Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Ultra large optical modulation of electrochromic porous WO_3 film and the local monitoring of redox activity

Guofa Cai, Mengqi Cui, Vipin Kumar, Peter Darmawan, Jiangxin Wang, Xu Wang, Alice Eh, Kai Qian, and Pooi See Lee*

Author Address: School of Materials Science and Engineering Nanyang Technological University 639798, Singapore

*Corresponding Author

E-mail: pslee@ntu.edu.sg

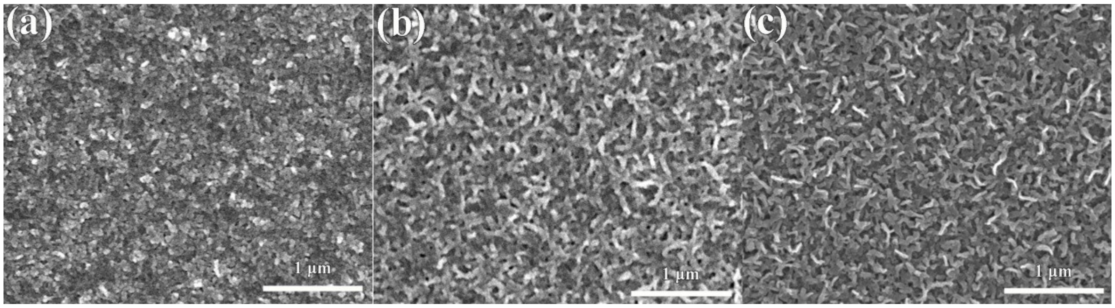

Fig. S1 SEM images of the WO_3 films prepared by pulsed deposition with different duty cycle length (a) 4 s, (b) 1 s, (c) 0.5 s.

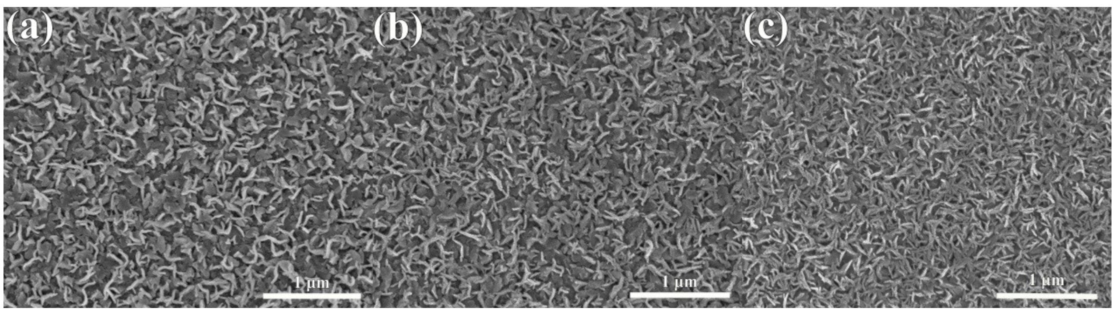

Fig. S2 SEM images of the WO_3 films prepared by pulsed deposition with different interval time (a) 0.4 s, (b) 0.6 s, (c) 0.8 s.

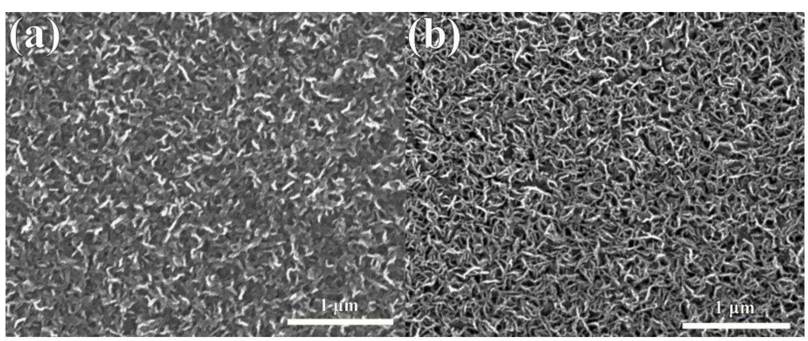

Fig. S3 SEM images of the porous WO_3 films deposited on different substrates (a) FTO- coated glass, (b) ITO-coated PET.

