

Supporting Information

Multicolor electrochromic polyaniline–WO₃ hybrid thin films: one-pot molecular assembling synthesis

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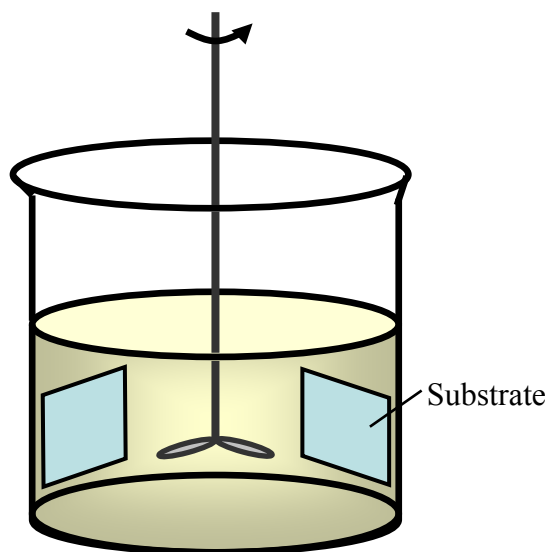
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Scheme S1. Schematic diagram of the deposition equipment.

Scheme S1 shows the chemical bath deposition (CBD) system, which is according to the references with some improvements.^{1,2} This equipment was kept in a refrigerator, and the stirring speed was adjusted using a controller. The substrates were fixed on the wall of beaker with double faced adhesive tapes. The substrates were masked with polyimide tape to prevent unwished deposition.

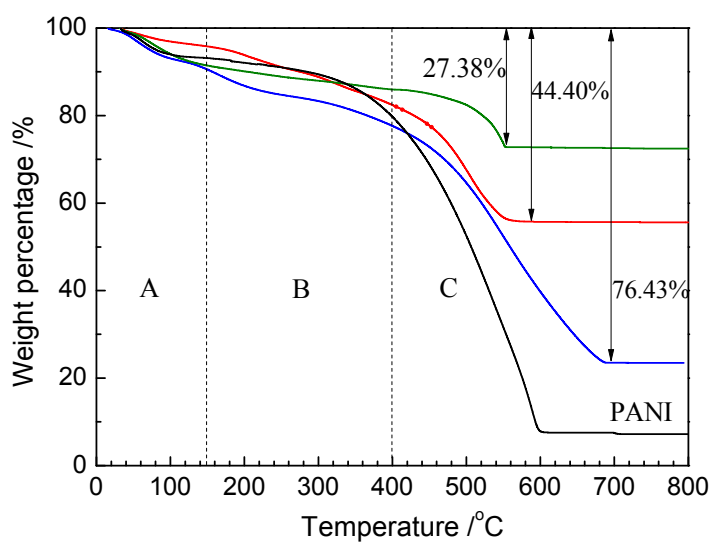


Figure S1. TGA curves of sulfuric acid doped PANI and PANI-WO₃ hybrids with various weight percentage of WO₃.

Figure S1 shows the TGA curves of sulfuric acid doped PANI and PANI-WO₃ hybrids with various weight percentage of WO₃. The thermal degradation mainly includes two stages. The slight weight loss from room temperature to 150 °C is attributed to the elimination of the moisture in the samples. The major weight loss of the samples from 400 to 700 °C is due to the degradation of PANI, leaving WO₃ as the residue. For neat PANI, there is a platform between 150 to 400 °C, while for the PANI-WO₃ composites, an extra stage is found there, which is because of the dehydration in WO₃ (as is well known that there is lots of hydration water in amorphous tungsten oxide). The composition by mass of the three samples containing WO₃ is 76.43% PANI + 23.57% WO₃, 44.40% PANI + 55.60% WO₃, 27.38% PANI + 72.62% WO₃, which are expressed as PANI-WO₃-1, PANI-WO₃-2 and PANI-WO₃-3. With the addition of dopant, the mass percentage of the residue increases. From the TGA curves, it is found that the thermal stability is enhanced due to small addition of dopant, while decreases when PANI was heavily doped. Some previous literatures reported that low thermal stability of PANI-inorganic composite was due to the weakened interfacial interaction between the two components.³ Other works, however, showed enhanced thermal stability because of the tight bonds between the inorganic fillers and the polymer.⁴ The disagreement among our result and those previous reports can be explained as follows. The thermal stability of PANI-inorganic composite depends on the intrinsic structure of PANI and the interfacial interaction between the two components. In our case, small dopant lead to more ordered structure and stronger interfacial interaction between two polymer chains with (W₂O₁₁)²⁻. The

polymer chains in the heavily doped PANI have weakened interaction with each other because too much inorganic fillers lead to a random network.

