Supplementary Information (SI) for Dalton Transactions.

Supporting Information

for

Synergistic WO_3-PBI Hybrid Electrochromic Materials with Enhanced Diffusion Coefficient and Cycling Reversibility Inspired by "Big Rocks" Theory

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Contents

1. Experimental Section

1.1 Chemicals and materials

Acetone, ethanol, $Na_2WO_4 \cdot 2H_2O$, H_2O_2, sulfuric acid, propylene carbonate (PC), $LiClO_4$, chloroform (TCM), toluene, and tetrahydrofuran (THF) used in this study were reagent grade and used as received without further purification. Indium tin oxide (ITO) substrates (1 cm × 4 cm) were ultrasonically cleaned sequentially in acetone, ethanol ,and deionized water for 30 minutes each.

1.2 Preparation of pure WO_3 films

The pure WO_3 film was prepared according to previously reported methods[1, 2]. Briefly, 5 μL of H_2O_2 was mixed with 8 mL of a 0.125 mol/L Na_2WO_4 solution, followed by the addition of 1 mol/L H_2SO_4 to reach a final volume of 10 mL, forming the electrolyte. The electrochemical synthesis of the pure WO_3 film was conducted using a two-electrode system, with the CHI 660E serving as the power source. The film was deposited onto an ITO-coated glass substrate at a constant current density of 2 mA/cm^2 for various durations, employing a Pt sheet as the counter electrode. After solvent evaporation, transparent to yellow films were obtained.

1.3 Preparation of hybrid WO_3/PBI films

The PBI derivative, PBI-CB, was synthesized following the method previously reported[3]. A stock solution of PBI-CB (1.0×10^{-3} mol/L) was prepared by dissolving an appropriate amount of PBI-CB in chloroform. The stock solution was then drop-coated onto pristine WO_3 films and air-dried at ambient temperature. Subsequently, hybrid WO_3/PBI films were obtained by annealing the dried films at various temperatures for 2 h under vacuum conditions. This process yielded hybrid WO_3/PBI films with varying compositions.

1.4 measurements

The morphologies of the films were characterized using a field emission scanning electron microscope (SEM, Hitachi SU8220, 5 kV). The structural properties of the films were analyzed using X-Ray Diffraction (XRD, D8 Advance) measurements for 2θ diffraction angle scans of 10°-

55°. The electrochemical behavior of hybrid WO_3/PBI films deposited on ITO substrate was investigated using cyclic voltammetry (CV). Experiments were conducted in a three-electrode system, with the WO_3/PBI coated ITO serving as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. CV curves were recorded by scanning from 1.0 V to -1.3 V at a scan rate of 50 mV/s. Spectroelectrochemical measurements were performed using a CHI-660E electrochemical workstation (Shanghai Chenhua instrument Co. Ltd.) coupled with a fiber optic spectrometer (QEpro, Ocean Optics). All measurements were conducted under quiescent condition in a supporting electrolyte of 1 mol/L $LiClO_4$ dissolved in a propylene carbonate/acetonitrile mixture at room temperature.

2. Chemical and optimized structures of PBI-CB

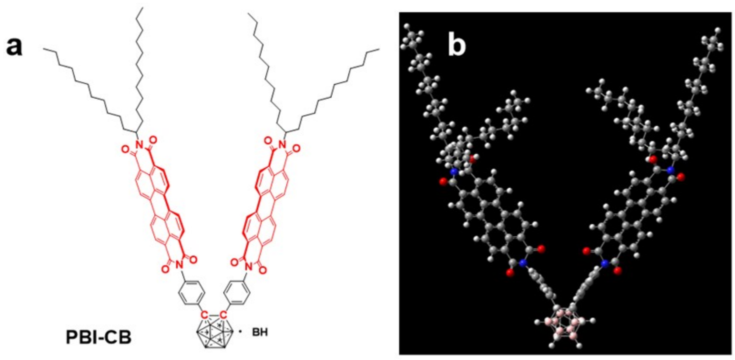

Figure S1. Chemical and optimized structures of PBI-CB (a, b)

