

Supporting Information

Lithium trapping as degradation mechanism of electrochromic properties of WO₃//NiO device

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1. Design of electrochromic device

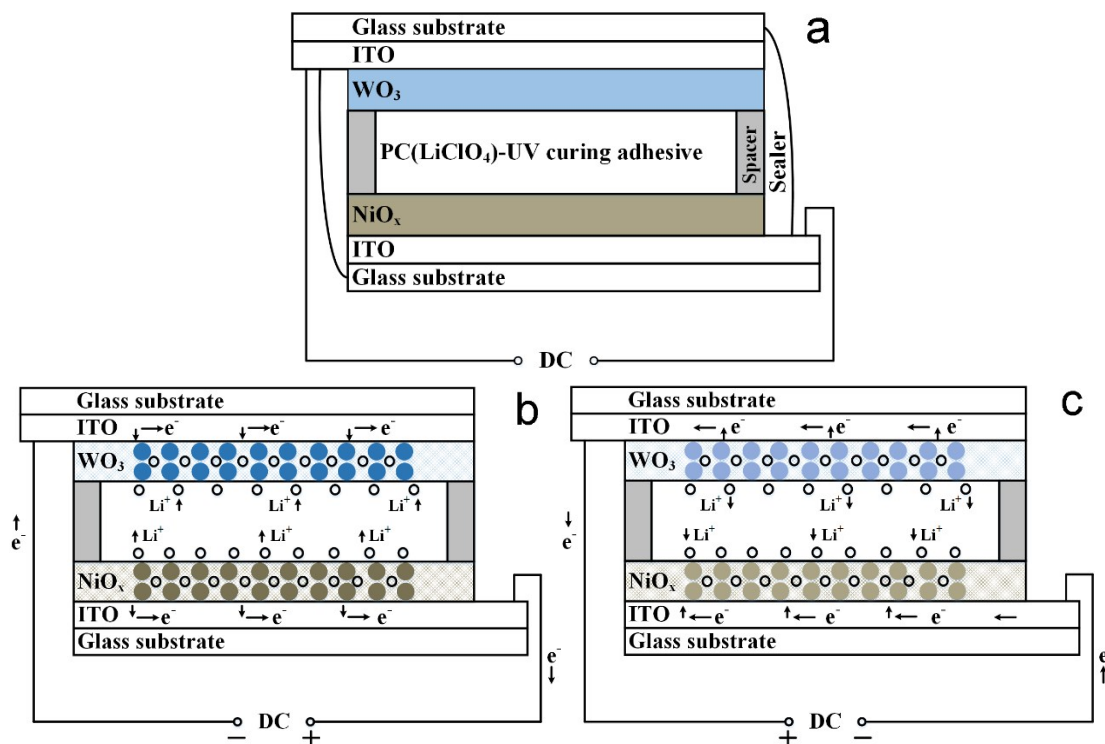


Fig. S1 Schematic cross-sectional view of design and working principle of the full laminated ECD: ITO/WO₃/LiClO₄(PC)-UV curing adhesive/NiO/ITO at (a) as-deposited, (b) coloring and (c) bleaching states.

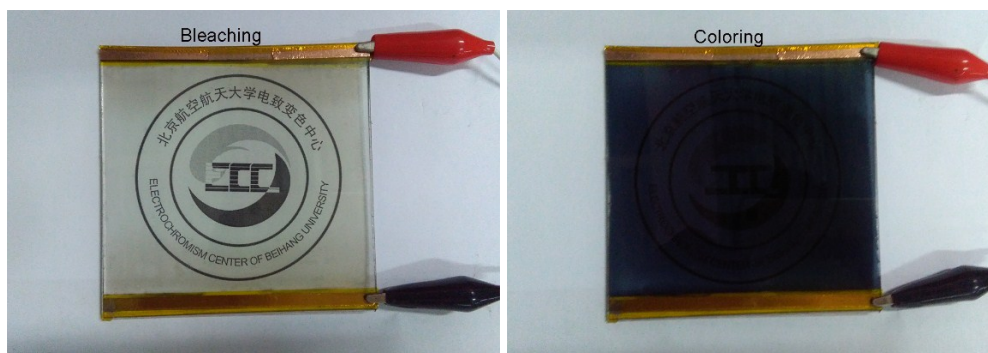


Fig. S2 Pictures of the full electrochromic device at bleaching and colored states.

