Supplementary Information

Structure evolution of electrochromic devices from 'face-to-face' to 'shoulder-by-shoulder'

Xiufeng Tang *, Guoxin Chen, Zhixin Li, Hua Li, Zehui Zhang, Qinghao Zhang, Zhijun Ou, Yongxian Li, Chengjian Qi and Jianyi Luo *,

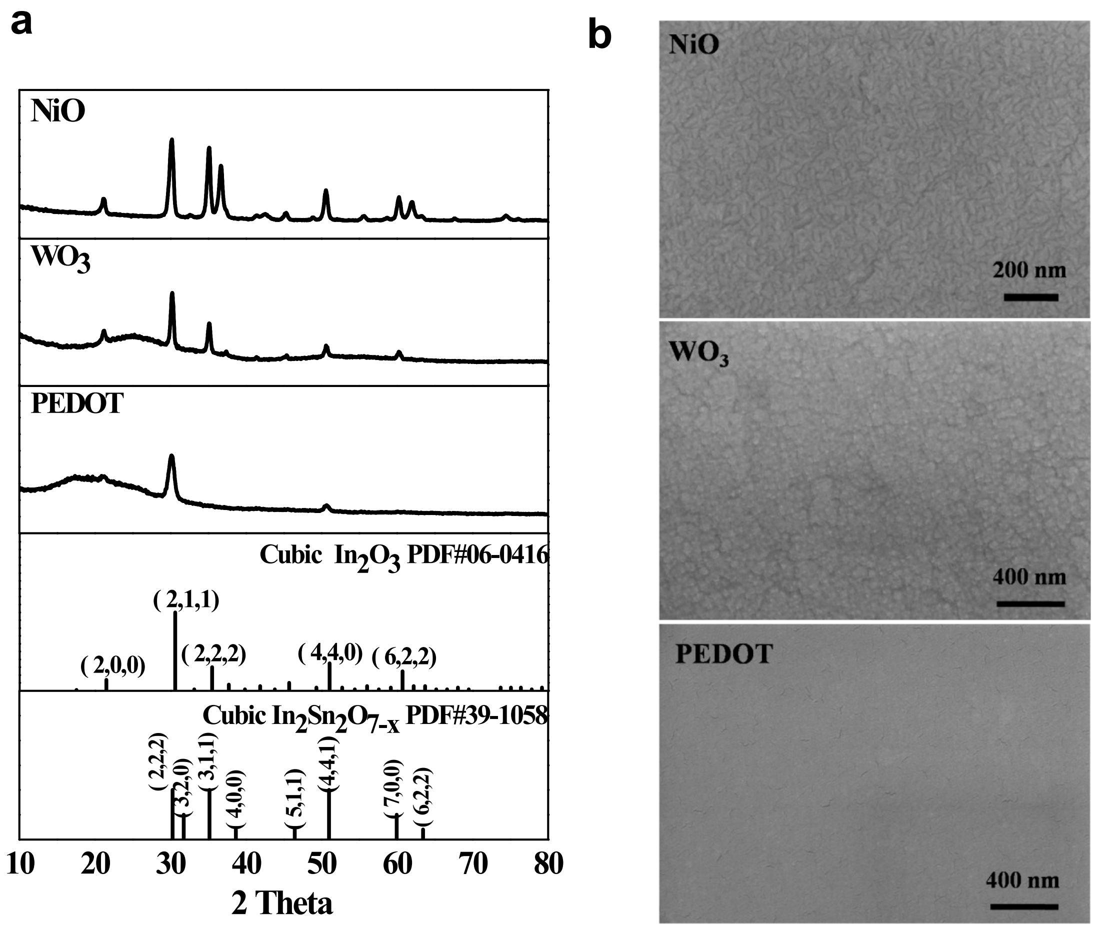

Figure S1 Characterization of the three EC films on ITO glass substrates used in this work. **a.** XRD spectra; **b.** SEM morphologies. These films were all amorphous.

