

## Supporting Information

### **Towards to large-scale and high-performance smart window based on Prussian blue: A revolutionary Two-dimensional materials assisted *in-situ* growth preparation method utilizing MXene**

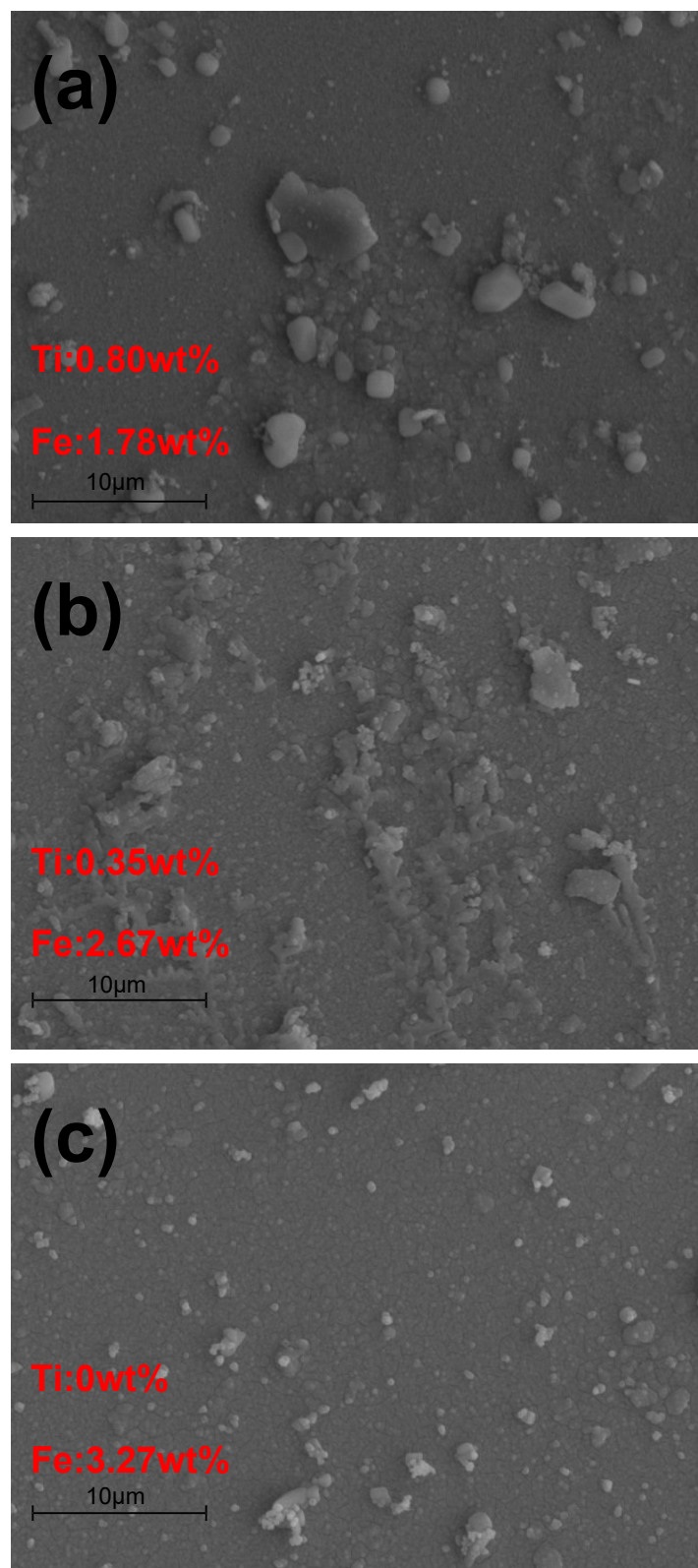
Maofei Tian<sup>1†</sup>, Mengshan Lu<sup>1†</sup>, Wenjun Wu<sup>1</sup>, Rongzong Zheng<sup>1, 2\*</sup>, Yanbang Tang<sup>1</sup>, Zhongquan Wan<sup>2</sup>, Junsheng Luo<sup>2</sup>, Chunyang Jia<sup>2\*</sup>

<sup>1</sup>College of Materials and Metallurgy, Guizhou University, Guiyang 550025, China;

