Electronic Supplementary Information

Amorphous bismuth and GO co-doped WO_3 electrochromic film with fast-switching time and long-term stability

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S1. Experimental Section

1.1 Materials

Tungstic acid (H_2WO_4, 99.9%), and bismuth (III) oxide (Bi_2O_3, 99.9%) were purchased from Aladdin®. Hydrogen peroxide (H_2O_2, 30%) from SCR®. Sulfuric acid (H_2SO_4, 95-98 wt%). Oxygenated graphene (GO,4 mg/mL), Fluorine-doped tin oxide (FTO)-coated glass (sheet resistance: 6 Ω/sq) was purchased from South China Xiang Science & Technology Co., Ltd. The FTO-coated glass substrates (size: 30 × 20 × 2.2 mm) were cleaned with deionized (DI) water, ethanol, and DI water under sonication for each 15 min and finally dried in the atmosphere at room temperature before use.

1.2 Preparation of GO-Bi-WO_3/FTO films

Firstly, 15 g H_2WO_4 was first dissolved in 100 mL of 30% H_2O_2 via continually stirring for about 4 days, and the concentration of 0.3 mol/L transparent peroxotungstic acid ($H_2W_2O_{11}$, denoted as PTA) solution was obtained. Secondly, Bi_2O_3 powder with a molar ratio of Bi: W ≈ 1: 30 was completely dissolved in the PTA solution at 80 °C water bath with magnetic stirring (300 rpm, about 8 h). Then withdraw 2 mL of the solution and add 100, 200, or 400 μL of GO nanosheet dispersion (1 mg/mL), mix thoroughly heat at 80 °C for 4 h to obtain a homogeneous GO-Bi-PTA sol. The Bi-PTA sol with high concentration has a higher viscosity, which is conducive to preparing film by the spin-coating method.

Transparent GO-Bi-PTA film was formed by spin coating the GO-Bi-PTA sol on FTO glass with a speed of 1500 rpm for 40 s via a spin coater, and then annealing it at 300 °C for 2 h in the air via a muffle furnace. For comparison, the different Bi-WO_3 films were obtained by calcinating at different temperatures of 200 °C, 250 °C, 350 °C, and 400 °C for 2 h. To research the doping effect on electrochromic properties, the evaluations of the pure WO_3 (W), Bi-doped WO_3 (BW), and GO-Bi co-doped WO_3 (GBW) films were carried out.

1.3 Characterization

X-ray diffraction (XRD, D8 Advance, Cu Kα) patterns were used to check the chemical structure and crystallinity of the films. Raman spectroscopy was recorded at ambient temperature on the LabRAM HR Evolution with a wavelength laser of 532 nm as the excitation source. An atomic force

microscope (AFM, BenYuan CSPM5500) and field-emission scanning electron microscope (SEM, FEI QUANTA FEG 250) with energy-dispersive spectroscopy (EDS, EDAX Element) were used to evaluate the morphology and elemental composition of the Bi-WO_3 film. X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha) analyses were performed and calibrated by the binding energy of C1s 284.8 eV. with a wavelength laser of 514 nm as the excitation source.

Electrochemical and electrochromic measurements were conducted using an electrochemical workstation (CHI660e, Shanghai Chenhua Instrument, Inc.) at room temperature in a three-electrode system. The GO-Bi-WO_3/FTO, an Ag/AgCl (with saturated KCl), and a Pt foil were used as working, reference, and counter electrodes, respectively. The electrolyte was 0.5 mol L^{-1} H_2SO_4. The in-situ electrochromic and optical measurements were performed on the electrochemical workstation and an ultraviolet−visible (UV−vis) spectrometer (Thermo Scientific GENESYS 50). Cyclic voltammetry (CV) measurements were carried out from +0.5 V to −0.3 V at scan rates of 0.01~0.3 V/s. Chronoamperometry (CA) measurements were performed at −0.3 V for coloring and +0.5 V for bleaching and the duration for each step was 60 s. The coloration efficiencies were calculated at the wavelength of 630 nm.

