Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Revealing Nanomechanical Deformation at Interface and Degradation in All-Thin-Film Inorganic Electrochromic Device

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Contents of Supporting Information

1. Configuration of the electrochromic device

As depicted in Fig. S1, the ECD consists of a cathodic EC layer WO_3 on transparent electrode ITO, an anodic EC layer NiO on ITO, and between them an electrolyte containing Li cations and anions. It is widely accepted the EC effect involves the simultaneous insertion/extraction of electrons provided by an external potential and Li cations from the electrolyte and the subsequent formation of coloring centers W^{5+} and Ni^{3+} or bleaching W^{6+} and Ni^{2+}.[1] The cathodic W oxide film, which has high transparency in the oxidized state W^{6+} and exhibits blue color when it is reduced to W^{5+} by electron insertion together with Li^+, or vice versa, and the anodic Ni oxide film, which has an opposite electrochromism to the former, or turns to be brownish in Ni^{3+} states accompanying the extraction of electrons and Li^+.

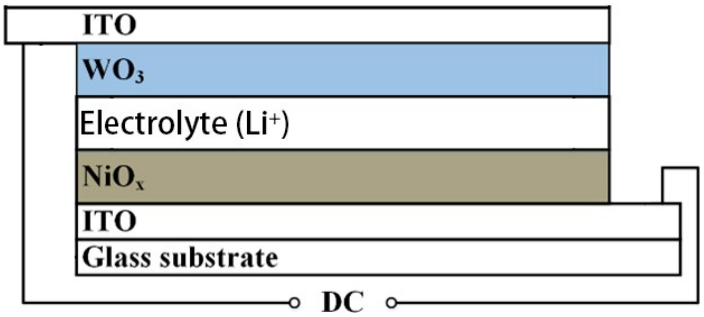

Fig. S1 Schematic cross-sectional view of design and working principle of the ECD: ITO/WO_3/Electrolyte (Li^+)/NiO/ITO.

2. Nanoidentation measurement cross-section analysis

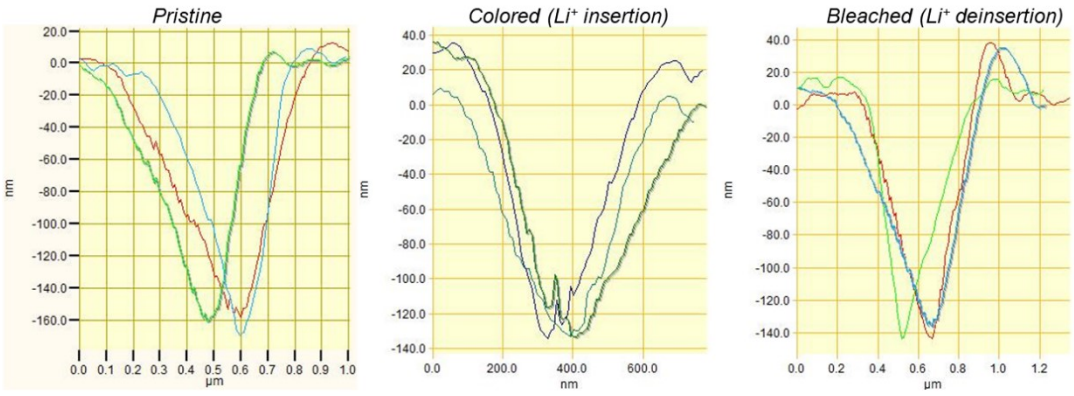

Fig. S2 The cross-section profile along with the line of three repetitive nanoindentation measurements of pristine, colored (Li^+ insertioin) and bleached (Li^+ de-insertion) WO_3 film.

