

## Supporting Information:

# The anodized crystalline WO<sub>3</sub> nanoporous network with enhanced electrochromic properties

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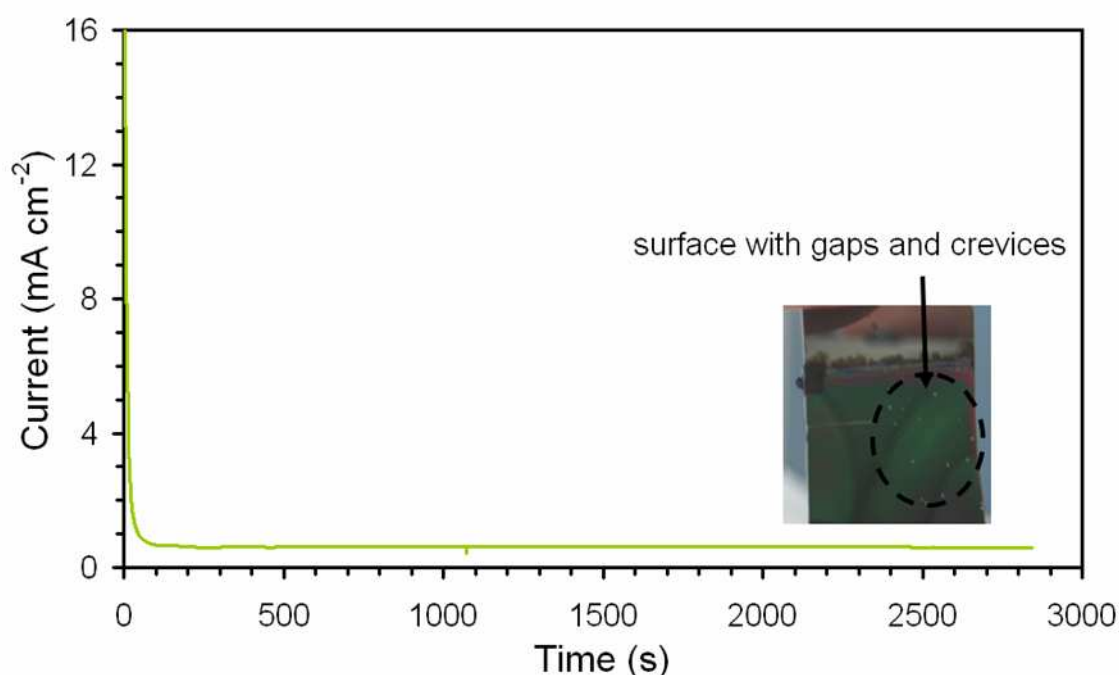
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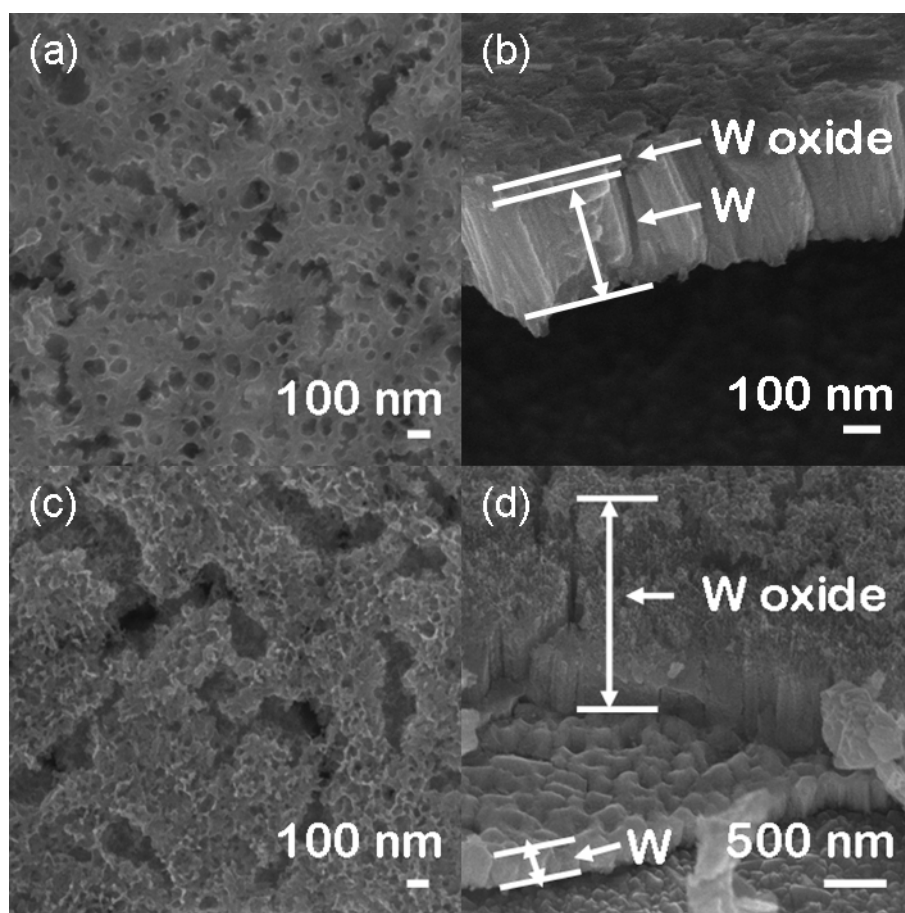
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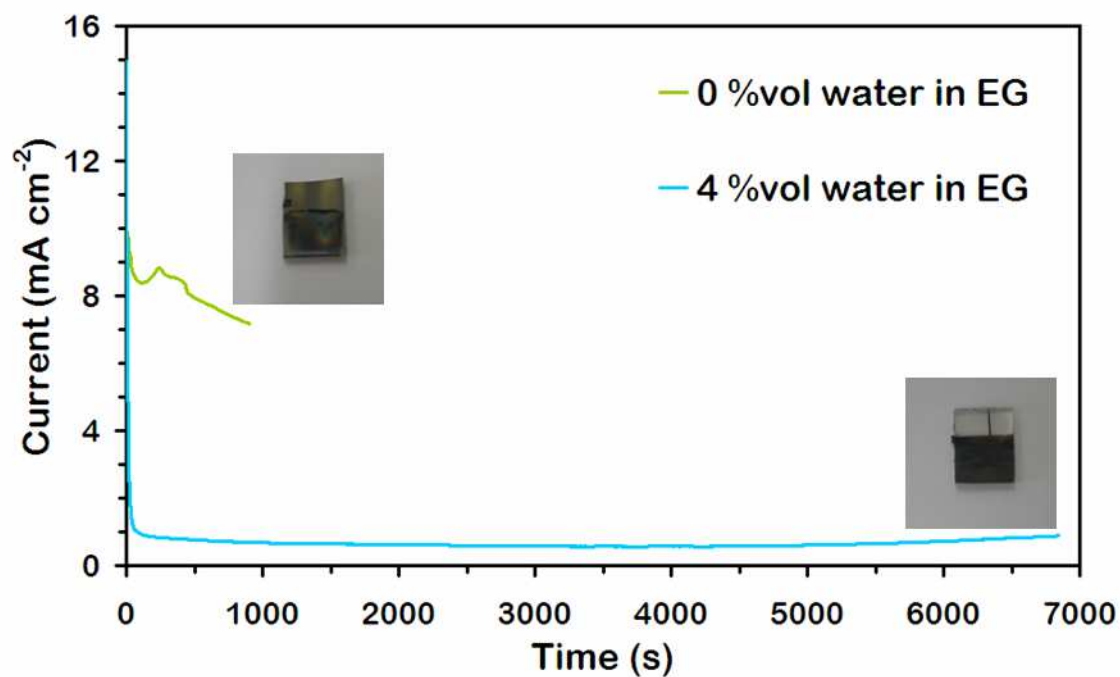