S2. Supplementary Figures

According to previous research, it has been noted that the optical modulation range of crystalline WO_3 material is constrained and its response speed is sluggish.[1] As a result, the annealing temperature of 300 ℃ was selected. XRD pattern reveals that the thin film demonstrates an amorphous structure.

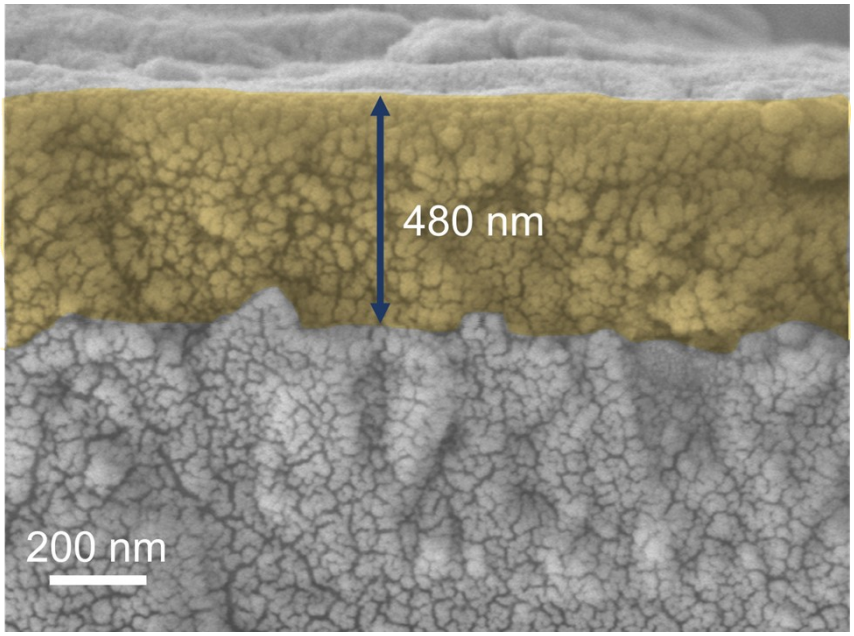


Fig. S1 Cross-sectional SEM image of GBW-2 film.

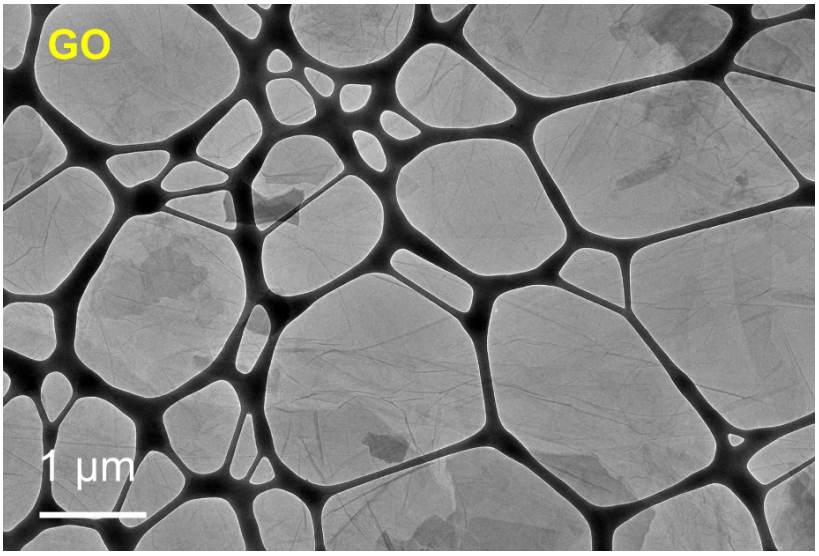


Fig. S2 TEM image of GO nanosheets.

