

Supporting information

An all-solid-state bistable electrochromic device based on the amorphous WO_{3-x} nanostructured film

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1. Experimental details

Materials

Polyvinyl pyrrolidone (PVP, $M_w \sim 1,300,000$), nickel chloride (NiCl_2), oleylamine (OA) and aluminum perchlorate nonahydrate ($\text{AlClO}_4 \cdot 9\text{H}_2\text{O}$) were purchased from Energy Chemicals, China. Ammonium metatungstate (AMT, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$) was purchased from Aladdin Chemicals, China. Propylene carbonate (PC) was purchased from Adamas-beta Reagent, China. The precursor nanofibers were produced by the ET-2535DC electrospinning equipment. The Nafion film was purchased from Alfa Aesar (Nafion-NRE-212 film, thickness ~ 0.05 mm, conductivity ~ 0.083 S/cm). The FTO glass electrodes were purchased from South China Xiang Science & Technology company (Sheet Resistance < 8 Ω/sq ; Transmittance $> 80\%$; the thickness of FTO is 500 nm). All the materials were used as received without any further purification.

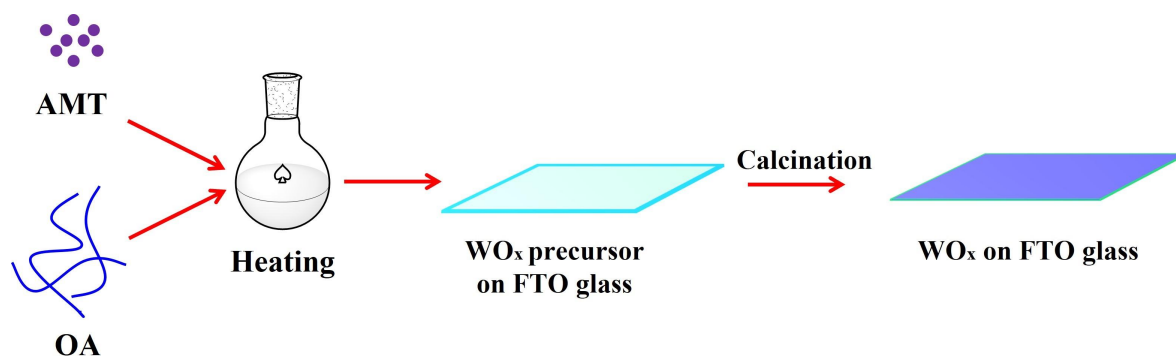
Synthesis of the WO_x (WO_{3-x}) precursor

Firstly, 1.3 g AMT was mixed with 50 mL OA in a 250 mL flask, and degassed at 120 °C for 10 minutes. Then, the mixture was further heated to 250 °C quickly under a nitrogen (N_2) atmosphere and held there for two hours. During this process, the mixture changed from colorless to dark blue. After cooling to the room temperature, the precipitate was formed by adding excess anhydrous ethanol, and separated by centrifugating with 10,000 rpm for 10 min. The obtained product was washed in the mixture solution of toluene and anhydrous ethanol, followed by centrifugation under 10,000 rpm for 10 min. The washing process was repeated three times. The solid precursors of the WO_x (WO_{3-x}) film were prepared and dispersed in toluene with the concentration of 50 mg/mL.

Fabrication of the liquid bistable electrochromic devices (BECDs)

(1) Electrochromic (EC) layer preparation (**Scheme S1**): The precursor material of WO_x was deposited on the FTO electrode by scrape coating. The thickness was controlled by the

distance from the scraper to the FTO electrode. After the precursor material was completely deposited, the composite electrode was heated at a 400 °C for 1 hour with a heating rate of 2 °C/min, and then cooled down to the room temperature with a rate of 2 °C/min. Finally, EC layer was fabricated by a 1 μm thickness of WO_x film on FTO.



Scheme S1. Preparation process of the EC layer on FTO electrode.

(2) Ion storage layer preparation: For LD-1, there was no ion storage layer. For LD-2, the preparation process was below: the NiO film deposited on the FTO electrode was synthesized by a two-step process of electrospinning and calcination. The precursor solution was prepared by dissolving 1.3 g NiCl₂, 1.3 g PVP in a mixture solvent of 7 mL DMF and 9 mL anhydrous C₂H₅OH firstly, and stirred at 45 °C until a clear green precursor solution formed. After that, the precursor solution was loaded into a plastic syringe with a 21G needle. The electrospinning was conducted under the operation voltage of 15 kV with a distance of 15 cm between the needle tip and the FTO electrode on the grounded stainless-steel plate at a flow rate of 1 mL h⁻¹ for 4 mins. The nanofibers-coated FTO was heated in air at 200 °C for 1 hour with a heating rate of 2 °C/min, and then heated at 520 °C for 2 hours with a heating rate of 1 °C/min. NiO nanostructured film modified FTO was fabricated.

(3) Liquid ion conductive layer preparation: Aluminum perchlorate nonahydrate (AlClO₄·9H₂O) was put into an oven (120 °C for overnight) to remove crystal water before using. And, the liquid electrolyte was prepared by AlClO₄ dissolved in PC with a concentration of 1 mol/L.