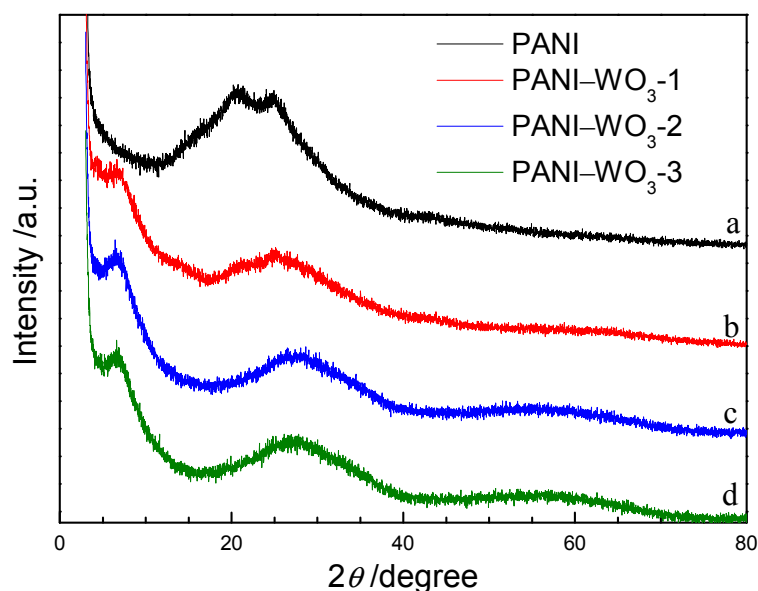


Figure S2. XRD patterns of (a) sulfuric acid doped PANI; (b) PANI-WO₃-1 hybrid; (c) PANI-WO₃-2 hybrid; (d) PANI-WO₃-3 hybrid

Figure S2 shows the XRD patterns of PANI films. XRD patterns of the PANI-WO₃ hybrids show a sharp peak at $2\theta = 6.6^\circ$ ($d = 13.3 \text{ \AA}$), which is close to the PANI repeat distance. However this peak is absent in the sulfuric acid doped PANI. This result suggests that PANI doped with tungstic acid leads to a more ordered structure with relative distinct Bragg reflections.^{5, 6} The peak centered at 20.42° , which is found in the sulfuric acid doped PANI and ascribed to the periodicity parallel to PANI chains. However, this peak is not distinctive in the PANI-WO₃ hybrid films, instead a broad band is found to be centered at $2\theta = 27.7^\circ$ ($d = 3.22$), which is

ascribed to the periodicity perpendicular to PANI chains. This result confirms the preferential growth of PANI doped with tungstic acid.