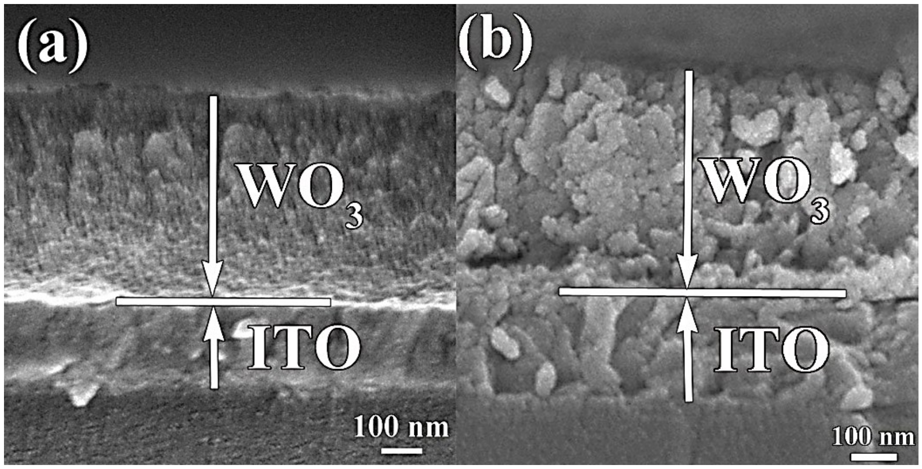

Fig. S4 The cross-section morphologies of (a) compact and (b) porous WO_3 film.

Table S1 Chemical state and composition of W and O obtained by deconvolution of the corresponding region spectra of porous WO_3 film.

Elements	Peak Binding Energy (eV)	Composition (At%)
W4f WO_3	35.9 38.0	25%
O1s O-W	531.0	75%
O/W	—	3.0

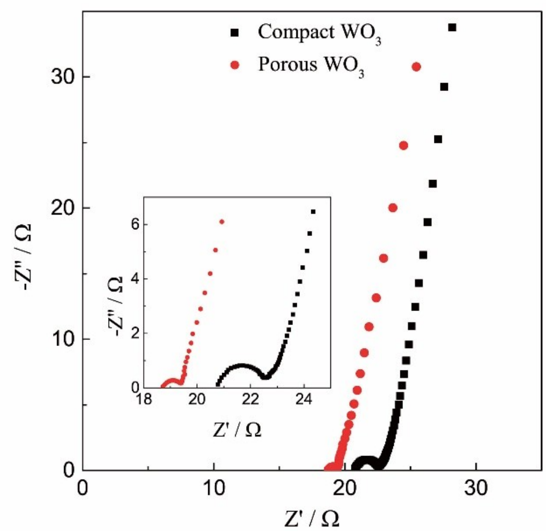

Fig. S5 Nyquist plots of compact and porous WO_3 film, the inset shows the magnified high-frequency region.

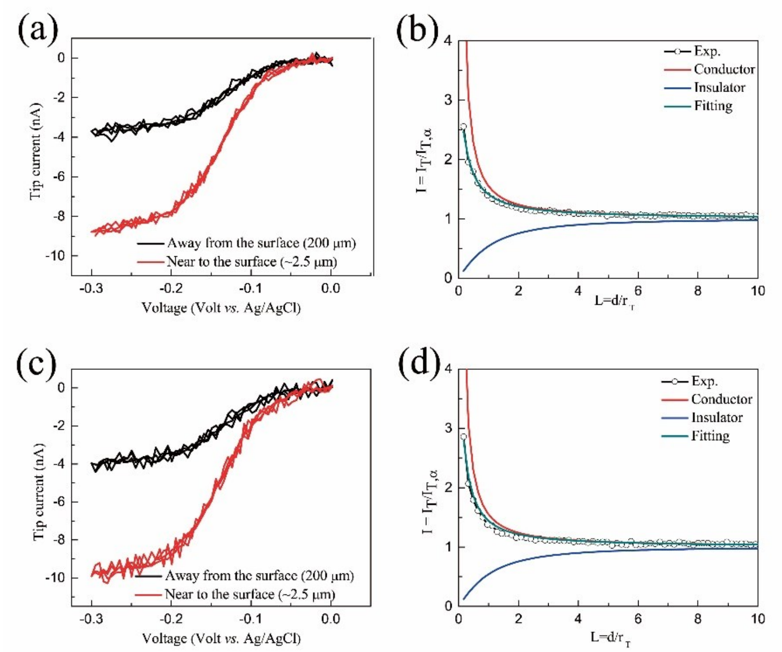

Fig. S6 The localized CVs and approach curves of Pt miroelectrodes recorded on the surface of WO_3 electrodes $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$ redox mediator: (a-b) compact WO_3 film electrode, (c-d) porous WO_3 film electrode.

Effective heterogeneous charge transfer rate constants k of WO_3 films were calculated using the relation $k_{eff} = \kappa D/ r_T$, where κ is the normalized heterogeneous rate constant which is obtained from the normalized approach curves I_T vs. L were fitted to the analytical approximation of Cornut and Lefrou.[1] The κ value of compact and porous WO_3 films are 3.91 and 5.19 obtained from Figure S5b and d, respectively. r_T is the radius of microelectrode (12.5 μm). D is the diffusion coefficient for redox species ($D = 8.4 \times 10^{-6}$ cm^2/s). The k_{eff} of porous WO_3 film is 3.49×10^{-2} cm s^{-1}, which is higher than that of the compact WO_3 film (2.63×10^{-2} cm s^{-1}).

1. R. Cornut and C. Lefrou, *J. Electroanal. Chem.*, 2008, 621, 178-184.