(4) Fabrication of the liquid bistable electrochromic device (BECD): The device was fabricated by the combination of above three layers. There was a spacer prepared between electrochromic layer and ionstorage layer (For LD-1, FTO electrode without any material; For LD-2, FTO electrode deposited with NiO nanostructured film), which was made by a heating-curing adhesive (height was 260 μm). The liquid electrolyte was injected into the spacer and then the spacer was sealed by UV curing adhesive. After that, the liquid bistable electrochromic device (BECD) was fabricated and the EC mechanism was shown in the following reaction.



Scheme S2. EC mechanism of the liquid BECD.

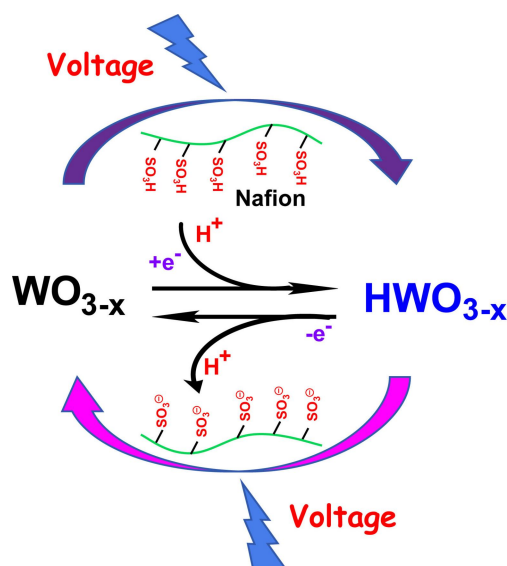
Fabrication of the all-solid-state bistable electrochromic devices (BECDs)

(1) Preparation of electrochromic (EC) layer: The precursor material of WO_{3-x} was deposited on the FTO electrode by scrape coating. And the thickness was controlled by the distance from the scraper to the FTO electrode. After the material was completely deposited, the composite electrode was heated at a specific temperature for 1 hour with a heating rate of 2 $^\circ\text{C}/\text{min}$, and then cooled to the room temperature with a cooling rate of 2 $^\circ\text{C}/\text{min}$. With all the above treatments finished, FTO modified with EC layer (WO_{3-x} film) was fabricated. (The optimization of thickness and calcination temperature are discussed in the manuscript)

(2) Preparation of ion storage layer: The NiO film deposited on the FTO electrode kept the same with the preparation of ion storage layer in “*Fabrication of the liquid bistable electrochromic devices (BECDs)*”.

(3) Preparation of the solid ion conductive layer: The Nafion film was cut into an appropriate shape/size and dipped into propylene carbonate (PC) for 24 hours. Then, the film was taken out and the PC on the surface of was dried completely by a filter paper.

(4) Fabrication of the all-solid-state bistable electrochromic device (BECD): The device was fabricated by the combination of above three layers tightly and efficiently. The treated Nafion film was put between electrochromic layer and ion storage layer. And then, a UV-sealing gum was used for device packaging. After that, the all-solid-state BECD was fabricated and the EC mechanism was shown in **Scheme S3**.



Scheme S3. EC mechanism of the all-solid-state BECD.

Patterning method of devices

FTO glass electrode was photo-etched to the specific pattern by layer mask machine FB30-Z HPWU0300-SKS. The etched FTO coated with the electrochromic layer was used as the working electrode. Then, the device was fabricated according to the procedure of the fabrication of the bistable electrochromic devices.

Instruments and Characterizations

X-ray diffraction (XRD) patterns were recorded using Empryan x-ray diffractometer (Cu K α radiation). Scanning electron microscopy (SEM) images were taken using field-emission scanning electronic microscopy (FE-SEM; SU8020, HITACHI) operated at an accelerating voltage of 3.0 kV. SEM energy spectrum analysis was evaluated using the FE-SEM at 20.0 kV. The electrochemical data were obtained from Bio-logic SP-150 electrochemical work station. Optical transmittance spectra and the kinetic data were measured using a Analitik

Jena Specord®210 plus UV/VIS spectrophotometer and a UV-Vis-IR spectrophotometer (UV-3600i Plus, SHIMADZU). FTO glasses were etched by the Xi-Ai FB30-Z HPWU0300-SKS Laser marking machine.

Electrochemical measurements

Cyclic voltammetry (CV) analysis of WO_x film was measured using a three-electrode system containing AlClO_4 (0.1 mol/L) in PC as the supporting electrolyte. The three-electrode system contained a WO_x film (area:1 cm*1 cm) as the working electrode, a Pt wire as the counter electrode (IDA, China), and an Ag wire as the reference electrode (IDA, China).