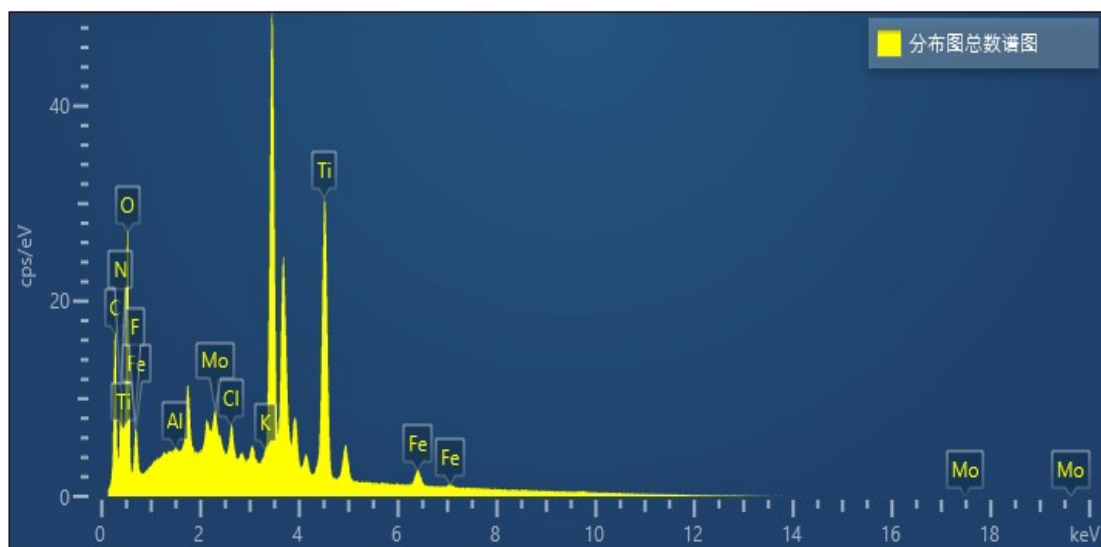
<sup>2</sup>State Key Laboratory of Electronic Thin Films and Integrated Devices, National Engineering Research Center of Electromagnetic Radiation Control Materials, School of Integrated Circuit Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, PR China;

Correspond authors: [zzheng@gzu.edu.cn](mailto:zzheng@gzu.edu.cn), [cjia@uestc.edu.cn](mailto:cjia@uestc.edu.cn)

