Electronic Supplementary Information

Eliminating degradation and uncovering ion-trapping dynamics in electrochromic WO_3 thin films

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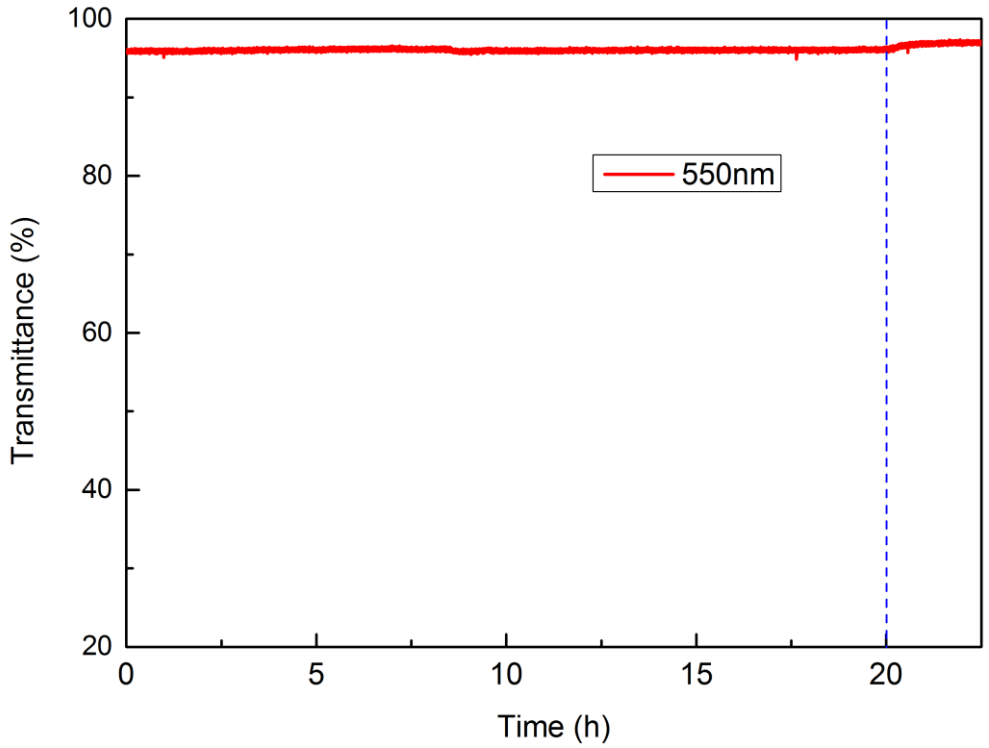

Fig. S1. Optical response a WO_3 film at 550 nm upon constant current loading. The measurement started with the film in its bleached state after 400 cycles and persisted for 20 h. The film was then kept for ~2 hours without current loading. The optical transmittance was barely altered.

