Fast response of complementary electrochromic device based on WO$_3$/NiO electrodes

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Nanoporous structures have proven as an effective way for enhanced electrochromic performance by providing a large surface area can get fast ion/electron transfer path, leading to larger optical modulation and fast response time. Herein, for the first time, application of vacuum cathodic arc plasma (CAP) deposition technology to the synthesis of WO$_3$/NiO electrode films on ITO glass for use in fabricating complementary electrochromic devices (ECDs) with a ITO/WO$_3$/LiClO$_4$-perchlorate solution/NiO/ITO structure. Our objective was to optimize electrochromic performance through the creation of electrodes with a nanoporous structure. We also examined the influence of WO$_3$ film thickness on the electrochemical and optical characteristics in terms of surface charge capacity and diffusion coefficients. The resulting 200-nm-thick WO$_3$ films achieved ion diffusion coefficients of $(7.35 \times 10^{-10}$ (oxidation) and $4.92 \times 10^{-10}$ cm$^2$/s (reduction)). The complementary charge capacity ratio of WO$_3$ (200 nm thickness)/NiO (60 nm thickness) has impressive reversibility of 98%. A demonstration ECD device $(3 \times 4$ cm$^2$) achieved optical modulation ($\Delta T$) of 46% and switching times of 3.1 sec (coloration) and 4.6 sec (bleaching) at a wavelength of 633 nm. In terms of durability, the proposed ECD achieved $\Delta T$ of 43% after 2500 cycles; i.e., 93% of the initial device.

Over the past decades, electrochromic devices (ECDs) have been used in energy efficient buildings, optical information displays, variable-reflectance mirrors, switchable mirrors, and electronic papers$^{1-5}$. Electrochromism materials change their optical characteristics (transmittance, reflectance, and absorption) reversibly through applying a dc voltage$^6$. Electrochromism has attracted much attention because it could provide a tremendous promising application in energy-saving smart windows. Smart windows based on electrochromic (EC) materials easily control the indoor sunlight and solar heat and can be effectively reduced the heating or cooling loads of building interiors$^8$. A wide variety of electrochromic materials have been developed, including metal oxides$^{7-9}$, small organic molecules$^{10}$, and conductive polymer thin films$^{11-13}$. Complementary ECDs are composed of anodic and cathodic coloring materials in a five-layer structure. A pair of transparent conducting layers sandwich an ionic conduction layer (electrolyte) in contact with an electrochromic (EC) layer and an ion storage (complementary) layer$^{14-16}$. Tungsten oxide (WO$_3$) is known as one of the most popular cathodic coloring material and nickel oxide (NiO) as typical anodic coloring material, which has been intensively investigated$^{14-17}$.

WO$_3$ film is a transition metal oxide, which can be reversibly switched between colorless and blue under positive or negative voltage, respectively$^{18,19}$. The chemical reaction underlying the electrochromic behavior of WO$_3$ films is based on reversible oxidation/reduction reactions induced by the electrochemical double injection/extraction of positive ions (lithium or proton) and electrons into/out of the host WO$_3$ lattice in the transition from $W^{5+}$ to $W^{6+}$ $\pm$ $e^-$. WO$_3$ films have been fabricated in a variety of nanostructures, including nano-rods$^{18,21,22}$, nanosheets$^{20}$, and nanotrees$^{23}$. Note however that a dense structure, low diffusion coefficient, and/or long diffusion length for ion insertion tend to hinder optical modulation performance. By increasing the contact area between the electrode and electrolyte, nanoporous WO$_3$ structures reduce the diffusion path of ions and providing channels to facilitate the rapid transfer of ion/electrons, resulting in particularly good electrochemical and electrochemical performance$^{9,20,23}$. Electrochromic WO$_3$ films have been fabricated using a variety of methods, including sputtering$^{24-27}$, chemical vapor deposition (CVD)$^{28-30}$, spray pyrolysis$^{31,32}$, thermal evaporation$^{33}$, electron-beam deposition$^{34}$, and sol-gel$^{35-37}$ methods. Lee et al.$^{19}$ recently reported on the synthesis of uniform WO$_3$ nano-rods, resulting in films with fast coloration/bleaching times (28.8/4.5 sec at 633 nm). Zhang et al.$^{23}$

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$\Delta T$ : Optical modulation

Wavelength : 633 nm
used thermal annealing in the synthesis of WO₃ electrodes within a one-dimensional structure, which resulted in good CE (43.6 cm²/C), and fast coloration/bleaching times (7.6/4.2 sec at 633 nm).