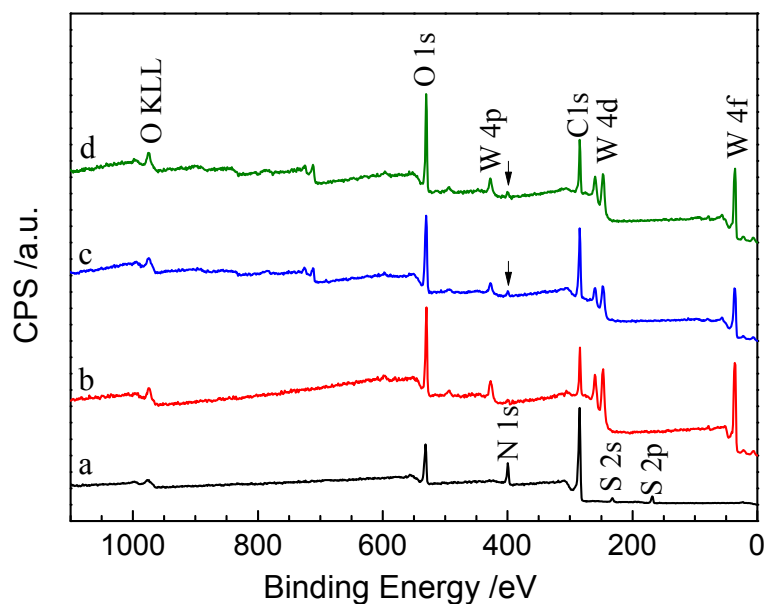
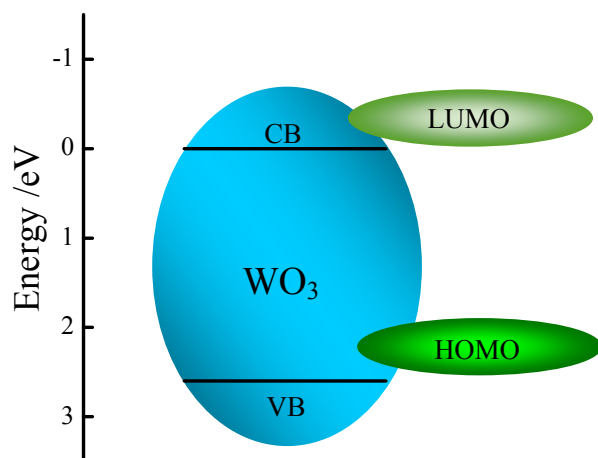
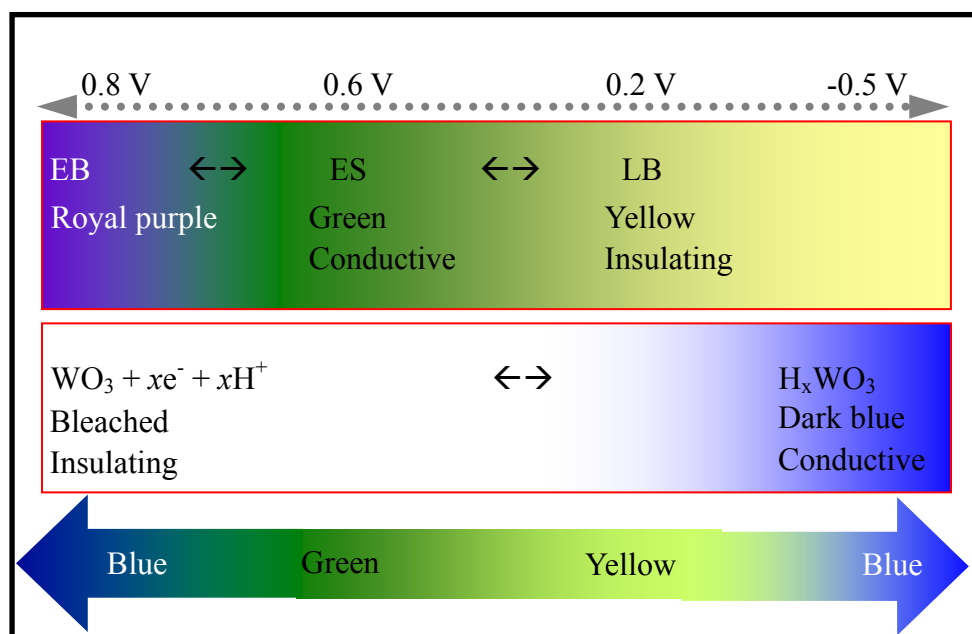


Figure S3. XPS spectra of (a) sulfuric acid doped PANI; (b) WO_3 xerogel; (c) PANI- WO_3 -1; and (d) PANI- WO_3 -2. (Arrows mark out the N 1s peaks in PANI- WO_3 hybrids).

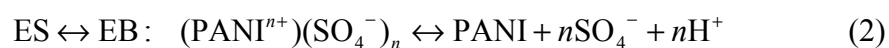


Scheme S2. The mechanism scheme of the energetic correlation between conduction band (CB) and valance band (VB) of WO_3 , and the highest occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) of PANI.⁷



Scheme S3. Illustration of the dual electrochromic mechanism of PANI- WO_3 hybrid films.

Scheme S3 illustrates the dual electrochromic mechanism of PANI–WO₃ hybrid films. EB = emeraldine base, ES = emeraldine salt, LB = leucoemeraldine base. The transformation equations in PANI are listed below:



Overlapping the two components, the hybrid films show blue–green–yellow–blue colors changing.

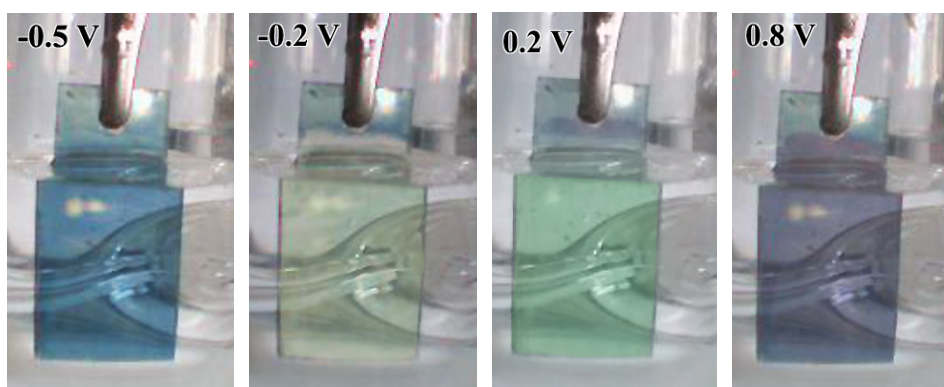


Figure S4. Digital photos of PANI–WO₃-2 hybrid film at each potential: -0.5 V, -0.2 V, 0.2 V and 0.8 V.

