Supplementary Information

Self-seeded growth of nest-like hydrated tungsten trioxide film film directly on FTO substrate for highly enhanced electrochromic performance

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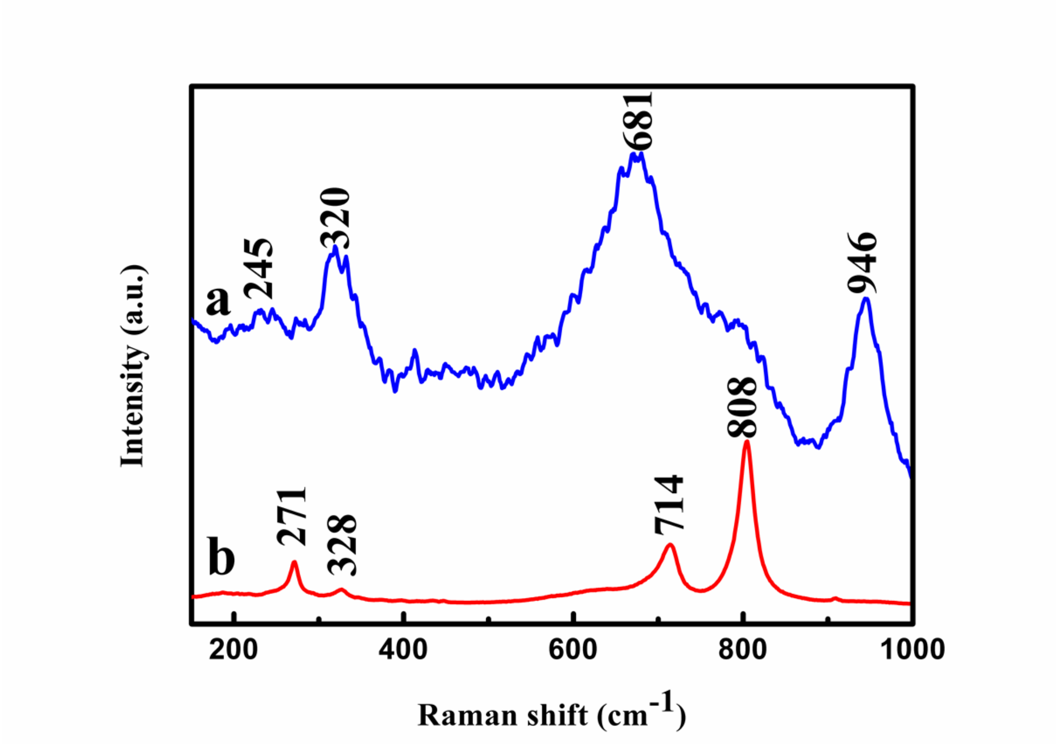

Fig. S1 Raman spectra of the films: (a) as-prepared and (b) annealed at 500 °C for 2 h.

Fig. S1 displays the Raman spectra of the as-prepared $WO_3 \cdot 0.33H_2O$ film and annealed film. The band at 681 cm^{-1} arises from the O-W-O stretching vibrations of the bridging oxygen atoms, the band at 245 cm^{-1} belongs to W-O-W bending mode and the bands at 320 cm^{-1} and 946 cm^{-1} can be assigned to the stretching of W-$(OH)_2$ and W=O, respectively. These vibrations are commonly found in tungsten trioxide hydrates ($WO_3 \cdot nH_2O$).[1-5] After annealed at 500 ºC for 2h, the bands centered at 714 and 808 cm^{-1} arise from the O-W-O stretching vibrations of the bridging oxygen atoms, and the two bands located at 271 and 328 cm^{-1} belong to W-O-W bending modes. These vibrations indicate that the as-prepared $WO_3 \cdot 0.33H_2O$ film transforms into pure WO_3 after heattreatment.[6,7]

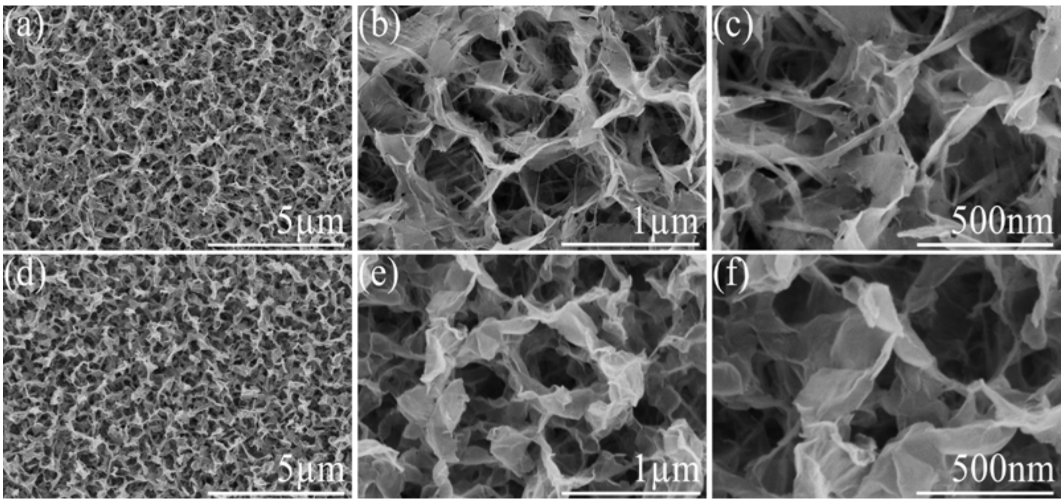

Fig. S2 FE-SEM images and corresponding high-magnification images of $WO_3 \cdot 0.33H_2O$ electrode prepared without(a,b,c) and with(d,e,f) seed layer.

