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Supplementary Information

Uncovering Phase Transformation, Morphological Evolution, and Nanoscale Color Heterogeneity in Tungsten Oxide Electrochromic Materials

Anyang Hu[1], Zhisen Jiang[2], Chunguang Kuai[1], Scott McGuigan[1], Dennis Nordlund[2], Yijin Liu[2], Feng Lin[1]*

1 Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA.

2 Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA.

*E-mail: fenglin@vt.edu

Supplementary Figures

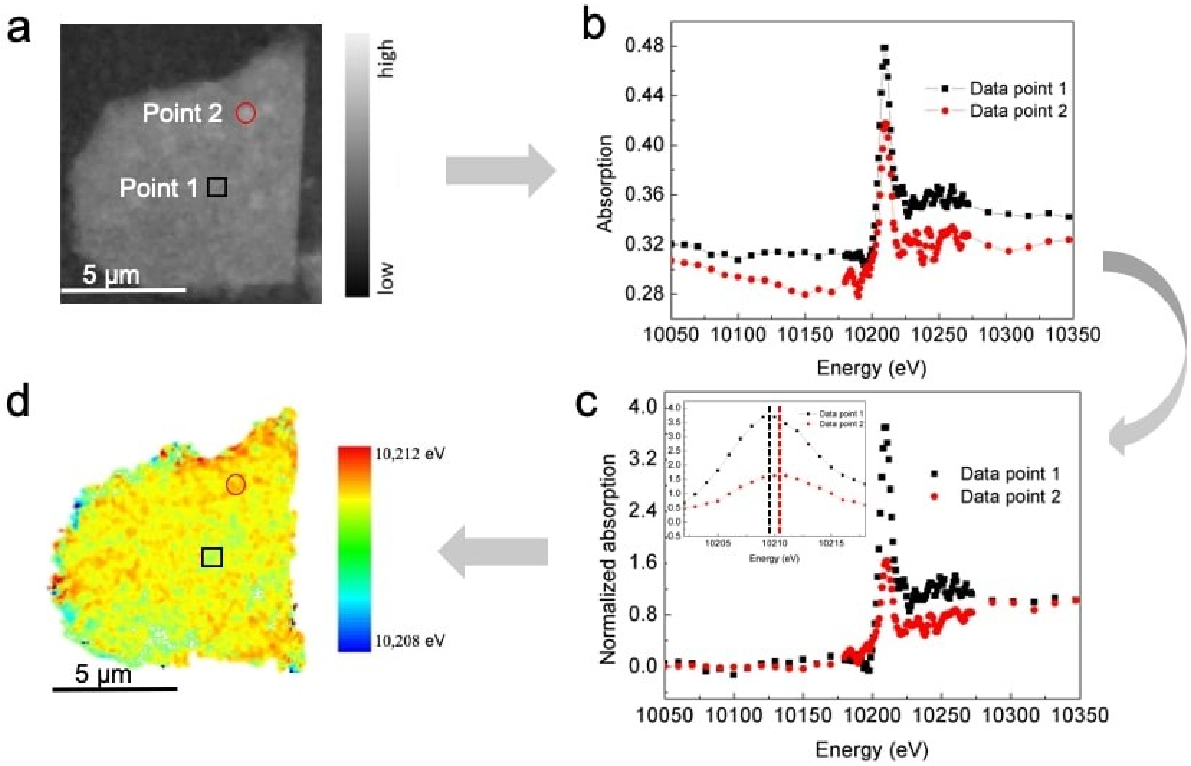

Fig. S1 Explanation of the TXM data normalization protocol. (a) An absorption image of a scratched WO_3 film sample (the one after 600 CV cycles in Fig. 3d) at a specific energy, where the X-ray absorption intensity is indicated by the gradient bar on the right. Two domains with different states of charge were selected to explain the normalization protocol. (b) XANES spectra of the two selected domains before the normalization process. The two spectra marked in (a) exhibit a difference in terms of rising edge energy intensity, suggesting a difference in the absolute amount of W within these two domains (due to the locally different concentrations of W in WO_3 film or different sample thickness). (c) XANES spectra of the two selected domains after the normalization procedure, the pre-edge intensity of the spectra is set to be zero and the post-edge intensity is set to be one. This protocol is applied to normalize all XANES spectra of all pixels of all of the samples presented in this work. The white-line (peak) energy is used to highlight the change of local valence state of W. Two dash lines of the inserted figure indicate the peak energy position of two data points (the black line is for data point 1 and the red line is for data point 2). Data point 2 is shifted to the right relative to data point 1, which means that the local valence state of data point 2 is higher than data point 1. (d) 2D mapping of the local W valence state after the normalization process. Compared with data point 1, data point 2 has a higher valence state and its color is closer to red.