3. Electrodeposition process of WO_3 films with different deposition time

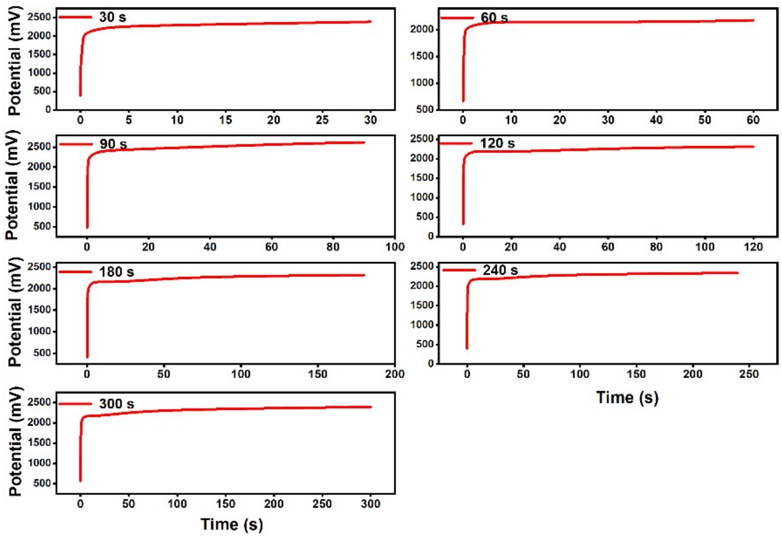

Figure S2. Potential recorded during the electrodeposition process of WO_3 films with different deposition time.

4. Transmittance spectra of the WO_3 films with different deposition time

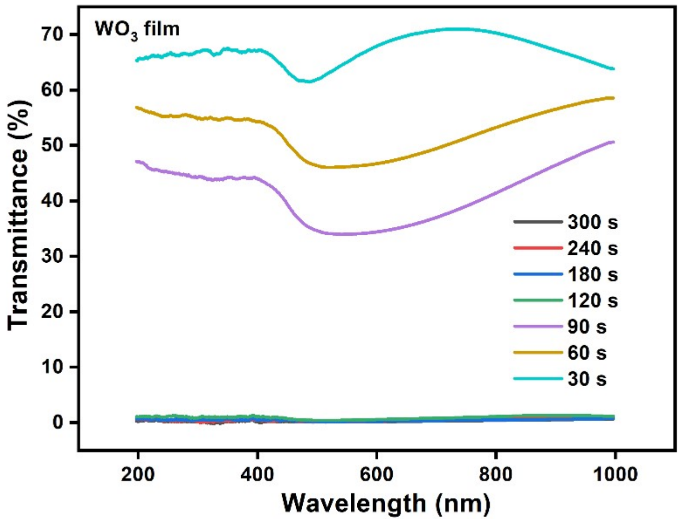

Figure S3. Transmittance spectra of the WO_3 films prepared with different electrodeposition time.

5. The levels of all factors for orthogonal design experiment

Table S1. The levels of all factors for orthogonal design experiment

Factor level	Deposition time (WO_3, s)	Volume (PBI-CB, μL)	Curing temperature (℃)
1	30	30	initial
2	60	60	100
3	90	90	120

6. Transmittance spectra of the hybrid PBI/WO_3 film in the orthogonal design

experiment of the orthogonal table

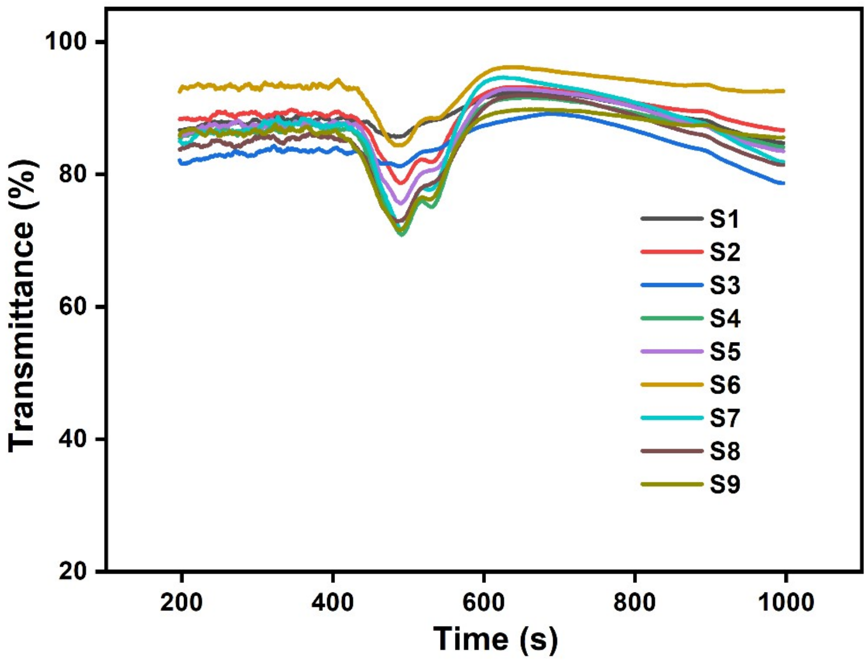

Figure S4. Transmittance spectra of the hybrid PBI/WO_3 film of the orthogonal table in the electrolyte with a concentration of 0.2 mol/L.