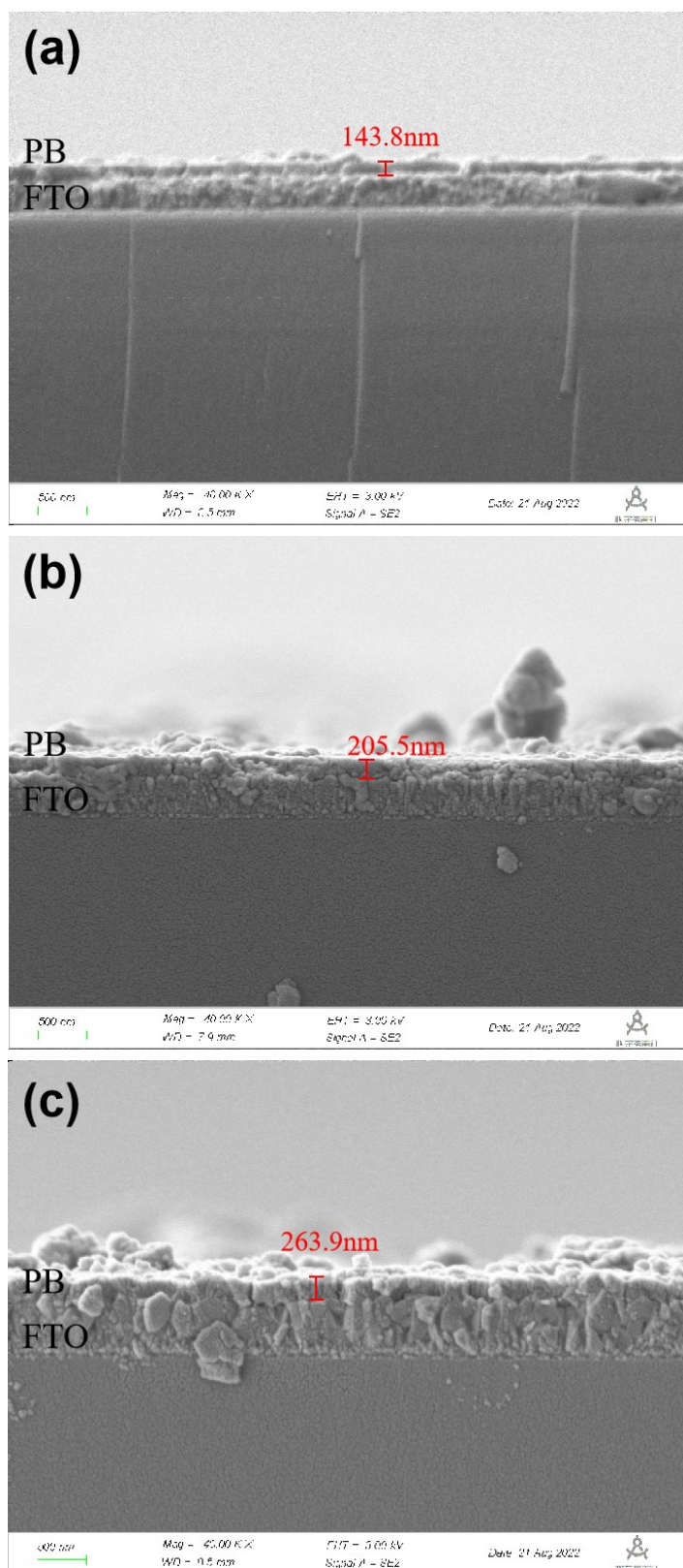
## 1. Supporting figures



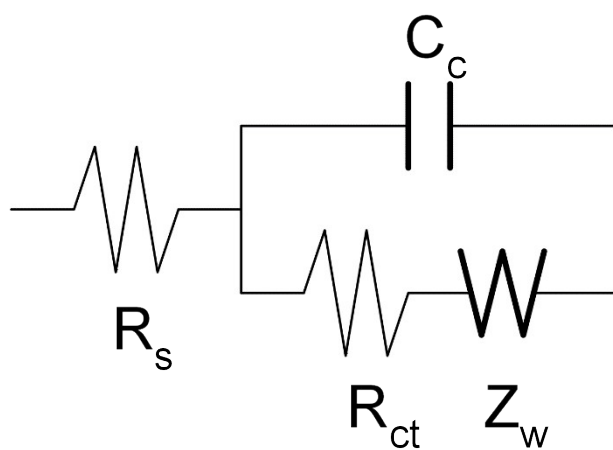
**Figure S1** The SEM and elemental content of PB films at (a) 10min, (b) 15min, (c) 20min immersion times respectively.



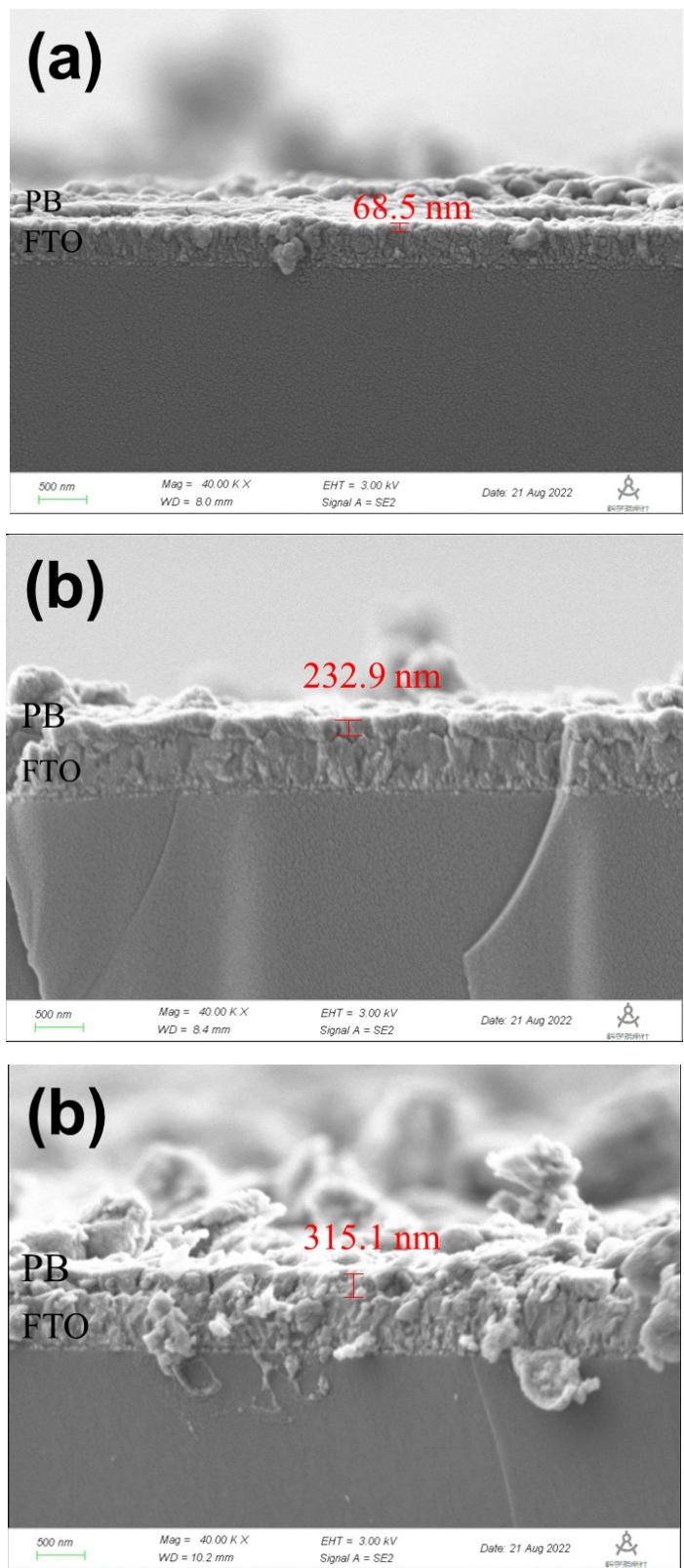
**Figure S2.** Energy dispersive X-ray (EDX) spectrum of the PB films prepared by TAIG.