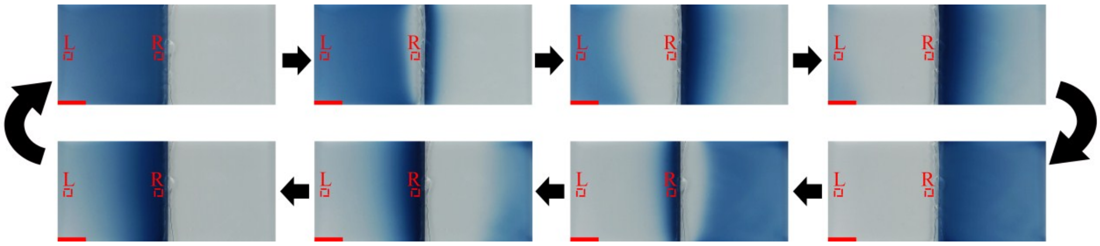

Figure S2 Optical photographs of the 2nd and 3rd processes of the WO_3 vs WO_3 shoulder-by-shoulder structure. Scale bars, 1 cm. After initialization of the first coloring process, the experimental phenomena of the subsequent processes were all the same.

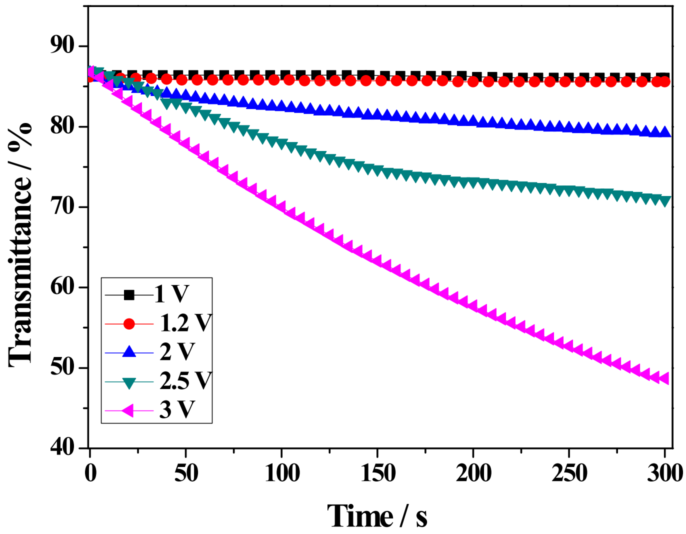

Figure S3 Transmittance variation of Spot L (as shown in **Figure 2 a** in the manuscript) as a function of the driving voltage during the first process when both EC films were transparent.

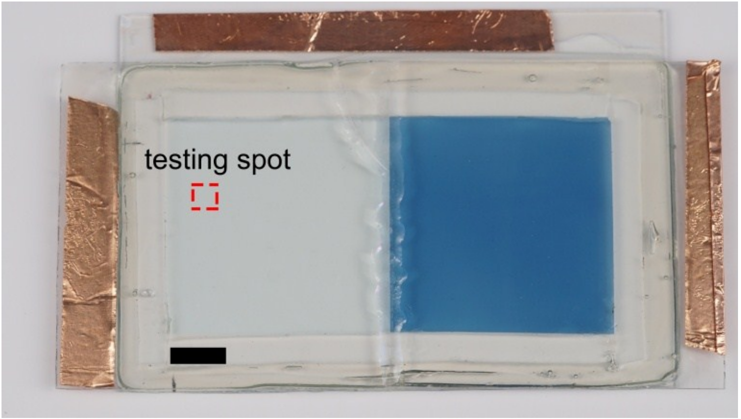

Figure S4 An optical photograph of the shoulder-by-shoulder device after being cycled for 15, 000 processes, where the red dashed square denoted the in situ monitored spot of the film transmittance during life cycling as shown in **Figure 3 c** in the manuscript. Scale bar, 1 cm.

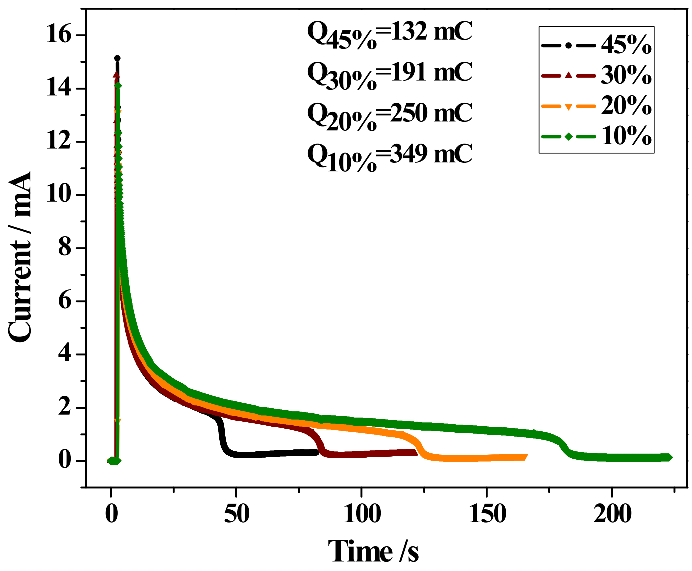

Figure S5 Current-time curves and calculation of the inserted charges in the first-initialized WO_3 film at different transmittances of 10%, 20%, 30% and 45%.