7. CV curves of the hybrid PBI/WO_3 film in the orthogonal table

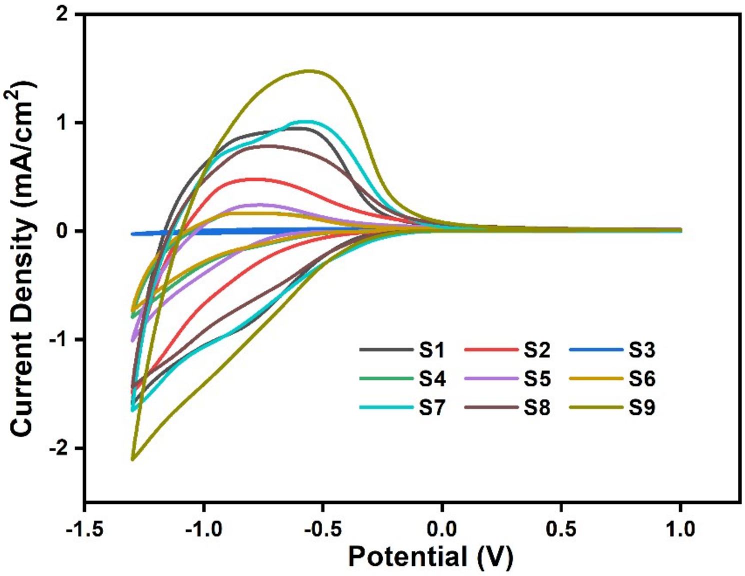

Figure S5. CV curves of the hybrid PBI/WO_3 film in the orthogonal table.

8. CV curves of the hybrid PBI/WO_3 film in the orthogonal table

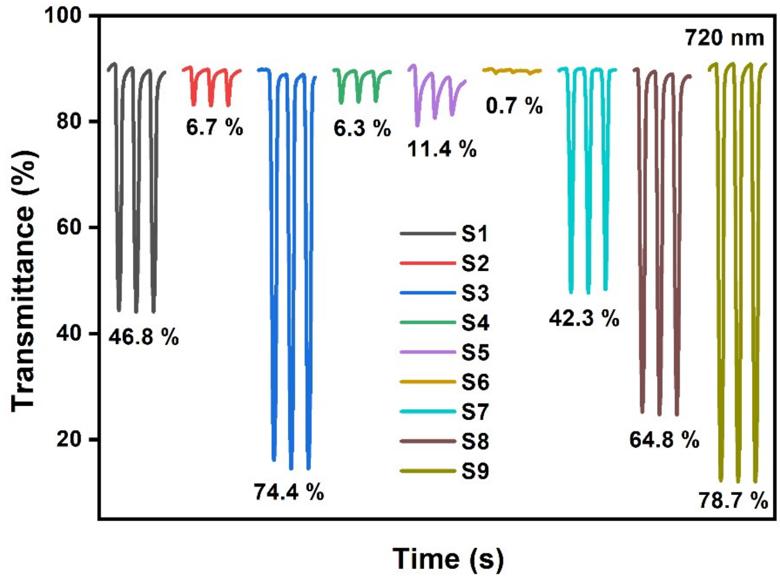

Figure S6. The corresponding transmittance-time spectra for hybrid PBI/WO_3 film of the orthogonal table plans in the CV process.