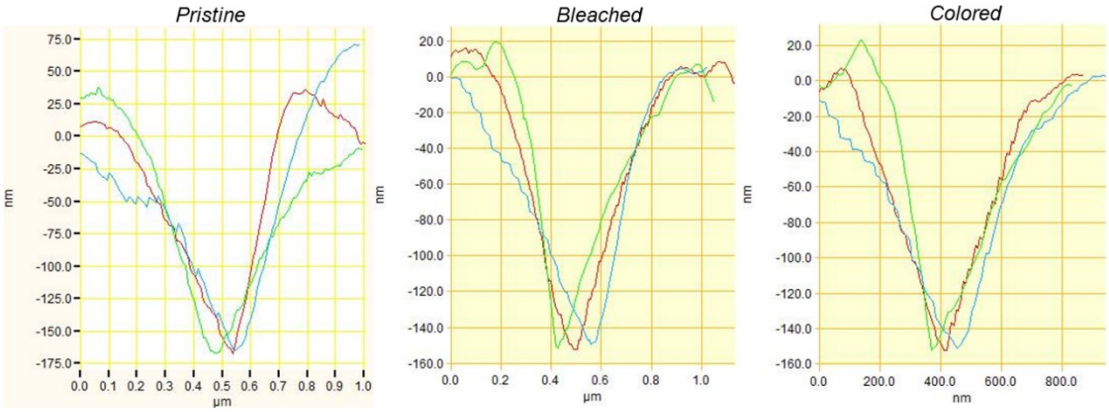

Fig. S3 The cross-section profile along with the line of three repetitive nanoindentation measurements of pristine, colored and bleached NiO film.

3. Charge/Discharge of WO_3 and NiO by multi-step chronoamperometry (CA)

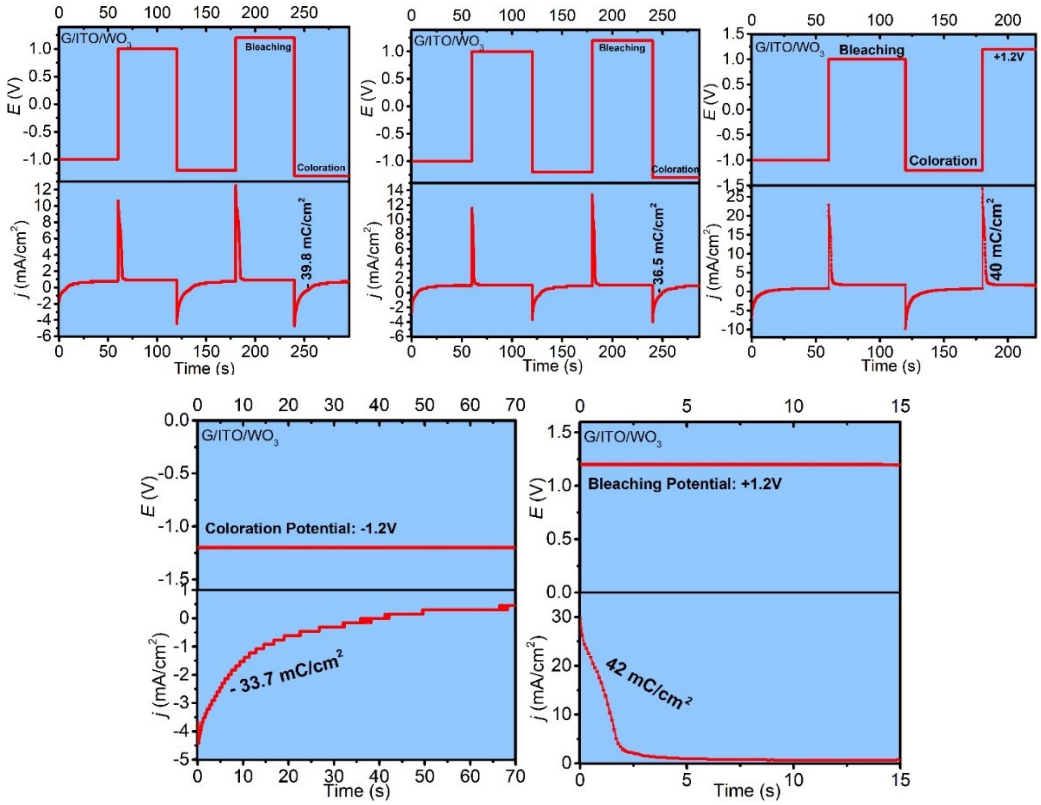

Fig. S4 The asysmetry in WO_3 coloration/bleaching response in multi-step chronoamperometry characterizations: much faster response time ~2s in the bleaching (Li^+ de-insertion).

