

Bifunctional $\text{MoO}_3\text{--WO}_3/\text{Ag}/\text{MoO}_3\text{--WO}_3$ Films for Efficient ITO-Free Electrochromic Devices

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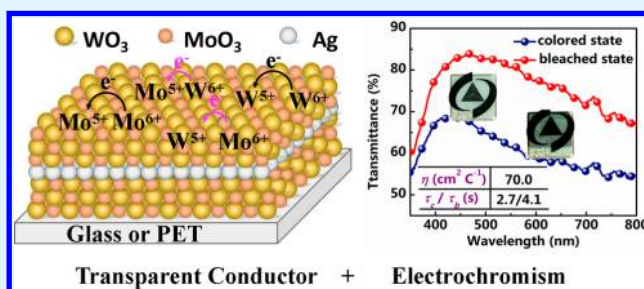
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S Supporting Information

ABSTRACT: Dielectric–metal–dielectric (DMD) trilayer films, served as both electrochromic (EC) film and transparent conductor (TC), have exhibited great potential application in low-cost, ITO-free electrochromic devices (ECDs). However, recent reports on the DMD-based ECDs revealed that the response time and the optical modulation properties were not very satisfactory. Here, the mixed $\text{MoO}_3\text{--WO}_3$ materials were first introduced as the dielectric layer to construct an EC–TC bifunctional $\text{MoO}_3\text{--WO}_3/\text{Ag}/\text{MoO}_3\text{--WO}_3$ (MWAMW) film, which demonstrates strong and broad-band optical modulation in the visible light region, fast color-switching time (2.7 s for coloration and 4.1 s for bleaching), along with high coloration efficiency ($70 \text{ cm}^2 \text{ C}^{-1}$). The electrical structure and electrochemical reaction kinetics analysis revealed that the improved EC performances are associated with the increased electron intervalence transition together with the fast charge-transfer and ion-diffusion dynamics.

KEYWORDS: electrochromic, transparent conductor, dielectric-metal-dielectric, mixed oxide, doping



1. INTRODUCTION

Electrochromic devices (ECDs) with dynamic changes in transparency, color, or other optical properties in response to applied potential^{1–3} show extremely promising applications in displays,^{4,5} adjustable mirrors,^{6,7} and energy-saving smart windows.^{8–11} However, the economic, large-scale, and reliable development of commercial ECDs is still facing some hurdles due to the restricted acquirability of low-cost transparent conductor (TC) and electrochromic (EC) materials with the desired functionality and durability.^{12,13}

The traditional ECD structure comprises three superimposed layers (EC film, electrolyte, and ion-storage film or complementary EC film) positioned between two TCs.¹⁴ The TC may be the most costly part in ECDs, especially if they are based on an indium-containing oxide, e.g., indium tin oxide (ITO).¹⁵ Some new TC materials such as metal grids,¹⁶ graphene,^{17,18} and dielectric–metal–dielectric (DMD) films^{19–21} have been used in ECDs as alternatives to ITO. Among them, the DMD structure is new and striking for potential application in large-scale and low-cost ITO-free ECDs due to its superior combination of low resistance (usually less than $15 \Omega \square^{-1}$) and high transparent (over 80%).^{20,21} Recently, by exploring EC materials such as WO_3 and MoO_3 as the dielectric layer, the DMD films have been demonstrated to have both TC and EC functionalities, which can not only simplify the device structure and significantly reduce the fabrication cost, but also improve the EC performances.^{22–24} However, the overall EC performances especially response

time, optical modulation property, and durability of the reported DMD-based ECDs are not very satisfactory. Therefore, the large improvement in EC performance for DMD-based ECD is still highly desired.