9. The trend chart between the levels of factors and the mean values

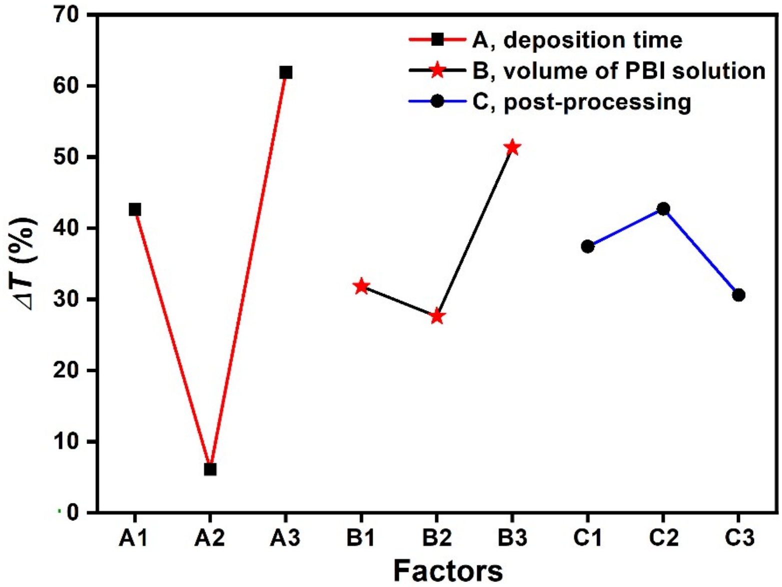

Figure S7. The trend chart between the levels of factors and the mean values.

10. FTIR spectra of the pure WO_3 and WO_3/PBI hybrid films on ITO substrate

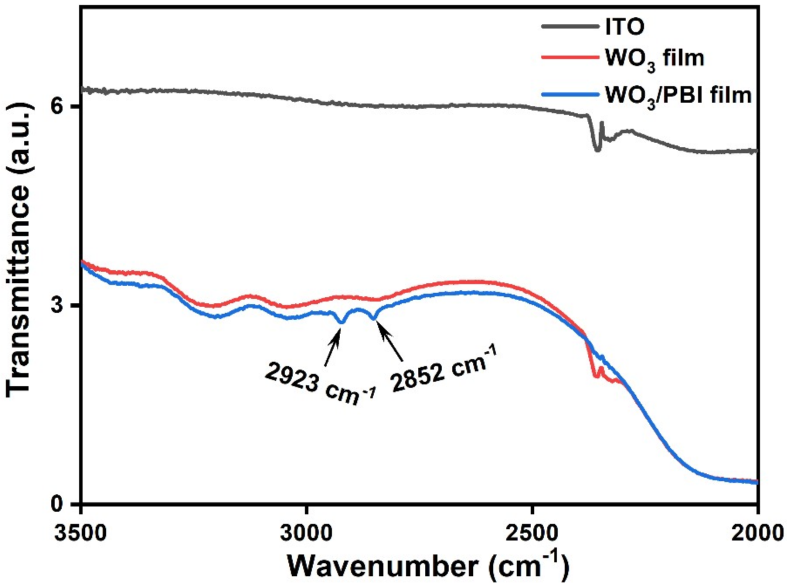

Figure S8. FTIR spectra of the pure WO_3 and WO_3/PBI hybrid films on ITO substrate

11. XRD patterns of the pure WO_3 and WO_3/PBI hybrid films on ITO substrate

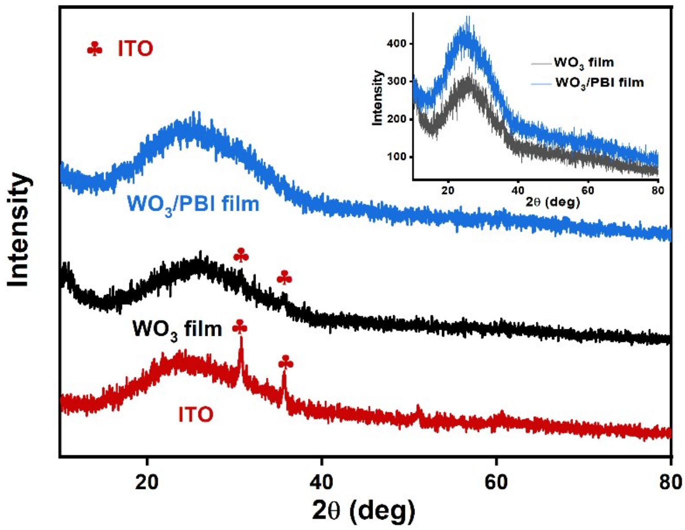

Figure S9. XRD patterns of the ITO substrate, WO_3 film and WO_3/PBI hybrid film.