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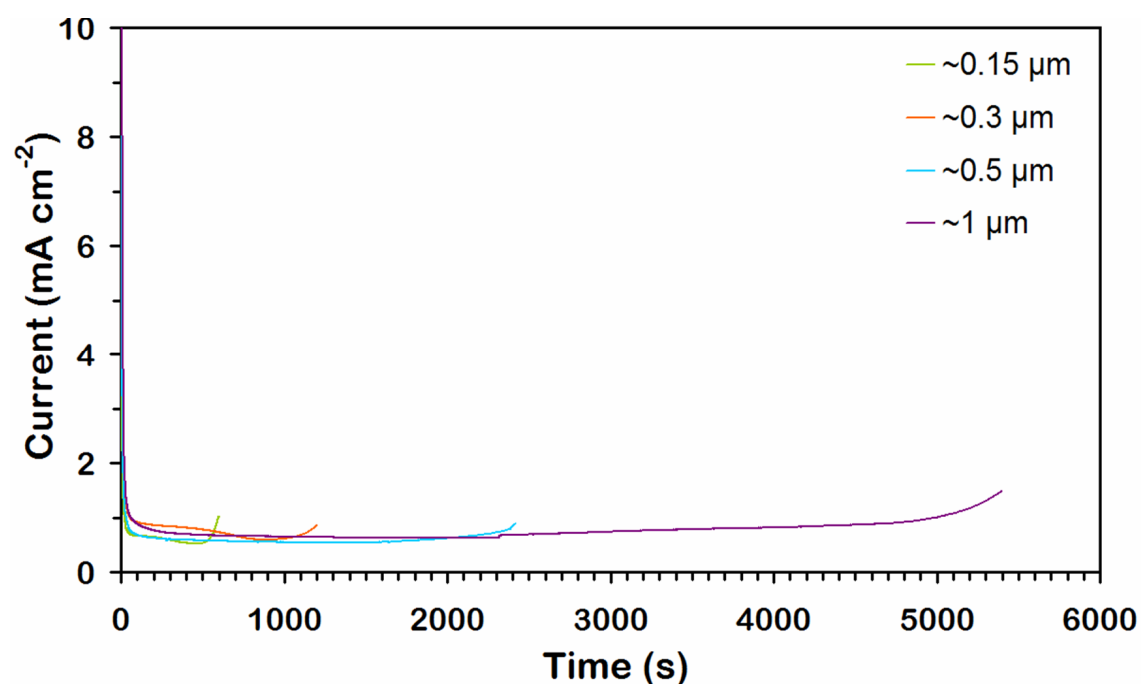
**Fig S1.** Anodization current transient of a ~1  $\mu\text{m}$  thick RF-sputtered W film anodized at 20 V in a 50 ml ethylene glycol electrolyte mixed with 0.5 g NH<sub>4</sub>F and 2 %vol H<sub>2</sub>O for 45 min. The insert is the optical image of this sample with a surface with gaps and crevices.