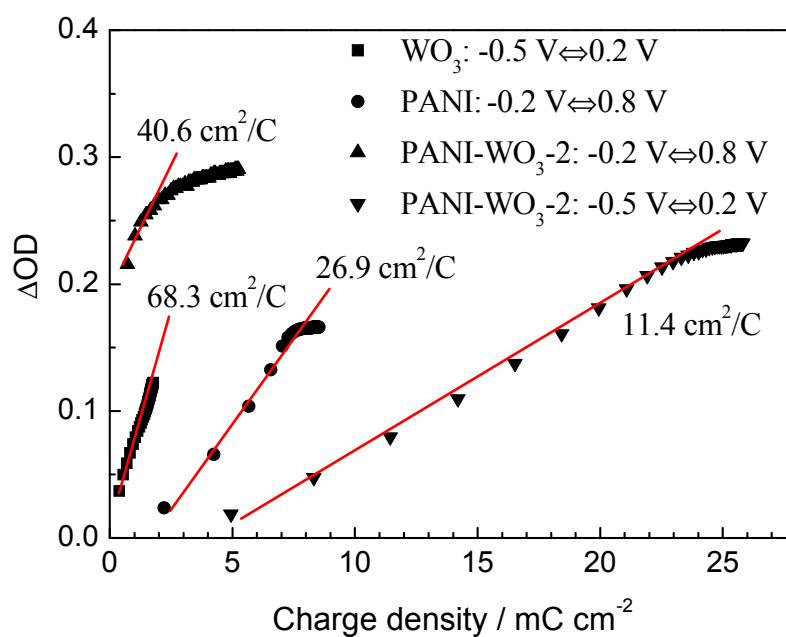


Figure S5. Optical density variations vs. charge density

The coloration efficiency (CE), which is defined as the change in optical density (OD) per unit of charge (Q) used for coloration of the film, is a characteristic parameter for comparing different electrochromic materials. i.e.:

$$CE = \Delta OD / Q = \log(T_b / T_c) / Q, \quad (3)$$

where T_b and T_c refer to the transmittance of the film in its bleached and colored states, respectively. The variation of optical density at 633 nm vs. charge density of these films is plot in Figure S4. The CE values are extracted as the slope of the lines fitted to the linear region of the ΔOD vs. charge density.

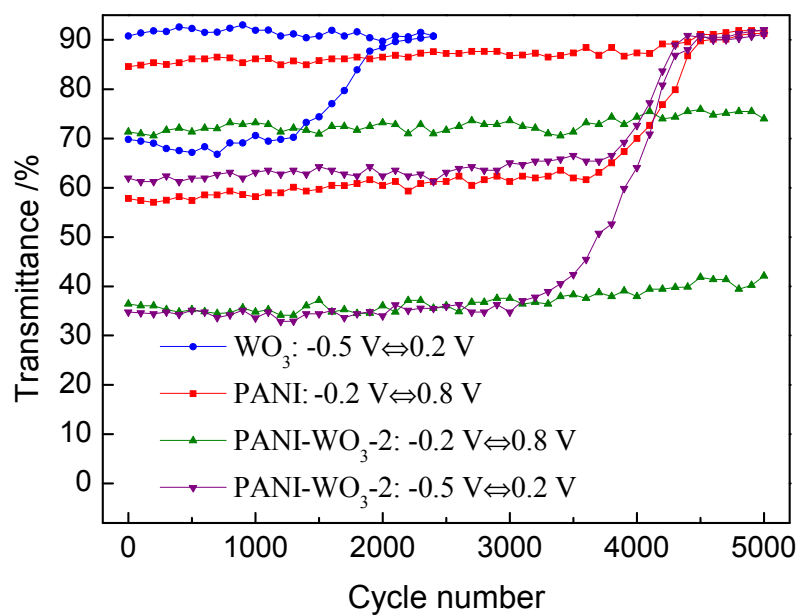


Figure S6. Electrochromic durability of WO₃ film, sulfuric acid doped PANI film and PANI-WO₃-2 hybrid film under different potential steps.

References

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