**Figure S3** The cross-sectional SEM images of the PB films after (a) 10 min, (a)15 min and (c)20 min of immersion, respectively.



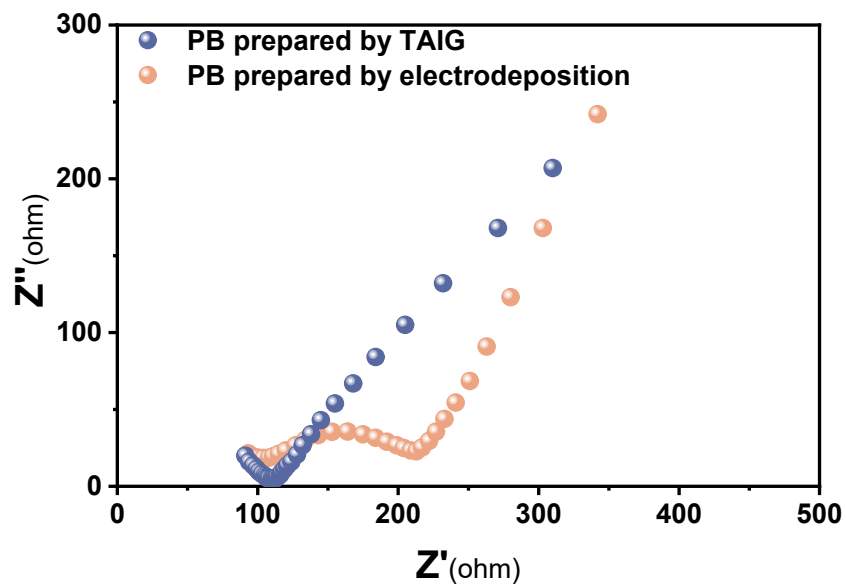
**Figure S4** The equivalent circuit of the PB films for different preparation temperatures.