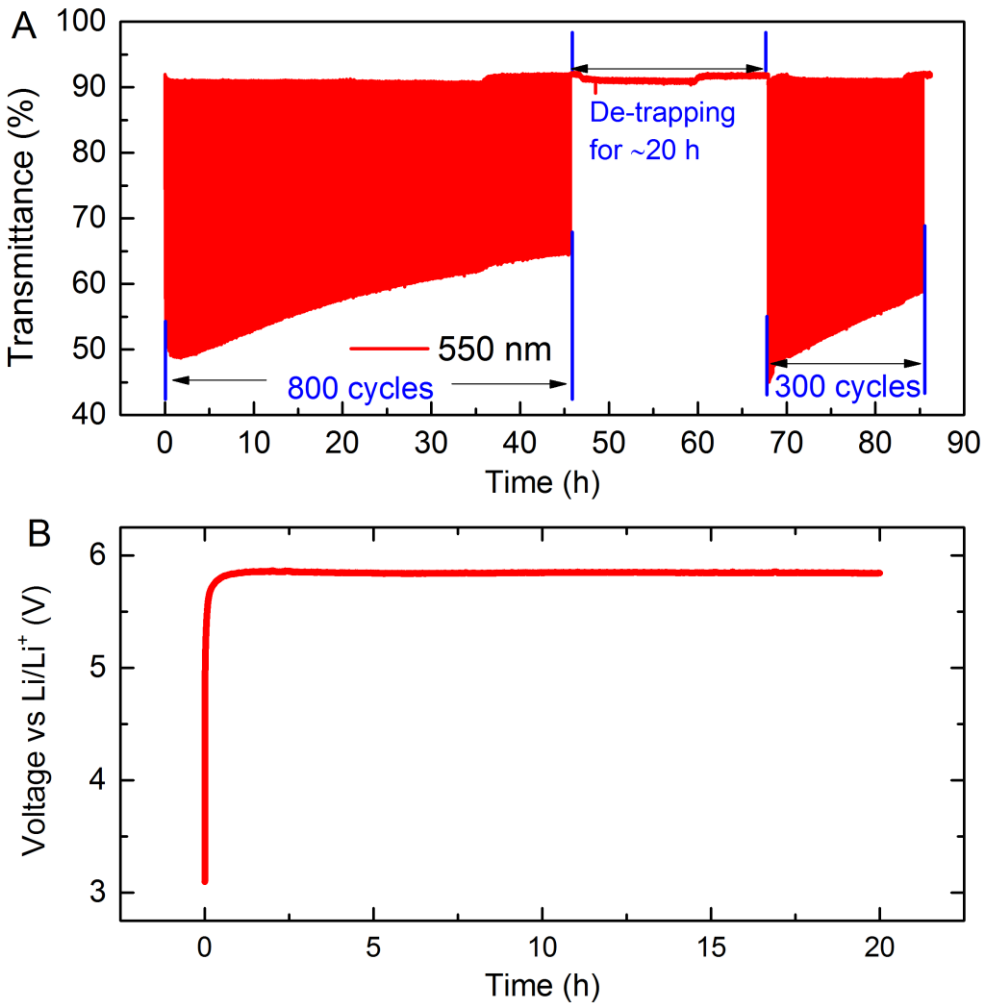

Fig. S2. (**a**) Optical transmittance for WO_3 films at 550 nm *vs*. time under extended CV cycling. The measurement was performed as follows: The film was first cycled for 800 times at a scan rate of 20 mV s^{-1} in the potential window 2.0–4.0 V *vs*. Li/Li^+; optical transmittance degradation is manifest. A constant current of 1×10^{-5} A was then applied for 20 h to accomplish ion de-trapping. After de-trapping, CV cycling was performed for 300 times. Clearly the film has the same electrochromic performance as in the initial state and follows the same degradation behavior. (**b**) Voltage upon extraction of trapped ions by a constant current. The films were deposited at a pressure of 30 mTorr.