As depicted in Fig. S1(a), the ECD consists of a cathodic EC layer WO₃ on transparent electrode ITO, an anodic EC layer NiO on ITO, and between them a gel polymer 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 gel polymer electrolyte (GPE) and the subsequent formation of coloring centers W⁵⁺ and Ni³⁺ or bleaching W⁶⁺ and Ni²⁺.¹ Fig. S1(b) & (c) demonstrates the diagram of the coloring and bleaching process of the device,

respectively. 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 opposite electrochromism to the former, or turns to be brownish in Ni^{3+} states accompanying the extraction of electrons and Li^+ . The digital pictures of the full electrochromic device at bleaching and colored states are presented in Fig. S2.

2. Structural characterization of degraded films

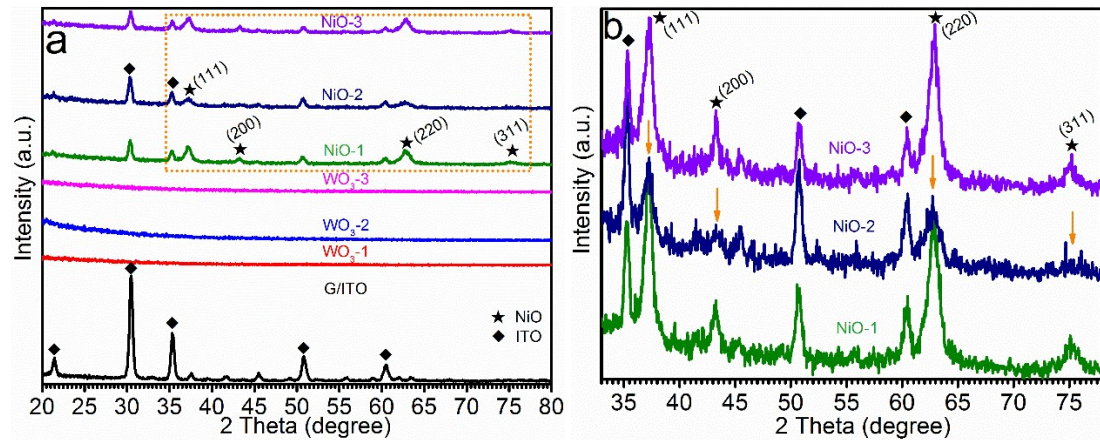


Fig. S3 (a) XRD patterns of the non-cycled and cycled films from as-prepared and degraded ECDs; (b) Partial enlarged drawing of rectangular region indicated by the yellow dashed line.

The XRD patterns of the films from degraded devices are presented in Fig. S3. A small incidence angle ω of 0.3 degree is used to avoid the strong signal intensity of ITO. No diffraction peaks are found in all WO_3 films, suggesting the amorphous feature of non-cycled WO_3 -1 as well as cycled WO_3 -2 and WO_3 -3. Conversely, NiO films show a polystalline NaCl-type structure indexed as (111), (200), (220) and (311) crystal planes recide by a noticable extent for cycled NiO-2, as indicated by the yellow arrows, which implies the crystallinity of the films tends to be weakened in ECD2 life-time cycling process. Moreover, 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.