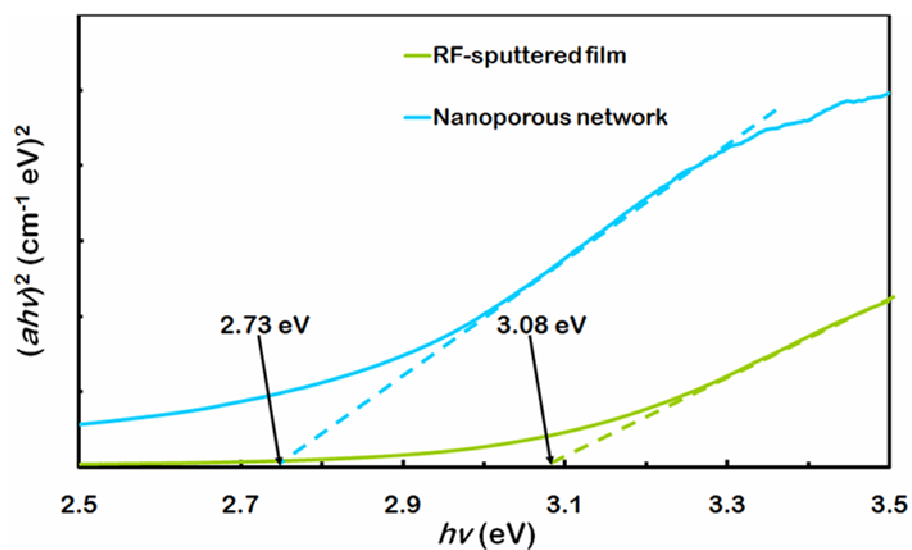
**Fig S2.** Top and cross-sectional SEM images of  $\sim 1 \mu\text{m}$  thick RF-sputtered W films anodized at 10 V in 50 ml ethylene glycol electrolytes mixed with 0.5 g  $\text{NH}_4\text{F}$  and (a), (b) 0 and (c), (d) 4 %vol  $\text{H}_2\text{O}$  for 15 and 120 min, respectively.