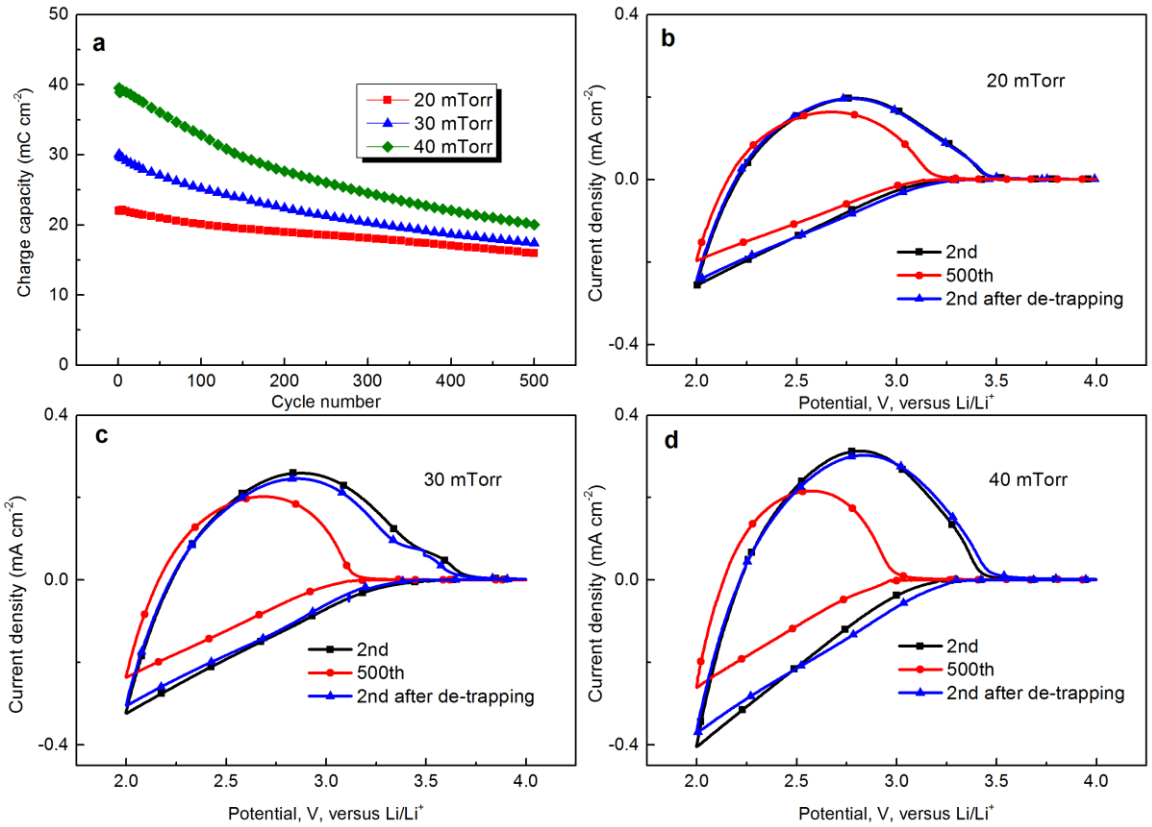

Fig. S3. (a) Charge capacity as a function of cycle number for WO_3 films (thickness ~300 nm), deposited with different pressure during sputtering, giving different porosities. (b) (c) (d) Cyclic voltammograms for films deposited at 20 mTorr, 30 mTorr and 40 mTorr, respectively. The CV's were measured with a scan rate of 20 mV/s and in the range 2.0 – 4.0 V *vs*. Li.

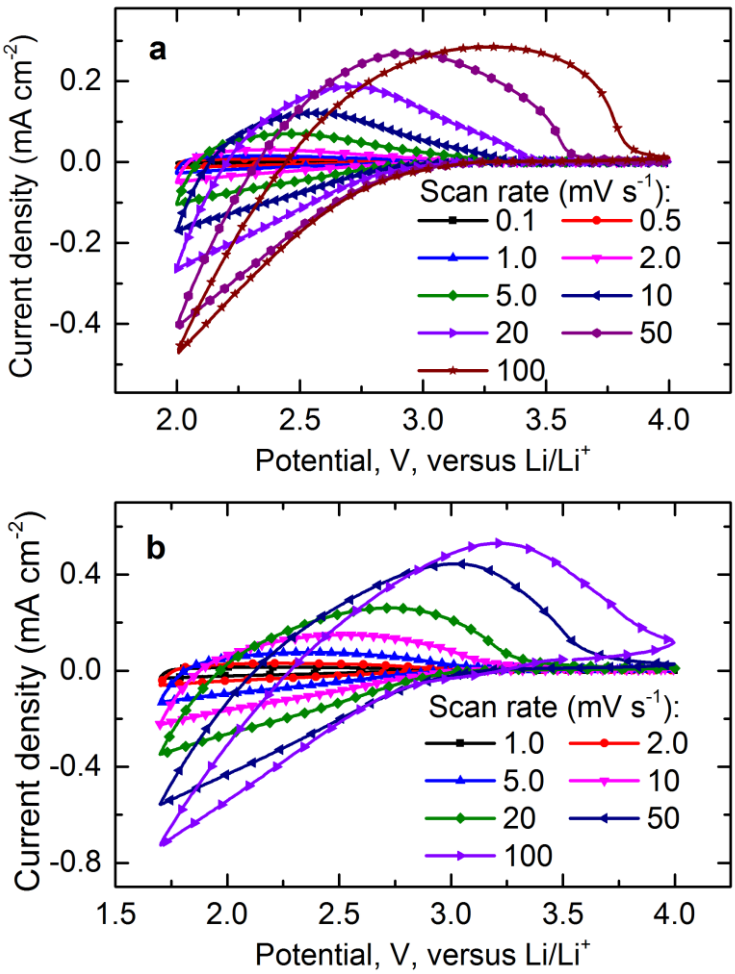

Fig. S4. Cyclic voltammograms for WO_3 films at different scan rates and potential windows: (**a**) 2.0–4.0, (**b**) 1.7–4.0 V *vs*. Li/Li^+. The films were deposited at a pressure of 30 mTorr.