2. Supplementary figure for devices

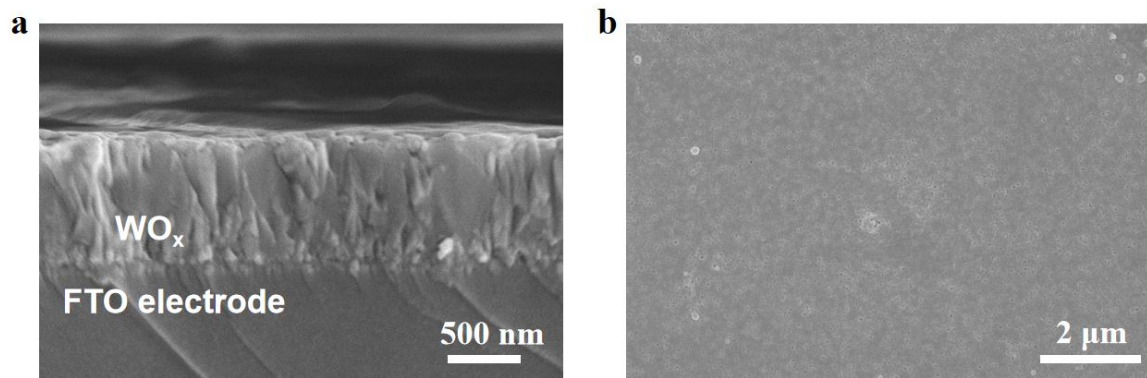


Fig. S1 SEM images of (a) cross-sectional and (b) surface microstructures of the WO_x film deposited on a FTO electrode.

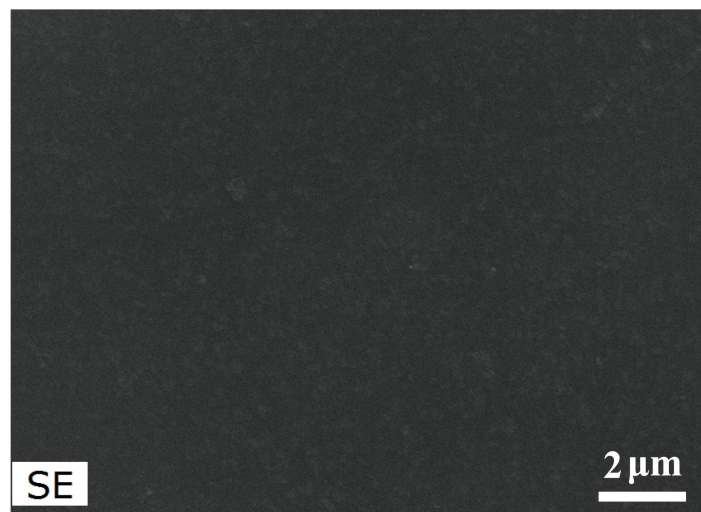


Fig. S2 SEM image used as EDS elemental mappings of the WO_x film. (SE: the original image measured by SEM in the mapping mode)

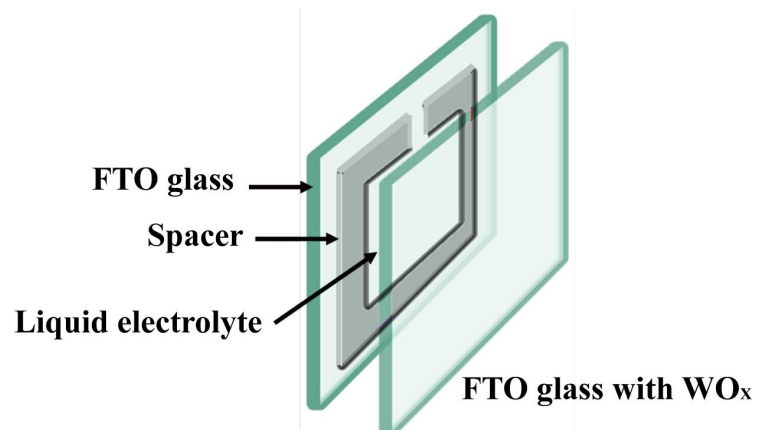


Fig. S3 Device structure of LD-1 (liquid electrolyte: 1 M AlClO₄/PC).

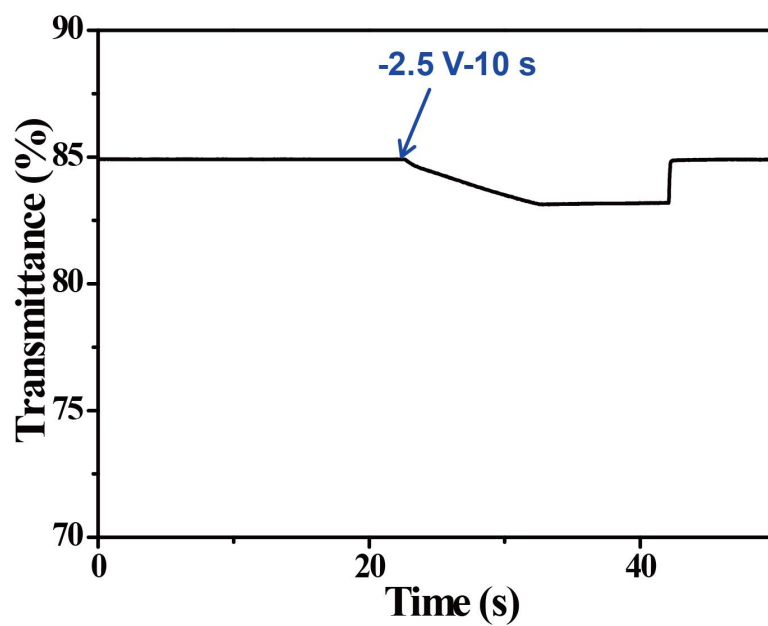
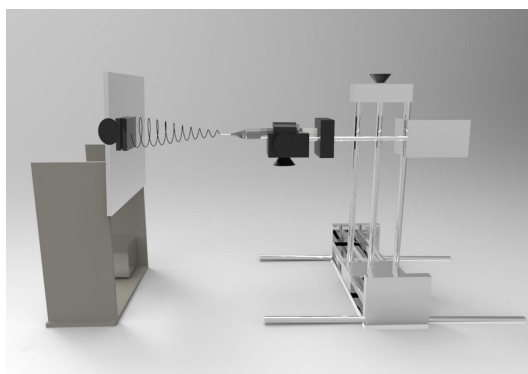