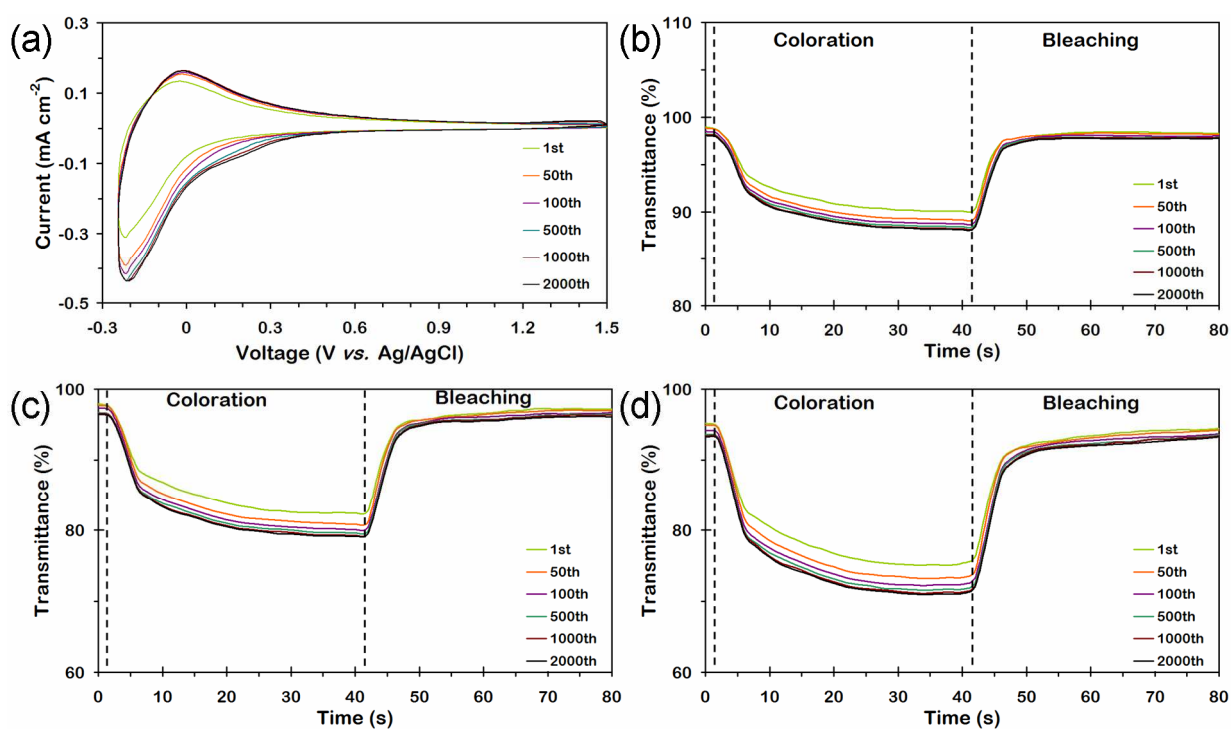
**Fig S3.** Anodization current transient of a  $\sim 1$   $\mu\text{m}$  thick RF-sputtered W film anodized at 10 V in a 50 ml ethylene glycol electrolyte mixed with 0.5 g  $\text{NH}_4\text{F}$  and 0 (green line) or 4 %vol  $\text{H}_2\text{O}$  (blue line) for 15 and 120 min, respectively. The inserts are the optical images of the corresponding samples.