Fig. S2 displays the difference of hydrothermally grown films with and without SL. The morphologies of the self-seeded grown electrode is shown in Fig. S2(a,b,c), while the morphologies of the crystal-seed-assisted grown film is shown in Fig. S2(d,e,f). The nest-like nanosheets of the self-seeded grown film are formed of nanoribbons while the nanosheets of the crystal-seed-assisted grown film are pure nanosheets. The hierarchical nanostructures create a large surface area for electrolyte to come in complete contact with the $WO_3{\cdot}0.33H_2O$ and could make the Li^+ ion intercalation and deintercalation processes easier.

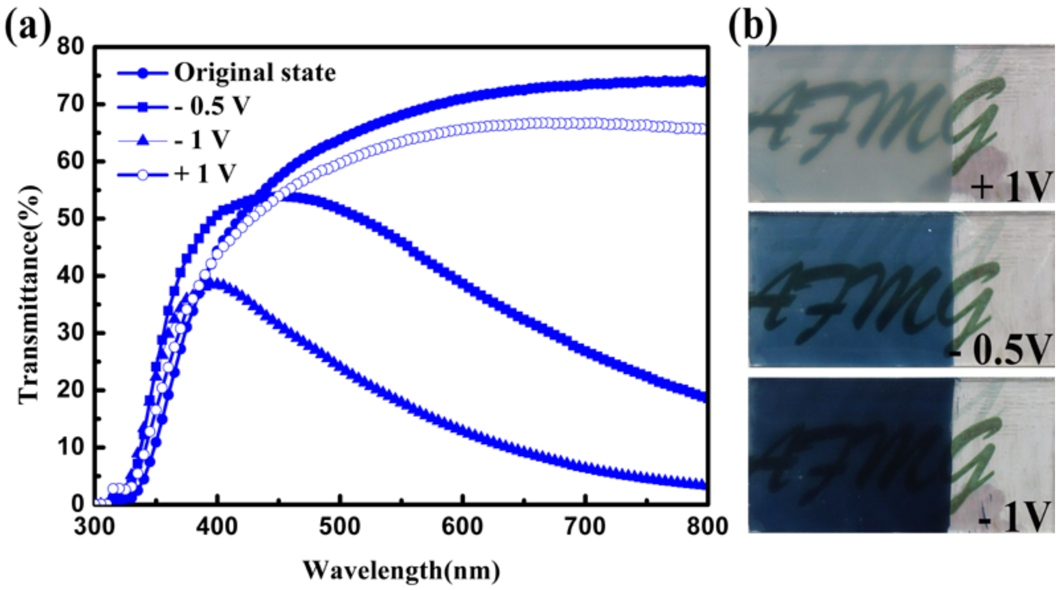

Fig. S3 (a) UV-vis transmittance spectra of the crystal-seed-assisted grown film measured at 0.5 V, 1.0 V and +1.0 V, respectively. (b) Digital photographs of the crystal-seed-assisted grown film.

The modulation range of the crystal-seed-assisted grown film at 632.8 nm after applying voltages of − 0.5 and −1.0 V is calculated to be 32.2 and 56.2 %, respectively (Fig. S3(a)), these modulation range is poor compared with that of the self-seeded grown film. Besides, the crystal-seed-assisted grown film can not recover to the original state completely after applying voltage of + 1.0V.

