

**Electronic Supplementary Information**

**A Large Area, Flexible, High Contrast and Long-life Stable Solid-state**

**Electrochromic Device Driven by Anion-assisted Method**

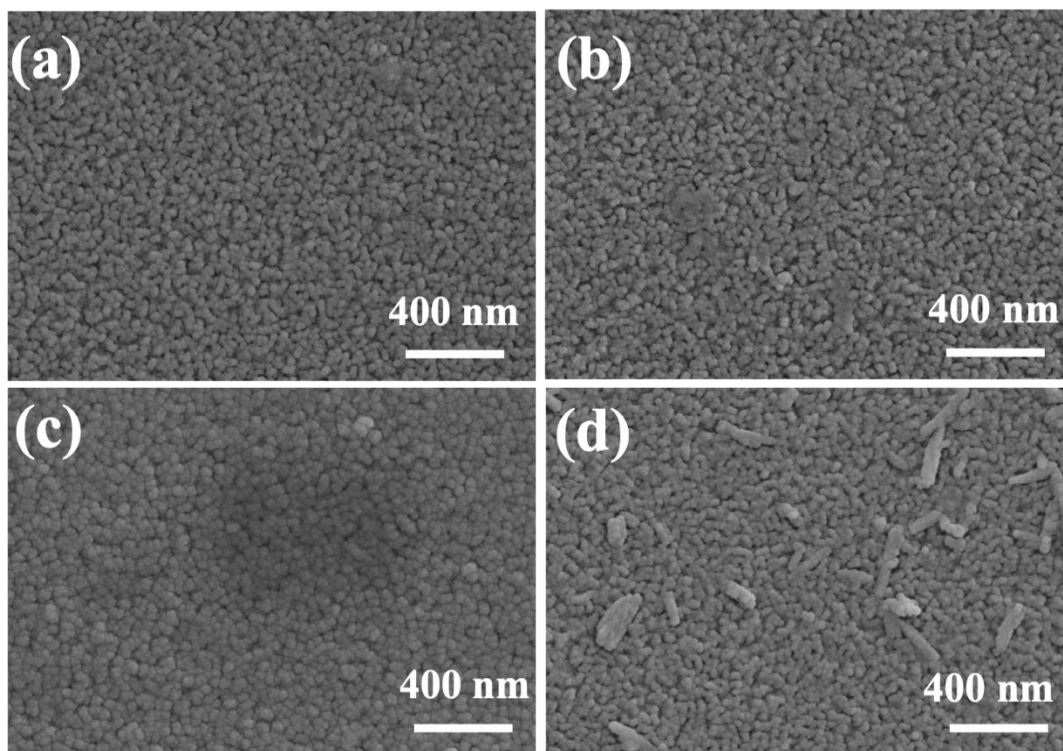
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**Fig. S1.** SEM images of NiO films after 10 cycles in lithium electrolyte with different content of H<sub>2</sub>O: (a) 0 wt.%, (b) 4 wt.%, (c) 6 wt.%, and (d) 8 wt.%.

As indicates in **Fig. S1**, with the increase of H<sub>2</sub>O content, the grain interface on the surface of the film gradually becomes smaller. When the H<sub>2</sub>O content is 8%, some surface attachments appear on the surface, which can be proved as NiOOH by XRD. This phenomenon can be explained by the electrochromic mechanism of NiO films. For less hydrated samples, evolution of NiO into Ni(OH)<sub>2</sub> will take place with potential cycling. When the film is cycled in an aqueous electrolyte, NiOOH will form during oxidation. And for more hydrated samples, excessive hydration produces NiOOH·H<sub>2</sub>O, resulting in isolation of NiO films [1].