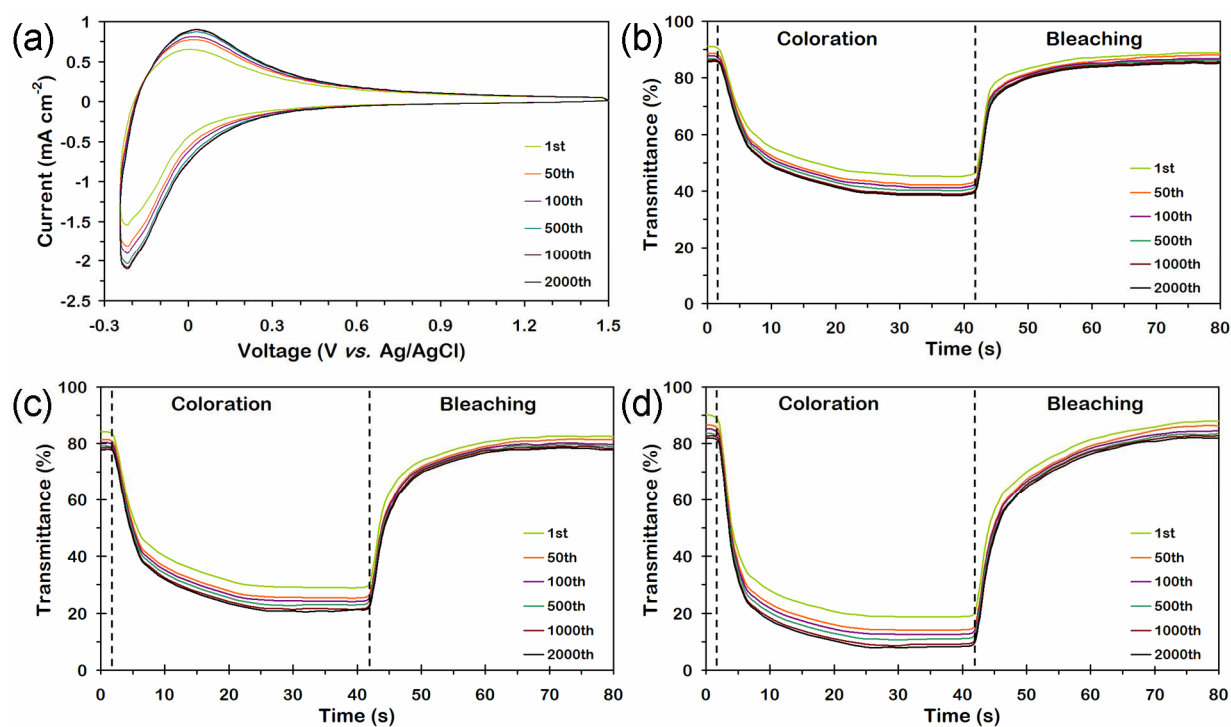
**Fig S4.** Anodization current transient of RF-sputtered W films with the thicknesses of 0.15, 0.3, 0.5 and 1 μm anodized at 10 V in a 50 ml ethylene glycol electrolyte mixed with 0.5 g NH<sub>4</sub>F and 2 %vol H<sub>2</sub>O. The anodization durations for the W films with the thicknesses of 0.15, 0.3, 0.5 and 1 μm were ~10, ~20, ~40 and ~90 min, respectively.