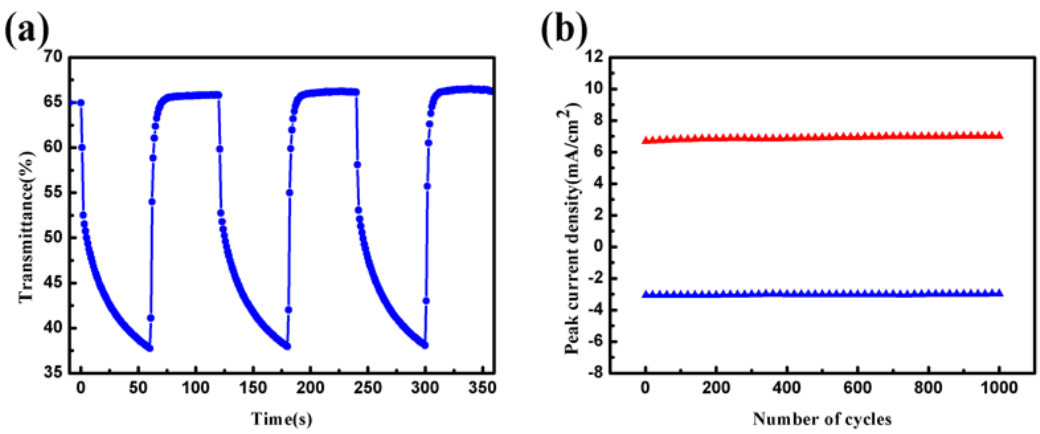

Fig. S4 (a) Switching time characteristics between the colored and bleached states for crystal-seed-assisted grown $WO_3{\cdot}0.33H_2O$ film measured at 632.8 nm, ± 3.0 V bias. (b) Peak current evolution of crystal-seed-assisted grown $WO_3{\cdot}0.33H_2O$ film during the step chronoamperometric cycles.

Fig. S4(a) shows the switching response of the crystal-seed-assisted grown film. The coloration time t_c and bleaching time t_b are calculated to be 36 s and 5.5 s respectively, while they are 26 s and 5.5 s respectively of the self-seeded grown film shown in Fig. 6(a).

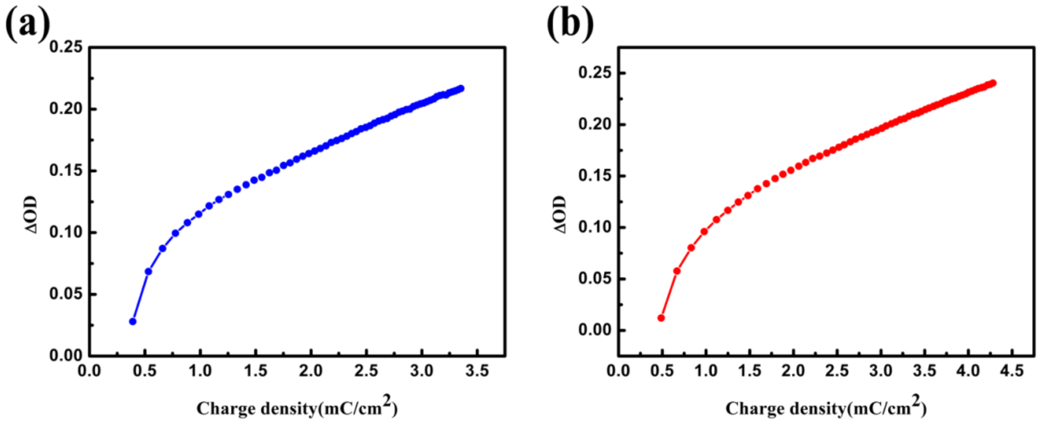

Fig. S5 OD variation with respect to the charge density for the (a) self-seeded grown $WO_3{\cdot}0.33H_2O$ film and (b) crystal-seed-assisted $WO_3{\cdot}0.33H_2O$ film measured at 632.8 nm at a potential of - 3.0 V.

Fig. S5 shows the coloration efficiency (CE) of the self-seeded grown film and crystal-seed-assisted WO_3 film. The CE values are found to be 126.34 cm^2C^{-1} and 122.06 cm^2C^{-1} respectively.

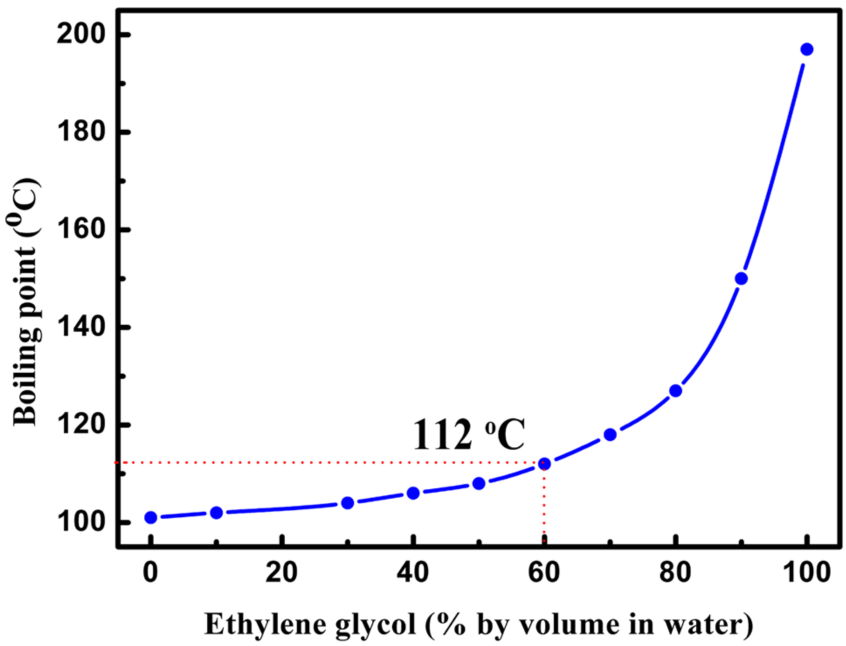

Fig. S6 Boiling point variation with respect to the composition of aqueous ethylene glycol solution

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