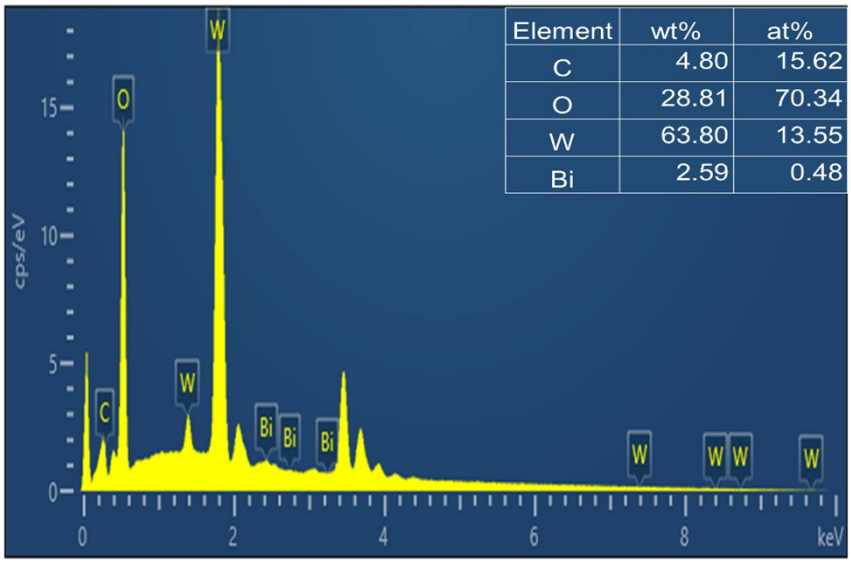


Fig. S3 EDS analysis of GBW-2 film.

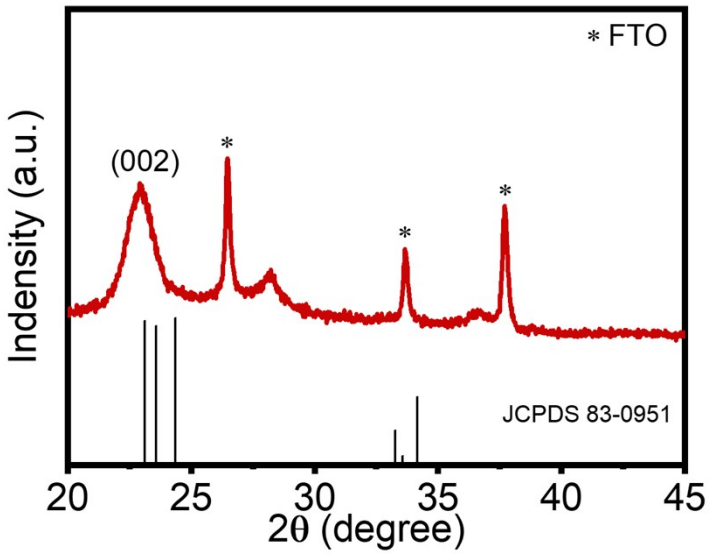


Fig. S4 XRD pattern of GBW-2 film.

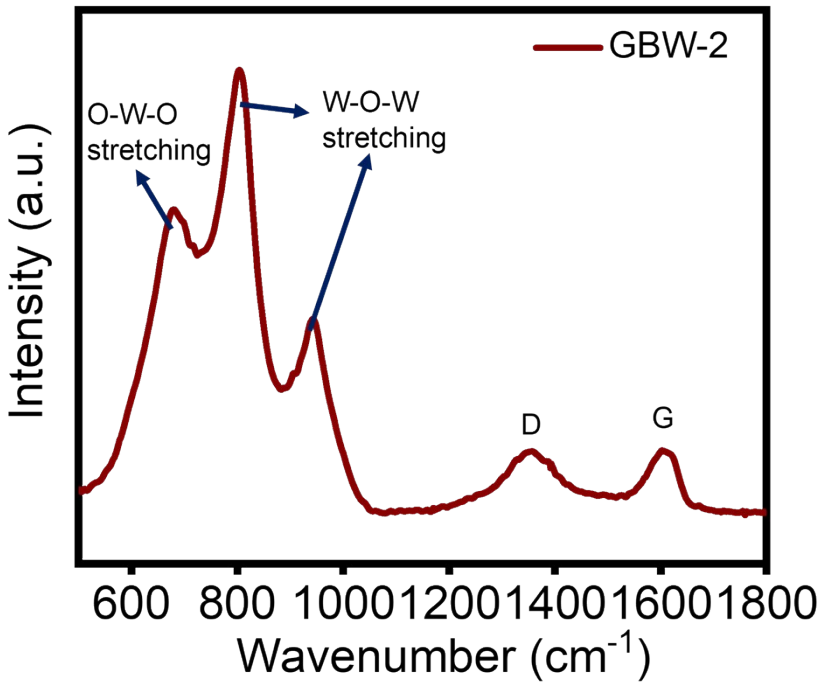


Fig. S5 Raman spectra of GBW-2 film.

