Supplementary Information

Self-healing electrochromic energy storage device based on PEDOT:PSS

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Preparation of PEI-self-healing film

A solution with a mass fraction of 0.4wt% was prepared by taking an appropriate amount of PEI. The solution was spin-coated on the cleaned FTO glass at a speed of 3000 rpm / min using a spin coater for 40 s. The spin-coated FTO glass was dried in an oven at 60 ℃. Take 3mL PEDOT : PSS solution, add 4% PEG solution to it, stir well, and then add 4.5% PA solution. The mixed solution was placed in an oven at 90 °C for 3 h. Finally, the mixed solution was dropped onto the dried FTO glass, and the spin-coated film was dried in an oven at 60 °C.

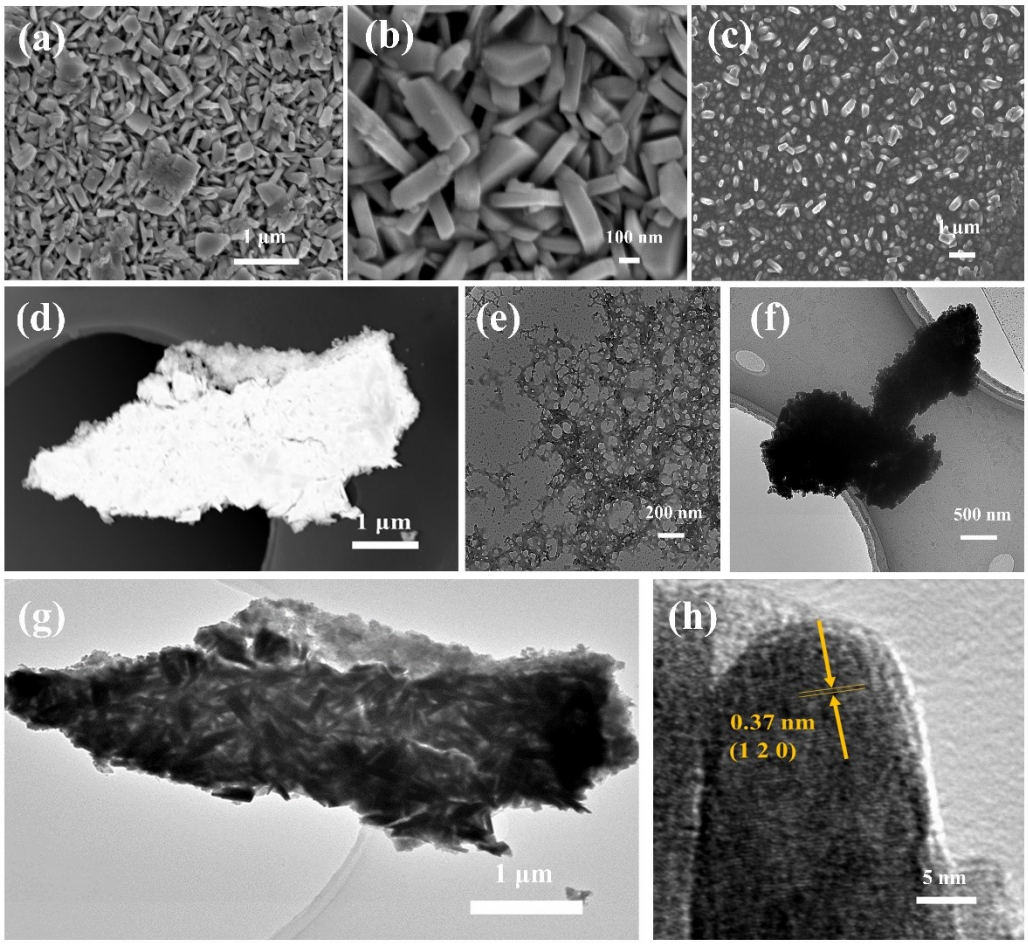

Fig. S1. The (a) low magnification SEM image and (b) high magnification SEM image of WP film. (c) low magnification SEM image of WPSH film. (d) TEM image in dark field of WP film. TEM image of (e) PSH film and (f-g) WPSH film. (h) HRTEM image of WPSH film.