**Figure S5** The cross-section SEM image of films at preparation temperature of (a)30°C, (b)45°C, (c)60°C.

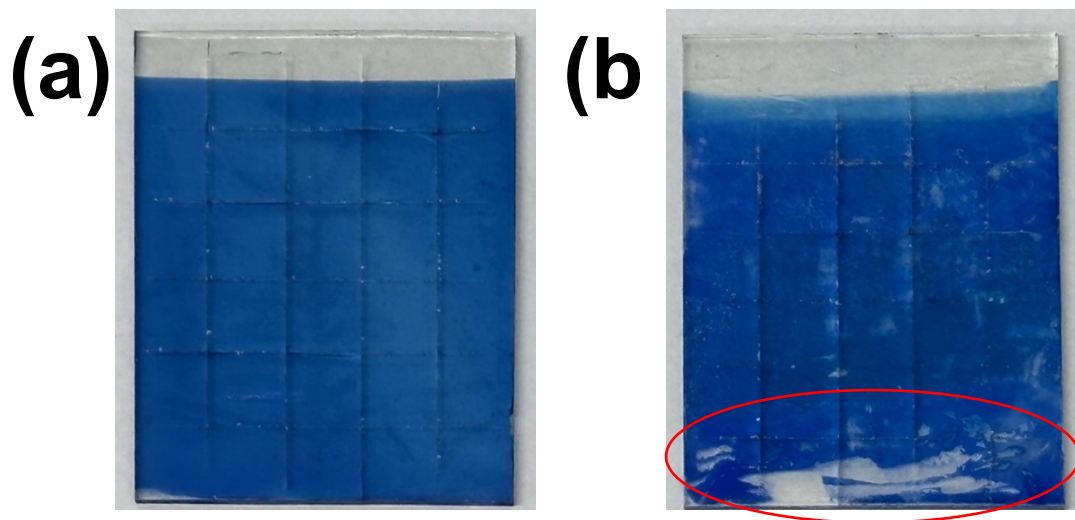


**Figure S6** The digital photo of the PB films at different preparation temperature.

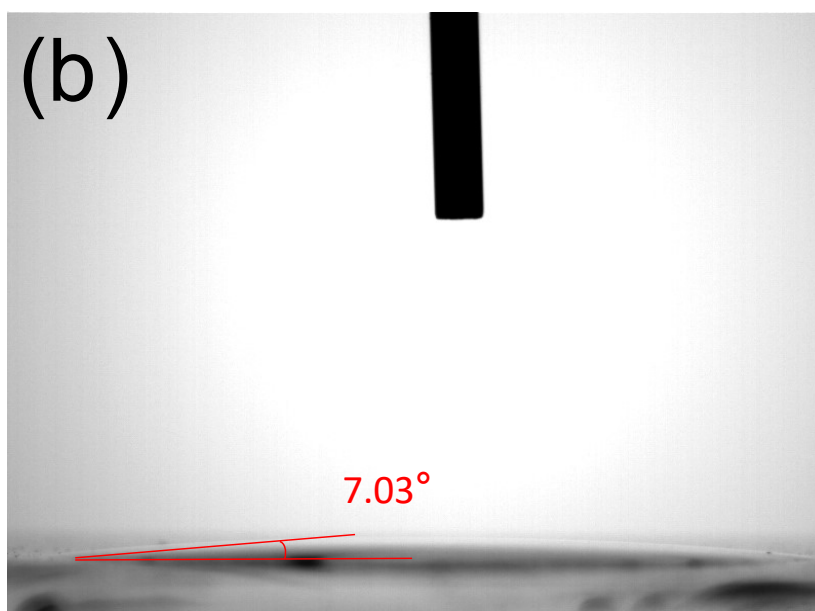
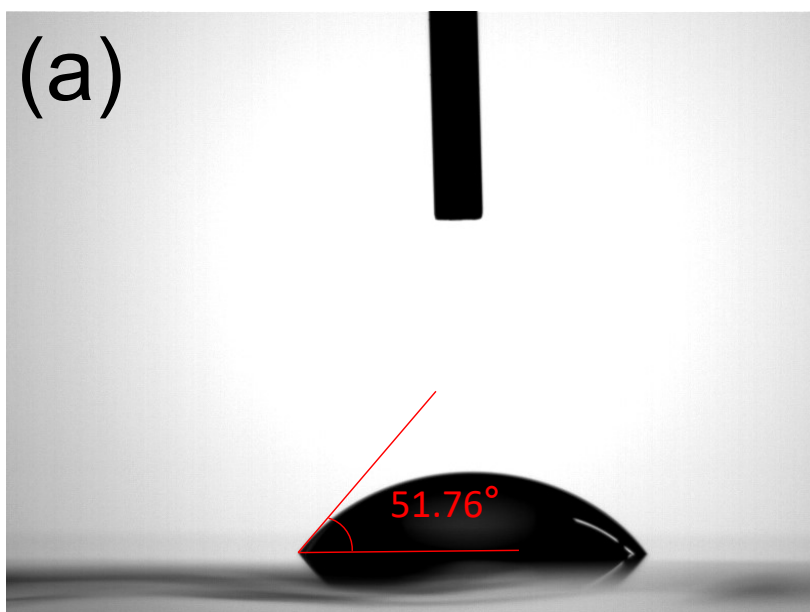