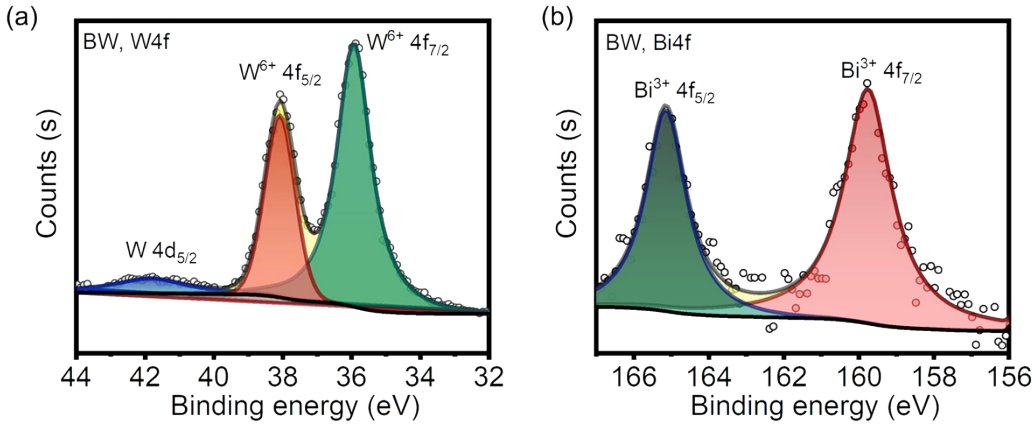
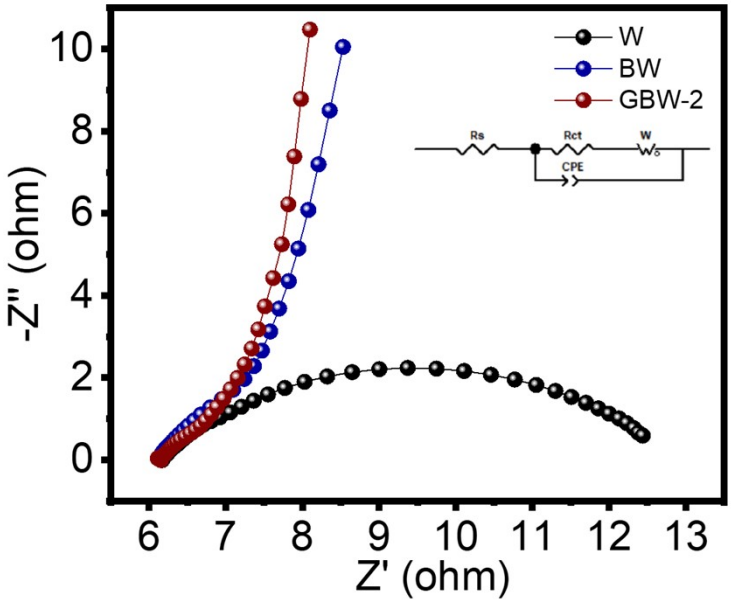


Fig. S6 XPS spectra of (a) W 4f and (b) Bi 4f for the BW film.



Samples	R_s	R_{ct}
W	6.195	6.51
BW	6.138	2.96
GBW	6.158	1.28

Fig. S7 EIS curves and simulated R_s and R_{ct} values of GBW-2, BW, and W films.