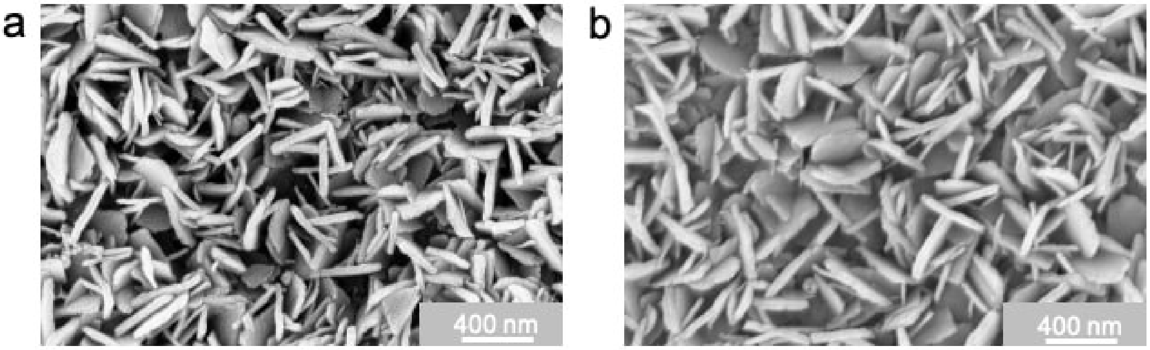

Fig. S2 These newly formed nanoflakes stably exist on the FTO substrate. a) the typical nanoflake formation after 3,000 CV cycles at 60 mV/s with -0.2V-0.6V vs. SCE. b) the nanoflakes after using a 6x20 mm magnetic stirrer to stir the same nanoflake film for 20 hours at 100 rpm. The WO_3 film has a thickness of ~1,000 nm. After long-term stirring, these nanoflakes do not disappear significantly, and the marginal disturbance of the electrolyte caused by stirring is even more severe than that in the flow cell. Therefore, the possibility of these newly formed nanoflakes flowing into the electrolyte is quite low, the main reason for the less formation of nanoflakes is the suppressed redeposition process with a lower concentration of dissolved W species by flowing the electrolyte.

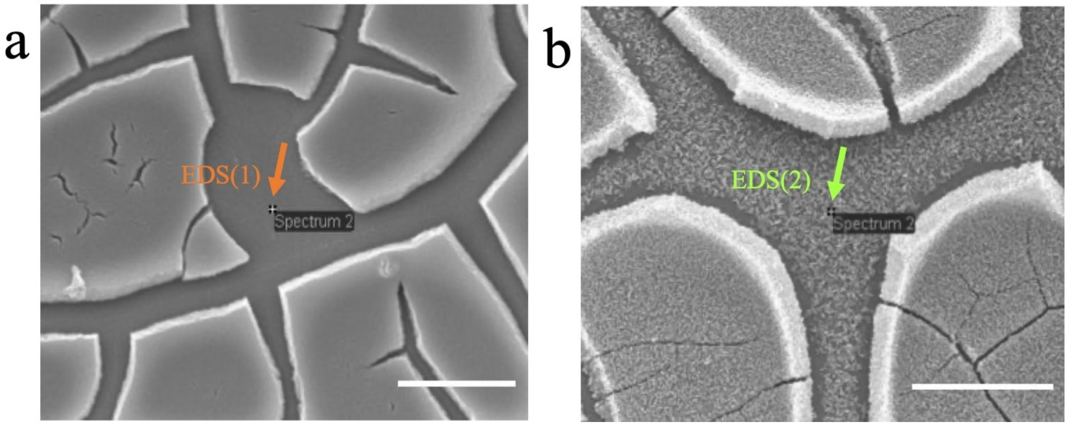

Fig. S3 SEM/EDS of the cracked area of WO_3 film (thickness about 1,000nm) before and after 3,000 CV cycles. (a) The SEM image and the selected cracked area for EDS before electrochemical cycling. (b) The SEM image and the selected cracked area for EDS after 3,000 CV cycles. Scale bars:10 μm.

