

## Supporting Information

### **High-Performance Multifunctional Three-Electrode Electrochromic Device Based on a Zn Auxiliary Electrode**

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### 1.The area capacity of TRECD at different scan rates

As shown in the Fig. S1, the area capacity of TRECD is 10.38 mF/cm<sup>2</sup> at a scan rate of 10 mV/s, and 8.07 mF/cm<sup>2</sup> at a scan rate of 100 mV/s.

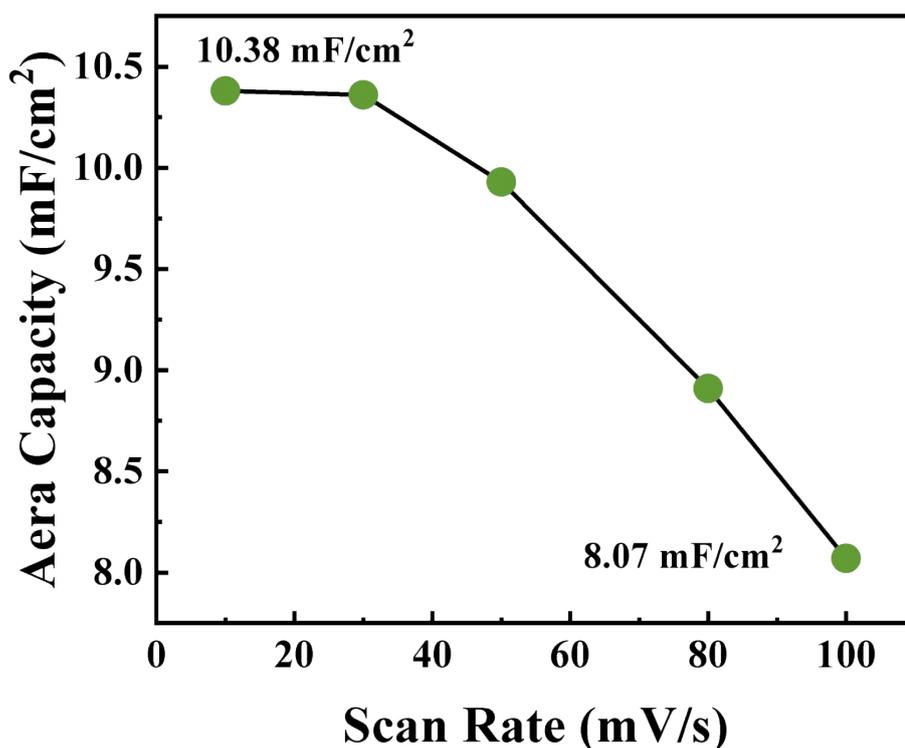


Fig. S1. The area capacity of TRECD at different scan rates

### 2.The coloration efficiency of TECD and TRECD

The coloration efficiency is defined as the change in optical density ( $\Delta OD$ ) at a specific wavelength caused by the charge injected per unit area, and can be calculated using the following equation:

$$CE = \Delta OD / Q = \log\left(\frac{T_b}{T_c}\right) / Q$$

where Q represents the inserted and extracted charge per unit area,  $T_b$  represents the transmittance of the bleached state,  $T_c$  represents the colored state, and  $\Delta OD = \log(T_b/T_c)$  represents the change in optical density. CE is a practical parameter that can be used to estimate the energy conversion efficiency of electrochromic device.

As shown in the Fig. S2, the coloration efficiency of TECD is  $76.24 \text{ cm}^2/\text{C}$  (Fig. S2a), while that of TRECD is  $95.32 \text{ cm}^2/\text{C}$  (Fig. S2b).

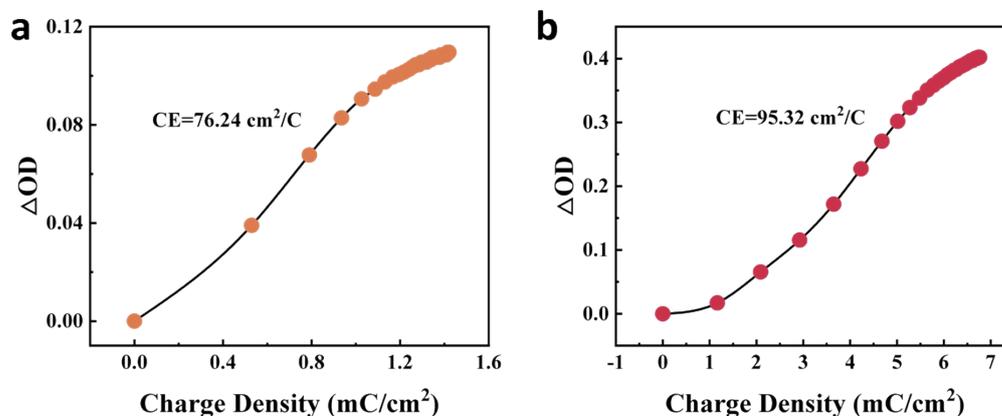


Fig. S2. (a) The coloration efficiency of TECD and (b) TRECD.