**Table S1.** Reagents for experiment in this study.

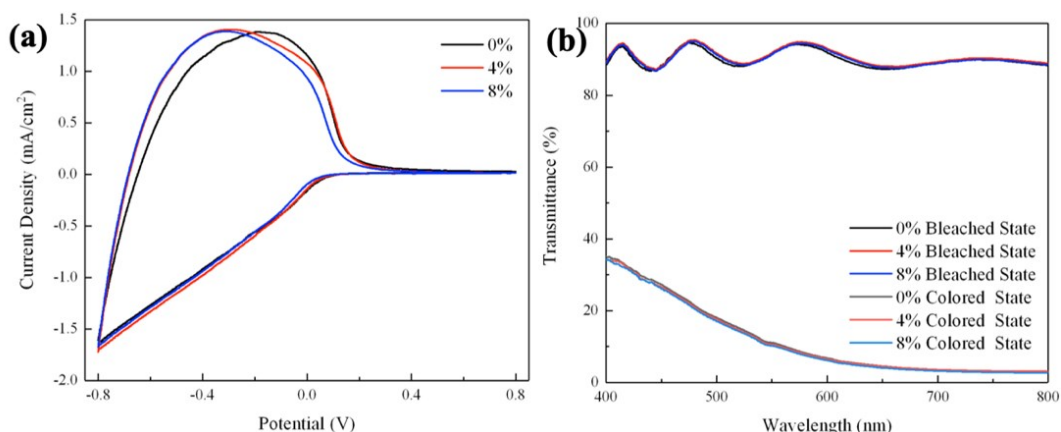
	Reagent and material	Specification	Origin
1	ITO/glass	1×4 cm <sup>2</sup> and 10×10 cm <sup>2</sup> , sheet resistance of 10 Ω/□, visible region transmittance of 85%.	Kaivo Technology Co., Ltd.
2	ITO/PET	4×4 cm <sup>2</sup> , sheet resistance of 10-15 Ω/□, visible region transmittance of 85%.	Kaivo Technology Co., Ltd.
3	PC	AR	Aladdin Biochemical Technology Co., Ltd.
4	LiClO <sub>4</sub>	AR	Aladdin Biochemical Technology Co., Ltd.
5	UV-adhesive	One-component UV light curing adhesive, product number No.8500.	Jisheng Photoelectric Co., LTD.

The reagents and materials required for this study are listed in **Table S1** as their origins.

**Table S2.** Detail data of XPS results.

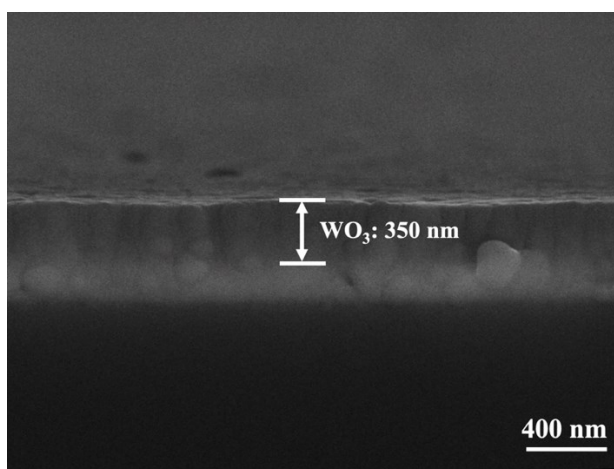
	Ni <sup>2+</sup>			Ni <sup>3+</sup>		
	Position/eV	Area /%	FWHM/eV	Position /eV	Area /%	FWHM/eV
0 wt.%	855.6	54.60	1.59	856.9	45.50	1.99
2 wt.%	855.5	53.50	1.59	856.7	46.50	1.99
4 wt.%	855.2	45.50	1.59	856.5	54.50	1.99
6 wt.%	855.6	15.40	1.59	856.7	84.60	1.99
8 wt.%	855.6	0	1.59	856.7	100	1.99

As shown in **Table S1**, the atomic ratio of Ni<sup>2+</sup>/Ni<sup>3+</sup> is calculated by deconvolution peaks area ratio, decreasing with the increased content of H<sub>2</sub>O. More coloration is caused by the extra Ni<sup>3+</sup>, so that lager optical modulation is obtained.



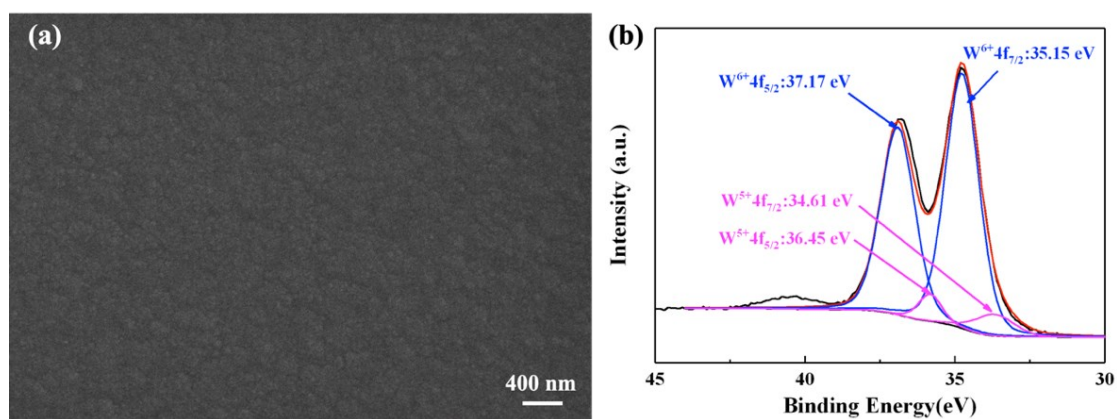
**Fig. S2.** The CV curves (a) and optical transmittance spectra (b) of WO<sub>3</sub> films in their colored (-0.8V) and bleached (+0.8V) state in electrolyte with different content of H<sub>2</sub>O.