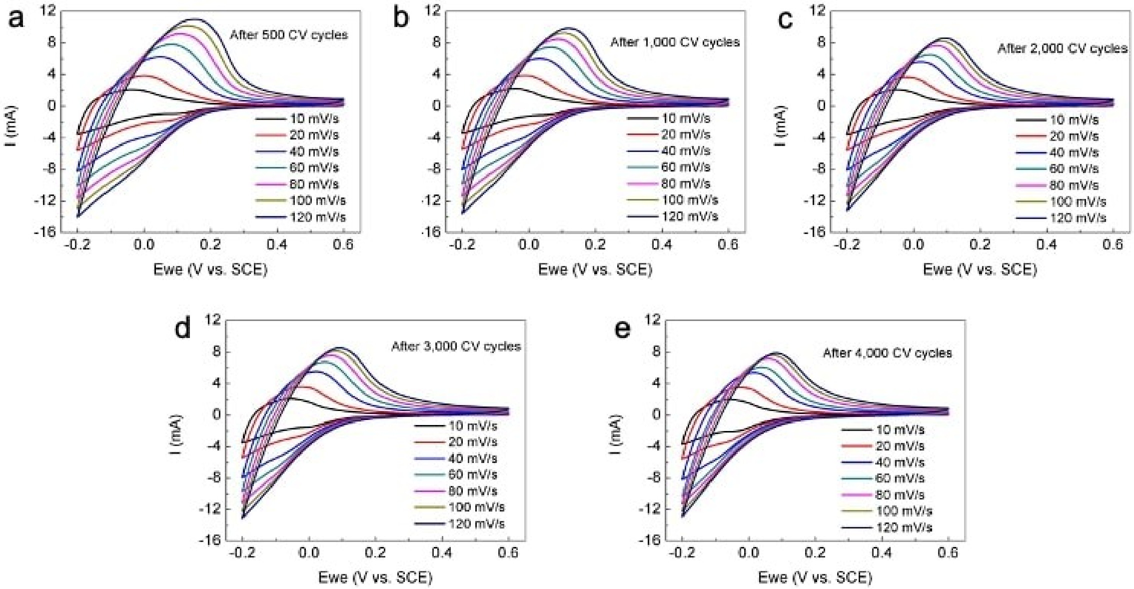

Fig. S4 The CV curves with various scan rates after different number of electrochemical cycling. The various scan rates including 10, 20, 40, 60, 80, 100, and 120 mV/s are used between long-term CV cycling to calculate the apparent diffusion coefficients. The long-term CV cycling is performed in 0.5M H_2SO_4(aq.) at 60 mV/s with -0.2V-0.6V vs. SCE. (a) after 500 CV cycles, (b) after 1,000 CV cycles, (c) after 2,000 CV cycles, (d) after 3,000 CV cycles, and (e) after 4, 000 CV cycles.