Different above technology, in the current study, we used cathodic arc plasma (CAP) technology to fabricate WO₃/NiO films with a porous surface structure with the aim of enhancing electrochromic performance and accelerating switching speeds. We also examined the degree to which the thickness of WO₃ layers affects the electrochemical and optical properties of ECDs.

**Results**

**Electrochromic mechanism for NiO-WO₃ system.** As shown in Fig. 1(a–c), the application of voltage (an electric field) to the device causes positive ions to move toward the electric field, while the electrons move in the opposite direction. The movement of ions (electrons) into the electrochromic (ion storage) layers is responsible for the coloration (bleaching) of the ECDs. The underlying physics involved in the electrochromic reactions can be represented using the following the redox equations:

\[
\text{WO}_3(\text{bleaching}) + x(M^+ + e^-) \rightleftharpoons M_x\text{WO}_3(\text{coloration}),
\]

where \(M\) indicates the lithium ions (Li⁺) or hydrogen ions (H⁺) ions. The WO₃ thin film changes from transparent to deep blue under the effects of electron insertion (i.e., photo-effected intervalence electron transfer from \(W^{6+}\) to \(W^{5+}\) sites). The electrochromic mechanism governing the behavior of Li⁺ ions against ion insertion/extraction in the NiO electrode can be represented using the following the redox equations:

\[
\text{NiO}_x + y(M^+ + e^-) \rightarrow M_y\text{NiO}_x(\text{coloration})M_y\text{NiO}_x(\text{bleaching}) + z(M^+ + e^-).
\]

The reduction of Ni³⁺ to Ni²⁺ leads to the bleaching of the NiO film (during the cathodic scan), and coloration of NiO film via the oxidation of Ni²⁺ to Ni³⁺ (in the reverse process). Continuously applying negative voltage to the NiO electrode (ion storage layer) causes the insertion of electrons and Li⁺ ions leading to the oxidation of Ni²⁺ to Ni³⁺, with the result that the coloration state is dominant. In Fig. 1(c), for test step, to understand surface charge capacity for WO₃/NiO electrode films, which were integrated CA curves defined as both intercalation surface charges \(Q_{in}\) and extraction surface charges \(Q_{out}\). Here, the complementary surface charge capacity ratio \(R\) is defined as the insertion WO₃ electrode divided by the extraction NiO electrode.

**WO₃/ITO and NiO/ITO films: surface charge capacity ratio.** The complementary ECD in the current study included two electrochromic electrodes, as in thin-film batteries. Thus, we calculated the surface charge capacity ratio of the electrodes in both directions. We first sought to elucidate the electrochemical and energy storage properties of the WO₃/ITO/glass by constructing three electrode cells, which comprised a working electrode (WO₃ film on ITO/glass), a counter-electrode (Pt mesh) and a reference electrode (Ag/AgCl) in 0.5 M LiClO₄/Perchlorate (LiClO₄/PC) solution.

The surface charge capacity of the WO₃ layers was based on integral to CA curves was carried with from −1.5 to 0.3 V versus AgCl/Ag in intercalation surface charges \(Q_{in}\) and extraction surface charges \(Q_{out}\). As shown in Fig. 2(a), the 200-nm-thick WO₃ electrode returned the following values: \(Q_{in}\) (7.38 mC cm⁻²), \(Q_{out}\) (8.4 mC cm⁻²), and reversibility, \(Q_{in}/Q_{out}\) is about 87% better than the other samples. Here, complementary charge capacity ratio \(R\) is defined as the intercalation WO₃ electrode divided by the extraction NiO electrode according to following equation:

\[
R = \frac{Q_{in}(\text{WO}_3)}{Q_{out}(\text{NiO})},
\]