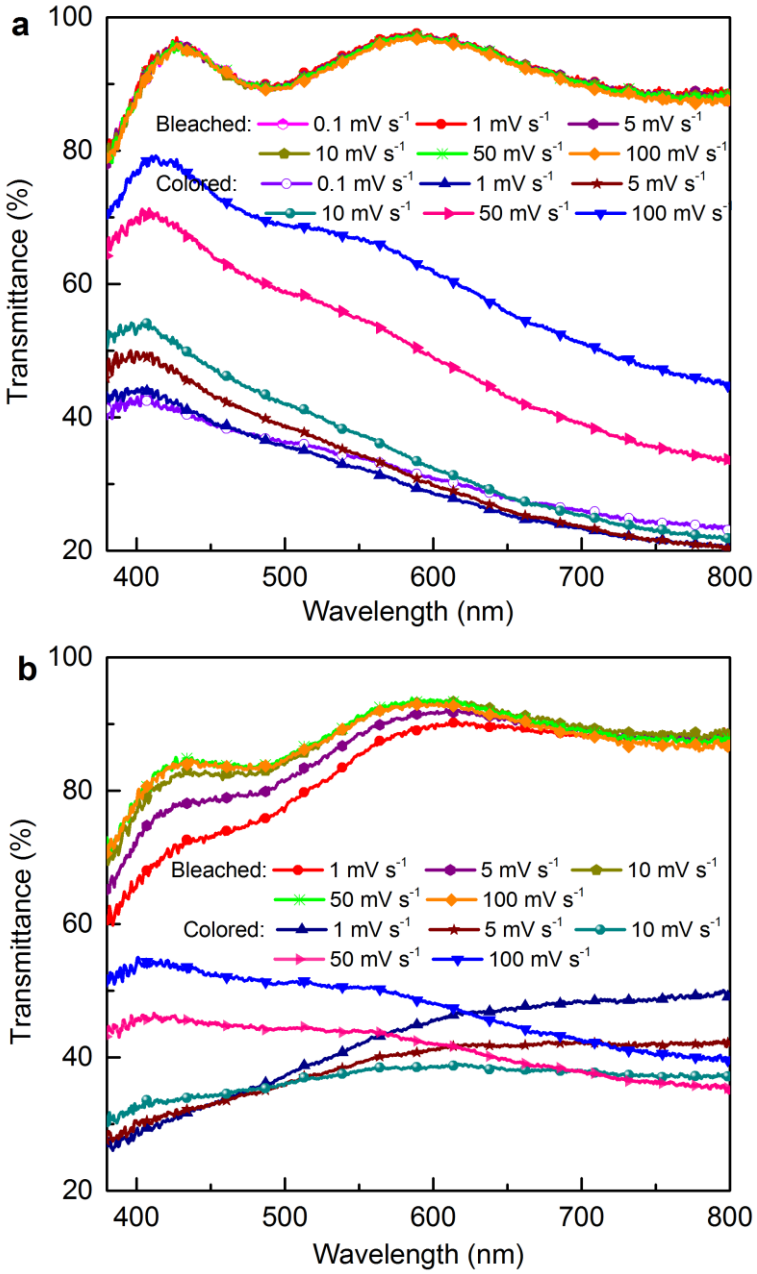

Fig. S5. *In situ* spectral optical transmittance of WO_3 films. (**a**) Data for 2.0–4.0 V *vs.* Li/Li^+. The scan rate was varied from 100 to 0.1 mVs^{-1}. There is a slight increase of the colored-state transmittance at 0.1 mVs^{-1}, whereas the colored state transmittance persistently decreases from 100 to 1 mV s^{-1}. The transmittance for the bleached state remains the same for all scan rates. (**b**) Data for 1.7–4.0 V *vs.* Li/Li^+. The scan rate was varied from 100 to 1 mV s^{-1}. Strong increase (decrease) of colored-(bleached)-state transmittance is observed when the scan rate is lower than 10 mVs^{-1}, which we ascribe to ion-trapping. The transmittance for the bleached state remains the same when the scan rate is above 10 mV s^{-1}. The films were deposited at a pressure of 30 mTorr.