The utilization of mixed oxides as EC layers has been proved to be an effective way to systematically modulate the absorption band and consequent EC performance by simply varying the ratio of the constituent oxides.²⁵ To date, by utilizing W–Ti,^{26,27} W–Mo,²⁸ W–Li,²⁹ and other mixed oxides,^{30,31} relative enhancements in device stability and coloration efficiency have been achieved. It can be inferred that introducing mixed oxides in DMD structure will be favorable to the performance improvement of DMD-based ECDs. Unfortunately, there is no report on the usage of this approach in DMD film for improving the device performance to the best of our knowledge. In this paper, by utilizing mixed $\text{MoO}_3\text{--WO}_3$ as the dielectric layer, the EC–TC bifunctional $\text{MoO}_3\text{--WO}_3/\text{Ag}/\text{MoO}_3\text{--WO}_3$ (MWAMW) film was successfully constructed and applied in highly efficient ITO-free ECDs for the first time. After optimizing the composition and thickness of the MWAMW film, the bifunctional film presents improved optical absorption in visible light range, very fast response time, and high coloration efficiency. The essence of these improvements was also discussed.

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2. EXPERIMENTAL SECTION

2.1. Materials. Tungsten oxide (WO_3 , 99.9%) and molybdenum oxide (MoO_3 , 99.9%) were purchased from Chnos elemental technology Co., Ltd. Lithium perchlorate (LiClO_4 , 98%) and propylene carbonate (PC, 99.7%) was acquired from Sigma–Aldrich. All the chemicals were used without further purification.

2.2. Film Preparations. The MWAMW, $\text{MoO}_3/\text{Ag}/\text{MoO}_3$ (MAM), and $\text{WO}_3/\text{Ag}/\text{WO}_3$ (WAW) films were deposited onto glass and PET substrates via electron–beam evaporation at room temperature. The glass and PET substrates were ultrasonically cleaned with a mixture of ether and ethanol ($V/V = 1/1$) for 15 min, and finally dried under an oven lamp (250 W). For the deposition of MW mixed films, the pure MoO_3 and WO_3 powders with various Mo/W atom ratios of 3:2, 1:1, and 1:2 were first ground in an agate mortar to form uniform mixed oxide powder. Afterward, the mixed powers were compression molded using a powder pressing molding machine and finally dried in a vacuum oven (-0.1 MPa) at 120°C for 12 h before use. The deposition rates of MW and Ag were 0.05 – 0.15 and 0.5 – 1.0 nm s^{-1} , respectively, at pressures below 3×10^{-3} Pa.

2.3. Characterizations. The surface resistances of the films were measured by a four-point probe instrument. The bulk carrier concentration and Hall mobility of the films were determined using a HMS–3000 Hall effect measurement system with an applied magnetic field of 0.55 T. The transmittance spectra of the films were performed on a Shimadzu UV-3101PC spectrophotometer. The ratios of WO_3 and MoO_3 in the mixed MW films were determined by X-ray photoelectron spectra (XPS) using a Thermo Scientific ESCALAB 250 with Multitechnique Surface Analysis. Energy dispersive X-ray (EDX, EMAX, Japan) elemental analysis was also adopted for reference. The structures of the films were measured by X-ray diffraction (XRD, D8 Focus, Bruker, Germany). The atomic force microscopy (AFM) measurement was taken from a Shimadzu SPM-7900 (tapping mode). The film thickness during the material deposited was monitored by quartz crystal thickness monitor, which was calibrated with Ambios XP-1 surface profiler by testing the actual thickness of a series of single layer thick films with the apparent thickness of 150, 200, and 300 nm. Herein, a thick film was adopted to reduce the measurement error and improve the accuracy. The thicknesses of the deposited films were also confirmed by SEM (S-4800, Hitachi, Japan).

The electrochemical and EC behaviors of the films were studied in a CHI 920 electrochemical workstation (Shanghai Chenhua Instruments Inc., China) equipped with an Ocean Optics QE-Pro spectrometer using a standard three-electrode arrangement in a quartz electrochemical cell. The titanium plate ($5\text{ mm} \times 20\text{ mm}$), Ag/AgCl (3.5 M KCl), and the investigated films ($18\text{ mm} \times 18\text{ mm}$) were used as the counter electrode, reference electrode, and working electrode, respectively. The LiClO_4 (1 mol L^{-1}) in propylene carbonate (PC) solution was used as the electrolyte, which was degassed with nitrogen for 30 min before use. The bending properties of the flexible films were tested at a home-made cyclic bending test system with an 5 mm radius of curvature. All experiments were carried out at room temperature.