**Figure S7** The Nyquist plots of the PB films prepared by TAIG and electrodeposition.

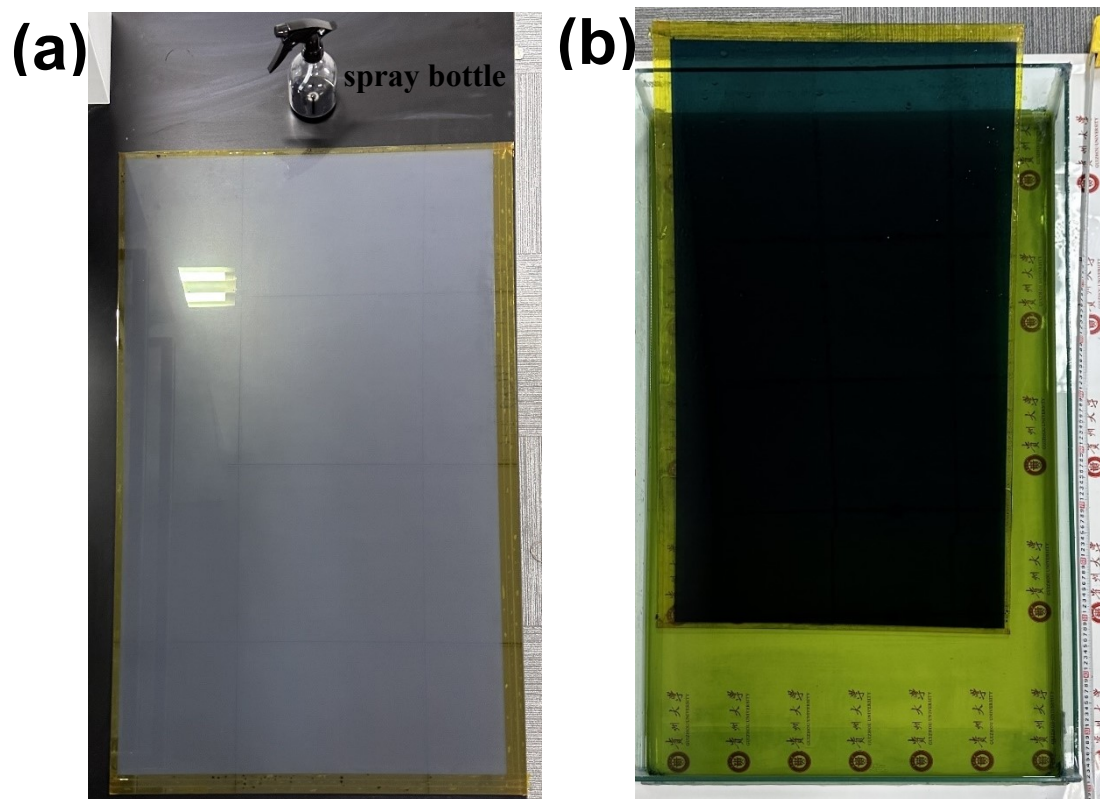




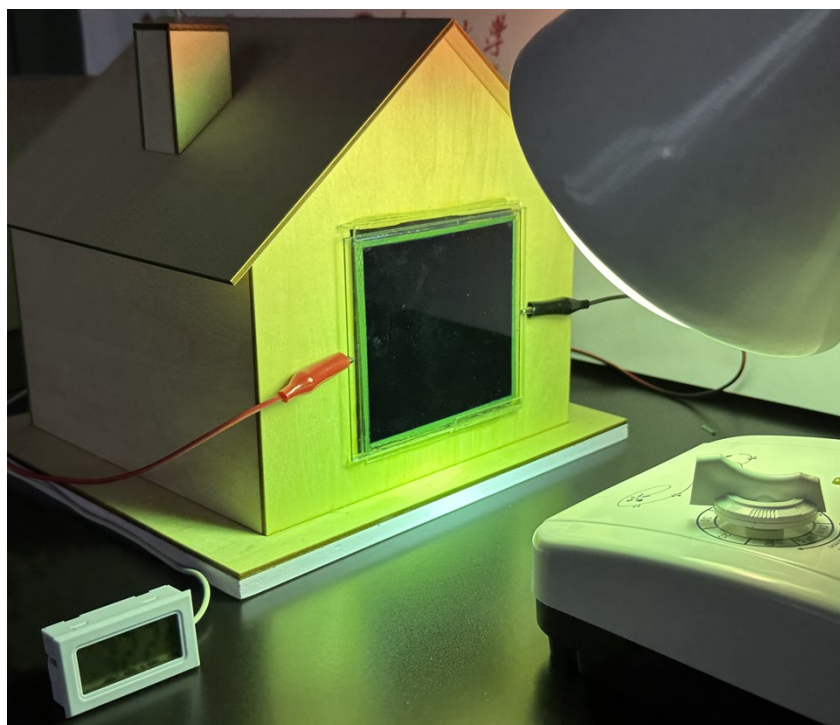
**Figure S8** The photos of PB films prepared by (a) TAIG and (b) electrodeposition after adhesion strength tests



**Figure S9** The contact angles of (a) pure FTO, (b)MXene/FTO.



**Figure S10** The digital photographs of (a) FTO substrate after spraying with MXene and (b) the finished PB film after growth.