### 3. CV curves of single WO<sub>3</sub> and PANI electrodes with Zn as the reference electrode

Fig. S3a and S3b show the comparison plots of CV curves of WO<sub>3</sub> and PANI electrodes, respectively, with Zn serving as the reference electrode at a scan rate of 10 mV/s. The areal capacitance of the WO<sub>3</sub> electrode is  $6.65 \text{ mF}/\text{cm}^2$ , and that of the PANI electrode is  $18.1 \text{ mF}/\text{cm}^2$ .

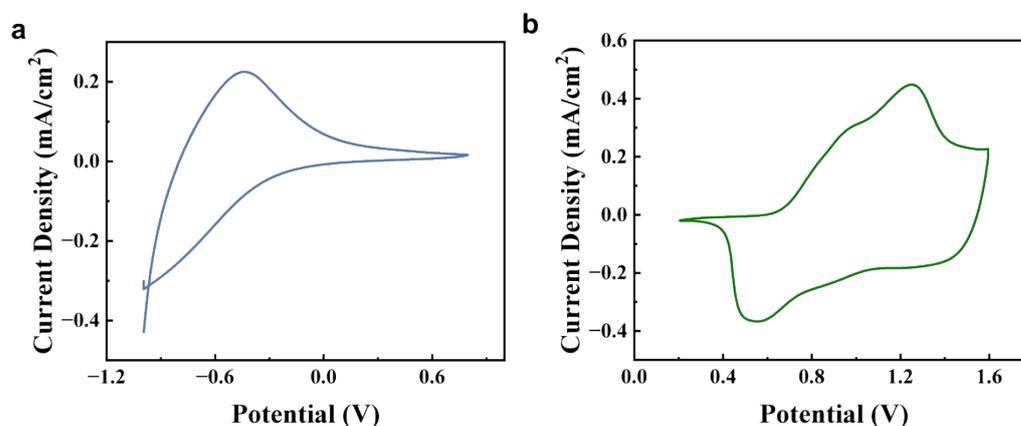


Fig. S3. CV curves of single WO<sub>3</sub> (a) and PANI (b) electrodes with Zn as the reference electrode at the scan rate of 10 mV/s

### 4. XPS spectra of Zn content in the WO<sub>3</sub> electrode before and after the reaction

As shown in Fig. S4, there were no obvious characteristic peaks observed in the original WO<sub>3</sub> and PANI electrodes. After 100 cycles of CV testing at a scan rate of 100 mV/s, distinct Zn 2p characteristic peaks appeared in the XPS spectrum of the WO<sub>3</sub> electrode in the colored state, whereas these peaks disappeared in the bleached state.

Since the electrolyte system in this experiment originally contained no  $Zn^{2+}$ , this phenomenon indicates that the  $Zn^{2+}$  precipitated from the zinc auxiliary electrode participated in the electrochromic reaction process.

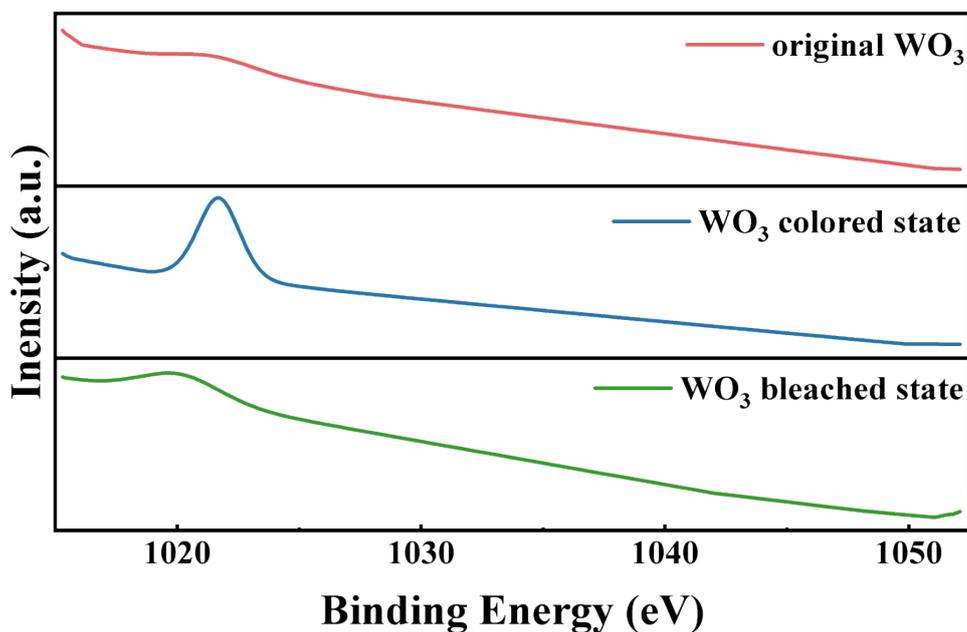


Fig. S4. XPS spectra of Zn content in the original WO<sub>3</sub> electrode (upper plot), before reaction (middle plot) and after the reaction (bottom plot).