EC performance was determined in terms of transmittance variation (optical contrast, ΔT), response time (τ), and coloration efficiency (η), shown in eqs 1 and 2:³²

$$\Delta T(\%) = T_b - T_c \quad (1)$$

$$\eta = \log(T_b/T_c)/Q \quad (2)$$

where T_b and T_c denote the transmittance of the samples in the bleached state and colored state, respectively, and Q represents the charge intercalation/deintercalation per unit area.

3. RESULTS AND DISCUSSION

3.1. Thickness Optimization. The optical and electrical properties of stacked DMD films are strongly affected by the thickness of each layer. Thin but continuous middle metal layer ensures small absorption and low sheet resistance of the films.

Adequate thickness of inner and outer dielectric layer would enable high transmittance and excellent EC performance.^{33,34}

Based on the previous studies,^{23,24} the MWAMW films with two different thicknesses of $30/10/40\text{ nm}$ (F40 for short) and $30/10/50\text{ nm}$ (F50 for short) were prepared to optimize the optical transmittance and electrical property of the mixed-oxide films. From the cross-section SEM micrographs of these films (Figure S1 in the Supporting Information), well definite trilayer structures can be observed on the substrate. As shown in Figure 1a, the maximum transmittance of F40 and F50 reached 81.8%

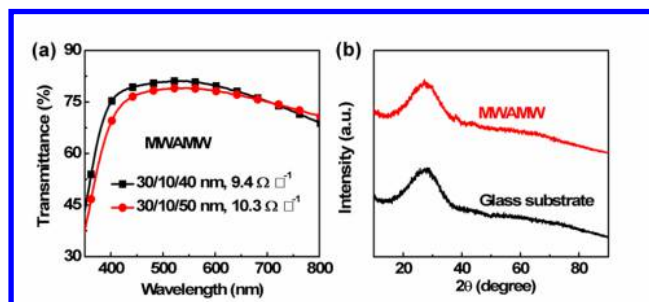


Figure 1. (a) Measured optical transmittance spectra of MWAMW films on glass with different thickness; (b) XRD patterns of glass substrate and MWAMW film deposited on glass at room temperature.

and 79.1% at 544 nm, respectively. Compared with the F50, F40 presented a slightly higher average transmittance (77.4% vs 76.2%) over the wavelength range of 400 – 800 nm and a lower sheet resistance (9.4 vs $10.3\ \Omega\ \square^{-1}$). Considering the high transparency and low sheet resistance for a film is conducive to the high performance ECDs, the mixed-oxide film with the thickness of $30/10/40\text{ nm}$ was chosen for further study.

3.2. Structural and Morphology. The microstructure and surface morphology of the mixed-oxide film were determined by XRD and AFM. The XRD pattern suggests that the room temperature-deposited MWAMW films are completely amorphous due to the absence of any well-defined diffraction peaks except a broad hump that from substrate (Figure 1b). The result is in good agreement with the previous reports on DMD films prepared under the similar conditions. It has been demonstrated that the amorphous films usually possess improved EC performance in comparison to the ordered crystalline films because the quite disordered and loose structure in an amorphous film offers an easier path for ion migration and charge–transfer during the electrochemical process and allow rapid changes of its optical properties.^{35,36} Figure 2 gives the AFM images of the WAW, MWAMW, and MAM films. It can be seen that all three films present fine granula-like surface feature without any crack. For the WAW film, some big grain agglomeration with the size ca. 20 – 50 nm is evenly dispersed on the surface, causing a relative rough surface morphology with the root-mean-square (RMS) of 1.4 nm . When doping $50\text{ at } \%$ MoO_3 into the WO_3 , a quite smooth and uniform morphology without any bulky aggregation on the surface was observed, leading to the RMS value decreased from 1.4 to 0.74 nm for the MWAMW film. The surface feature of the doped MWAMW film is even similar to that of pure MAM film, implying that MoO_3 -doping into the WAW film can significantly improve the surface uniformity of the film. This smooth surface lineament would contribute to the uniform electrical field distribution in the electrochemical process, which