Fig. S4 Transmittance changes at 650 nm of the liquid device (LD-1). (Measurement of the starting voltage).



Electrospinning

Calcination



NiO on FTO glass

Fig. S5 Preparation process of the NiO film deposited on the FTO electrode.

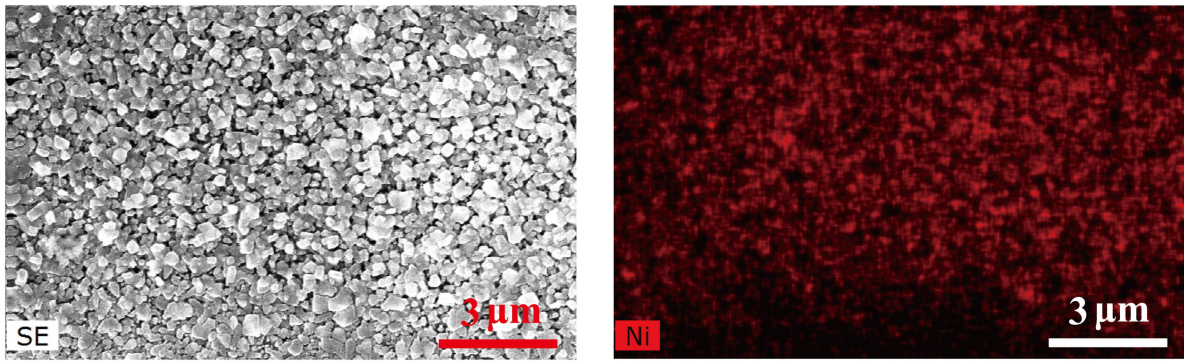


Fig. S6 SEM and Ni element mapping images of the NiO film. (SE: the original image measured by SEM in the mapping mode)

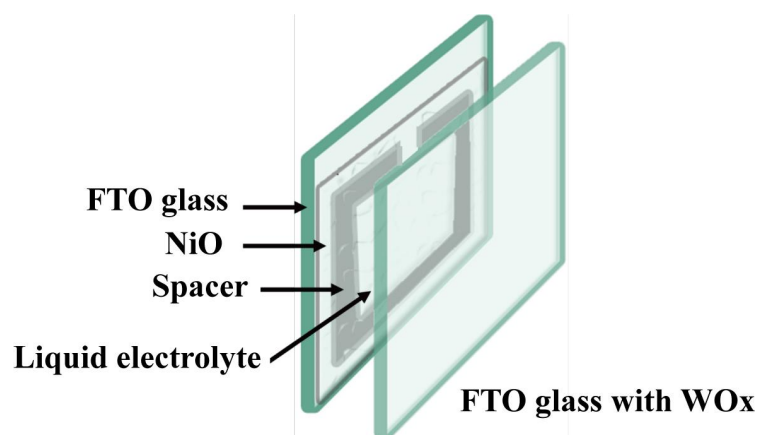


Fig. S7 Device structure of LD-2 (liquid electrolyte: 1 M AlClO_4 in PC).

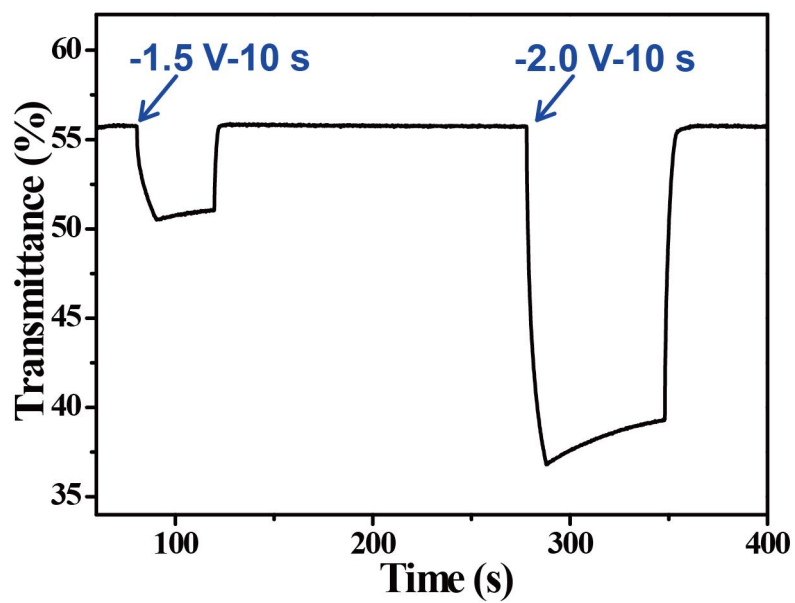


Fig. S8 Transmittance changes at 650 nm of the liquid device (LD-2). (Measurement of the starting voltage).