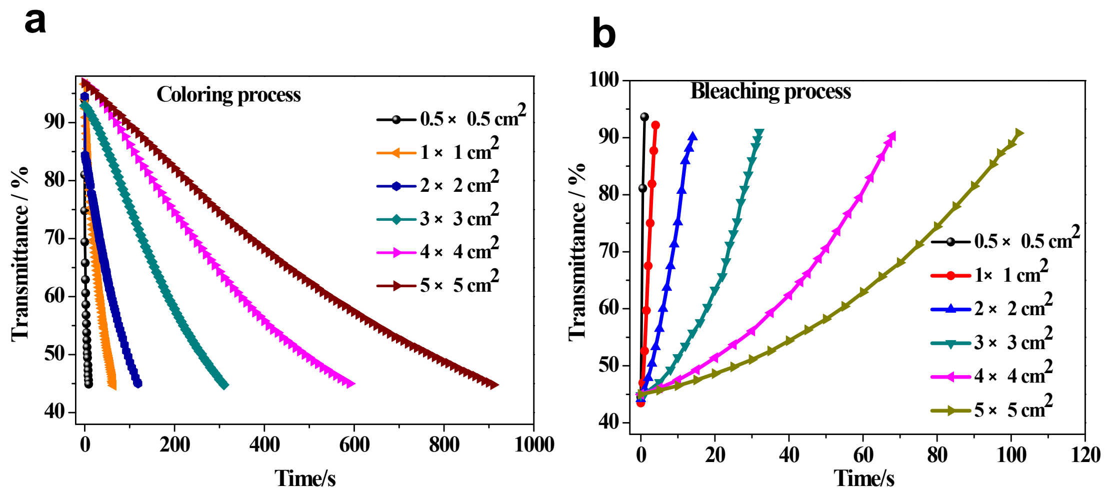

Figure S6 In-situ transmittance variation of Spot L (as denoted in **Figure 2 a** in the manuscript) in the subsequent processes of the WO_3 vs WO_3 shoulder-by-shoulder structure as a function of the film size. **a.** Coloring process; **b.** Bleaching process. The driving voltage was 3 V and at the beginning, the counterpart film was initialized at a transmittance of 40%.

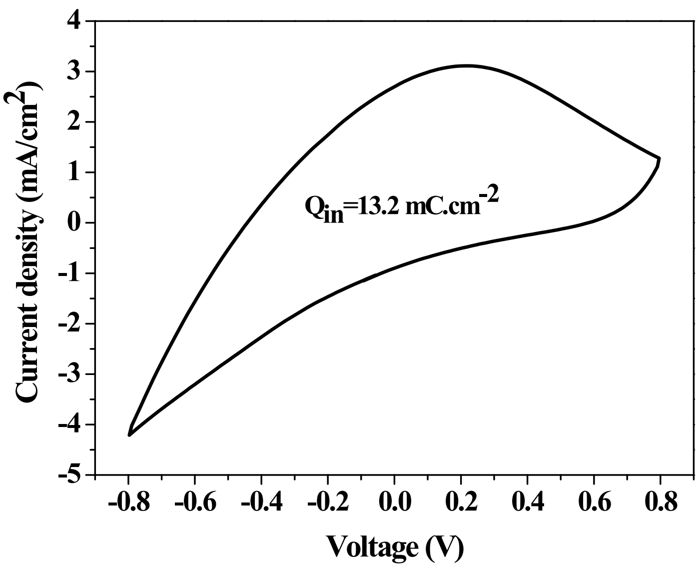

Figure S7 The cyclic voltammogram of the WO_3 film recorded at a voltage scan rate of 100mV s^{-1}, where the inserted charge was calculated to be 13.2 mC.cm^{-2}, and T_b and T_c of the film were recorded as 83% and 38% at 550 nm. Thus, the coloration efficiency of the WO_3 film at 550 nm could be calculated as 38.9 cm^2/C.