where \(Q_{in}(\text{WO}_3)\) is the surface charge capacity of the WO₃ electrode during intercalation and \(Q_{out}(\text{NiO})\) is the surface charge capacity of the NiO electrode during the extraction process. \(Q_{out}(\text{NiO})\) was carried with from 0.7 V versus Ag/AgCl and observed \(Q_{out}(\text{NiO})\) value is 7.45 mC cm⁻². As shown in Fig. 2(b), we also assessed the degree to which the thickness of the WO₃ layer (175 nm, 200 nm, 225 nm and 250 nm) affected the charge capacity ratio when using an NiO/ITO/glass electrode of 60 nm in thickness. With the change capacity of the NiO
electrode fixed at 7.45 mC cm$^{-2}$, the $R$ values varied as a function of WO$_3$ thickness, as follows: 175 nm (0.54), 200 nm (0.98), 225 nm (1.04), and 250 nm (2.0). Note that under these conditions, the sample with a 200 nm-thick layer of WO$_3$ achieved reversibility of nearly 98%. Figure 2(c) shows the reversibility of $R = \frac{Q_{\text{in}}(\text{WO}_3)}{Q_{\text{out}}(\text{NiO})}$ about 0.98–1.02 value between 60 and 72 cycles. It appears that the high $R$ value reduced the likelihood of ion blocking, making it an ideal structure for the movement of ions at electrode/electrolyte interfaces in an electrochromic film.

**Diffusion coefficient and transmittance optical modulation as a function of WO$_3$/ITO film thickness.** Figure 3(a1,b1,c1,d1) showed cycle voltammetry (CV) curve of WO$_3$/ITO films at four different thicknesses and applied the potential voltage from $-1.5 \text{ V}$ (coloration) to $0.3 \text{ V}$ (bleaching) at a scan rate of 200 mV/s. In Fig. 3, the CV curve of WO$_3$/ITO films were measured at 25th-cycle for four different thicknesses 175 nm, 200 nm, 225 nm, and 250 nm respectively. Furthermore, the diffusion coefficient $D$ of Li$^+$ ions during injection/extraction of ions into/out of the WO$_3$ film can be calculated using the Randles–Servick Eq. (4)$^9$.

$$J_p = 2.69 \times 10^5 n^{3/2} C_0 D^{1/2} v^{1/2},$$  

where $C_0$ indicates the concentration of electrolyte solution (mol $\cdot$ cm$^{-3}$); $v$ is the scan rate (V $\cdot$ s$^{-1}$); $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$) and $J_p$ is the peak current. Table 1 lists the values for $J_{pa}$ (cathodic peak current density), $J_{pa}$ (anodic peak current density), and diffusion coefficient $D$ (working area $3 \times 4 \text{ cm}^2$). Sample 2 (with 200 nm-thick) of WO$_3$/ITO films in Table 1 presented the highest ion diffusion coefficients of $7.35 \times 10^{-10} \text{ cm}^2/\text{s}$ (oxidation) and $4.92 \times 10^{-10} \text{ cm}^2/\text{s}$ (reduction). From Table 1, the higher diffusion coefficient indicates a larger contact area and greater porosity resulting in faster ion insertion/extraction.
Figure 3(a1,b1,c1,d1,1,4) presents the optical transmittance spectra of WO3/ITO/glass between bleached and colored states at different various thicknesses (175 nm, 200 nm, 225 nm, and 250 nm). At a fixed wavelength of 633 nm, optical transmittance varied as a function of thicknesses from 38.35% to 52.68%. Note that the modulation of optical transmittance of 200-nm-thick WO3 film (ΔT = 52.68%) was higher than that of the other samples, as indicated by the larger enveloped area in the CV curve. Actually, the area of the CV curve is deeply related to the charge stored (capacity) at porous WO3 film20 indicates that more charges are taking part in redox reactions.

**Microstructural characteristics.** The cross-sectional SEM image in Fig. 4 shows the hemispherical surface structures of the WO3 film deposited using CAP. Top-view SEM image of WO3 pattern inset of Fig. 4. Figure 5(a1) presents the X-ray diffraction (XRD) patterns of the WO3 film deposited on a glass substrate. The porous WO3 film presented only one broad peak at ~23°, indicating an amorphous structure, as described in previous studies36. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the WO3 film surface. The electrochemical testing of Li_{x}WO_{3}(WO_{3}:Li) samples in 0.5 M liquid-electrolyte of LiClO_{4}/PC solution was performed using a three-electrode cell, comprising a working electrode (WO3 electrode film on ITO/glass), a counter-electrode (Pt mesh) and a reference electrode (Ag/AgCl). The color of the WO3/ITO/glass changed from deep blue (colored state; −1.35 V) to transparent (bleached state; 0.2 V), is accordance with the intercalation/extraction of ions (Li\(^{+}\)) into/out of the WO3 electrode. The thickness of the WO3 film was shown to have considerable influence on the electrochromic properties by XPS analysis. Figure 5(c,e) show XPS spectra of W 4f in tungsten oxide films (200 nm) and (250 nm) in coloration states. In Fig. 5(c,e), the peaks W 4f\(_{7/2}\) and W 4f\(_{5/2}\) of W\(^{6+}\) and W\(^{5+}\) that are located at binding energies of 35.17 and 37.24 eV corresponding to W4 f\(_{7/2}\) and W4 f\(_{5/2}\) of W\(^{5+}\) in the Li\(_{x}\)WO\(_{3}\). The coloration process indicates the movement of Li\(^{+}\) ions and electrons into the WO3 films, such that the W\(^{6+}\) obtained an e\(^{-}\) to become W\(^{5+}\), resulting in a corresponding shift in the peak to a lower energy level. The content of W\(^{5+}\) in Li\(_{x}\)WO\(_{3}\) film (i.e., \(\eta(W^{5+})\)) can be calculated using the following equation:

\[
\eta(W^{5+}) = \frac{W^{5+} (W^{5+} + W^{6+})}{100%}.
\]

Table 1. Diffusion coefficients of WO3/ITO glass of various thicknesses.

| Sample | Thick(nm) | Cathodic Current(Ipc) | Anodic Current(Ipa) | D from Jpc/Jpa |
|--------|-----------|-----------------------|--------------------|----------------|
| 1      | 175       | 1.19 × 10\(^{-3}\)    | 9.28 × 10\(^{-4}\) | 3.92 × 10\(^{-10}\) |
| 2      | 200       | 1.63 × 10\(^{-3}\)    | 1.33 × 10\(^{-3}\) | 7.35 × 10\(^{-10}\) |
| 3      | 225       | 1.41 × 10\(^{-3}\)    | 1.14 × 10\(^{-3}\) | 5.46 × 10\(^{-10}\) |
| 4      | 250       | 1.10 × 10\(^{-3}\)    | 8.90 × 10\(^{-4}\) | 3.36 × 10\(^{-10}\) |

Figure 3(a2,b2,c2,d2) presents the optical transmittance spectra of WO3/ITO/glass between bleached and colored states at different various thicknesses (175 nm, 200 nm, 225 nm, and 250 nm). At a fixed wavelength of 633 nm, optical transmittance varied as a function of thicknesses from 38.35% to 52.68%. Note that the modulation of optical transmittance of 200-nm-thick WO3 film (ΔT = 52.68%) was higher than that of the other samples, as indicated by the larger enveloped area in the CV curve. Actually, the area of the CV curve is deeply related to the charge stored (capacity) at porous WO3 film20 indicates that more charges are taking part in redox reactions.
The fitted spectrum can be separated into two gaussian doublets shown Fig. 5(c–f). In this redox reaction Eq. (5), we evaluated ions transformed from the W⁶⁺ to the W⁵⁺ state. In Fig. 5(c–e), we calculated that approximately 30% (200 nm) and 35% (250 nm) of the ions transformed from the W⁶⁺ to the W⁵⁺ state, see Table 2. This is an indication that a larger number of W⁶⁺ (bleaching) Li⁺ ions took part in the reduction reaction to become W⁵⁺ (blue). As shown in Fig. 3(b₁, d₁), we found that as the thickness of the film increased, Qₙₑ (WO₃) curve gradually increased as did the power of lithium-ion injection, optical transmittance of 200-nm-thick WO₃ film (T_coloration = 25.12%) and 250-nm-thick WO₃ film (T_coloration = 18.13%) at a fixed wavelength of 633 nm. Figure 5(d–f) presents high-resolution XPS spectra of W 4f in tungsten oxide films (200 nm) and (250 nm) in bleaching states. In the W 4f spectrum in the bleached state (Fig. 5(d)), the peaks at binding energies of 35.6 and 37.7 eV (T_coloration approximately 80% (250 nm) of the ions transformed from the W 5⁺ to W⁶⁺ state). But when the film thickness reaches 250 nm, the film can't completely fade, which is still light blue, which means that W⁵⁺ (blue) can't completely convert to W⁶⁺ (bleaching).