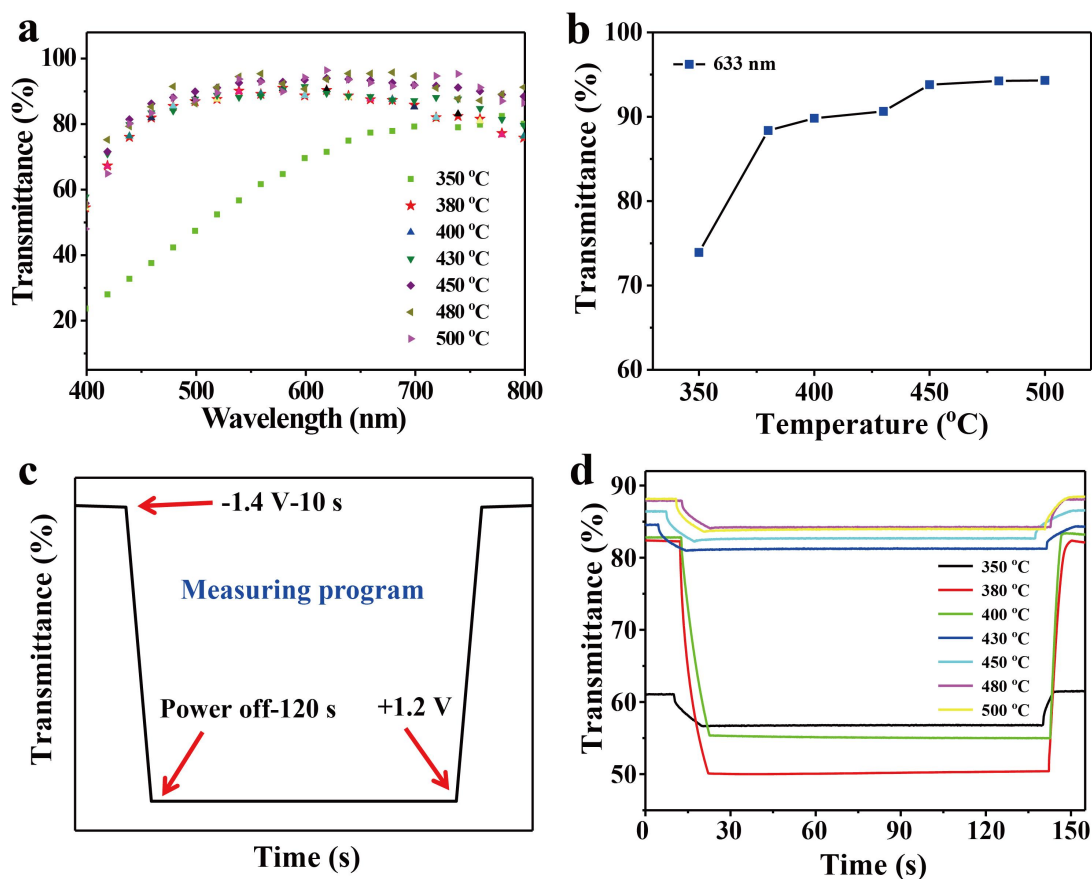


Fig. S9 (a) Transmittance spectra (400-800 nm) of the WO_x film deposited on FTO electrode with the treatment of various temperatures for 1 h. (b) Transmittance at 633 nm of the WO_x film deposited on FTO electrode with the treatment of various temperatures for 1 h. (c) The schematic diagram of the stimulation program of “-1.4 V with 10 s for coloring, then power off with 120 s, +1.2 V for bleaching”. (d) Transmittance change at 633 nm of the devices using the WO_x film deposited on FTO electrode with the treatment of various temperatures for 1 h as electrochromic materials under the stimulation program of “-1.4 V with 10 s for coloring, then power off with 120 s, +1.2 V for bleaching”.

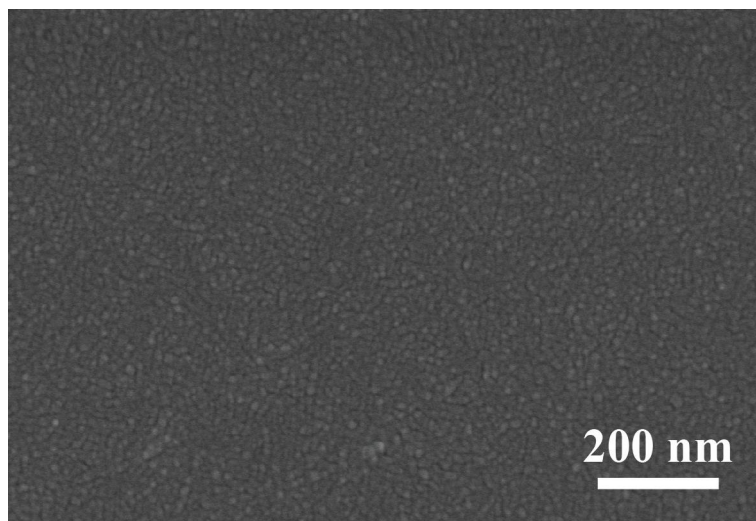


Fig. S10 SEM image of the optimized WO_x film.