3. Surface characterization of degraded films

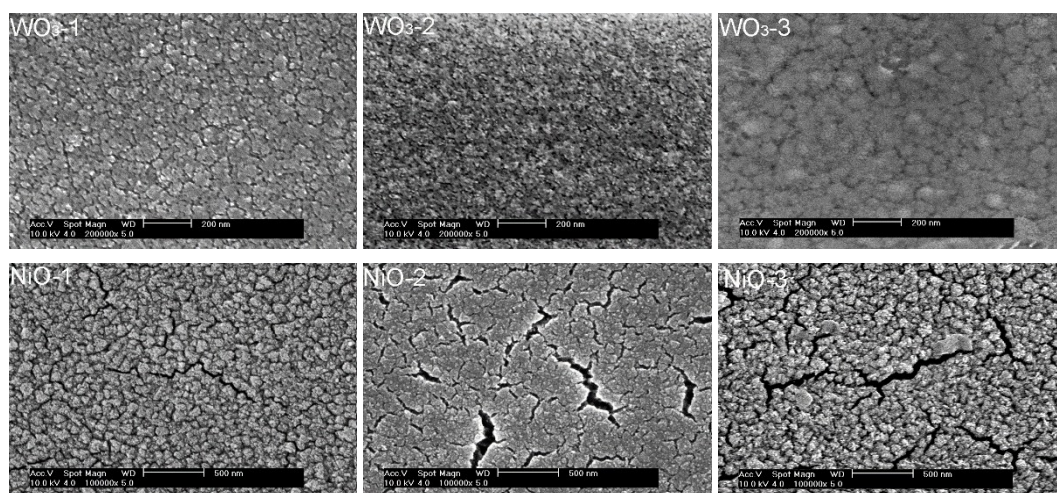


Fig. S4 SEM images for WO₃ and NiO films.

In Fig. S4 & S5, it is clearly demonstrated for WO₃-3 with a very dense and flat morphology totally different from non-cycled WO₃-1 that this micro change is closely associated with the irreversible coloring in WO₃-3. Evidently, the accelerated harsh voltammetric cycling procedure leads to deterioration of the WO₃-3 films' morphology. In contrast, for WO₃-2, from ECD2 after conventional long-term voltammetric cycling, a less porous morphology with even smaller particles than WO₃-1 is presented. Thereby, surface analysis reveals that two cycling protecoles will give two different micro evolutions in WO₃ films. For NiO thin films, NiO-1 and NiO-3 display unambiguous particles (see SEM graphs) in accordance with the crystallinity feature induced in XRD. After conventional long-term CV cycling, the particle distribution in NiO-2 micrograph is getting more uneven, which means they tend to be clustered in certain areas as exhibited in 3D AFM figure. For NiO-3, the harsh electrochemical cycling also results in the agglomeration development.

Moreover, in the SEM figures for uncycled NiO-1 and degraded NiO-2 and NiO-3 films, there are significant macroscopic cracks, which tend to expand in the degradation process. These cracks will increase the permeability of the electrode, and at the same time, decrease the homogeneity of charge transfer due to the unevenness of the surface. These changes would induce a reduction of the cycling life, which is a fatal flaw of the ECDs. What is more, excess cracks will lead to deterioration of the film's microstructure, and the adhesion between Ni oxide grains and between film and

substrate will become weak. The weak mechanical adhesion will make the film peel off from the substrate at last.⁴