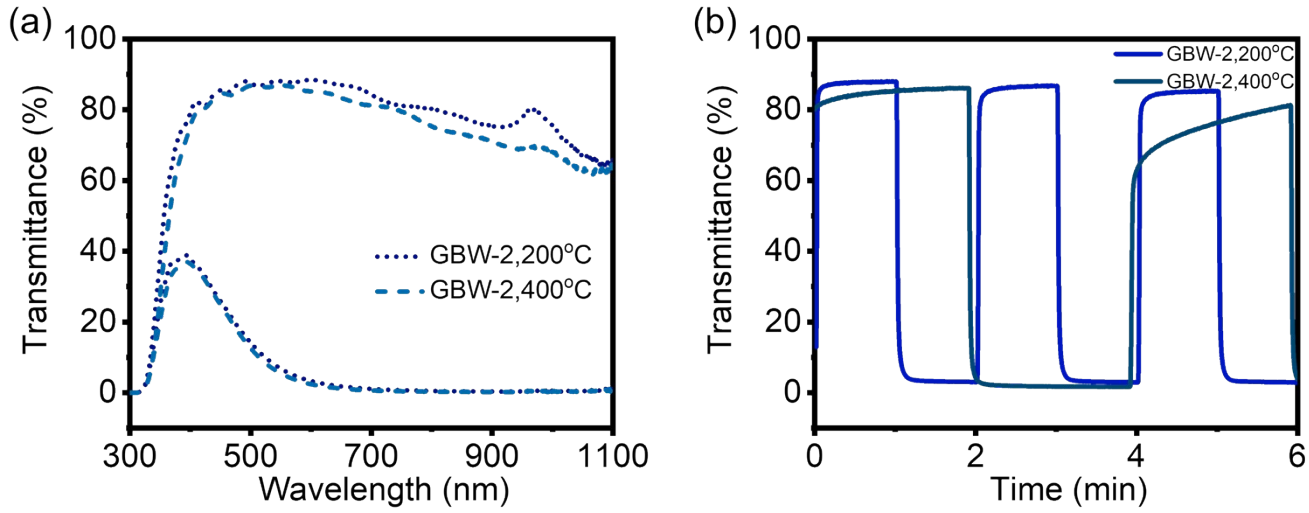


Fig. S8 (a) Transmittance changes versus wavelength in the colored state (−0.3 V) and bleached state (0.5 V), and (b) *in-situ* transmittance curves at 630 nm under square wave potentials of −0.3 V (coloring) and 0.5 V (bleaching) for 60 s of GBW-2 (annealing at 200 °C and 400 °C) films.

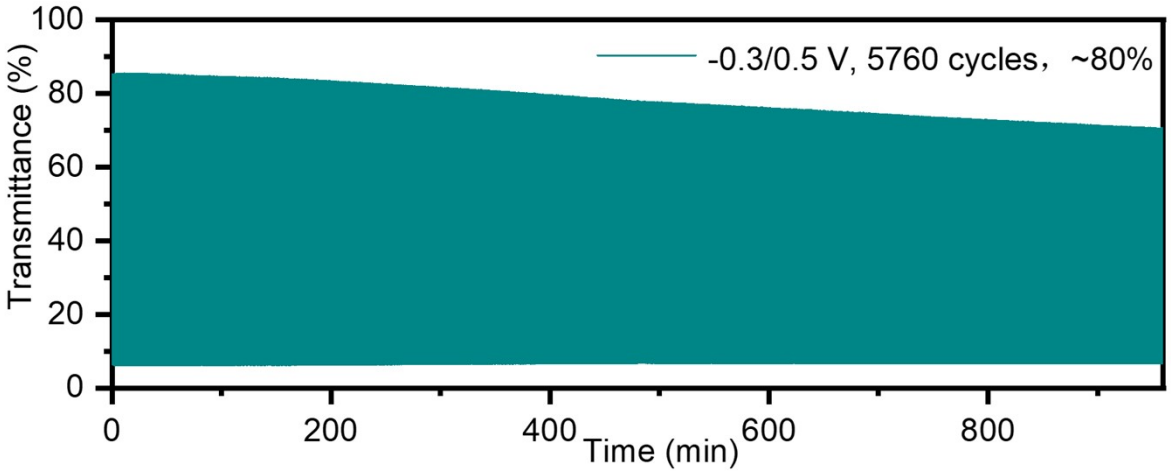


Fig. S9 Long-term stability of GBW-2 film prepared by annealing at 200 °C.