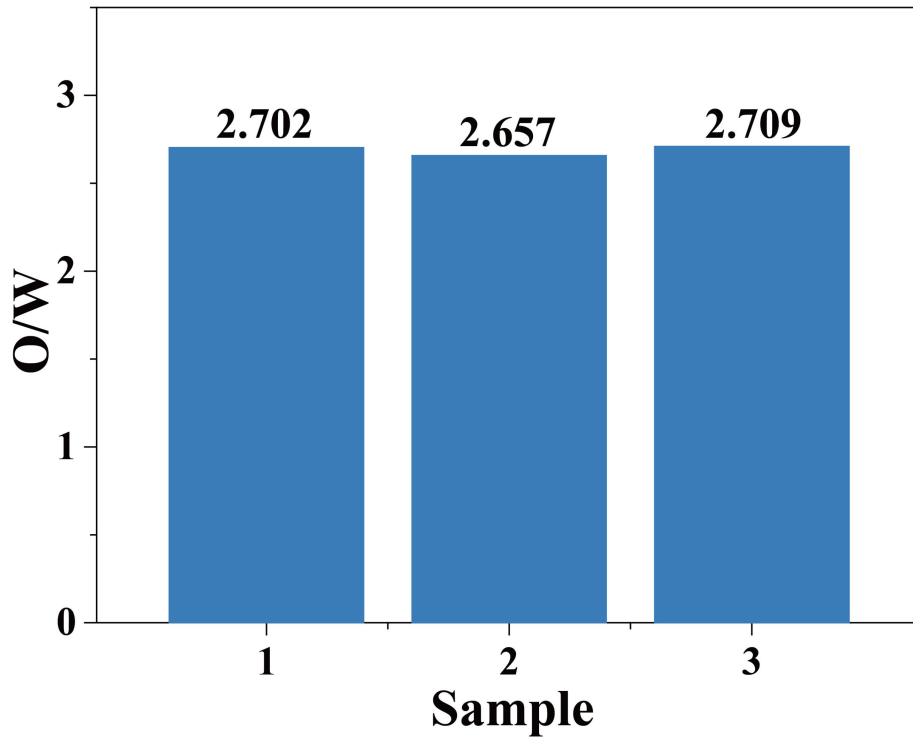


Fig. S11 EDS results of three samples (WO_x films, molar ratio of O to W) measured by SEM.