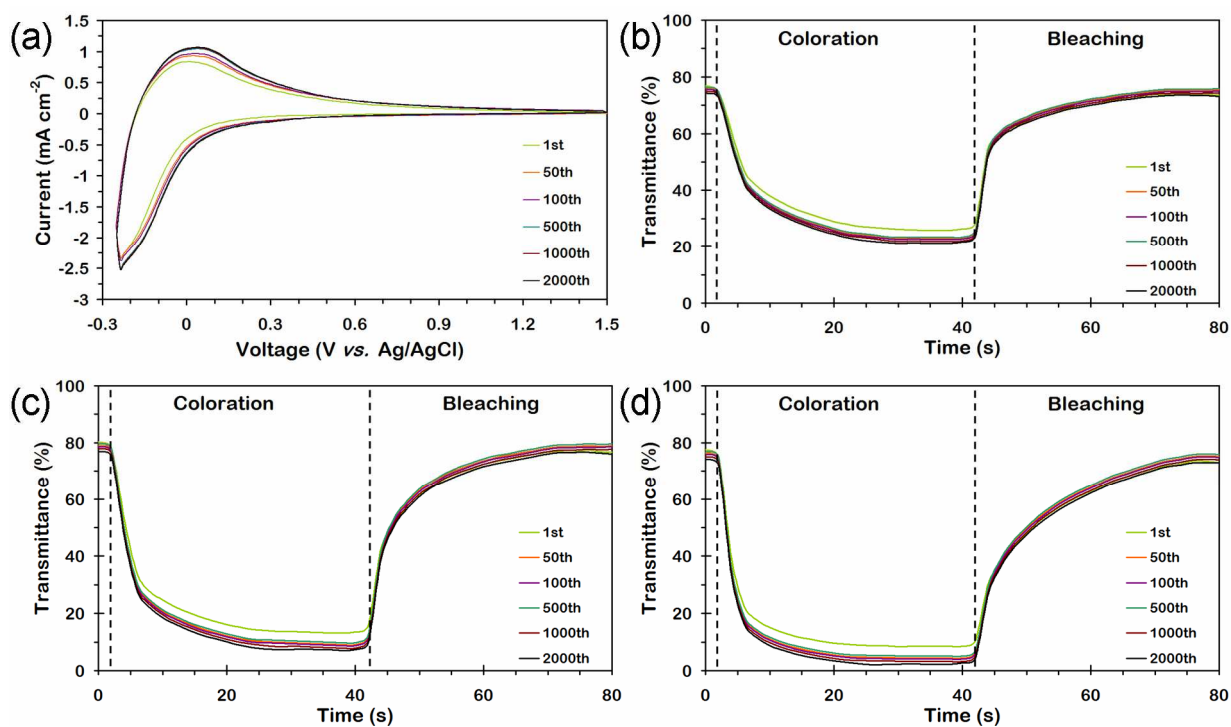
**Fig S5.** Optical band gap estimation of a crystalline 3D WO<sub>3</sub> nanoporous network (Orthorhombic phase) and a RF-sputtered film (monoclinic phase).



**Fig S6.** (a) Cyclic voltammograms (CVs) performed between  $-0.25$  and  $1.5$  V (vs. Ag/AgCl) with a scan rate of  $100 \text{ mV s}^{-1}$  in  $0.1 \text{ M H}_2\text{SO}_4$  for a  $\text{WO}_3$  layer with the thickness of  $0.2 \text{ }\mu\text{m}$  for up to 2000 cycles; (b)-(d) The corresponding *in situ* transmittance changes at the wavelength of (b) 550, (c) 650 and (d) 750 nm after the specified CV cycles.