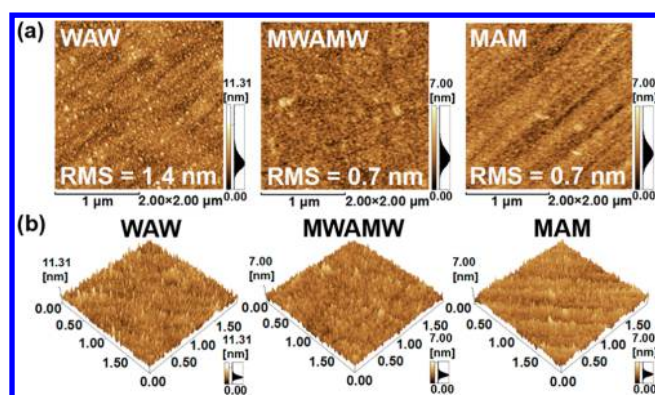


Figure 2. AFM images in (a) surface topography and (b) 3D stereogram of WAW, MWAMW, and MAM films deposited on glass substrates.

facilitates even ion-diffusion and electron-transfer kinetics and subsequently results in good EC performance.³⁷

To further study the composition–property relationship, a series of MWAMW films with various Mo/W ratios are deposited. The similar evaporation temperature for WO_3 ($\sim 800^\circ\text{C}$) and MoO_3 ($\sim 600^\circ\text{C}$) made the deposition of mixed MW film from single boat (single-source evaporation) possible, which was more straightforward and controllable to traditional multi-source deposition method.³⁸ The XPS spectra of the deposited films are shown in Figure 3. All the mixed films

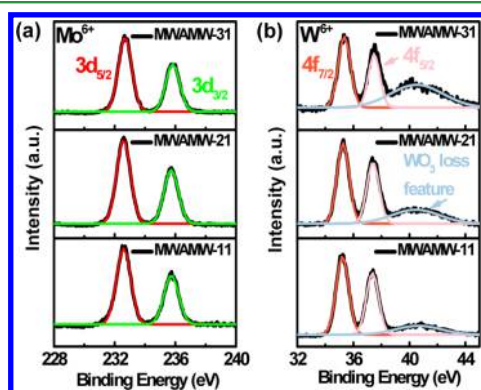


Figure 3. XPS lines corresponding to (a) Mo ($3d_{5/2}$, $3d_{3/2}$) and (b) W ($4f_{7/2}$, $4f_{5/2}$) from MWAMW films.

exhibit the characteristic $3d_{5/2}$ and $3d_{3/2}$ doublet for MoO_3 caused by the spin–orbit coupling. The component peaks located at 232.70 and 235.83 eV are expected to Mo^{6+} . The binding energies of $4f_{7/2}$, $4f_{5/2}$, and loss feature lines characteristic for W^{6+} have been found at 35.28, 37.40, and 40.86 eV, respectively. All these peak positions are in excellent agreement with the reports in the literature.^{39–41} The XPS analysis results of MWAMW films are given in Table S1. The calculated chemical composition ratio of the MWAMW films is Mo:W = 3:1, 2:1, 1:1 (in at %, hereafter, referred to as MWAMW–31, MWAMW–21, and MWAMW–11, respectively). In the all MWAMW films, the at % of MoO_3 was slightly larger than that in the raw material, maybe caused by the lower evaporation temperature of MoO_3 than WO_3 .⁴² The EDX spectra of the deposited films are shown in Figure S2. The absence of any other characteristic peaks except those attributed to Mo, W, O, and Ag from the film indicates that

the high-quality mixed films without any other elemental impurity were successfully obtained.

3.3. Electrochemical and Electrochromic Properties.

In order to evaluate the EC properties of the deposited films, potential step chronoamperometry was executed by concurrent recording the corresponding changes of the optical transmittance. As shown in Figure 5a, the average transmittance of as-deposited MAM, MWAMW–31, –21, –11, and WAW films in the wavelength range of 400–800 nm are 72.9%, 76.5%, 77.4%, 73.9%, and 79.3%, respectively, showing that WO_3 doping can improve the visual transparency of WAW film. By successively changing the potential from -0.50 to $+0.55$ V (vs Ag/AgCl), the color of these films changed reversibly from dark gray blue (colored state for MAM and MWAMW) to transparent (bleached state) or from dark blue (for WAW) to transparent (Figure 4), which could be relevant to the

