Supplementary Information

Correlation of the Electrochromic Absorption with the $W^{6+/5+}$ Energetic States in WO_3

Huaqing Rong[a] *and Yimeng Ma**[a]

College of Chemistry and Chemical Engineering, Donghua University, Shanghai, 201620, China

AUTHOR INFORMATION

Corresponding Author

*Correspondence: yimeng.ma@dhu.edu.cn

1 Experimental section

1.1. Materials

Fluorinated tin oxide conductive glass (FTO, sheet resistance <15 $\Omega\cdot sq^{-1}$, transmittance >83%) was purchased from Zhuhai Kaiwo Optoelectronic Technology. Sodium tungstate dihydrate was purchased from Mercury, while hydrogen peroxide and nitric acid were obtained from Sinopharm Reagent. All electrolytes were prepared using deionized water (18.25 MΩ·cm, YL400BU, Ereeran).

1.2. Fabrication of WO_3 electrodes

This WO_3 film was fabricated using the previously reported electrodeposition method[1, 2].

FTO pretreatment: First clean the FTO substrate (3×2.5 cm) surface with deionized water containing glass cleaner. Then ultrasonically clean it in ethanol (95%) for 30 minutes. After cleaning and drying, place the FTO substrate in a muffle furnace (Nabertherm, LE 6/11/R7) and calcine it at 500°C for 3 hours to remove organic impurities.

Fabrication of WO_3 electrodes: Sodium tungstate dihydrate (0.025 mol) was dissolved in deionized water (50 mL). After stirring continuously until complete dissolution, hydrogen peroxide (0.03 mol) was added to the solution. The pH of the mixture was adjusted to 1.3 using nitric acid. After thorough mixing, the precursor solution was obtained. A three-electrode system was employed with a platinum mesh as the counter electrode, fluorine-doped conductive glass (FTO) as the working electrode and a Ag/AgCl in saturated KCl solution electrode as the reference electrode. A potential of -0.45 $V_{Ag/AgCl}$ was applied to the three-electrode system. Deposition was carried out for 10 minutes at this potential to obtain the required sample. Finally, the surface was rinsed with deionized water to remove excess precursor solution, and the sample was air-dried at room temperature to yield the WO_3 electrode film. In order to tune the colour of the WO_3 electrode, a -0.5 $V_{Ag/AgCl}$ or 1 $V_{Ag/AgCl}$ was applied to the WO_3 electrode to obtain a blue or a pale yellow transparent colour of the electrode, respectively. These colours were able to last over 24 hours after being tried in air without electrochemical connections.

1.3. Materials characterization

The X-ray diffraction data of the WO_3 and FTO were recorded using a Bruker D8 Advance X-ray diffractometer at a tube voltage of 40 kV with Cu Kα radiation (λ = 1.5405 Å). Surface morphology, cross-sectional morphology images of WO_3 and FTO were obtained using a field emission scanning electron microscopy (S-4800, Hitachi). The ground state optical absorption of the WO_3 electrode was recorded using UV-vis spectrophotometer (UV-1099i, Shimadzu). Escalab 250 X-ray photoelectron spectrometer was employed to characterize the oxidation states and bonding energies using Al as the exciting source and the X-ray photoelectron spectroscopy (XPS) data were corrected based on the C 1s peak at 284.8 eV.

1.4. Electrochemical measurements

For all electrochemical tests, a custom-made transparent quartz reactor was employed, with WO_3 (2.5 cm × 2 cm) serving as the working electrode, a platinum mesh (1.5 cm × 1.5 cm) as the counter electrode, and the Ag/AgCl in saturated KCl solution as the reference electrode. Measurements were conducted in 0.1 M H_2SO_4 (pH = 1) electrolyte solution. In the tests described in this paper, all applied voltages are expressed relative to the Ag/AgCl electrode; any conversions are indicated. The Nerst equation is used to convert the potential relative to the Ag/AgCl electrode (reference electrode) ($V_{Ag/AgCl}$) to the potential relative to the reversible hydrogen electrode (V_{RHE}), as shown in formula S1:

$$V_{(RHE)} = V_{(Ag/AgCl)} + pH \times 0.0591 + 0.197 \quad \text{(S1)}$$

In this paper, pH = 1; $V_{(Ag/AgCl)}$ is the voltage applied in the experiment relative to the Ag/AgCl reference electrode.