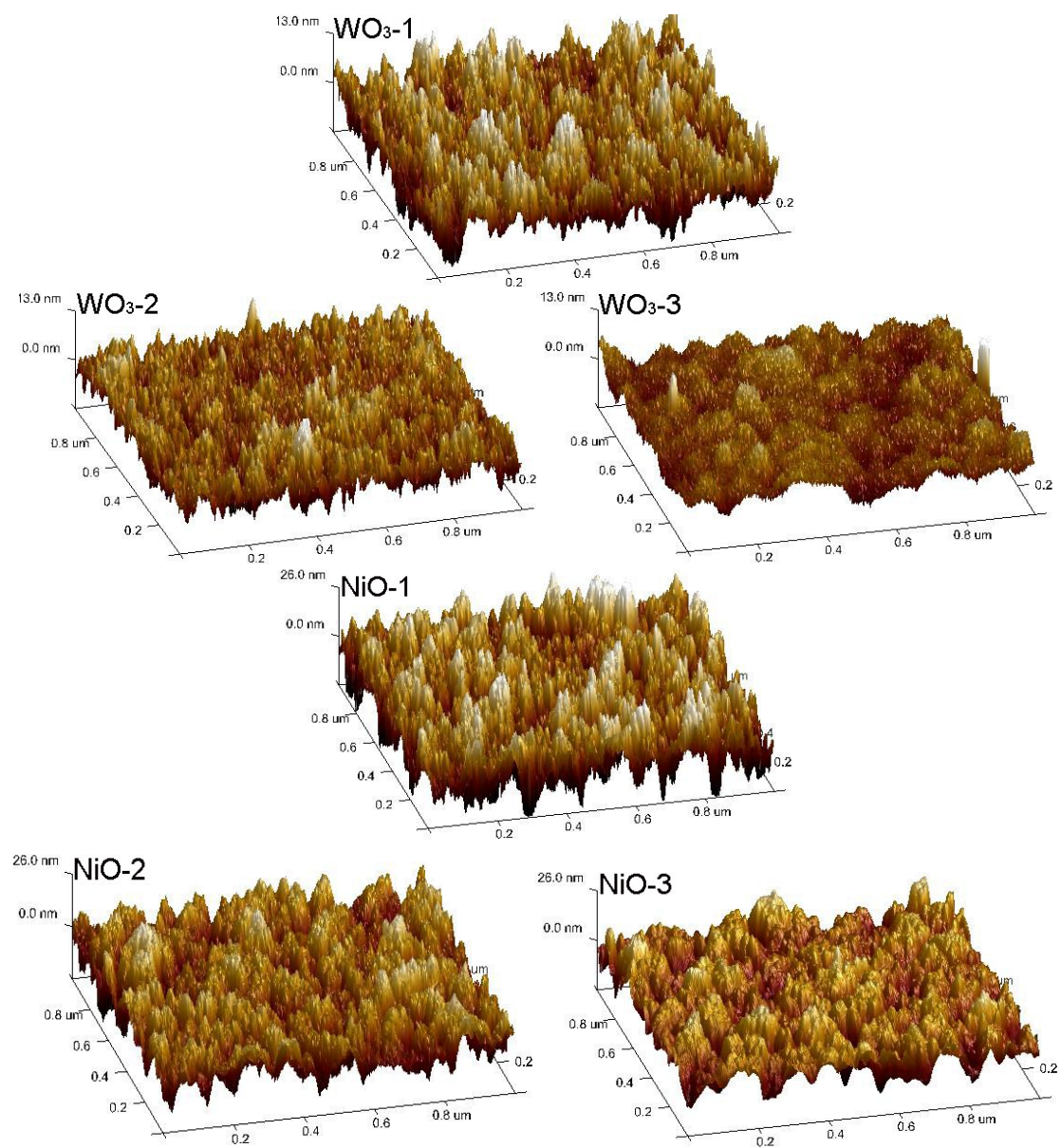


Fig. S5 Three dimensional AFM images for WO₃ and NiO films.

