Electronic Supplementary Information

Facile Preparation of Aqueous Suspensions of WO_3/Sulfonated PEDOT Hybrid Nanoparticles for Electrochromic Applications

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1. Investigation of Conditions for the Polymerization of EDTS

WO_3 NPs (100 mg) were dispersed in 20 mL DI-water and sonicated for 20 mins. EDTS (40 mg) was dissolved in the dispersion. Four sample dispersions were prepared with the same amount of WO_3 NPs and EDTS, and named as S1, S2, S3 and S4. The original sample dispersion is a milk-like liquid. The experiments were conducted as described below:

- S1 was stirred and heated at 80 °C for ca. 4 hours in N_2 condition. No colour change observed.
- S2 was stirred and heated at 80 °C for ca. 4 hours in air. No colour change observed.
- The pH of S3 was adjusted by HCl to around 1~2, and then stirred and heated at 80 °C for ca. 4 hours under N_2. No color change observed.
- The pH of S4 was adjusted by HCl to around 1~2, and then stirred and heated at 80 °C for ca. 4 hours in air. Blue colored observed.

The blue colour indicates the oxidative polymerization of EDTS. The PEDTS (light blue) can be formed by oxidation of EDTS. From the above experiments, the EDTS can only be oxidized by oxygen in strong acidic conditions. WO_3 NPs cannot oxidize the EDTS under the same conditions (S3). Without WO_3 NPs, EDTS can also be oxidized to form PEDTS under the same conditions, but the polymerization product can be dissolved in water to form a blue polymer solution, instead of suspensions of hybrid nanoparticles.

2. Further Oxidization of PEDTS Oligomers

The products of EDTS oxidization is likely to be a mixture of polymers and oligomers. By applying positive potentials to the hybrid thin films fabricated, the PEDTS can be further polymerized. Therefore, before the spectro-electrochemical characterization, the thin films were subjected to positive potential of + 1.3V for 250 s in 1 M $LiClO_4$/PC solution to further polymerize PEDTS. The spectro-electrochemical measurements were all taken at the stable condition of the films. It means that the transimittance values of the hybrid films are stable under positive potentials.

3. Morphology of FTO Glasses

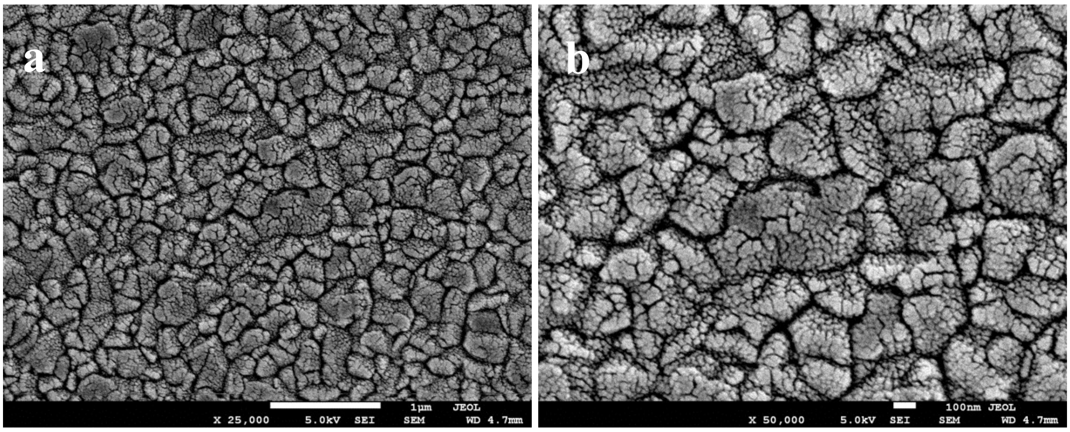

Fig. S1. SEM images of FTO glasses at different magnifications: 25K(a) and 50K (b).

4. Fabrication of PEDTS-based ECDs

The WO_3-NP and hybrid ECDs were fabricated by air brush spray of a certain amount of suspension. If the same volume of the PEDTS solution is used to produce PEDTS films via air-brush spraying, the films formed are too thin due to its low PEDTS concentration, which barely show any colour change. Therefore, PEDTS films of ca. 400 nm were coated onto FTO glasses through drop casting. The EC performances of the ECDs based on PEDTS films are characterized using the same instruments and conditions as reported for WO_3-NP and hybrid based ECDs.

5. Switching Responses of the ECDs

In this work, the neat PEDTS based ECDs show fast coloration and bleaching speeds of less than 3 seconds; and the WO_3-NP based ECDs present slower speeds. So the switching speeds of hybrid ECDs are determined by the major component, WO_3. The hybrid ECDs exhibit faster coloration and slower bleaching speeds compared with that of the WO_3 based ECDs. It may be caused by the morphology of the EC films. The morphology of the WO_3-NP films obtained via air-brush spraying is porous with many voids among the nanoparticles. In the hybrid system, the voids are filled with the conductive PEDTS. During the coloration, the WO_3 is reduced and exhibits metallic conductivity. The hybrid films hence exhibits enhanced conductivity, leading to fast coloration switching speed. On the other hand, WO_3 is the major component in the hybrid system, and is an insulator at fully oxidized states. In this case, the conductivity of the hybrid system may be lower during bleaching process. The porous morphology of the WO_3-NP film may assist the ion extraction, whereas the PEDTS may block this process in the hybrid system during the bleaching process. As a result, the hybrid ECD shows relatively slow bleaching process. Nevertheless, the initial bleaching of the hybrid ECD is very fast; it can achieve higher contrast than both WO_3-NP and PEDTS ECDs in just few seconds.

6. Cyclic Voltammetry of Sample Films

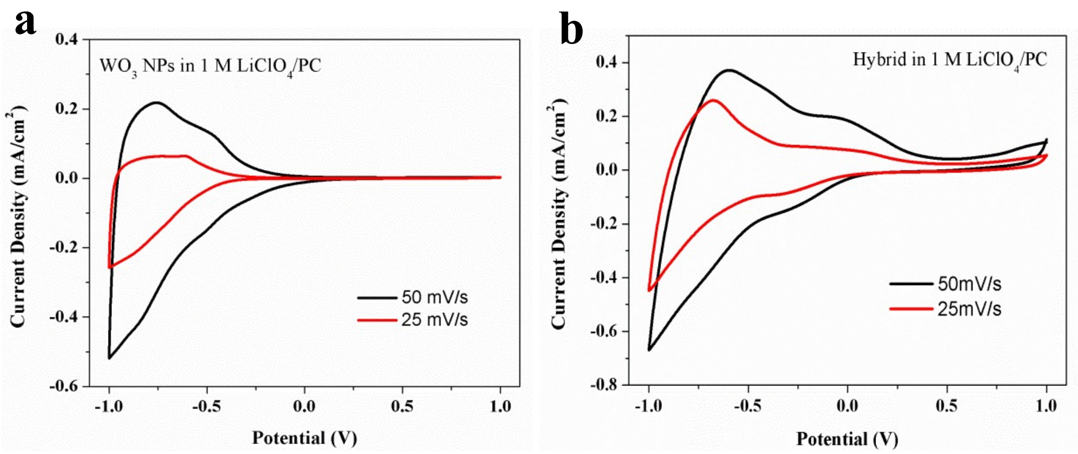

Fig. S2. Cylic voltammetry plots of (a) WO_3-NP and (b) hybrid films of the same thickness coated on FTO glasses in 1 M $LiClO_4$/PC solution at scan rates of 25 and 50 mV/s.