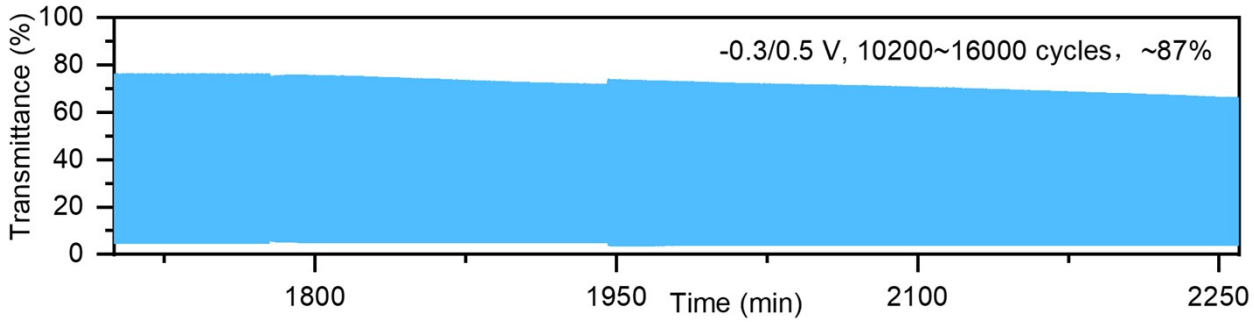


Fig. S10 The switching response curve of GBW-2 thin film for cycles from 10200 to 16000 cycles.

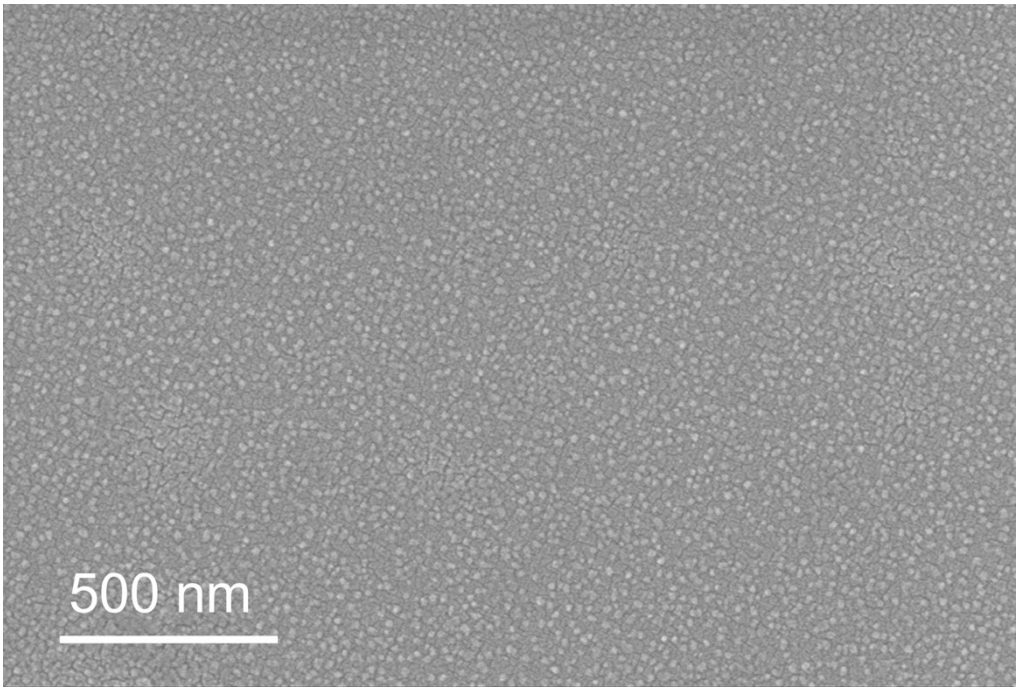


Fig. S11 SEM image of GBW-2 after 16000 cycles.