This is confirmed by the detection of W⁵⁺ in a later XPS analysis of the 250 nm bleached film. This shows that there are residual W⁵⁺ ions in the process of fading oxidation when lithium ion is injected into the coloring reduction reaction Therefore, appropriate film thickness, will help improve the electrochromic optical modulation performance. The 200-nm-thick film contained only W⁶⁺ ions; however, some of the W⁵⁺ ions in the 250-nm-thick film did not convert into W⁶⁺ ions, thereby decreasing the penetration of the bleaching state, as shown in Fig. 3(b₂, d₂), we found optical transmittance of 200-nm-thick WO₃ film (T_bleaching = 78.85%) and 250-nm-thick WO₃ film (T_bleaching = 70.05%) at a fixed wavelength of 633 nm. In Fig. 5(f), we calculated that approximately 80% (250 nm) of the ions transformed from the W⁵⁺ to the W⁶⁺ state, see Table 2. Ning et al. claimed that lattice strain can affect the diffusion and migration of lithium ions, such that the coefficient of lithium ion diffusion decreases under the effects of pressure-induced strain. Thus, the failure of the 250-nm-thick film to recolor may be due to the thickness of the film, which extended the lithium ion migration path, such that the remaining stress hindered the transfer of lithium ions and the conversion of W⁵⁺ to W⁶⁺. Therefore, tungsten oxide film as a cathodic electrochromic layer, the film thickness should be selected appropriately, can improve modulation optical transmittance to optimization conditions.

Coloration efficiency of WO₃/ITO films as a function of thickness. Coloration efficiency (CE) is an important criterion in the evaluation of electrochromic materials. CE is defined as the optical density charge (ΔOD) per unit of inserted charge Qₙₑ (Qₑ = Q/A, where A is the ²⁶;

$$CE = \frac{\Delta OD}{Q_{in}}$$

$$\Delta OD = \ln (T_{bleaching}/T_{coloration})$$

where T_bleaching and T_coloration refer to the transmittance of bleaching and coloration state. Generally, a high CE value is an indication of large optical modulation under small charge insertion. Figure 6(a–d) plots ΔOD at a wavelength of 633 nm as a function of the charge inserted into films. The CE value of the as-synthesized WO₃/ITO/glass was estimated from the slopes of the quasi-linear curves. The CE values at 633 nm were as follows: 175 nm (79.8 cm² C⁻¹), 200 nm (90 cm² C⁻¹), 225 nm (77.5 cm² C⁻¹), and 250 nm (72.3 cm² C⁻¹).

Characterization of WO₃/NiO ECD. Figures 7,8 presents the electrochromic performance of ECD (glass/ITO/WO₃/liquid electrolyte/NiO/ITO/glass) with an active area of 3 × 4 cm². Figure 7(a) presents the in-situ transmittance of WO₃/NiO ECD at 633 nm, as analyzed during a continuous potential cycle from −1.5 V (colored potential, Vₜ) to 0.8 V (bleached potential, Vₜ). In Fig. 7(b,c) show that the coloration state (charge process) and bleaching state (discharge process) of ECDs were measured by CA curves and in-situ optical response of transmittance at fixed 633 nm. The coloration and bleaching of switching times or speed was a prominent characteristic for ECD system, which was defined as the time required for a 90% change in the full transmittance modulation. As shown in Fig. 7(c), ECD achieved a maximum optical modulation reached 46% and the switching times at a wavelength of 633 nm were obtained coloration (3.1 sec) and bleaching (4.6 sec) (see supplementary video). The electrochromic and optical properties of our work compared with other authors researches are detailed in

![Cross-sectional morphologies of WO₃/ITO film.](image)
Table 3. Figure 8 illustrates the durability of the ECDs in terms of transmittance optical modulation measured in intervals of 15 s. As shown in Fig. 8, even after 1000 cycles (approximately 10 hours), there was no significant degradation in the optical modulation performance of the ECD. As shown in Fig. 8, transitions between bleached and colored states remained steady until 1000 cycles, at which point switching performance degraded gradually, dropping to 93% of the as-synthesized samples by 2500 cycles.

Methods
Cathodic arcs can be used for the reactive deposition of various nitrides and oxides. Nonetheless, CAP technology has not been widely adopted, due to violent plasma-liquid pool interactions at cathode spots, which can cause the emission of macro-particles (MPs) that degrade the quality of the resulting film. This can largely be overcome by steering the arc rapidly across the surface of the cathode under high working pressure to reduce the spot residence
time and limit the formation of erosion craters. In recent years, researchers have shifted emphasis from monolithic coatings to higher performing multilayers and nano-composites. As shown in Fig. 9(a), the proposed arc gun set up relies on the flow of argon (for insertion) and oxygen (reaction) to control the formation of the electrode structure. It is difficult to measure the dynamics of a cathode spot; therefore, we employed a high-speed