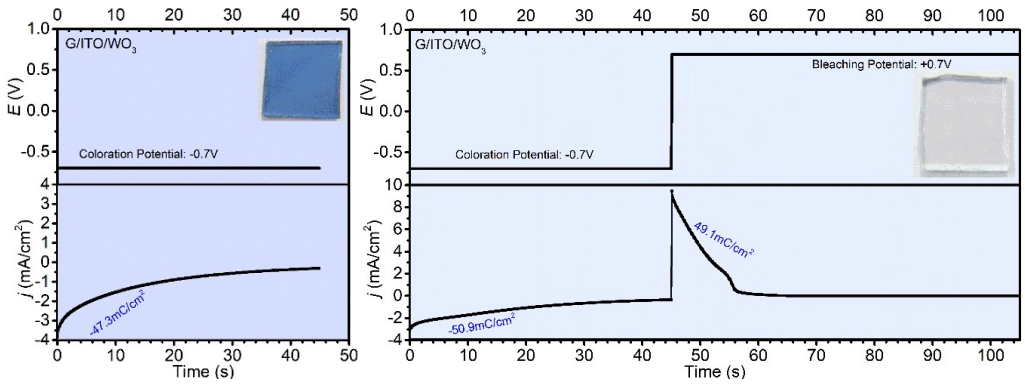

Fig. S5 Chronoamperometry (CA)/charge capacity of WO_3 at colored/bleached state. Inset is colored/bleached WO_3 digital photos.

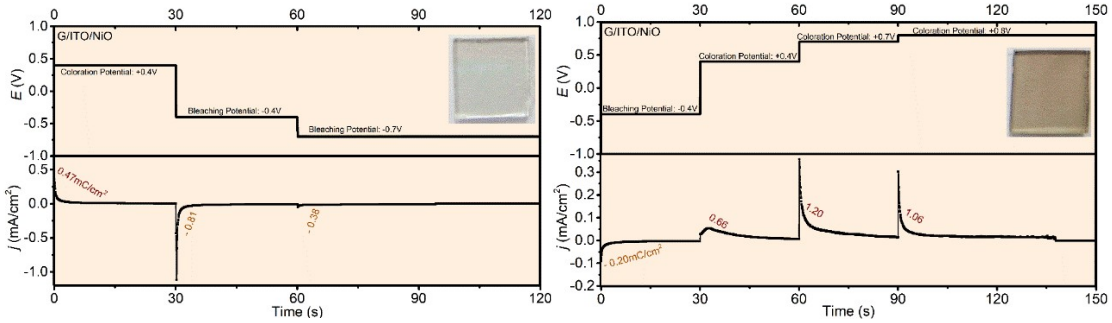

Fig. S6 Multi-step chronoamperometry (CA)/charge capacity of NiO at bleache/colored state. Inset is bleached/colored NiO digital photos.

4. Optical modulation of electrochromic WO_3 and NiO films

The spectra properties of EC WO_3 and NiO films colored and bleached by a step potential are investigated on a spectrometer after the sample has been subjected to 60 s in $LiClO_4$-PC electrolyte. The cathodic EC WO_3 films are colored by applying negative step voltages ranging from 0 to -3.5 V and the anodic NiO films get colored by positive voltages from 0 to +3.0 V. The results of the spectral transmission of WO_3 and NiO after cycling in two modes are shown in Fig.S7-9. The transmittance of both colored WO_3 and NiO decreases continuously due to significant reduction reactions of W^{6+} to W^{5+} and oxidation of Ni^{2+} to Ni^{3+}, respectively, by exerting an increasing potential. At fully colored and bleached states in modulation response, the optical properties are studied with the optical spectroscopy. For NiO, in the modulation response, the absorption band present a visible blue shift from ~460 to ~430 nm from coloration to following bleaching, which may be induced by the charge transfer. In general, for all NiO curves, the wide absorption valley ranges from ~500 to ~900 nm, and what is interesting, at the same wavelength range, the corresponding transmittance remains at a relatively high level, from which it can be indicated here the less absorbed, the more is passed through for transmission. This could equally apply to WO_3. In coloration, great changes have taken place in the film appearance (transparent→light blue→dark blue), manifested by the sharp increase in the intensity of its absorption in the wavelength > 600 nm. This almost shuts the window for the transmittance of the orange and red light, so WO_3 presents a blue colored state.