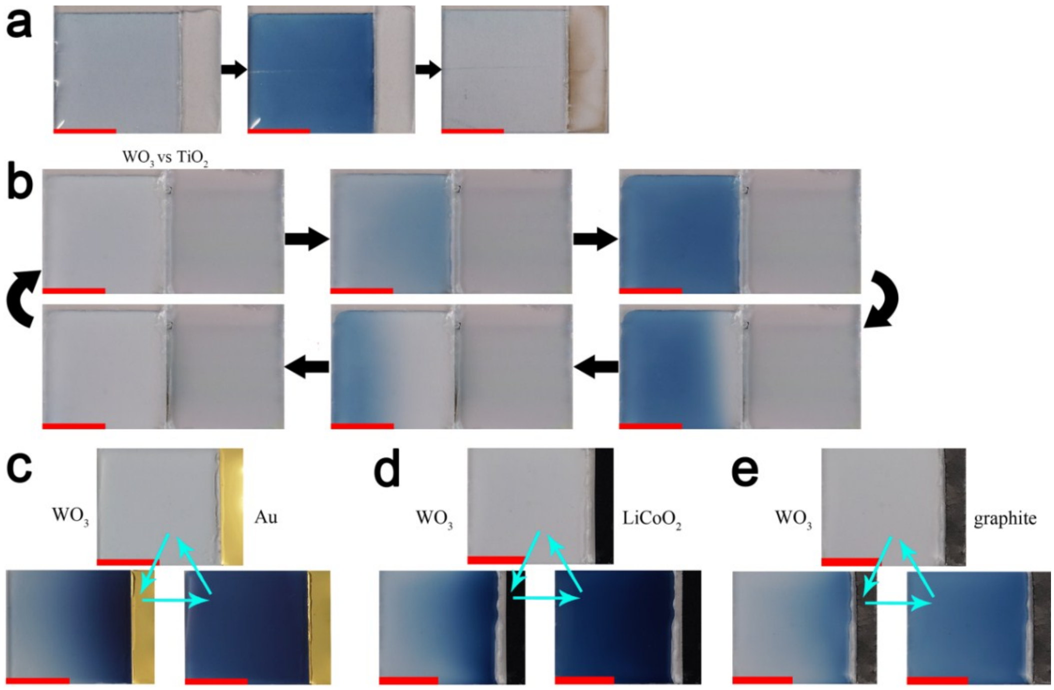

Figure S8 Optical photographs of the WO_3-based shoulder-by-shoulder structures with various counter electrodes. **a.** with bare ITO as the counter electrode, **b.** with TiO_2 film as the counter electrode, **c.** with Au film as the counter electrode, **d.** with $LiCoO_2$ as the counter electrode, **e.** with graphite as the counter electrode. The working voltage was 2 V. Scale bars, 1 cm. It turned out that the bare ITO cannot withstand the bombardment of Li ions and cannot work as the counter electrode, and those materials (TiO_2, Au, $LiCoO_2$ and graphite) that can withstand the bombardment of Li ions, all successfully colored the WO_3 films as the counter electrodes.

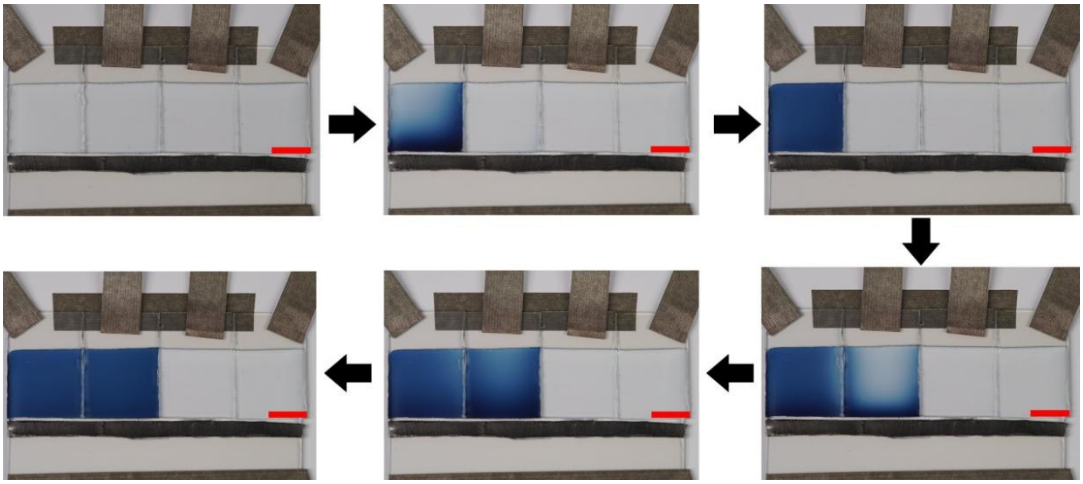

Figure S9 Integration of multiple EC films and one strip of graphite as the counter electrode, where the graphite could color every single EC unit at the working voltage of 2 V. Scale bars, 1 cm.