The relationship between peak current (i) and scan rate (v) can be described by the following equation:

$$i = av^b \quad \text{(S2)}$$

$$\log i = b\log v + \log a \quad \text{(S3)}$$

In the above equation, i is the peak current (mA); v is the scan rate (mV/s); a and b are constants. A value of b = 0.5 indicates diffusion-controlled battery behavior, while a value of b = 1 indicates surface-controlled capacitive behavior.

The relationship between electrode current and voltage was recorded at different scan rates using cyclic voltammetry scanning, with scan rates of 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1}, and 100 mV s^{-1}.

1.5. Voltage-induced absorption spectroscopy and operando spectroelectrochemical technique

Voltage-induced absorption (VIA) spectroscopy and operando spectroelectrochemical (SEC) technique were employed to detect transient changes in active species in the WO_3 electrodes. A 150 W tungsten lamp served as the probe light source, with a monochromator (TLS15-T150A, Zolix Instruments) to control the light wavelength. Long-pass filters (Hengyang Optics) and a band-pass filter (Rayan Optics) were then selected for the desired probe wavelength to block parasitic light. The VIA data were monitored using a homemade photodetector (Hamamatsu S5973) and recorded with a data acquisition device (USB-6361) and an oscilloscope (MDO34, Tektronix). The VIA data in this paper were obtained at a detection wavelength of 600 nm. To evaluate the wavelength dependence of the relaxation kinetics, additional VIA analyses were also conducted at 500 nm and 755 nm, and the time required for the maximum absorbance to decay by 50% at these two wavelengths was compared with that at 600 nm. The SEC data were collected using an Ocean Optics spectrometer (QE65pro) during the step potential measurements. All SEC spectra as a function of applied potential were obtained by subtracting the reference spectrum measured at -0.24 V_{RHE}.

2 Supplementary Figures

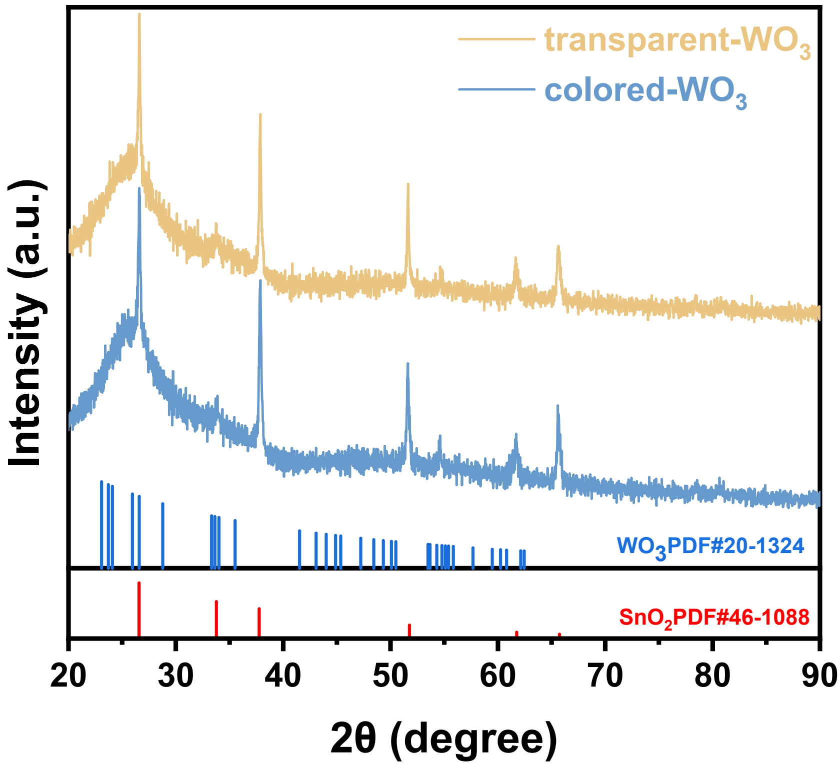

Fig S1. XRD data of the transparent WO_3 (yellow) and blue WO_3 (blue). The standard XRD pattern of WO_3 (ICDD 20-1324) and FTO (ICDD 46-1088) is used for reference.