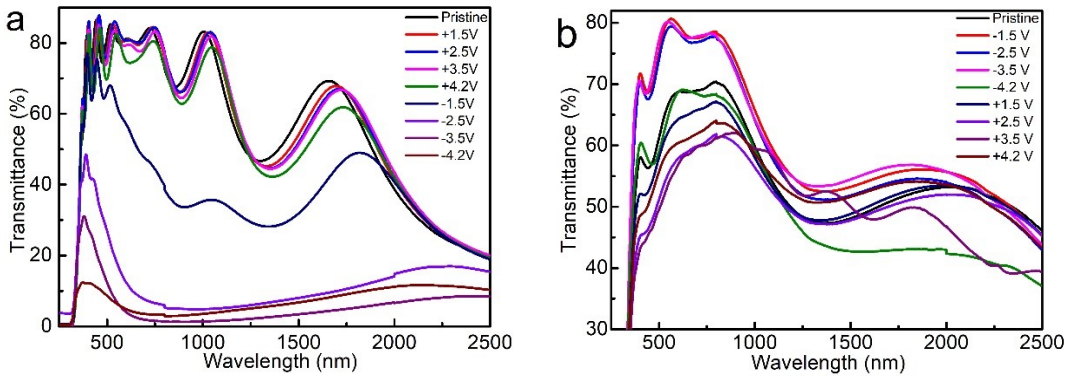

Fig. S7 Optical transmittance spectra of cathodic electrochromic WO_3 as a function of potential. (The symbol "+" correlates to bleaching for cathodic WO_3; In accordance, the symbol "-" correlates to coloration for cathodic WO_3. Solid line: bleached state; Dashed line: colored state; For clarity, the experimental sequence of applied potentials is indicated by a vertical arrow to the right side of the legend.)

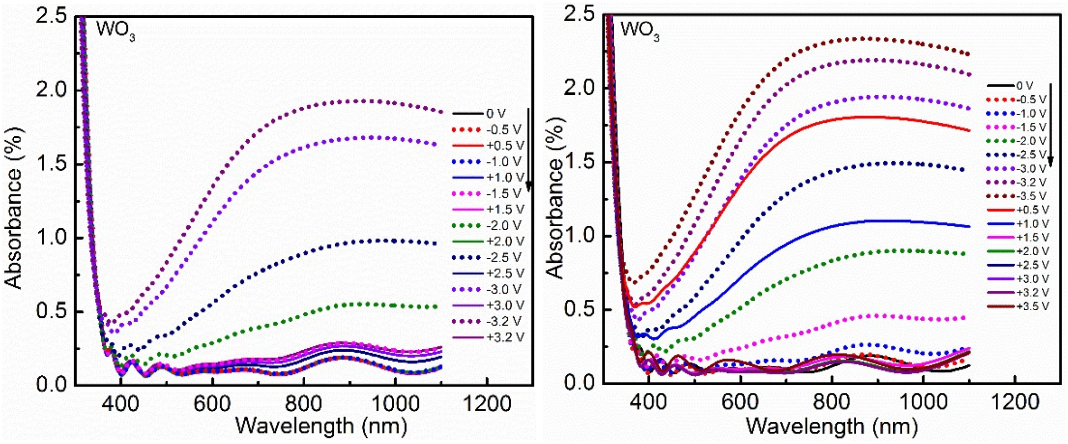

Fig. S8 Optical absorbance spectra of cathodic electrochromic WO_3 as a function of potential.