### 5. Coloration efficiency of TRECD ( Zn electrode in an open-circuit state)

As shown in the Fig. S5, the coloration efficiency of Zn-TECD is  $67.53 \text{ cm}^2/\text{C}$ , and TRECD (Zn electrode in an open-circuit state) is  $74.79 \text{ cm}^2/\text{C}$ .

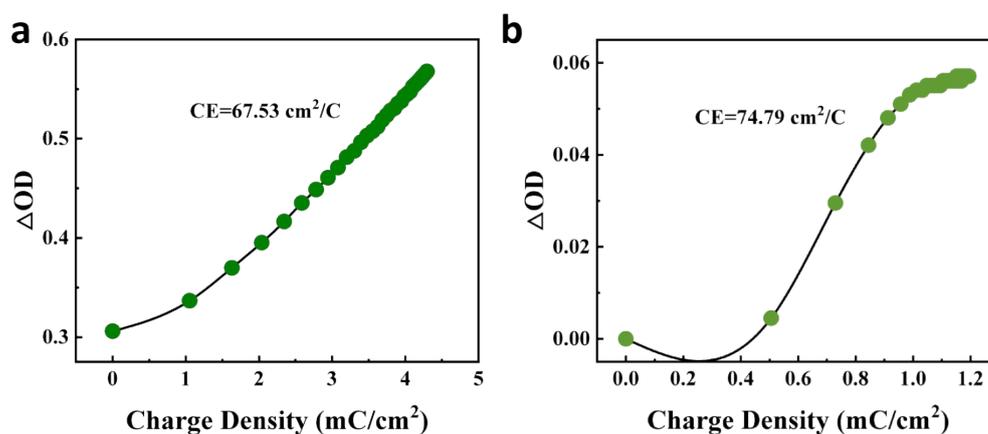


Fig. S5. Coloration efficiency of (a) Zn-TECD and (b) TRECD (Zn electrode in an open-circuit state).

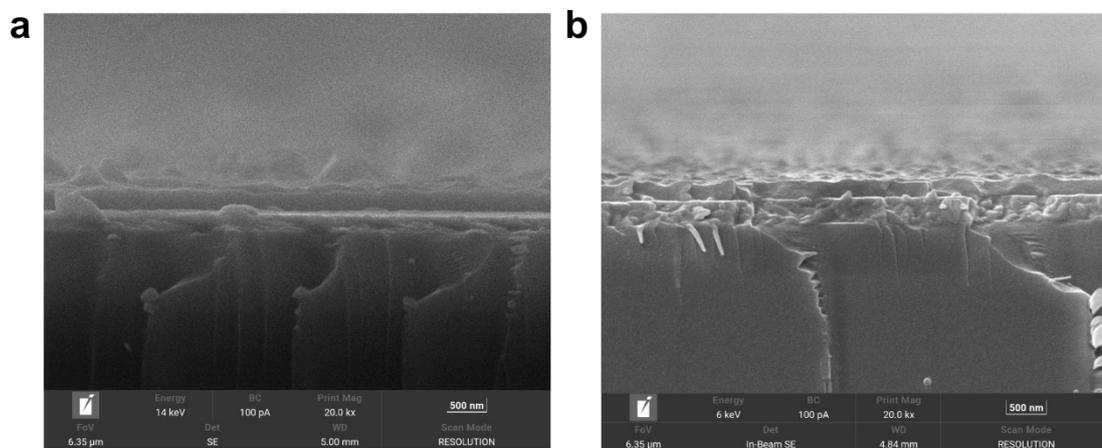
### 6. Photograph of the 0.1 M TRECD device under different voltages

As shown in the Fig. S6, the photograph of the 0.1 M TRECD device under different voltages, specifically, the device is transparent at a voltage of 0.2 V, pale yellow at 0.6 V, pale green at 0.8 V, dark green at 1.2 V, dark blue at 1.4 V, and opaque at 1.6 V, demonstrating excellent electrochromic performance.



**Fig. S6.** Photograph of the 0.1 M TRECD device under different voltages

### 7. Cross-sectional SEM images of the PANI and WO<sub>3</sub> films



**Fig. S7.** Cross-sectional SEM images of the (a)PANI film and (b)WO<sub>3</sub> film