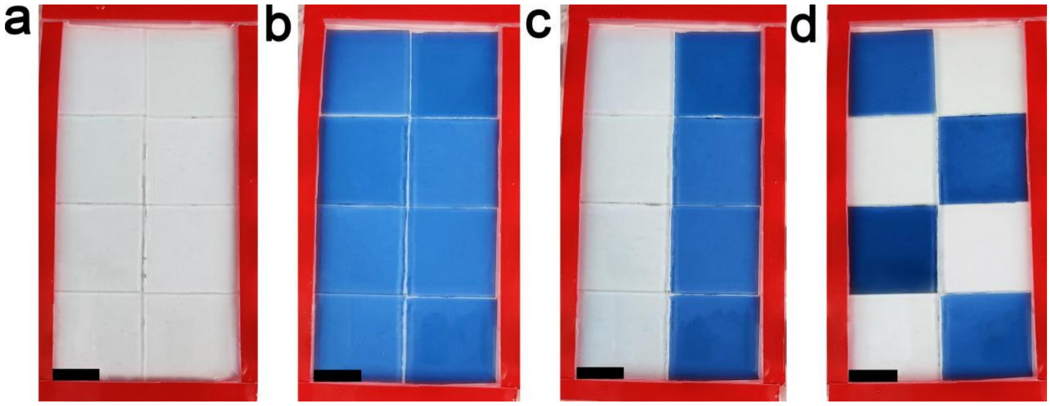

Figure S10 The prototype for an integrated display smart window based on the shoulder-by-shoulder structure, showing different patterns (**a-d**). The working voltage was 2 V. Scale bars, 1 cm.