| Film Thickness | states     | W oxidation | W 4f peak | Binding energy (eV) | FWHM (eV) | Area % |
|---------------|------------|-------------|-----------|---------------------|-----------|--------|
| 200           | Bleaching  | W⁶⁺        | W⁴⁺       | 35.6                | 0.8       | 100%   |
| 200           | Coloration | W⁶⁺        | W⁴⁺       | 35.5                | 1.6       | 70%    |
| 200           | Coloration | W⁶⁺        | W⁴⁺       | 35.6                | 2.2       | 30%    |
| 250           | Bleaching  | W⁶⁺        | W⁴⁺       | 35.6                | 1.7       | 80%    |
| 250           | Bleaching  | W⁶⁺        | W⁴⁺       | 16.2                | 1.8       | 20%    |
| 250           | Coloration | W⁶⁺        | W⁴⁺       | 35.6                | 1.7       | 65%    |
| 250           | Coloration | W⁶⁺        | W⁴⁺       | 16.3                | 1.8       | 35%    |

Table 2. W 4f peak fitting binding energy of WO₃ film with thick of 200 and 250 nm. *FWHM-Full width half maximum.

Figure 6. (Color online) Optical density change as a function of inserted charge for WO₃/ITO film with various thicknesses.
video camera to capture images of light emission from various spots across the target plane in sequences of 1 sec, as shown in Fig. 9(b,c). The deposition parameters are shown in Table 2 and 3, and the schematic drawing of the cathodic arc deposition is presented in Fig. 9(a).

Figure 10 presents a schematic diagram showing the process of ECD fabrication. Figure 10(a): Step 1 and 2 involved respectively depositing an EC film/ITO on one glass substrate and a counter film/ITO on another glass substrate. Step 3 involved fitting the two components together and sealing them with epoxy adhesive. Note glass beads were used as spacers to maintain a cavity between the EC film and the counter film to hold liquid electrolyte (<100 μm). Note also that a small gap was created in the epoxy for use as an inlet into the space. Step 5 showed ECD consisted of seven layers: A central ionic conduction layer (electrolyte) sealed between an electrochromic (EC) layer and an ion storage (complementary) layer, which were sandwiched between two transparent conducting layers, which were in turn sandwiched between two glass substrates. Figure 10(b) mainly describes the process of component packaging. Figure 10(b) Step 1: Dispensing for one side pre gluing. Step 2: UV glue curing. Step 3

**Figure 7.** (Color online) (a) While the optical modulation for applied voltage of −1.5 V for colored state and 0.8 V for bleached state within interval of each step was controlled at 15 s; (b) corresponding CA curve of ECD; (c) switching time between bleached and colored states measured at 633 nm between 0.8 V and −1.5 V.

**Figure 8.** The durability of ECDs in terms of transmittance optical modulation at 633 nm following 2500-cycles.
involved filling the space between the two layers with liquid electrolyte ion injection in a vacuum pump. Step 4 production components.

**Synthesis of porous electrochromic and dense transparent electrodes films.** Indium tin oxide (ITO, Solaronix SA, $R_s = 6.1 \, \Omega/\square$)-coated glass was cut into wafers (5 × cm²) for use as a conducting substrate in ECDs. The ITO wafers underwent ultrasonic cleaning respectively in deionized water and ethyl alcohol for 2 min each. WO₃/NiO films were deposited in series on the ITO glass using cathodic arc plasma (CAP) with targets of metallic tungsten (W) (99.95%) and Nickel (Ni) (99.95%) (76 mm in diameter and 12 mm in thickness) at room temperature.