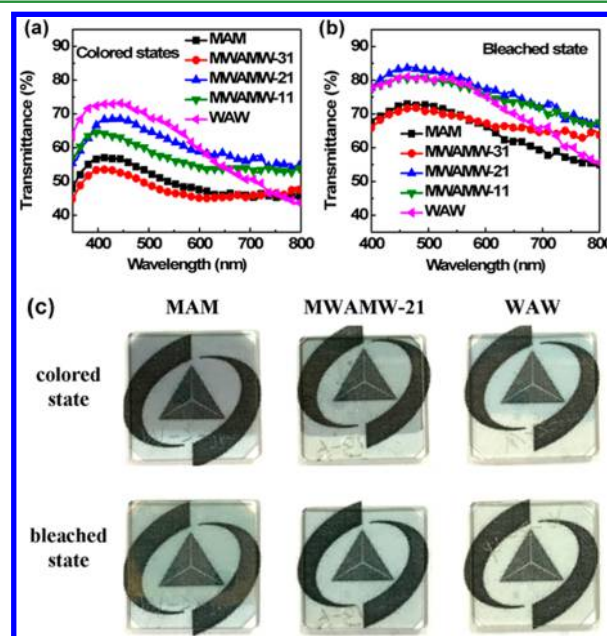


Figure 4. Measured optical transmittance spectra of MAM, MWAMW, and WAW films in (a) colored and (b) bleached states at potential steps from -0.50 to 0.55 V (vs Ag/AgCl) with a 20 s interval; the photographs of samples; (c) pictures of MAM, MWAMW-21 and WAW films in colored states and bleached states.

double injection and extraction of electrons and Li^+ ions. The optical contrast (ΔT) spectra of these films are given in Figure 5b. For the WAW film, the average transmittance alteration in visible light range is only 12.4% with the maximum ΔT of 15.8% at 683 nm. After MoO_3 doping, the obvious enhancement in ΔT (19.4–22.9%) was realized. Most importantly, the maximum ΔT peaks of these three MWAMW films (localized at ca. 550 nm) are blue-shifted significantly toward the eye-sensitivity peak. In addition, compared with bare MAM film, the mixed MWAMW films display increased ΔT in the wavelength range larger than 600 nm, resulting in stronger and broader band absorption of light in their colored state. These results suggested that the doped MWAMW films presented superior optical modulation properties over both MAM and WAW films.

The color-switching response time for a 90% transmittance variation and the coloration efficiency were also studied. From Table 1 and Figure S3, we can see that after WO_3 doping, a

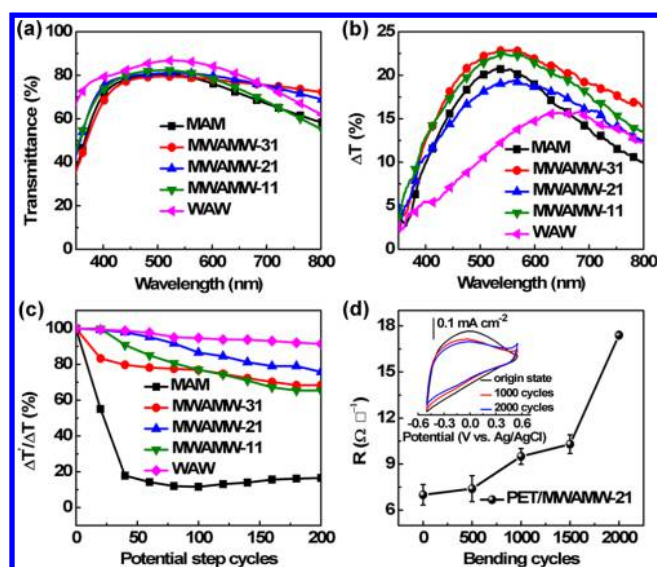


Figure 5. (a) Measured initial transmittance spectra, (b) calculated optical contrast, and (c) attenuation curves of optical contrast during 200 potential step cycles (from -0.50 to $+0.55$ V vs Ag/AgCl) of MAM, MWAMW, and WAW films on glass substrates; (d) changes in sheet resistivity of MWAMW-21 on PET after repeated bending at a 5 mm radius of curvature (changes in CV curves presented in the inset).