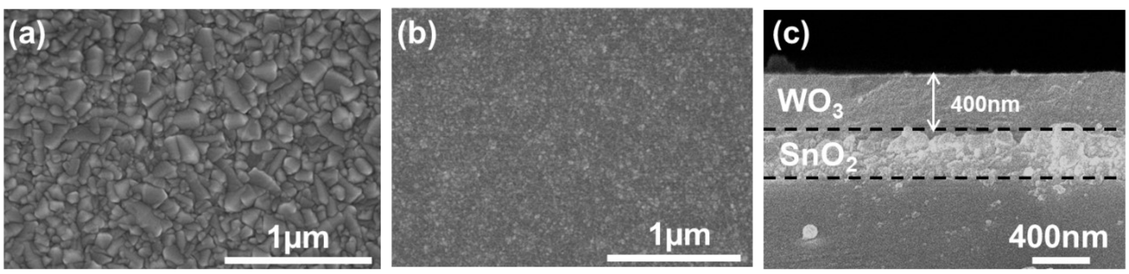

Fig S2. SEC images of (a) Top view of FTO. (b) Top view of WO_3 electrode. (c) Cross-sectional view of the WO_3 electrode.

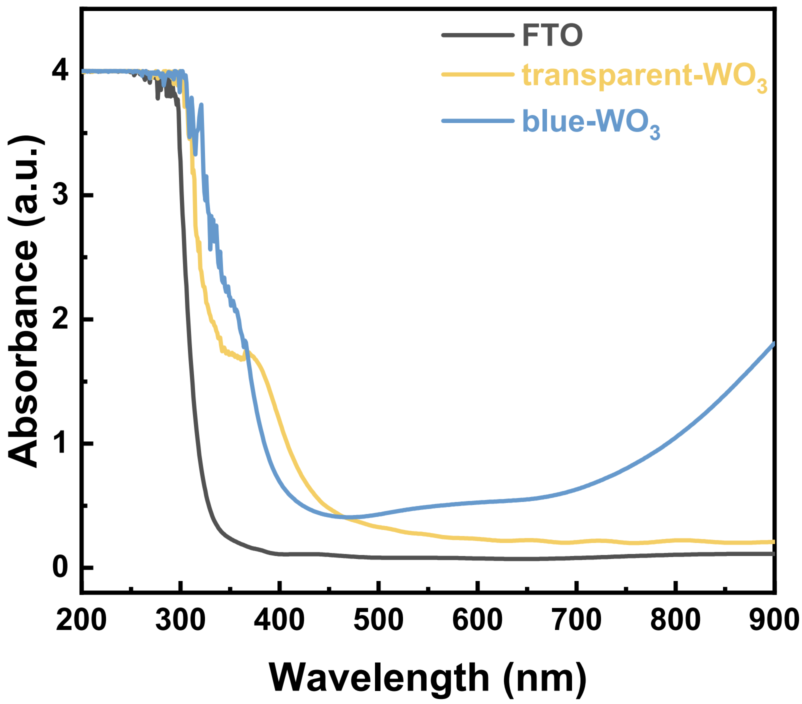

Fig S3. UV-vis absorption spectra of the transparent WO_3 (yellow) electrode, blue WO_3 (blue) electrode and FTO substrate (black).