As shown in **Fig. S2**, during the test process, H<sub>2</sub>O is added to the electrolyte in two times, one with 4 wt.% and the other with 8 wt.%. The result indicates that the content of H<sub>2</sub>O in the lithium electrolyte can't improve the electrochromic properties of WO<sub>3</sub> films. Similar charge capacity and optical modulation is obtained. This result can also be proved by Zhao's research [2]. According to Zhao's research, H<sub>2</sub>O can't improve the electrochromic properties in lithium electrolyte, while the interlayer water molecules within tungsten oxide can improve the near-infrared electrochromism.



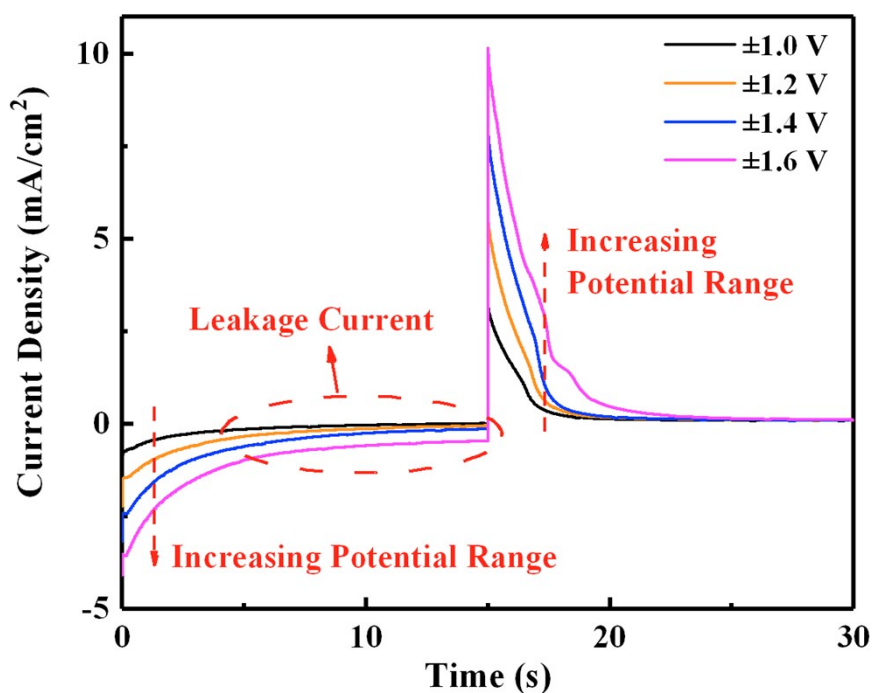
**Fig. S3.** The cross-section and thickness value of WO<sub>3</sub>.

The SEM image of  $\text{WO}_3$  film in cross-section is exhibited in **Fig. S3**, and the value of  $\text{WO}_3$  film thickness is 350 nm, which is consistent with the value obtained by quartz crystal oscillator in the fabrication process of  $\text{WO}_3$  films. The substrate is ITO/glass.



**Fig. S4.** (a) The SEM image of  $\text{WO}_3$  surface, (b) W4f core peak spectra of  $\text{WO}_3$  films.

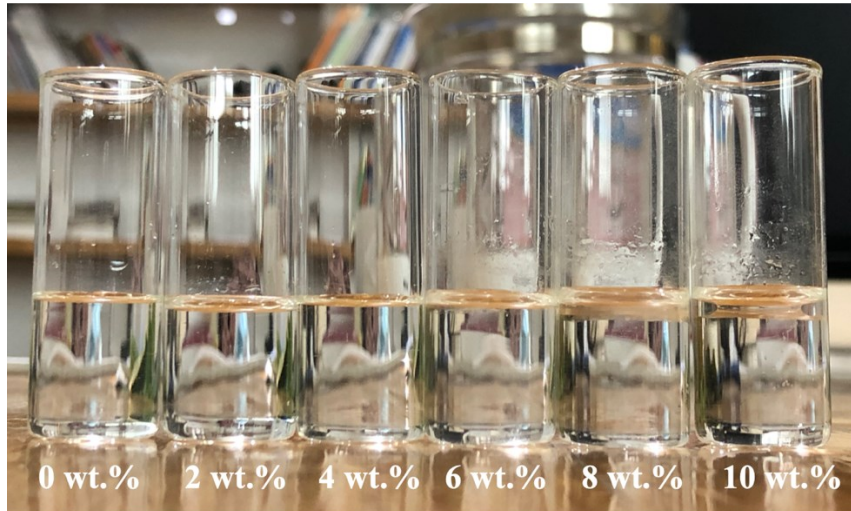
In order to examine characteristics of  $\text{WO}_3$  films in detail, we have examined characteristics of  $\text{WO}_3$  films using SEM and XPS in detail. A uniform and dense film surface of  $\text{WO}_3$  can be obtained according to **Fig. S4(a)**. And **Fig. S4(b)** is W4f core peak spectra of  $\text{WO}_3$  films. The peaks at binding energy of 37.17 eV and 35.15 eV can be assigned to  $\text{W}^{6+}$ , whereas the peaks at 34.61 eV and 36.45 eV are associated with  $\text{W}^{5+}$ . The atomic ratio of  $\text{W}^{6+}/\text{W}^{5+}$  is calculated by deconvolution peak area ratio, which is 91%/9%, indicating high quality preparation of  $\text{WO}_3$  for ECDs.