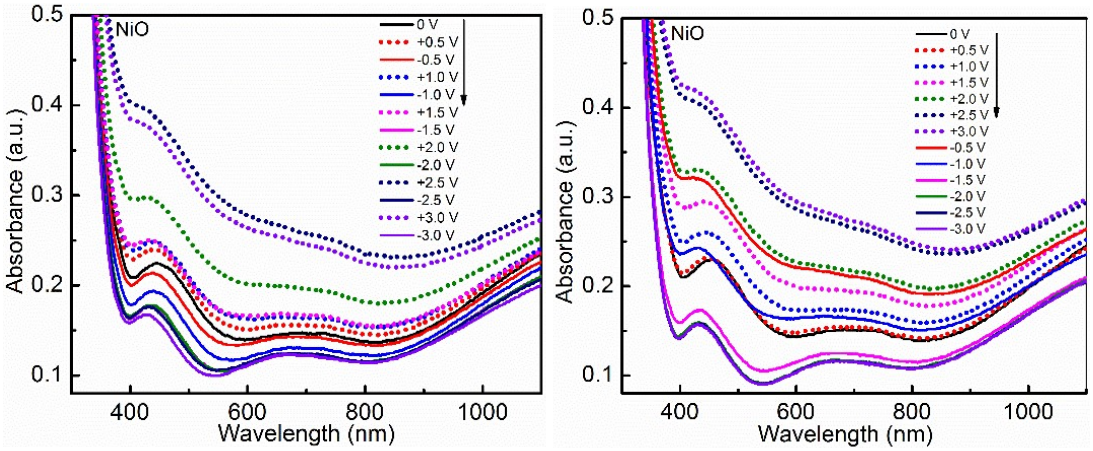

Fig. S9 Optical absorbance spectra of anodic electrochromic NiO as a function of potential. (The symbol "+" correlates to coloration for anodic NiO; In accordance, the symbol "-" correlates to bleaching for anodic NiO. Solid line: bleached state; Dashed line: colored state.)