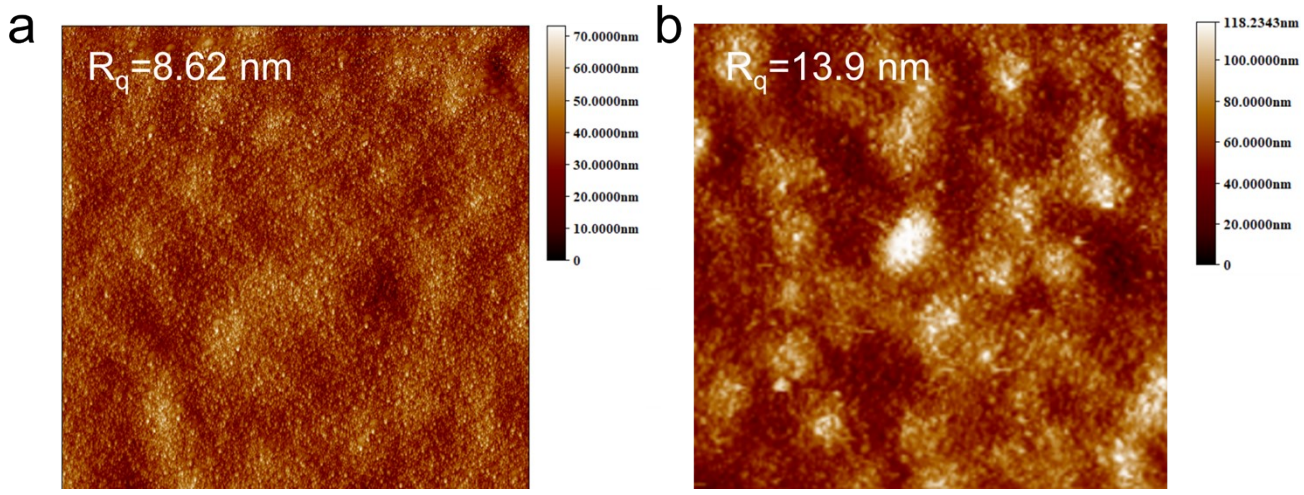


Fig. S12 AFM images of GBW-2 (a) before and (b) after 16000 cycles

Table S1 Comparison of the electrochromic performance of GBW-2 film with recent reports.

Composition and phase, film thickness (nm)	Electrolyte ion	ΔT (%)	t_c, t_b (s)	CE (cm^2C^{-1})	Cycle stability	Ref
GBW-2, 480	H^+	85 (630 nm)	1.8,1.8	65.9	10200, 86.4%	This work
c-WO_3/rGO, ~	Li^+	58.8 (633 nm)	4.7,4.5	122.2	2500, ~	2
c-WO_3-rGO, 800	Li^+	50 (632 nm)	5.3,6.2	386	500, 90%	3
c-$W_{18}O_{49}$ /rGO, 244	Al^{3+}	~55 (633 nm)	8,8.25	46	4000,96%	4
a-WO_3, 296	Li^+	75.7 (633 nm)	8.4,7.4	189.3	1000, 75.5%	5
a-WO_3*, 300	H^+	90 (650 nm)	0.7,7.1	109	3000, 90%	6
a-Tb-WO_3, 410	H^+	66.71 (680 nm)	9.99,3.7	48.33	600, ~	7
h-Sm-WO_3/P_1, 750	H^+	68.5 (633 nm)	7.4,2.9	72.7	5000, 90.2%	8
c-Ti-WO_3, 283	Li+	84.9 (633 nm)	25,3.3	114.9	1000, 89%	9
c-WO_3@GQD*, ~	Li^+	78.72 (700 nm)	4.1,4.6	78	10000, 90%	10
$W_{17}O_{47}$@PEDOT:PSS, ~	Li^+	79.7 (633 nm)	3.5,5.5	90.1	12400, 76%	11
P-CQD/a-WO_3, ~	Li^+	62.5 (633 nm)	4.4,2.7	76.1	4000, 87.3%	12
a/c-WO_3, ~	Li^+	84.5 (633 nm)	1.2,3.6	83.6	3000, 91.9%	13

*: The performances were measured in the electrochromic devices.

References

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