**Figure S11** The digital photographs of testing solar shielding capabilities of smart window.

## 2. Experimental section

### Materials

Lithium fluoride (LiF) of high purity (99.99%), Titanium aluminium carbide ( $\text{Ti}_3\text{AlC}_2$ ) with a purity of 98%, Hydrofluoric acid (HF), Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) with a purity of 99.5%, Ferric chloride ( $\text{FeCl}_3$ ) of analytical reagent grade, concentrated Hydrochloric acid (12 M), Potassium molybdate ( $\text{K}_2\text{MoO}_4$ ) with a purity of 98%, Potassium chloride (KCl) of analytical reagent grade, Propylene carbonate (PC), and Lithium perchlorate ( $\text{LiClO}_4$ ), along with other chemicals and solvents, were procured from reputable commercial sources and employed without further purification. Fluorine-doped tin oxide (FTO) glass substrates boasting a sheet resistance of  $15 \Omega/\text{cm}^2$  were acquired from the market. The FTO substrates were subjected to sequential ultrasonic baths in detergent, isopropyl alcohol, and distilled water, each for a duration of 30 minutes. Following meticulous drying in an oven, the glass substrates underwent a 30-minute ozone cleaning process in an ozone cleaner. This stringent procedure culminated in the acquisition of clean FTO substrates.

### Preparation of MXene suspension

A mass of 0.2 g of Lithium fluoride (LiF) and 0.2 g of Titanium Aluminum carbide ( $\text{Ti}_3\text{AlC}_2$ ) was weighed and subsequently dissolved in a volume of 10 mL deionized water. Following this, 30 mL of 12 M HCl and 2 mL of HF (50%) were added to the solution. The prepared solution was transferred to a PTFE beaker and stirred vigorously at  $37^\circ\text{C}$  for 48 hours. Upon the completion of the stirring regimen, a series of centrifugation steps using water were executed multiple times at a rotational speed of

3500 (r/min), ensuring the solution achieved a neutral pH. The obtained MXene precipitation was added with an appropriate amount of ethanol, and the MXene suspension was further centrifuged at a higher speed of 10,000 r/min after 1 h ultrasound under ice water bath. The MXene precipitate was collected and dispersed in ethanol, and ultrasound and centrifuged again. Subsequently, the concentration of the suspension was determined and appropriately diluted to achieve a concentration of MXene suspension suitable for use in subsequent experiments as 1 mg/mL.

### **Preparation of PB precursor solution**

Initially, a amount of 0.062 g  $\text{FeCl}_3$ , 0.146 g  $\text{K}_3\text{Fe}(\text{CN})_6$ , and 0.5445 g KCl was dissolved in 100 mL of deionized water, resulting in the formation of a Prussian blue solution (FeHCF). Subsequent to this, a quantity of 0.095 g of  $\text{K}_2\text{MoO}_4$ , 0.124 g of  $\text{K}_3\text{Fe}(\text{CN})_6$ , and 2.928 g of KCl was weighed and dissolved in 25 mL of deionized water, resulting in the generation of a pale yellow, clarified solution of a molybdenum-based Prussian blue analogue (MoOHCF). The two distinct solutions were then combined in a ratio of 4:1 and subjected to sonication using an ultrasonic cleaner until no signs of precipitation were observed. This process produces the desired precursor solution of FeHCF/MoOHCF.

### **Preparation of PB films by TAIG method**

First, one end of the FTO substrate was covered with polyimide tape to preserve a portion of the conductive surface for easy subsequent performance testing. MXene suspension was coated onto the FTO substrate by spraying, the ratio of required MXene suspension volume to FTO area is roughly 35 mL/m<sup>2</sup>. After drying in an oven for 5

minutes, the FTO glass was placed in the prepared precursor solution. After 15 minutes of immersion at 45°C, the homogeneous PB films were produced.

### **Fabrication of the ESWs**

The ultra-large area electrochromic smart window (ESW) was constructed employing a PB as the cathode material, with methyl viologen serving as the anode material, and 1M LiClO<sub>4</sub>/PC employed as the electrolyte. A PB film spanning a considerable area of 100×70 cm<sup>2</sup> was fabricated utilizing TAIG method. Pure FTO substrates of the same size and PB film were bonded together with hot glue gun.