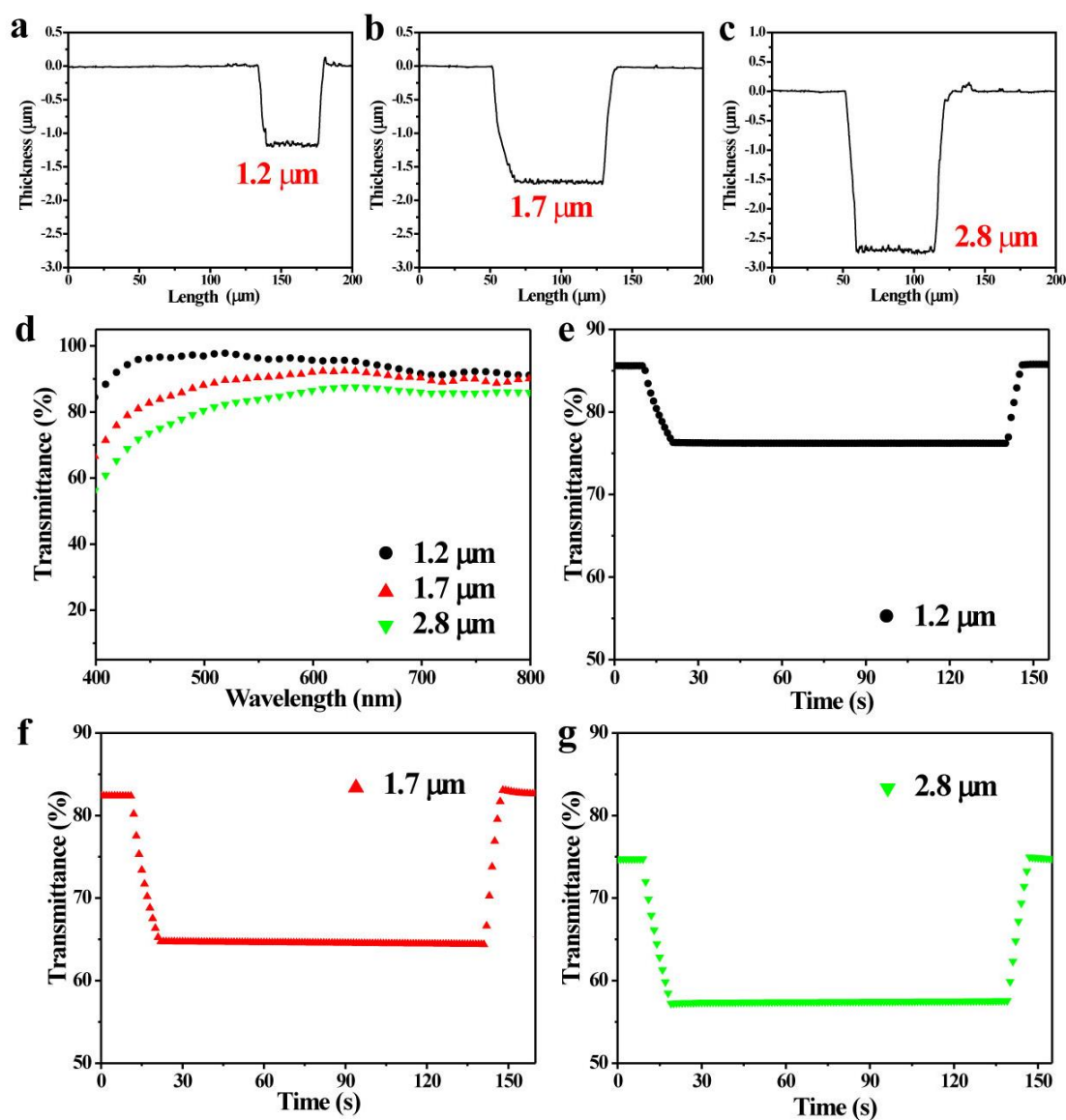


Fig. S12 The WO_x film combining FTO electrode was called working electrode. The optimization of thickness of WO_x film was shown here. The thicknesses of the WO_x film deposited on FTO electrode which measured by a probe surface profiler. (a) 1.2 μm; (b) 1.7 μm; (c) 2.8 μm. (d) Transmittance spectra of working electrode which deposited with various thicknesses of WO_x film. Transmittance at 633 nm of devices under stimulation mode of “-1.2 V-10 s, open circuit for 120 s, +1.0 V with appropriate time for back to the initial state” with various thicknesses of WO_x film: (e) 1.2 μm; (f) 1.7 μm; (G) 2.8 μm.

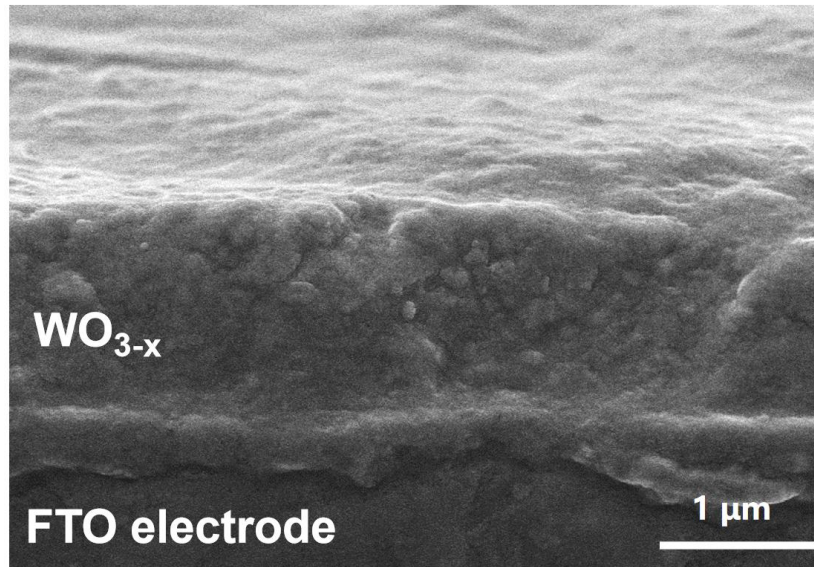


Fig. S13 SEM image of cross-sectional microstructures of the optimized WO_{3-x} film deposited on a FTO electrode.

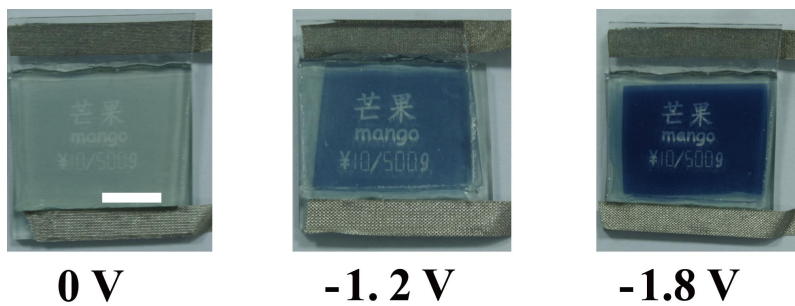


Fig. S14. Physical displays of BECDs when added various voltages. (Scale bar=1 cm)

