

Electronic Supplementary Information

## A rapid-response electrochromic device with significantly enhanced electrochromic performance

### Experimental Section

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , sulfuric acid,  $\text{H}_2\text{O}_2$ , acetone, ethanol,  $\text{LiClO}_4$ , propylene carbonate (PC), 3,4-ethylenedioxythiophene (EDOT), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim] $\text{PF}_6$ ) (various chemical suppliers) used in this study were reagent grade.

**Electrodeposition of three-dimensionally ordered macroporous  $\text{WO}_3$  films.** Indium-tin oxide (ITO) coated glass substrates ( $\sim 9 \Omega \text{ cm}^{-2}$ ,  $1 \text{ cm} \times 4 \text{ cm}$ ) and double-sided ITO-coated glass substrates ( $\sim 60 \Omega \text{ cm}^{-2}$ ,  $1 \text{ cm} \times 4 \text{ cm}$ ) were ultrasonically cleaned in acetone, ethanol and then distilled water for 20 min, separately. Monodispersed polystyrene (PS) latex spheres (diameters of 450 nm) were obtained using an emulsifier-free emulsion polymerization technique.<sup>1</sup> PS colloidal crystal templates were grown using a controlled vertical drying method.<sup>1</sup> The cleaned ITO-coated glass substrates were vertically placed into cylindrical glass vessels. The PS sphere suspension diluted to 0.5 wt% was added into glass vessels and then evaporated in an incubator at a stable temperature of 60 °C to obtain polystyrene colloidal crystal templates. Cathodic electrodeposition of  $\text{WO}_3$  into polystyrene colloidal crystal templates was performed at a constant current of 2 mA in an ice-water-bath mixture of 10 mL of 0.025 mol/L  $\text{Na}_2\text{WO}_4$ , 0.05 mol/L  $\text{H}_2\text{SO}_4$  and one drop of 30%  $\text{H}_2\text{O}_2$  for 5 min with Pt foil as the counter electrode. After electrodeposition, samples were immersed in the toluene for 24 h to remove the polystyrene templates. Finally, the as-prepared samples were dried at 70 °C for 30 min.

**Electropolymerization of PEDOT films.** [Bmim] $\text{PF}_6$  was used after drying under vacuum condition at 100 °C until the water content below 1 ppm. EDOT was used as delivered. PEDOT films were electropolymerized at a constant voltage of 1.4 V versus Ag (1.0 mm diameter wire) from [Bmim] $\text{PF}_6$  containing 0.1M EDOT monomer and Pt ring as the counter electrode. Then the films were immersed in ethanol to remove the residue monomers.

**Characterization.** The morphologies of 3DOM  $\text{WO}_3$  films and PEDOT films were characterized by scanning electron microscopy (SEM, Hitachi S-4800). Crystalline structures of the 3DOM  $\text{WO}_3$  films were investigated using a Rigaku D/mol/Lax-3C equipment with a sweep rate of 5°/min through a diffraction angle range of 20–70°. The Raman spectra were determined on a Renishaw in Via micro Raman spectroscopy system, using the TE air-cooled 576×400 CCD array in a confocal Raman system (wavelength: 633 nm). The incident laser power was kept at 0.1 mW, ×100 objective and an integration times of 5 s were employed. In situ visible and near-IR (NIR) electrochromic measurements of ECDs and NECDs were performed using an experimental setup produced in-house<sup>2</sup> in combination with a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd.). The experimental setup was sealed in an argon-filled glove box (Vigor Glove Box from Suzhou, China) before testing. One side of the setup was connected to a white lamp (DT-mini-2-GS, Ocean Optics) by an optical fiber; the other side was connected to an optic spectrometer (MAYA 2000-Pro, Ocean Optics). The transmittances of the ECDs and NECDs without electrochromic layers and electrolyte were used as a reference for 100% transmittance. Chronoamperometry measurements were done by applying +3 V for 1000 s to de-intercalate all  $\text{Li}^+$  ions present, then setting the potential back to -3 V for 20 s followed by +3 V for 20 s, and monitoring the current as a function of time during testing.

Fig. S1 shows the coloration/bleaching transmittance response curves of the  $\text{WO}_3$ -NECD and the PEDOT-NECD for the first, 150th and 300th cycles with alternately applied potentials of  $\pm 3$  V. The NECDs retain the electrochromic properties after 300 switching cycles, with little changes of optical contrast and switching time.

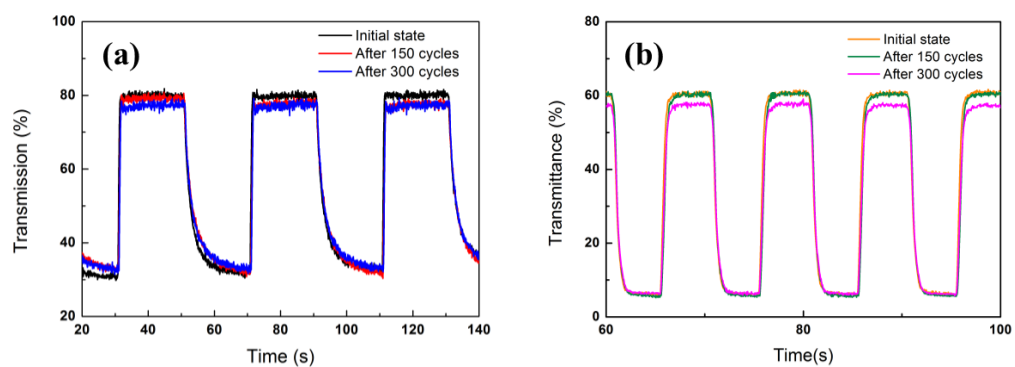


Fig. S1. Change in optical transmittance versus time for (a) the  $\text{WO}_3$ -NECD and (b) the PEDOT-NECD at initial cycle, after 150 cycles and after 300 cycles with alternately applied potentials of  $\pm 3$  V.

## References

- 1 M. A. McLachlan, N. P. Johnson, M. Richard and D. W. McComb, *Journal of Materials Chemistry*, 2004, **14**, 144.
- 2 G. Bar, N. Larina, L. Grinis, V. Lokshin, R. Gvishi, I. Kiryushev, A. Zaban and V. Khodorkovsky, *Solar Energy Materials and Solar Cells*, 2012, **99**, 123.