5. Structural characterization of electrochromic thin films

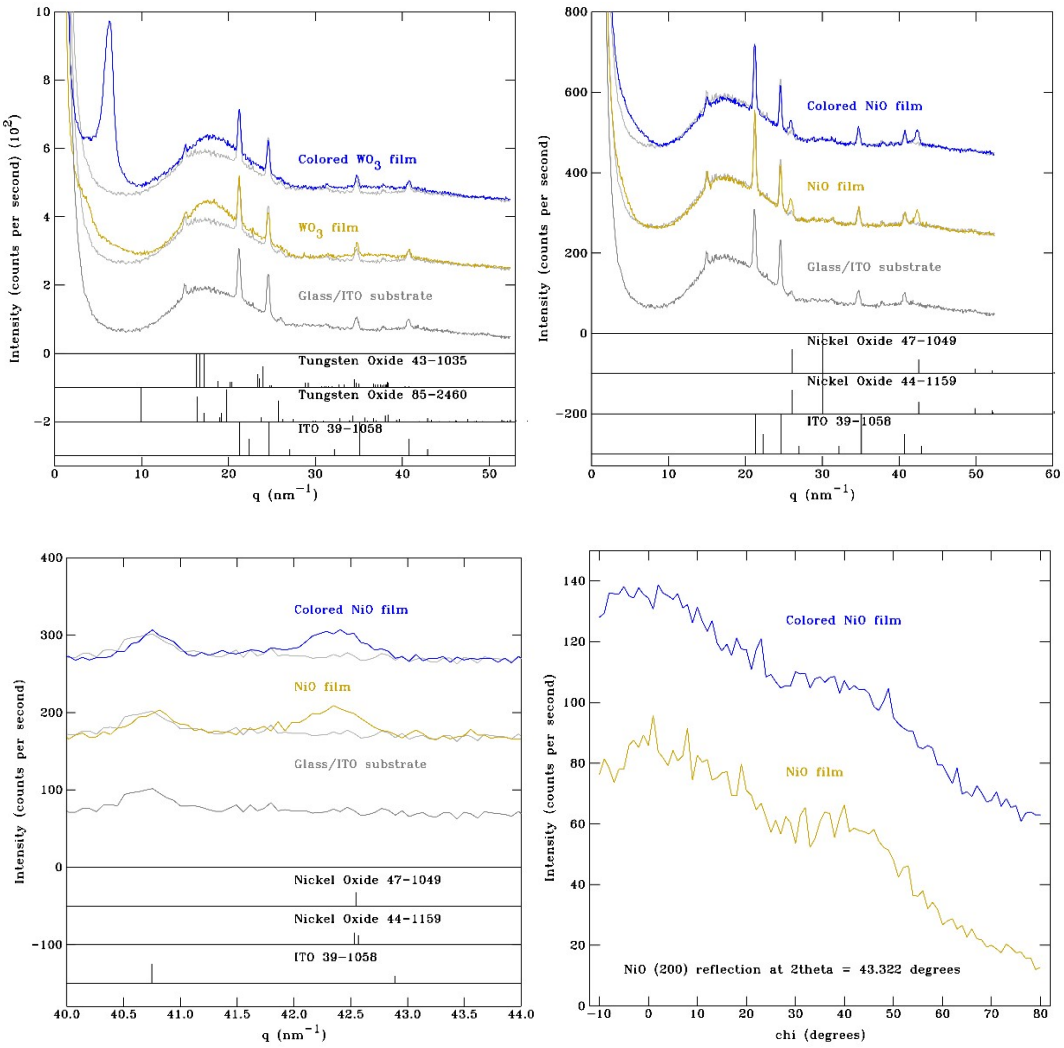

Fig. S10 XRD spectra of electrochromic WO_3 and NiO at initial, transparent and colored states.

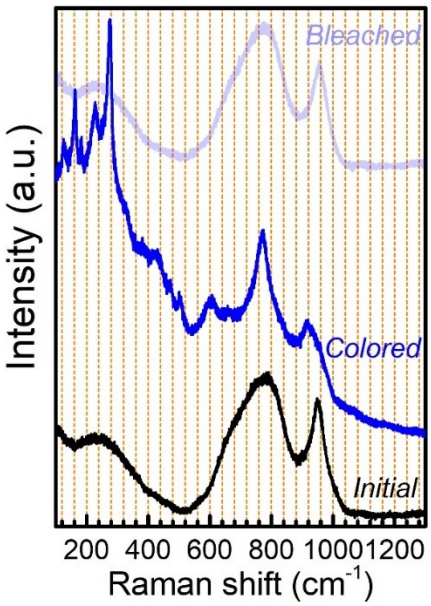

Fig. S11 Raman spectra of electrochromic WO3 at initial, colored and bleached states.

The XRD patterns of the films are presented in Fig. S10. NiO films show a polystalline

NaCl-type structure indexed as (111), (200), (220) and (311) crystal planes. No additional diffraction peaks representing other phases such as Ni_2O_3 or $LiNiO_2$ or any other compounds appear for cycled films. As described in Kitao et al.,[2] the Ni^{3+} ions are performed as color centers in films. Thus, the brownish samples contain not only Ni^{2+} ions but also a certain amount of Ni^{3+} ions, and they exists in amorphous state.