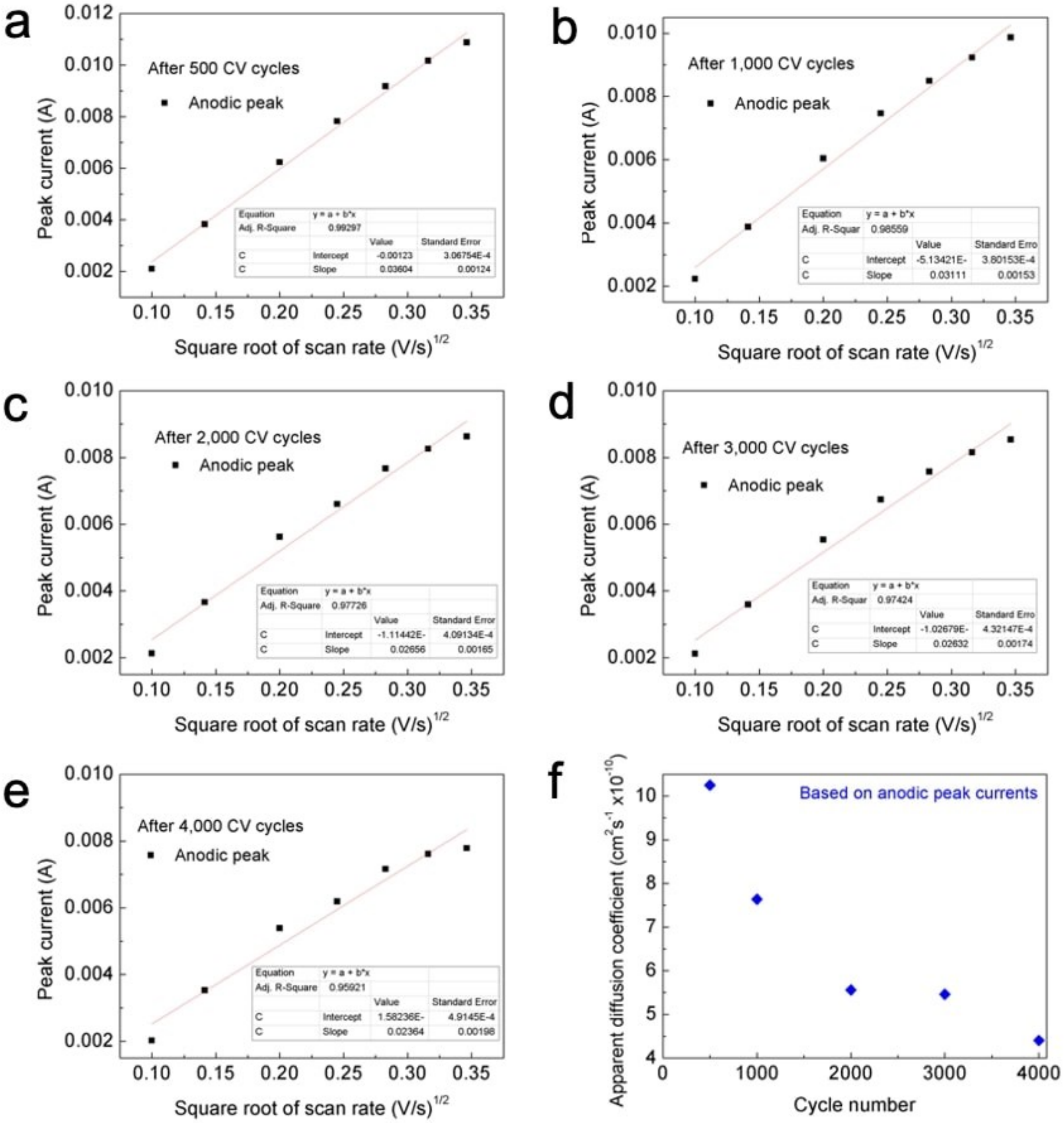

Fig. S5 The evolution of apparent diffusion coefficients during the long-term electrochemical cycling. The calculation of apparent coefficients is based on the Randles–Sevcik equation using various scan rates in CV measurements at room temperature. (a) after 500 CV cycles, (b) after 1,000 CV cycles, (c) after 2,000 CV cycles, (d) after 3,000 CV cycles, and (e) after 4, 000 CV cycles. The various scan rates including 10, 20, 40, 60, 80, 100, and 120 mV/s are used between long-term CV cycling to calculate the apparent diffusion coefficients. The long-term CV cycling is performed in 0.5M H_2SO_4(aq.) at 60 mV/s with -0.2V-0.6V vs. SCE. The linear relationship indicates that the proton intercalation/deintercalation process is diffusion-controlled. The film thickness is ~ 1,000 nm. (f), Calculated apparent diffusion coefficients decrease with the increase of CV cycle numbers based on anodic peak currents.

Randles–Sevcik equation at room temperature (25 °C):

$$i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{0.5}$$

i_p = current maximum in amps

n = number of electrons transferred in the redox event (usually 1)