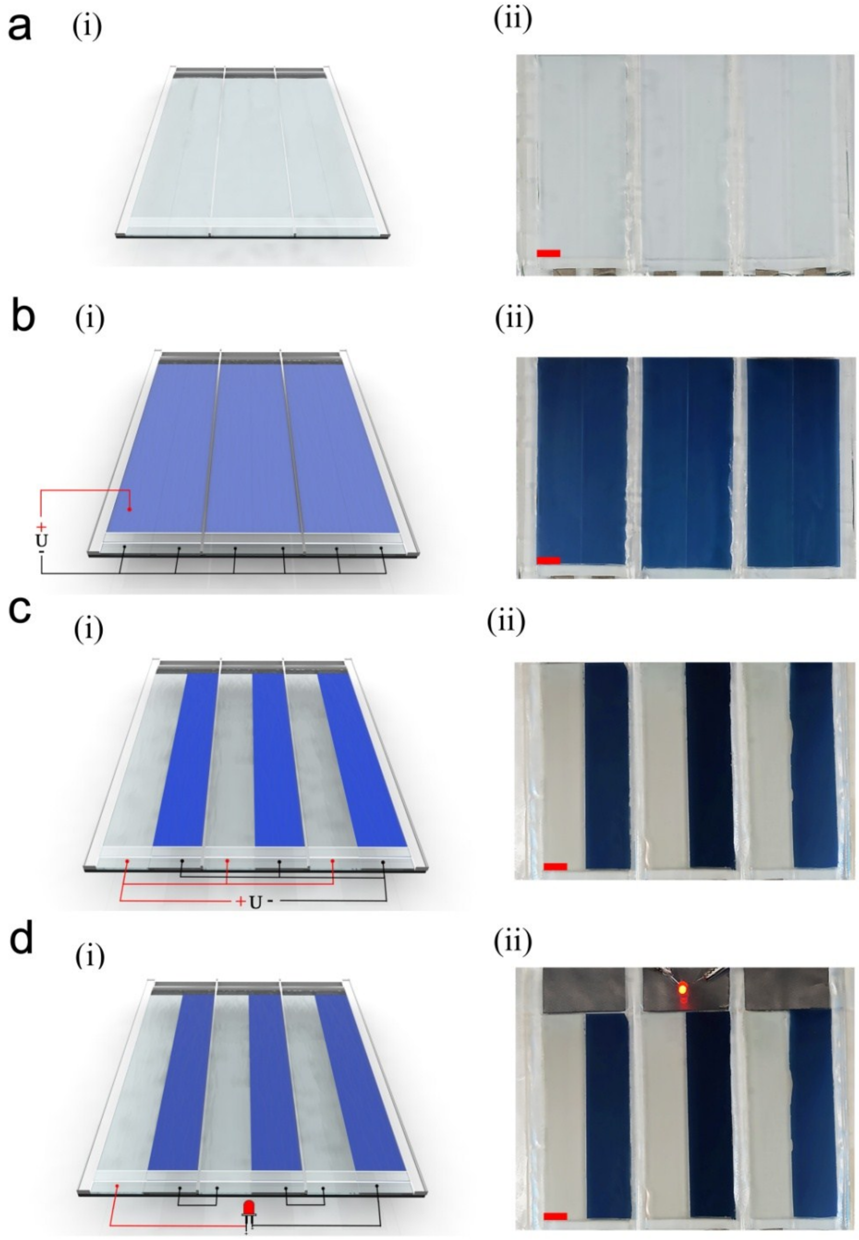

Figure S11. The prototype for a multifunctional smart window based on combination of the traditional face-to-face structure and the shoulder-by-shoulder structure. a. the wholly-transparent mode; b. the wholly-colored state; c. the shutter mode and d. the discharging mode. (i) illustrations of the working mode and (ii) corresponding optical photographs. The working voltage was 2 V. Scale bars in optical photos, 1 cm.

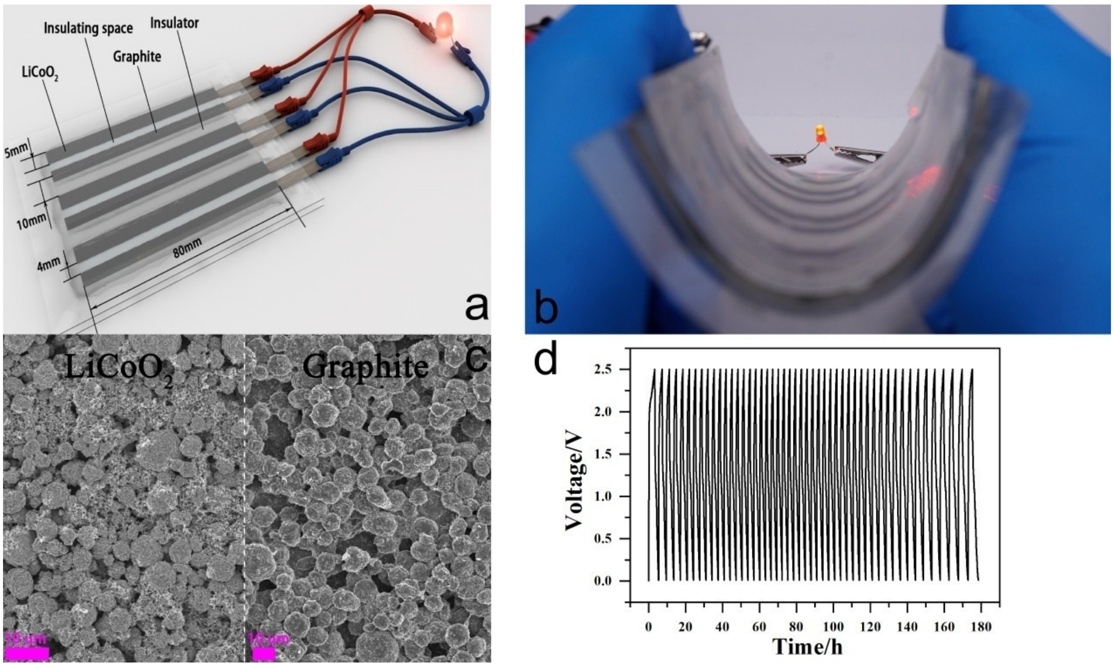

Figure S12 The prototype for a flexible separator-free lithium battery ($LiCoO_2$ vs graphite) based on the shoulder-by-shoulder structure. **a.** structure illustration; **b.** an optical photograph; **c.** SEM morphologies of the active materials; **d.** cyclic life curve. This flexible battery showed a good cyclic stability.

Supplementary movies

Movie S1

General applicability of the shoulder-by-shoulder structure in inorganic vs inorganic, inorganic vs organic hybrid and organic vs organic EC systems.

Movie S2

The prototype for an integrated display smart window based on the shoulder-by-shoulder structure.

Movie S3

The prototype for a flexible separator-free lithium battery ($LiCoO_2$ vs graphite) based on the shoulder-by-shoulder structure.