Table 1. Summary of Electrochromic Properties of MAM, MWAMW, and WAW Films

films	T_{ave}^a (%)	$\Delta T_{max}@ \lambda$ (%@nm)	$\tau_{c,90\%}$ (s)	$\tau_{b,90\%}$ (s)	η (cm ² C ⁻¹)	E_g (eV)	R ($\Omega \square^{-1}$)
MAM	72.9	20.8@531	10	11.8	32.5	2.75	12.0
MWAMW-31	76.5	22.9@541	6.5	10.9	38	3.19	14.7
MWAMW-21	77.4	19.4@561	2.7	4.1	70.0	3.21	9.4
MWAMW-11	73.9	22.5@543	4.3	4.4	48	3.27	12.3
WAW	79.3	15.8@683	6	3	63.0	3.38	11.5

^aThe average transmittance in the visible range (400–800 nm).

great decrease in response time and a significant enhancement in coloration efficiency were realized in these MWAMW films. The coloration/bleaching time (τ_c/τ_b) of MWAMW-21 film was found to be 2.7 and 4.1 s, which were about 2.7 and 2.9 times shorter than those of MAM film ($\tau_c = 10$ s and $\tau_b = 11.8$ s), respectively. The response time of MWAMW-21 is among the top values reported on film-state MoO₃–WO₃ materials, and even comparable to the response time of nanostructured MoO₃–WO₃ materials (Table S2). In addition, the coloration efficiency of the MWAMW-21 film realized a value of 70.0 cm² C⁻¹, which is 2.15 times as large as that of MAM (32.5 cm² C⁻¹). Usually, thicker film exhibits more intense coloration efficiency owing to the increased amount of electrochromic chromophores at the same inserted charge density. So, the achieved coloration efficiency of the MWAMW-21 film in this study is very competitive (Table S2), considering the effective thickness of the EC layer is only 40 nm in the film.

The large optical contrast, fast response time, and high coloration efficiency of the MWAMW films suggest the efficient use of charge, which can desirably induce long-term cycling stability. As shown in Figure 5c, among all films, WAW exhibits

the best stability with only 9% attenuation of optical contrast. While, the transmittance modulation ability of MAM is down to less than 20%, which may originate from the self-dissolution, degradation and ion-trapping of the film during the successive switching.^{43,44} By comparison, MWAMW films also have a high stability of optical contrast like the WAW film, which preserve over 70% transmittance modulation ability even after 200 successive potential step cycles.

To explore the essence reason for the enhanced EC performance of the mixed MWAMW film (larger absorption in visible light region, higher coloration efficiency, and faster response time), the band-gap energy and the electrochemical reaction kinetics of the films were thoroughly analyzed. The variation of $(\alpha h\nu)^{1/2}$ vs $h\nu$ in Figure 6a results in linear plots

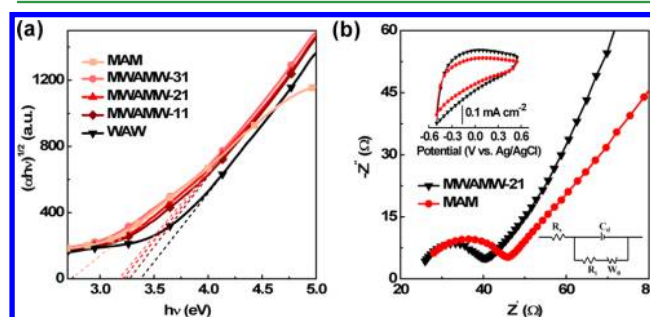


Figure 6. (a) Tauc plots of MAM, MWAMW, and WAW films. (b) Nyquist plots of MAM and MWAMW-21 films on glass; insets are their fitted equivalent circuit and CV curves at the scan rate of 50 mV s⁻¹.

indicating that the optical absorption in these samples takes place through indirect inter band transitions. The extrapolation of the linear region of the plot to zero absorption coefficient gives the band gap value. We noted that the values of band-gap decreased with the increasing of Mo content in WO₃ film, which can be attributed to the enhanced intervalency-transition, that is electron transition between metal ions with different valencies (e.g., Mo⁵⁺ to Mo⁶⁺ and Mo⁵⁺ to W⁶⁺).^{38,45} This increased electron transition in MWAMW film are causally expected to induce large optical absorption in the visible light region and high coloration efficiency.