The assembly procedure for devices with high-resolution customised patterns is very similar to the process described above, with one notable difference being that the MXene layer was covered with GZU pattern plate. Upon immersion in the solution, the film grows along the apertures, whereas the area covered by the tape does not. The rest of the device assembly step replicates the above sequence, resulting in an ECD with a high-resolution customized pattern.

### **Characterizations**

The morphology of PB films were characterized by SEM (ZEISS Gemini 300). XPS (Thermo Scientific K-Alpha) was conducted to characterize the chemical composition of the PB films. The phase and structural information of the PB films was conducted using D8 Advance (Bruker, Germany) XRD with a Cu Ka ( $\lambda = 0.154$  nm) radiation target, transmission electron microscopy (TEM, F200, Japan). GIWAXS data were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic of the light source was 1.54 Å. The data

were recorded by using the two-dimensional image plate detector of Eiger 2M from Dectris, Switzerland. The weight loss of the PB films was tested by TGA (TG 209 F3, Germany) during the temperature increase from 30°C to 650°C at a temperature increase of 10°C/min. Contact Angle Measuring Instrument (JC2000D1, Powereach, China) was used to investigate the hydrophilicity of FTO substrates coated with MXene. The electrochemical tests were recorded by an electrochemical workstation (CHI 760E, Shanghai Chenhua) with the three electrodes system. The transmittance curves were carried out by the UV (S6300, Shanghai Mapada), and the optical variation was also tracked in terms of the color coordinates  $L^*$ ,  $a^*$ ,  $b^*$  (CIELAB) by the Portable spectrophotometer (3NH, YS4510).

### **Electrochemical measurements**

A three-electrode electrochemical cell was used for electrochemical tests, the reference electrode was Ag/AgCl, and a platinum sheet served as the counter electrode, PB films coated on FTO as working electrode, while a two-electrode configuration was used for the test of ECDs. The CV was tested at different sweep rates ranging from -0.8 V to 1.8 V. The amperometric  $i$ - $t$  curve as parameterized for 400 s at -0.8 V. Multi-potential steps test was performed with two-step cycles at 0.6 V for 20 s, -0.8 V for 25 s. EIS analysis of the PB films was performed by employing an AC signal of small amplitude that is 5 mV when the corresponding frequency changed from 100 KHz to 0.01 Hz. The equivalent circuit were fitted by ZSimpWin software, and the fitting errors for each component is less than 10%.



## **Demonstration of solar thermal shielding capability**

First, a hollow window measuring  $10 \times 10 \text{ cm}^2$  was carved at the center of a wooden house model with dimensions of  $25 \times 25 \times 20 \text{ cm}^3$ . Subsequently, a  $10 \times 10 \text{ cm}^2$  ESW was fabricated employing TAGI method detailed earlier, and seamlessly integrated onto the house model. In order to monitor the fluctuation of the temperature inside the model in real time, a simple temperature sensor with a temperature probe reaching in center of the model was used. To emulate natural sunlight, a UV light source (ULTRA-VITALUX) possessing a power output of 300W was employed. The light source was fixed 10 cm in front of the model to simulate sunlight hitting the glass windows of the building. After starting the light source, the change in temperature inside the model was recorded over a period of 30 minutes by means of a temperature detector. Commercially available glass of the same size was affixed to the model as a comparison test and the above test operation was repeated.

## **Theoretical calculations**

The study used VASP to perform density functional theory calculations with projector augmented wave<sup>1,2</sup>. The Perdew-Burke-Ernzerhof (PBE) functional was employed for exchange-correlation effects<sup>3</sup>, while DFT+D3 was used for handling weak interactions<sup>4</sup>. The cut-off energy for the plane-wave basis was 450 eV. K-points were  $1 \times 1 \times 1$  in the Brillouin zone. 15 Å of layer vacuum was applied at Z-axis of heterojunction models to avoid the Periodic effect. Energy and maximum stress were converged to  $10^{-5} \text{ eV}$  and  $0.03 \text{ eV/\AA}$ , respectively.

## References

1. G. Kresse, & J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical review B*, 1996, **54**, 11169.
2. P. E. Blöchl, Projector augmented-wave method, *Physical Review B*, 1994, **50**, 17953-17979.
3. J. P. Perdew, K. Burke, & M. Ernzerhof, Generalized gradient approximation made simple, *Physical Review Letters*, 1996, **77**, 3865.
4. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *Journal of Chemical Physics*, 2010, **132**, 154104.