4. O1s peak analysis of X-ray photoelectron spectroscopy

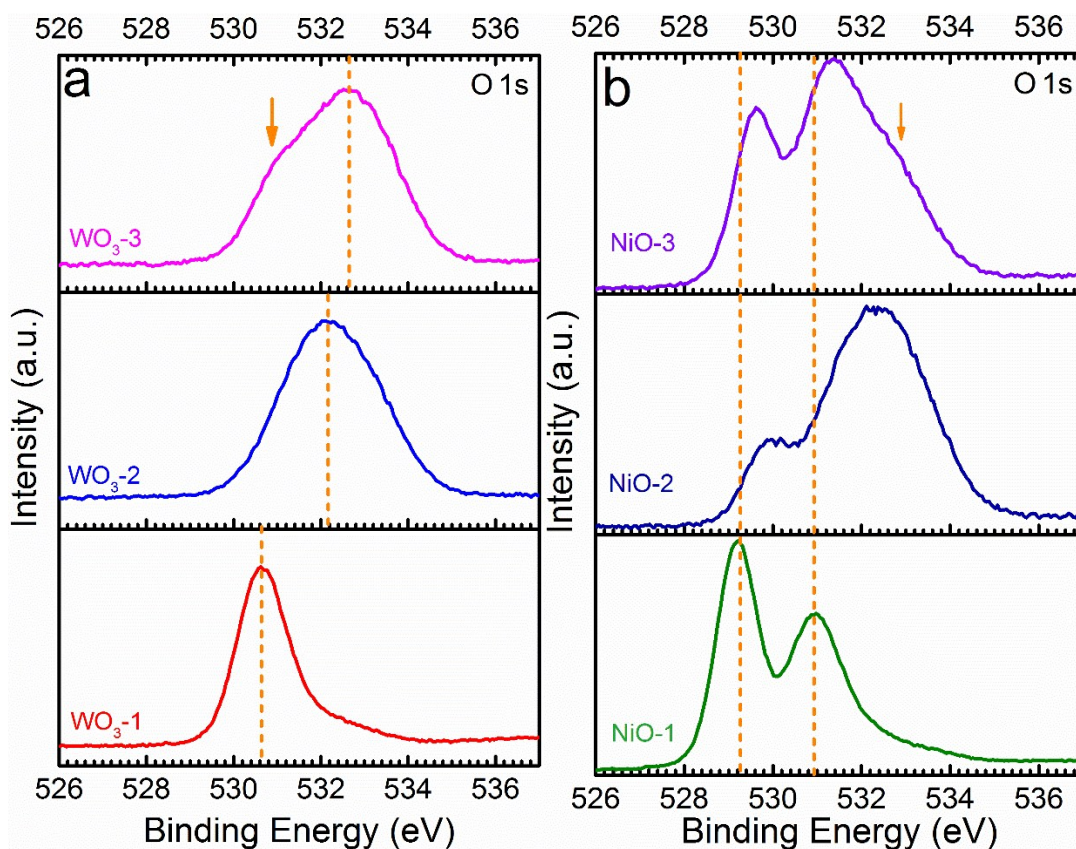


Fig. S6 XPS spectrum comparison of O1s peak of electrochromic films degraded in various cycling protocols.

XPS spectrum of O1s demonstrate that the sample contains W as well as Ni oxide in respect with the W4f and Ni2p analysis. In Fig. S6 (a) the scan of W oxide exhibits a sharp and asymmetric peak at 530.6 eV for bare WO₃-1 and a shifted broad peak for degraded WO₃-3. The peak broadening and shifting towards higher binding energy direction in O 1s XPS profile indicate that W⁵⁺ in matrix films is partly oxidized chemically. Another significant effect on NiO lies in the change of the relative intensity ratio of the two main peak in the O 1s scan as demonstrated in panel b. This change is more related to the relative concentration of Ni²⁺ and Ni³⁺.³ The increased complexity in degraded films is reflected by the shoulder of the main peak, as marked by the arrow in the figure. The increase in Ni³⁺ percentage in degraded films is also evidenced by XPS Ni 2p analysis. The O1s peaks of all the NiO based films mainly include two components, *i.e.* the left peak (LP) and the right peak (RP). The degraded NiO-2 and NiO-3 samples show significant peak shift towards higher binding energy direction as well as peak broadening, in accordance with the analysis of Ni 2p_{3/2} spectra, which is

attributed to the large amount of Li^+ ions trapping. Moreover, the relative intensity ratio of RP/LP increases for degraded films and it adds the complexity in analyzing, mainly due to the formation of Li_2O and/or the compound in $\text{Ni}_{1-x}\text{O}-\text{Li}_2\text{O}$ system. Here, we cannot go too far or determine what the specific compound is.

References

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