; Taweepreda, W.; Stoenescu, S.; Badilescu, S.; Truong, V.-V. Electrochromic properties of MoO₃–WO₃ thin films prepared by a sol-gel method, in the presence of a triblock copolymer template. *Surf. Coat. Technol.* **2017**, *327*, 66–74. [\[CrossRef\]](#)
21. Cholang, C.M.; Westphal, T.M.; Balboni, R.D.C.; Moura, E.A.; Gündel, A.; Flores, W.H.; Pawlicka, A.; Avellaneda, C.O. Thin films of V₂O₅/MoO₃ and their applications in electrochromism. *J. Solid State Electrochem.* **2017**, *21*, 1509–1515. [\[CrossRef\]](#)
22. Deepa, M.; Saxena, T.K.; Singh, D.P.; Sood, K.N.; Agnihotry, S.A. Spin coated versus dip coated electrochromic tungsten oxide films: Structure, morphology, optical and electrochemical properties. *Electrochim. Acta* **2006**, *51*, 1974–1989. [\[CrossRef\]](#)
23. Fang, Y.; Sun, X.; Cao, H. Influence of PEG additive and annealing temperature on structural and electrochromic properties of sol-gel derived WO₃ films. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 145–152. [\[CrossRef\]](#)
24. Shi, Y.; Sun, M.; Zhang, Y.; Cui, J.; Wang, Y.; Shu, X.; Qin, Y.; Tan, H.H.; Liu, J.; Wu, Y. Structure modulated amorphous/crystalline WO₃ nanoporous arrays with superior electrochromic energy storage performance. *Sol. Energy Mater. Sol. Cells* **2020**, *212*, 110579. [\[CrossRef\]](#)
25. Zhou, D.; Che, B.; Kong, J.; Lu, X. A nanocrystalline tungsten oxide electrochromic coating with excellent cycling stability prepared via a complexation-assisted sol–gel method. *J. Mater. Chem. C* **2016**, *4*, 8041–8051. [\[CrossRef\]](#)
26. Zhou, D.; Tong, Z.; Xie, H.; Sun, J.; Chen, F. Effects of additives on electrochromic properties of nanocrystalline tungsten oxide films prepared by complexation-assisted sol-gel method. *Materials* **2023**, *16*, 2681. [\[CrossRef\]](#)
27. Zhou, D.; Zhou, R.; Chen, C.; Yee, W.-A.; Kong, J.; Ding, G.; Lu, X. Non-volatile polymer electrolyte based on poly(propylene carbonate), ionic liquid, and lithium perchlorate for electrochromic devices. *J. Phys. Chem. B* **2013**, *117*, 7783–7789. [\[CrossRef\]](#)
28. Xiong, S.; Phua, S.L.; Dunn, B.S.; Ma, J.; Lu, X. Covalently bonded polyaniline-TiO₂ hybrids: A facile approach to highly stable anodic electrochromic materials with low oxidation potentials. *Chem. Mater.* **2010**, *22*, 255–260. [\[CrossRef\]](#)
29. Wang, Z.; Zou, Y.; Li, Y.; Cheng, Y. Metal-containing polydopamine nanomaterials: Catalysis, energy, and theranostics. *Small* **2020**, *16*, 1907042. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Griffith, W.P.; Pumphrey, C.A.; Rainey, T.A. Catecholato complexes of ruthenium, iridium, rhenium, molybdenum, and tungsten. *J. Chem. Soc. -Dalton Trans.* **1986**, *6*, 1125–1128. [\[CrossRef\]](#)
31. Elhendawy, A.M.; Griffith, W.P.; Pumphrey, C.A. Complexes of osmium, uranium, molybdenum, and tungsten with the catechol amines adrenaline, noradrenaline, dopamine, dopa, and isoproterenol. *J. Chem. Soc. -Dalton Trans.* **1988**, *7*, 1817–1821. [\[CrossRef\]](#)
32. Urdaneta, I.; Keller, A.; Atabek, O.; Palma, J.L.; Finkelstein-Shapiro, D.; Tarakeshwar, P.; Mujica, V.; Calatayud, M. Dopamine adsorption on TiO₂ anatase surfaces. *J. Phys. Chem. C* **2014**, *118*, 20688–20693. [\[CrossRef\]](#)