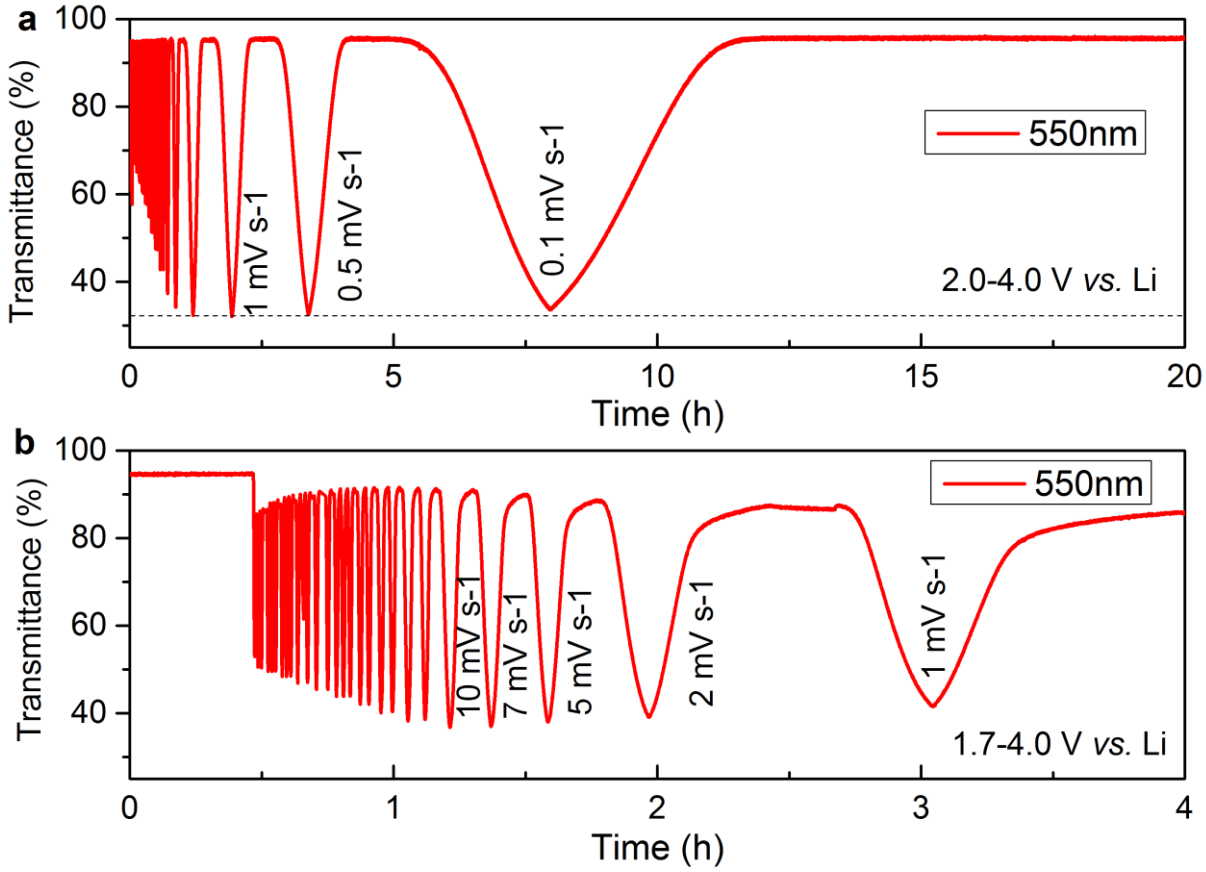

Fig. S6. *In situ* optical transmittance of WO_3 films at 550 nm. (**a**) Data for 2.0–4.0 V *vs.* Li/Li^+. The scan rate was varied from 100 to 0.1 mV s^{-1}. After measurements, the sample remained in the cell and no optical variation was observed. The dashed line indicates the lowest transmittance achieved. (**b**) Analogous data for 1.7–4.0 V *vs.* Li/Li^+. The films were deposited at a pressure of 30 mTorr.