### Table 3.

| Materials/Device | Method             | $\Delta T$ (%) | $\Delta E$ (V) | $\Delta R$ ($\Omega/\square$) | Switching time (t / t₀) | Ref. |
|------------------|--------------------|----------------|----------------|------------------------------|-------------------------|------|
| WO₃/NiO          | CAP                | 46             | 90             | 3.1/4.6 s                    | This work               |      |
| Mo-doped WO₃     | RF sputtering      | 44.3           | 42.5           |                             | 24                      |      |
| WO₃/NiO          | DC sputtering      | 55             | 87             | 10/20 s                      | 25                      |      |
| WO₃/NiO          | Electropolymerization | 37.4         | 98.4           | 9.9/13.6 s                   | 26                      |      |
| WO₃/NiO          | physicochemical    | 50             | 121.56         | 4.1 / 3.4 s                  | 47                      |      |
| WO₃/NiO          | Electrodeposition  | 88.51          | 137            | 3.7/5.2 s                    | 48                      |      |
| WO₃ nanorods      | Exposure           | 57             | 33.3           | 11.8 / 20.1 s                | 49                      |      |
| WO₃/0.3H₂O/PEDOT | sol-gel            | 50.9           | 74.6           | 5/25 s                       | 50                      |      |
| Mo-doped WO₃     | hydrothermal       | 66.71          | 48.33          | 3.7/9.99 s                   | 51                      |      |
| WO₃/NiO          | dip-coating        | 54.3           | 79.7           | 1.4/1.1 s                    | 43                      |      |
| WO₃              | spray              | 64             | —              | —                            | 44                      |      |
| (NH₄)₀.₃₃WO₃     | hydrothermal       | 51.6           | 60.9           | 5.7 / 4.2 s                  | 45                      |      |

Figure 9. (a) Cathodic arc plasma (CAP) gun; (b,c) WO₃/ NiO images showing the transient dynamics of cathodic spot motion.

Figure 10. (a) Experimental procedure for Step 1 to Step 4. (b) Packaging process for ECD.
Table 4. Details of WO$_3$ processing parameters.

| Sample | W$_p$ (Torr) | Ar$_2$ (sccm) | DC-power (W) | Time (min) | Dep. Rate (nm/min) | Dep. Temp. (°C) |
|--------|--------------|---------------|--------------|------------|-------------------|-----------------|
| Sample 1 | 8.3 $\times$ 10$^{-3}$ | 0.2 | 1250 | 11 | 15.9 | 25 |
| Sample 2 | 8.3 $\times$ 10$^{-3}$ | 0.2 | 1250 | 13 | 15.4 | 25 |
| Sample 3 | 8.3 $\times$ 10$^{-3}$ | 0.2 | 1250 | 15 | 15 | 25 |
| Sample 4 | 8.3 $\times$ 10$^{-3}$ | 0.2 | 1250 | 17 | 14.7 | 25 |

In conclusion, we have developed a CAP deposition as an alternative to sputtering in order to achieve high deposition rates with low-cost method of producing EC film based on WO$_3$ for ECD applications. The proposed deposition scheme was applied to the synthesis of WO$_3$ films with nanostructured surface features in various thicknesses (175 nm, 200 nm, 225 nm, and 250 nm). The complementary WO$_3$ (200 nm)/NiO (60 nm) ECD exhibits higher optical modulation (46% at 633 nm), faster response times ($t_c = 4.6$ s, $t_e = 3.1$ s) and higher CE (90 cm$^2$/C). During the durability test, the transmittance change of ECD remained 43% after 2500 cycles, which was about 93% of original state.

Electrolyte layer. The liquid electrolyte system comprised lithium perchlorate (LiClO$_4$, Mw = 106.39, Sigma-Aldrich, Darmstadt, Germany) and propylene carbonate (PC, C$_4$H$_6$O$_3$, Sigma-Aldrich) at a weight ratio of 0.1325 (LiClO$_4$/PC = 26.5 g/200 mL).

Measurements. Electrochemical characterization was performed using cycle voltammetric (CV) and chronamperometric (CA) (Autolab, model PGSTAT 30) measurements. In-situ UV-Vis measurements were obtained using a spectrophotometer (Ocean Optics, DH-4000-BAL) in conjunction with CA analysis.

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Table 5. More details of ECD deposition parameters.

| Target | W$_p$ (Torr) | Ar$_2$ (sccm) | DC-power (W) | Time (min) | Dep. Rate (nm/min) | Dep. Temp. (°C) |
|--------|--------------|---------------|--------------|------------|-------------------|-----------------|
| ITO    | 3 $\times$ 10$^{-3}$ | Ar = 100 | 500 | 60 | 5 | 200 | 300 |
| Ni Metal | 8.3 $\times$ 10$^{-3}$ | 1/3(Ar = 120) | 650 | 2.5 | 20 | 50 | 60 |
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Author contributions
The study was writing and review by P.-W.C.; the data collection and analysis for WO3 film by C.-T.C.; T.-F. K. prepared Figures 3 and 10; the experiments was performed by S.-C.H. and J.-Y.W.; K.-D. Li performed the XPS characterization.

Competing interests
The authors declare no competing interests.

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