33. Kleiman-Shwarsstein, A.; Laursen, A.B.; Cavalca, F.; Tang, W.; Dahl, S.; Chorkendorff, I. A general route for RuO₂ deposition on metal oxides from RuO₄. *Chem. Commun.* **2012**, *48*, 967–969. [\[CrossRef\]](#) [\[PubMed\]](#)

34. Valverde-Aguilar, G.; Prado-Prone, G.; Vergara-Aragon, P.; Garcia-Macedo, J.; Santiago, P.; Rendon, L. Photoconductivity studies on nanoporous TiO₂/dopamine films prepared by sol-gel method. *Appl. Phys. A-Mater. Sci. Process.* **2014**, *116*, 1075–1084. [[CrossRef](#)]
35. Dalavi, D.S.; Devan, R.S.; Patil, R.A.; Patil, R.S.; Ma, Y.-R.; Sadale, S.B.; Kim, I.; Kim, J.-H.; Patil, P.S. Efficient electrochromic performance of nanoparticulate WO₃ thin films. *J. Mater. Chem. C* **2013**, *1*, 3722–3728. [[CrossRef](#)]
36. Cheng, P.; Shi, L.; Li, W.; Fang, X.; Cao, D.; Zhao, Y.; Cao, P.; Liu, D.; He, D. Efficient Regulation of Polysulfides by MoS(2)/MoO(3) Heterostructures for High-Performance Li-S Batteries. *Small* **2023**, *19*, e2206083. [[CrossRef](#)] [[PubMed](#)]
37. Wen-Cheun Au, B.; Chan, K.-Y.; Knipp, D. Effect of film thickness on electrochromic performance of sol-gel deposited tungsten oxide (WO₃). *Opt. Mater.* **2019**, *94*, 387–392. [[CrossRef](#)]
38. Quy, V.H.V.; Jo, I.-R.; Kang, S.-H.; Ahn, K.-S. Amorphous-crystalline dual phase WO₃ synthesized by pulsed-voltage electrodeposition and its application to electrochromic devices. *J. Ind. Eng. Chem.* **2021**, *94*, 264–271. [[CrossRef](#)]
39. Huang, H.; Tian, J.; Zhang, W.K.; Gan, Y.P.; Tao, X.Y.; Xia, X.H.; Tu, J.P. Electrochromic properties of porous NiO thin film as a counter electrode for NiO/WO₃ complementary electrochromic window. *Electrochim. Acta* **2011**, *56*, 4281–4286. [[CrossRef](#)]
40. Cong, S.; Tian, Y.; Li, Q.; Zhao, Z.; Geng, F. Single-Crystalline Tungsten Oxide Quantum Dots for Fast Pseudocapacitor and Electrochromic Applications. *Adv. Mater.* **2014**, *26*, 4260–4267. [[CrossRef](#)]
41. Kondalkar, V.V.; Mali, S.S.; Kharade, R.R.; Khot, K.V.; Patil, P.B.; Mane, R.M.; Choudhury, S.; Patil, P.S.; Hong, C.K.; Kim, J.H.; et al. High performing smart electrochromic device based on honeycomb nanostructured h-WO₃ thin films: Hydrothermal assisted synthesis. *Dalton Trans.* **2015**, *44*, 2788–2800. [[CrossRef](#)] [[PubMed](#)]
42. Romero, R.; Dalchiele, E.A.; Martin, F.; Leinen, D.; Ramos-Barrado, J.R. Electrochromic behaviour of Nb₂O₅ thin films with different morphologies obtained by spray pyrolysis. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 222–229. [[CrossRef](#)]
43. Lee, S.H.; Deshpande, R.; Parilla, P.A.; Jones, K.M.; To, B.; Mahan, A.H.; Dillon, A.C. Crystalline WO₃ nanoparticles for highly improved electrochromic applications. *Adv. Mater.* **2006**, *18*, 763–766. [[CrossRef](#)]
44. Rai, V.; Singh, R.S.; Blackwood, D.J.; Zhili, D. A review on recent advances in electrochromic devices: A material approach. *Adv. Eng. Mater.* **2020**, *22*, 2000082. [[CrossRef](#)]
45. Deepa, M.; Srivastava, A.K.; Sood, K.N.; Murugan, A.V. Nanostructured tungsten oxide-poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) hybrid films: Synthesis, electrochromic response, and durability characteristics. *J. Electrochem. Soc.* **2008**, *155*, D703–D710. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.