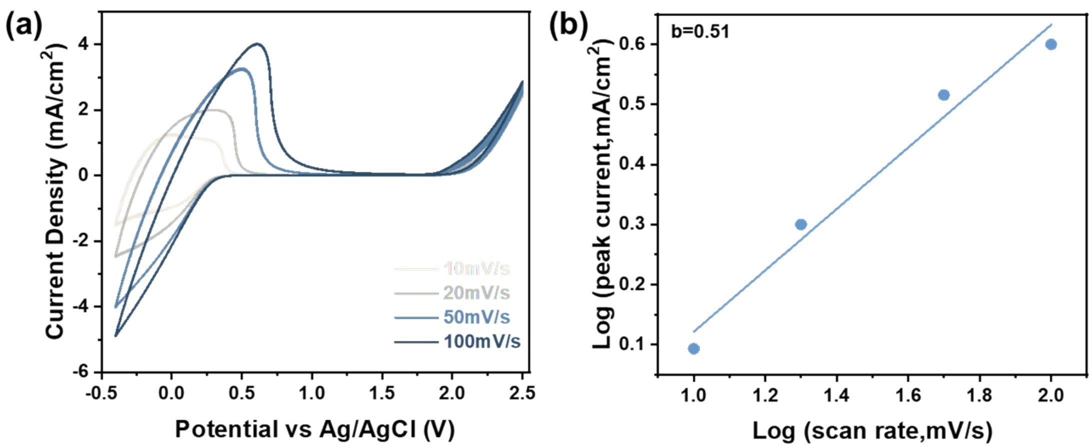

Fig S4. (a) Cyclic voltammetry curves of WO_3 measured as a function of scan rate. (b) Log (i) as a function of log (v) for the WO_3.

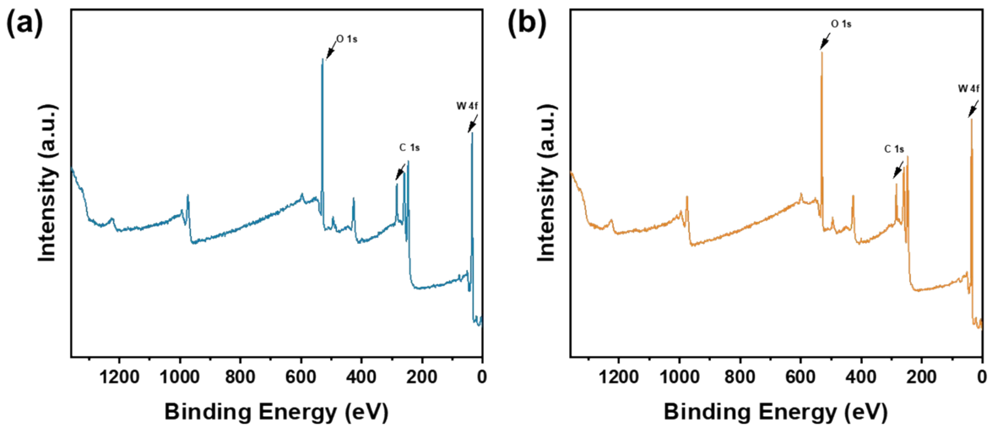

Fig S5. X-ray photoelectron spectrum of WO_3 electrodes: (a) Blue WO_3. (b) Transparent WO_3.

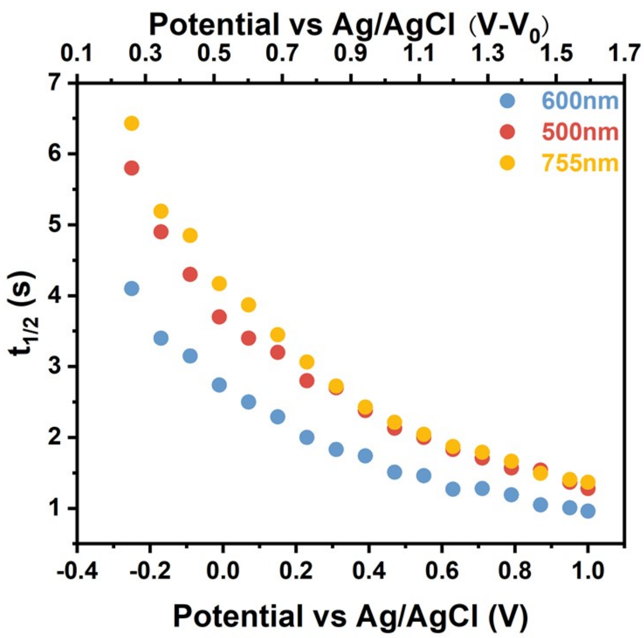

Fig S6. Half the time of voltage induced transient decay in VIA tested at three wavelengths (500nm, 600nm, 755nm) using WO_3 electrode.

Reference

1. E. A. Meulenkamp, *Journal of The Electrochemical Society*, 1997, DOI: 10.1149/1.1837657.
2. K. Ç. Demir, *Ceramics International*, 2020, **46**, 4358-4364.