To further understand the electrochemical behavior of the deposited films, the electrochemical impedance spectrum (EIS) were performed by applying an AC voltage of open-circuit voltage of each film in a frequency range of 0.01 to 100 Hz. The measured EIS curves in Figure 6b consist of a semicircle in high-frequency region and a straight line in low-frequency region, which correspond to the charge-transfer and ion-diffusion process, respectively.⁴⁶ The MWAMW-21 film possesses smaller semicircle and higher line slope than the MAM film, indicating the MWAMW-21 has a lower charge-transfer resistance and a higher ion-diffusion rate, which subsequently leading to superior electrical conductivity and reaction kinetics. The enhanced electrochemical activity for MWAMW-21 film can also be confirmed by CV curve analysis as a larger area under the CV curve can be observed for the MWAMW-21 film (inset of Figure 6b). The diffusion coefficients of the Li⁺ were also determined from CV curves at scan rates from 5 to 50 mV s⁻¹ (Figure S4) and calculated from the slope of the anodic peak current vs the square root of the scan rate according to the Randles-Sevcik equation.⁴⁷ The calculated diffusion coefficient of Li⁺ in MWAMW-21 film was

$7.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which was nearly 1.4 times larger than that in MAM film ($3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The above results suggest that the critical reasons of the enhanced coloration efficiency and fast color-switching response time of doped MWAMW films lie in its increased electron intervalence transition together with the fast charge-transfer and ion-diffusion dynamics.

By preparing the MWAMW-21 film onto the flexible PET substrate, we found that the flexible MWAMW-21 film owns excellent transparency in the visible light vision with a maximum transmittance of 82.2% at 514 nm (Figure S5). Meanwhile, the excellent EC performance was also impressive. It possessed fast response time ($\tau_c = 1.2 \text{ s}$, $\tau_b = 1.2 \text{ s}$, Figure S6), high coloration efficiency of $56.9 \text{ cm}^2 \text{ C}^{-1}$ (Figure S7), as well as promising mechanical stability. We observed that after 2000 bending cycles at a 5 mm radius of curvature, the area under CV curve was only slightly reduced compared to the original one. Moreover, the resistance of the film increased marginally from 7.0 to $17.4 \Omega \square^{-1}$ (Figure 5d) after the bending treatment. The results suggested the mixed-oxide stacked films also have the potential application in high performance flexible ITO-free ECDs.

4. CONCLUSION

In summary, the highly efficient rigid and flexible ECDs based on TC and EC dual-functional MWAMW films have been achieved by utilizing the mixed MoO_3 - WO_3 as the dielectric layer for the first time. The mixed MWAMW film displayed good overall performance, with a low sheet resistance of $9.4 \Omega \square^{-1}$, high average transmittance of 77.4%, strong and broad-band optical modulation in visible light range, fast color-switching time ($\tau_c = 2.7 \text{ s}$ and $\tau_b = 4.1 \text{ s}$), as well as a high coloration efficiency ($70 \text{ cm}^2 \text{ C}^{-1}$), considering the effective thickness of the EC layer is only 40 nm. These improved EC performances can be attributed to the increased electron intervalence transition together with the fast charge-transfer and ion-diffusion dynamics. The present study could provide an alternative route to improve EC performance for tungsten and molybdenum oxide materials and the demonstrated method could also be extended to other material system for adjusting the photoelectric performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b12346.

Cross sections of SEM images; EDX spectra; in situ corresponding transmittance and chronocoulometry switching curves; variation of the optical density vs charge density; composition summary of reported MWAMW films; performance summary of reported ECDs based on mixed MoO_3 - WO_3 materials. (PDF)

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Notes

The authors declare no competing financial interest.

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