12. Transmittance modulation of the WO_3 and WO_3/PBI hybrid films under

multi-step potential

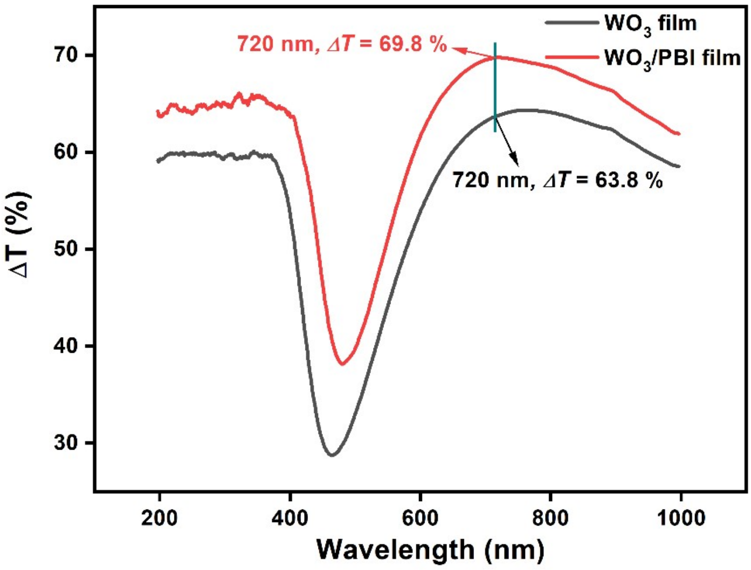

Figure S10. Transmittance modulation of the WO_3 film and WO_3/PBI hybrid film under the multi-step potential of 1.0 V (30 s) and -1.3 V (30 s) in 0.2 mol/L PC/$LiClO_4$ electrolyte.

13. Switching speed of the WO_3 and WO_3/PBI hybrid films under multi-step

potential

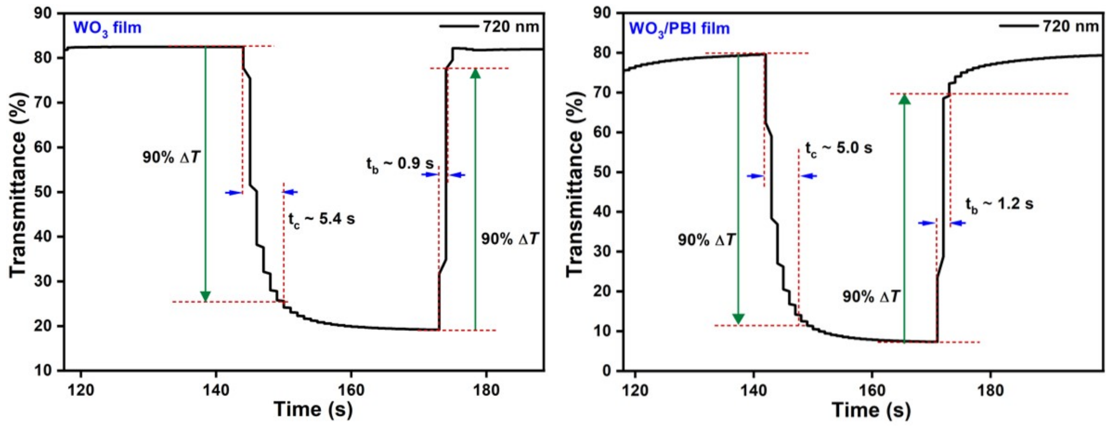

Figure S11. switching speed of the WO_3 film and WO_3/PBI hybrid film under the multi-step potential of 1.0 V (30 s) and -1.3 V (30 s) in 0.2 mol/L PC/$LiClO_4$ electrolyte.

References

[1] Hassab S, Padilla J. Using WO_3 as a transparent, optically-passive counter electrode in an unbalanced electrochromic configuration. *Electrochemistry Communications*, **2016**, 72, 87.

[2] Yang B, Barnes P R F, Bertram W, et al. Strong photoresponse of nanostructured tungsten trioxide films prepared via a sol-gel route. *J. Mater. Chem.*, **2007**,17, 2722.

[3] Liu, K.; Shang, C. D.; Wang, Z. L.; Qi, Y. Y.; Miao, R.; Liu, K. Q.; Liu, T. H.; Fang, Y. Non-Contact Identification and Differentiation of Illicit Drugs using Fluorescent Films, *Nat. Commun.* **2018**, 1, 1695.