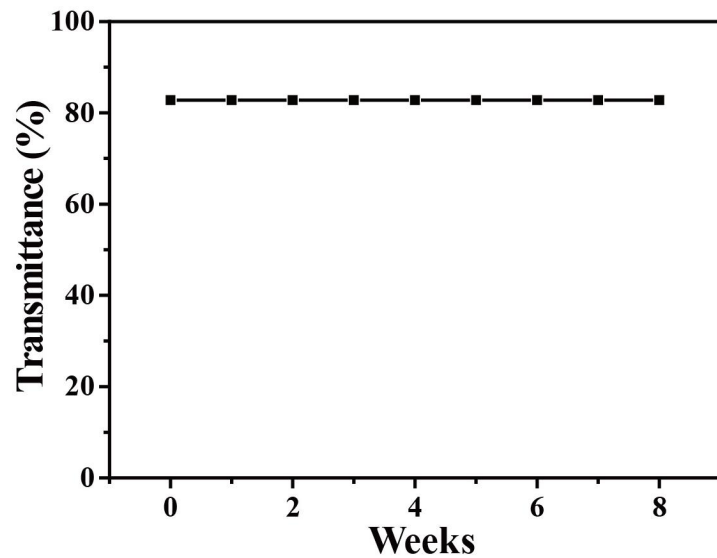


Fig. S15 Transmittance of the bleached state of the BECD at open circuit state with time.

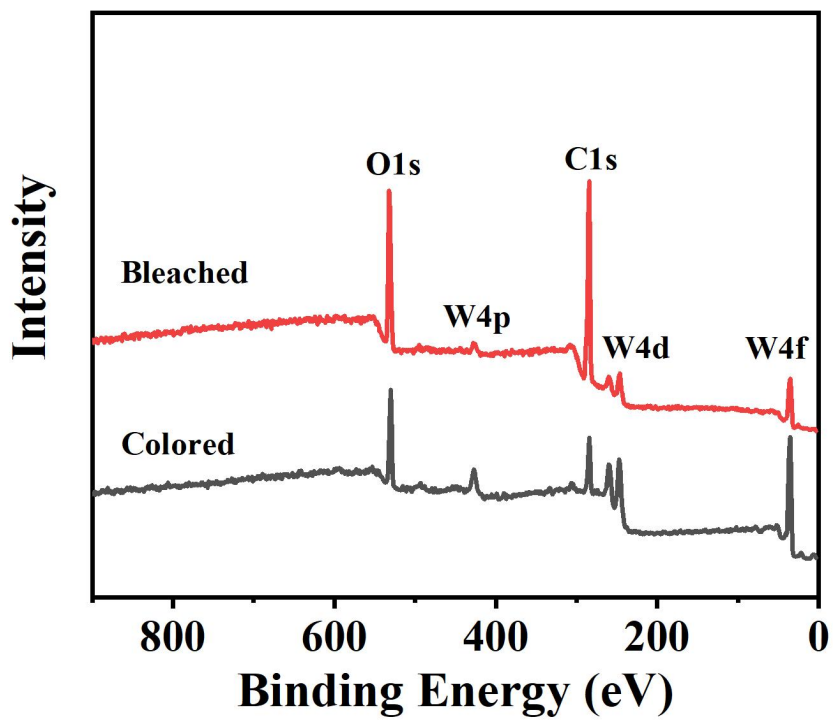


Fig. S16 Wide scanning XPS spectra of WO_{3-x} film at colored state and bleached state.

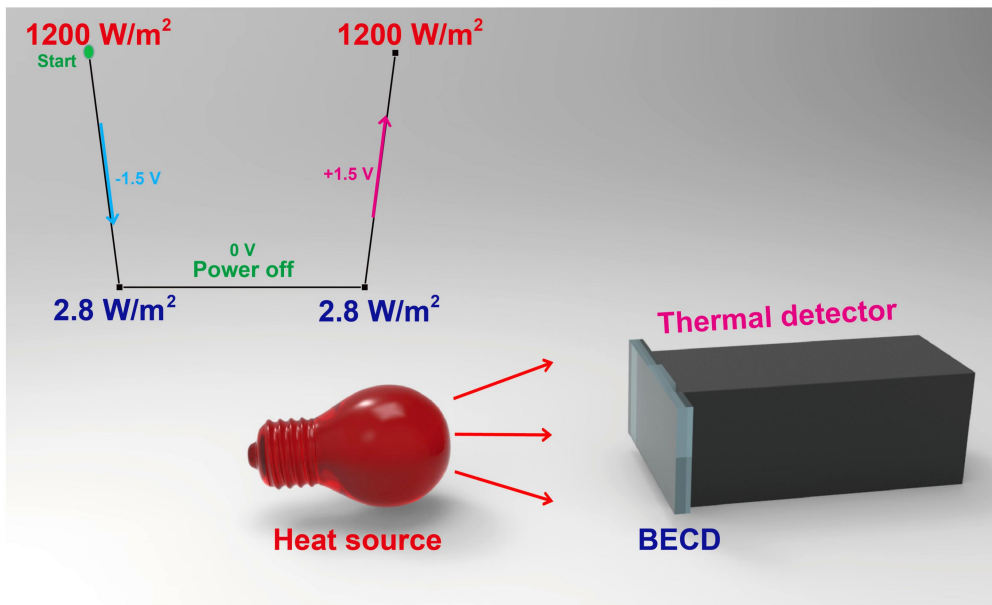


Fig. S17 Application mode of the BECD in smart heat-insulation windows.