**Fig. S5.** CA curves of ECDs applying different potential range.

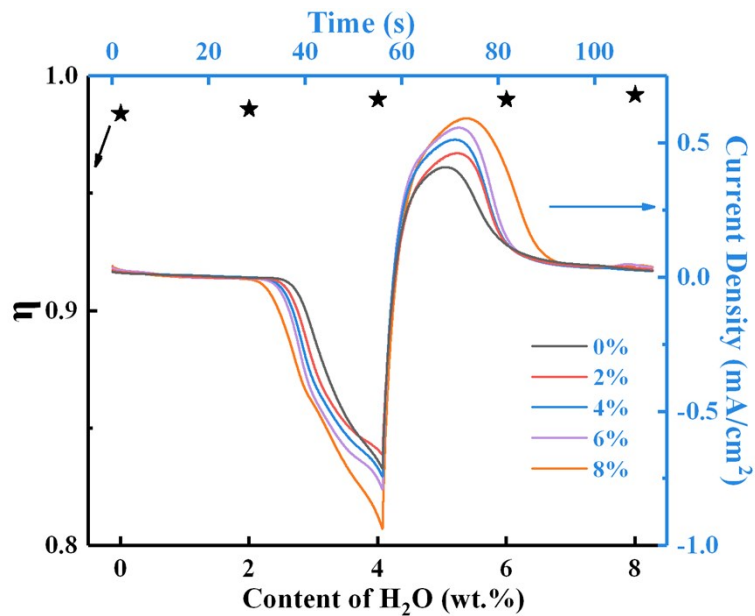
Voltage provides driving force for ion transfer. Generally, large driving force indicates fast ion transfer and more ions participate in the reaction, so the voltage is closely related to electrochromic performance. Some reasons for voltage selected are listed as follow.

We record the CA measurements of ECDs applying different voltages ( $\pm 1.0$  V,  $\pm 1.2$  V,  $\pm 1.4$  V and  $\pm 1.6$  V), and the results indicate that the leakage current becomes larger with the increase of potential range, as shown in **Fig. S5**. Poor coulomb efficiency and short memory time at open circuit of ECDs will be caused by the unexpected leakage current, leading the ECDs instability. Therefore, in order to obtain fast response, long-life stability, and high-quality EC performances of ECDs,  $\pm 1.4$  V is recommended for the cycling potential range.



**Fig. S6.** Lithium electrolyte with different content of H<sub>2</sub>O

As shown in **Fig. S6**, H<sub>2</sub>O is added into the lithium electrolyte. When the H<sub>2</sub>O content reaches 10 wt.%, there will be obvious two-phase interface after fully stirred, which means the maximum additive content is under 10 wt.%.



**Fig. S7.** The charge capacity ratio of the ECDs with different content of H<sub>2</sub>O in electrolyte.

A good charge capacity ratio is necessary for long-life stability of ECDs. In order to prove the stable performance and as the reviewer suggested, we have examined the

charge capacity ratio of the complementary ECDs. As shown in **Fig. S7**, the capacity ratio of ECDs is figured from the CV measurements (as shown in **Fig. 5(a)** in manuscript), and the value of  $Q_{in}/Q_{out}$  are 0.984, 0.986, 0.990, 0.990, and 0.992, respectively. All the ratios of ECDs are nearly equal to 1, indicating good cycling stability of the ECDs, regardless of the H<sub>2</sub>O content in electrolyte.

[1]. Y. Ren, W. K. Chim, L. Guo, H. Tanoto, J. Pan, S. Y. Chiam, *Sol. Energy Mater. Sol. Cells.* **2013**, *116*, 83-88.

[2]. Z. Wang, W. Gong, X. Wang, Z. Chen, X. Chen, J. Chen, H. Sun, G. Song, S. Cong, F. Geng, Z. Zhao, *ACS Appl. Mater. Interfaces.* **2020**, *12*, 33917-33925.