A = electrode area in cm^2, 4.1875 cm^2

F = Faraday Constant in C mol^{-1}, 96485.3 C mol^{-1}

D = diffusion coefficient in $cm^2\ s^{-1}$

C = concentration in mol/cm^3, 0.001 mol cm^{-3}

ν = scan rate in V s^{-1}

R = Gas constant in J K^{-1} mol^{-1}, 8.3145 J K^{-1} mol^{-1}

T = temperature in K, 298.1 5K

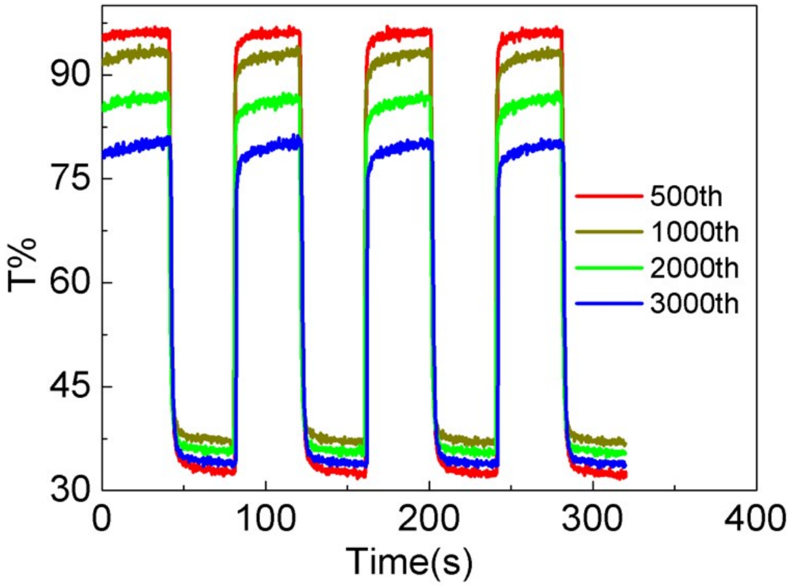

Fig. S6 In-situ transmittance at 600 nm monitoring the evolution of optical modulation during the long-term CV cycling. Chronoamperometry (CA) is performed after the different numbers of CV cycles in the regular cell. The test conditions of CA between the long-term CV cycling are holding 40s at 0.6V vs. SCE.(bleaching) and subsequently holding 40s at -0.2V vs. SCE.(coloration), repeated four times. The optical modulation measured by CA is greater than that measured by CV because the films are maintained for a longer time under both positive and negative potentials.

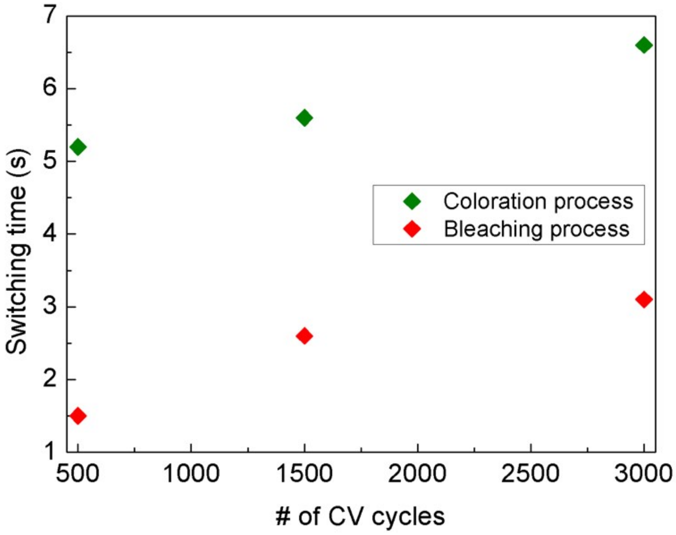

Fig. S7 The evolution of switching time during the long-term CV cycling. Chronoamperometry (CA) is performed after the different numbers of CV cycles in the regular cell. The switching time is calculated as the time needed to achieve 90% of transmittance change.

Supplementary Tables

Table S1 The element atomic ratio of two EDS measurements in Figure S3. The orange color indicates the EDS (1), which is the cracked area before the long-term CV cycling; The green color indicates the EDS (2), which is the cracked area after 3,000 CV cycles. The W atomic ratio is clearly increased after the long-term CV cycling. Sn and Si elements are from the FTO substrate.

Element	at. %	at. %
O	69.7	74.8
Si	14.4	8.8
Sn	15.5	14.0
W	0.4	2.4

Table S2 Based on the XPS data in Figure 3b, the atomic ratios of W^{5+} and W^{6+} are calculated in the WO_3 film before and after 3,000 CV cycles.

Oxidation state of W	Pristine film	Cycled film
+6	90.3%	80.1%
+5	9.7%	19.9%

Table S3 The linear fitting of the square root of scan rates and the anodic peak currents based on Figure S5. Based on the anodic peak current data, the calculated apparent diffusion coefficients decreases along with the increasing number of CV cycles. The cathodic peak is ill-defined so the cathodic peak current is not selected to indicate the trend.

Total # of cycles	Slope (Oxi.)	**D_{anodic} (cm^2s^{-1})**
500	0.036	$1.02*10^{-9}$
1000	0.031	$7.63*10^{-10}$
2000	0.027	$5.56*10^{-10}$
3000	0.026	$5.46*10^{-10}$
4000	0.024	$4.40*10^{-10}$