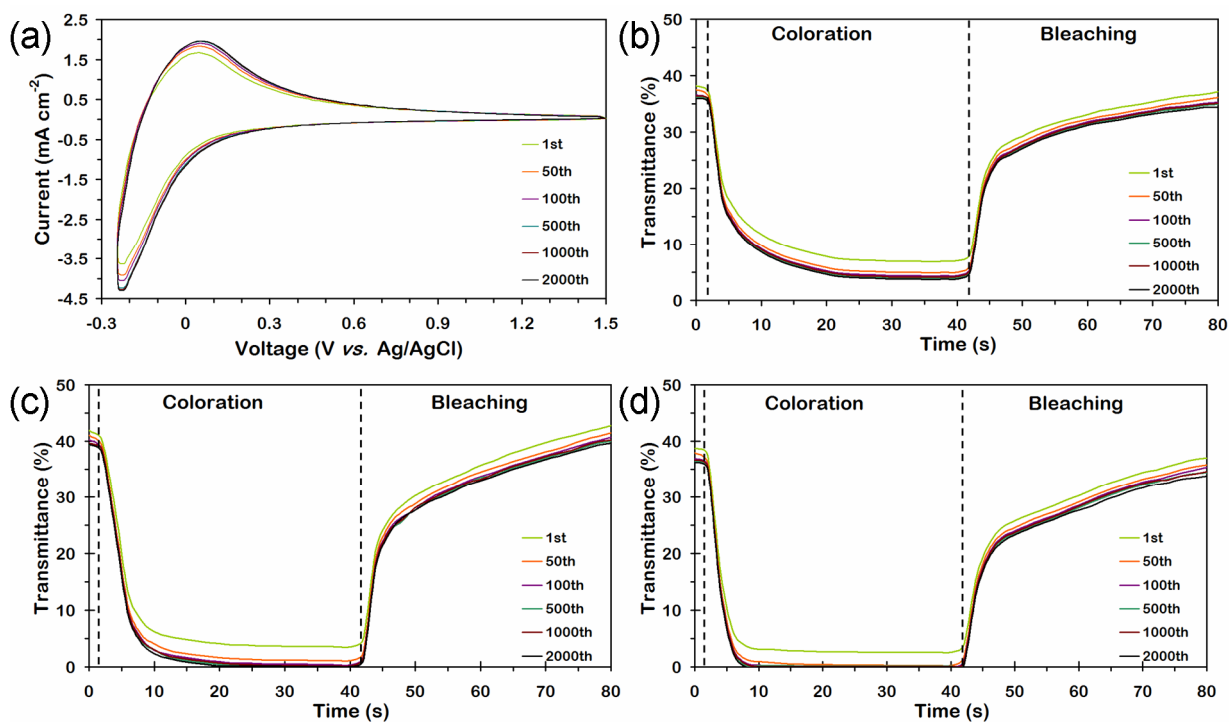


**Fig S7.** (a) Cyclic voltammograms (CVs) performed between  $-0.25$  and  $1.5$  V (vs. Ag/AgCl) with a scan rate of  $100 \text{ mV s}^{-1}$  in  $0.1 \text{ M H}_2\text{SO}_4$  for a  $\text{WO}_3$  layer with the thickness of  $0.6 \mu\text{m}$  for up to 2000 cycles; (b)-(d) The corresponding *in situ* transmittance changes at the wavelength of (b) 550, (c) 650 and (d) 750 nm after the specified CV cycles.

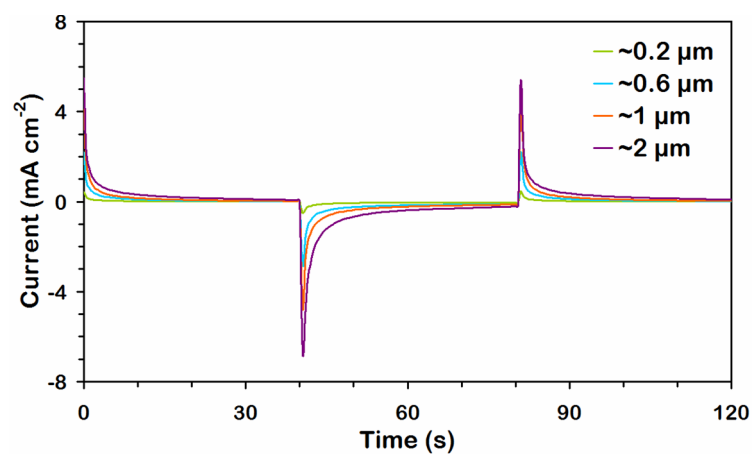


**Fig S8.** (a) Cyclic voltammograms (CVs) performed between  $-0.25$  and  $1.5$  V (vs. Ag/AgCl) with a scan rate of  $100 \text{ mV s}^{-1}$  in  $0.1 \text{ M H}_2\text{SO}_4$  for a  $\text{WO}_3$  layer with the thickness of  $1 \text{ }\mu\text{m}$  for up to 2000 cycles; (b)-(d) The corresponding *in situ* transmittance changes at the wavelength of (b) 550, (c) 650 and (d) 750 nm after the specified CV cycles.





**Fig S9.** (a) Cyclic voltammograms (CVs) performed between  $-0.25$  and  $1.5$  V (vs. Ag/AgCl) with a scan rate of  $100 \text{ mV s}^{-1}$  in  $0.1 \text{ M H}_2\text{SO}_4$  for a  $\text{WO}_3$  layer with the thickness of  $2 \text{ }\mu\text{m}$  for up to 2000 cycles; (b)-(d) The corresponding *in situ* transmittance changes at the wavelength of (b) 550, (c) 650 and (d) 750 nm after the specified CV cycles.



**Fig S10.** Chronoamperometric (CA) measurements with voltage step from  $-0.25$  V (40 s) to  $+1.5$  V (40 s) for  $\text{WO}_3$  layers with the thicknesses of 0.2, 0.6, 1 and 2  $\mu\text{m}$ .