6. SEM and EDS Analysis of electrochromic WO_3 thin films

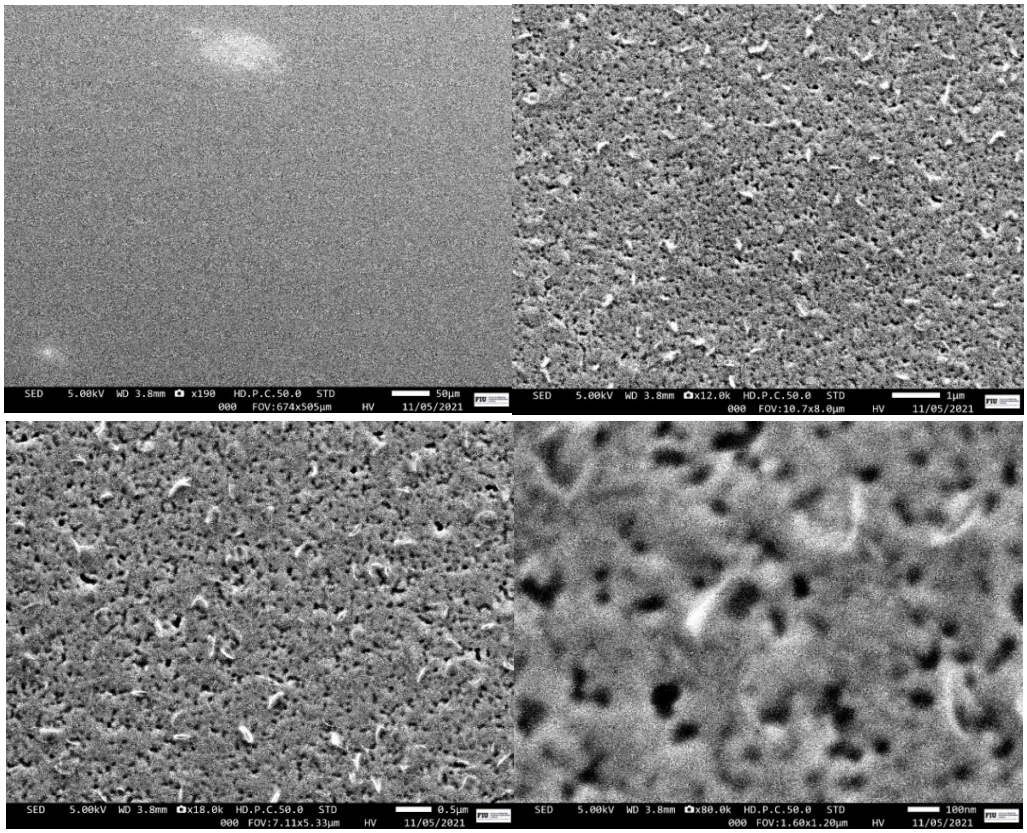

Fig. S12 SEM of electrochromic WO_3 films.

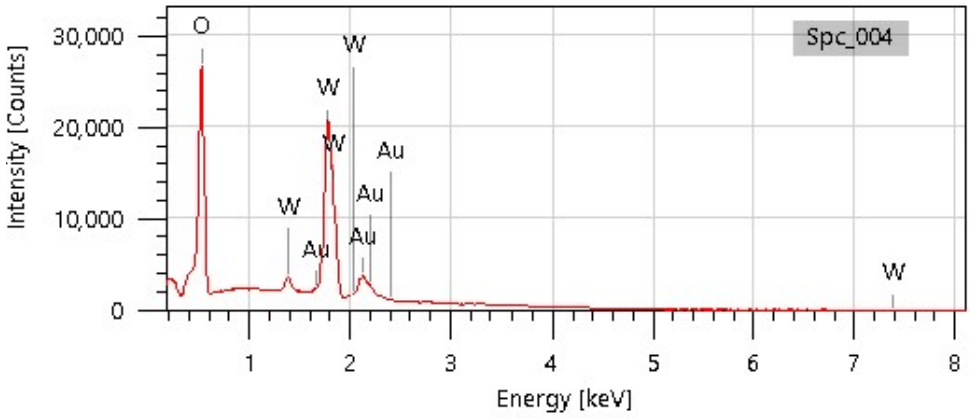

Fig. S13 EDS analysis of WO_3 thin films.

Table 1 Elemental analysis of WO_3 thin films

Element	Line	Mass%	Atom%
O	K	10.92±0.03	58.79±0.14
W	M	73.04±0.25	34.20±0.12
Au	M	16.03±0.17	7.01±0.07
Total		100.00	100.00

References

[1] S. Zhang, S. Cao, T. Zhang, A. Fisher, and J. Y. Lee, *Energy & Environ. Sci.* 2018, **2**, 11(10), 2884-2892.

[2] Y. Wang, E. L. Runnerstrom and D. J. Milliron, *Annu. Rev. Chem. Biomol. Eng.* 2016, **7**, 283-304.