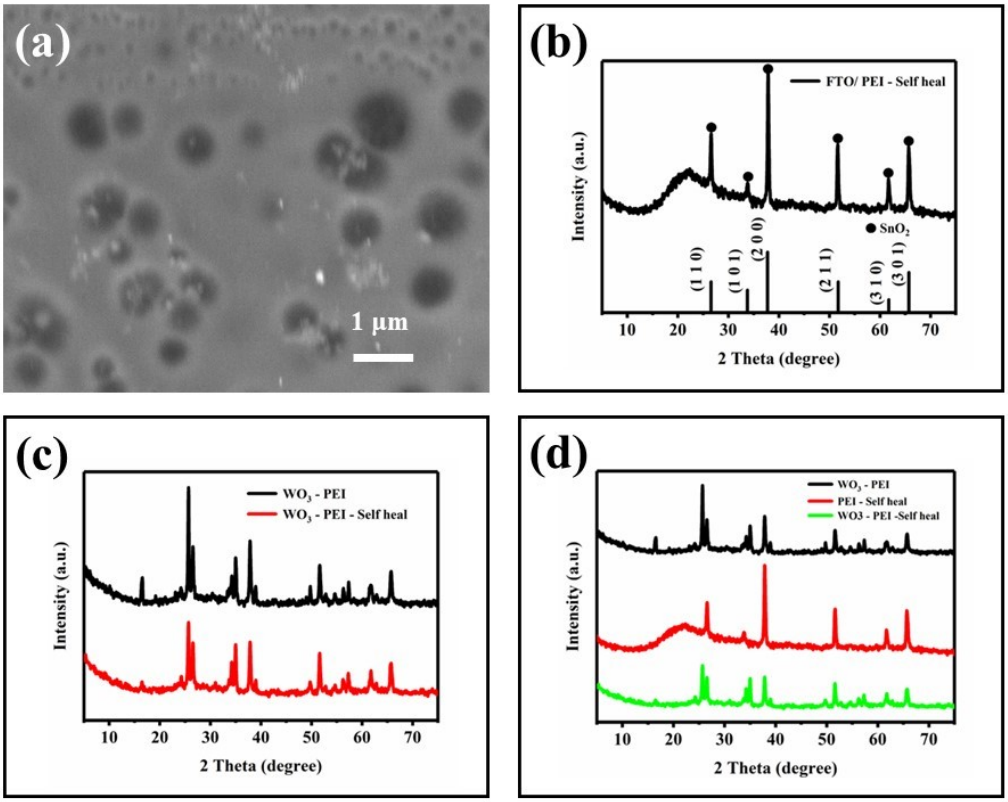

Fig. S2. (a) SEM image of PSH film, and corresponding XRDs of (b) PSH film, (c) XRD comparison of the two films. (d) XRD comparison of three films.

As shown in Fig. S3, the uniform distribution of N, P and S elements indicates the successful preparation of PSH films.

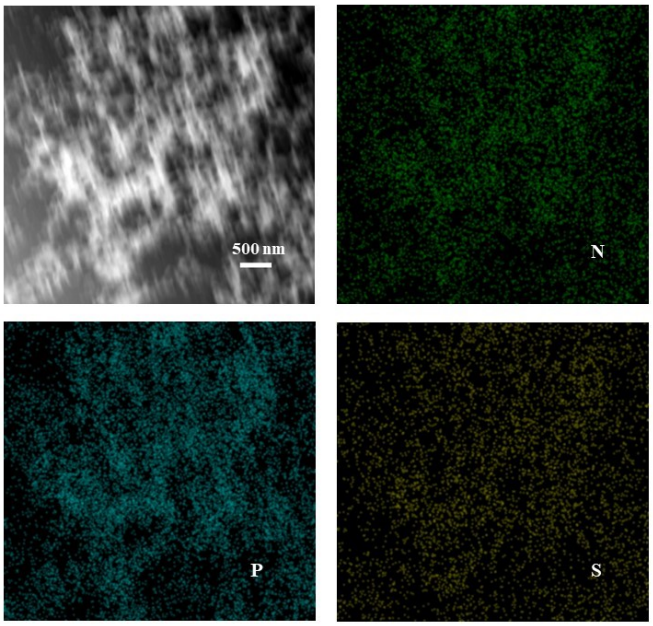

Fig. S3. EDS mappings images of PSH film.

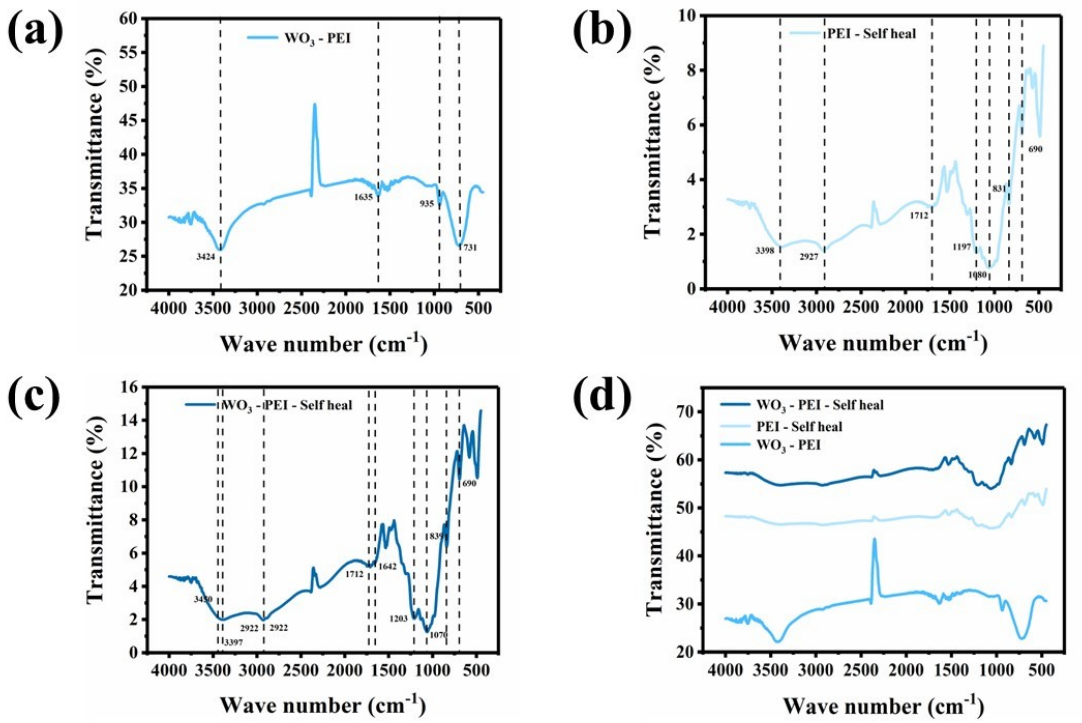

Fig.S4. (a) FTIR spectra of WP film, (b) FTIR spectra of PSH film, (c) FTIR spectra of WPSH film and (d) Comparison of FTIR spectra of three kinds of films.

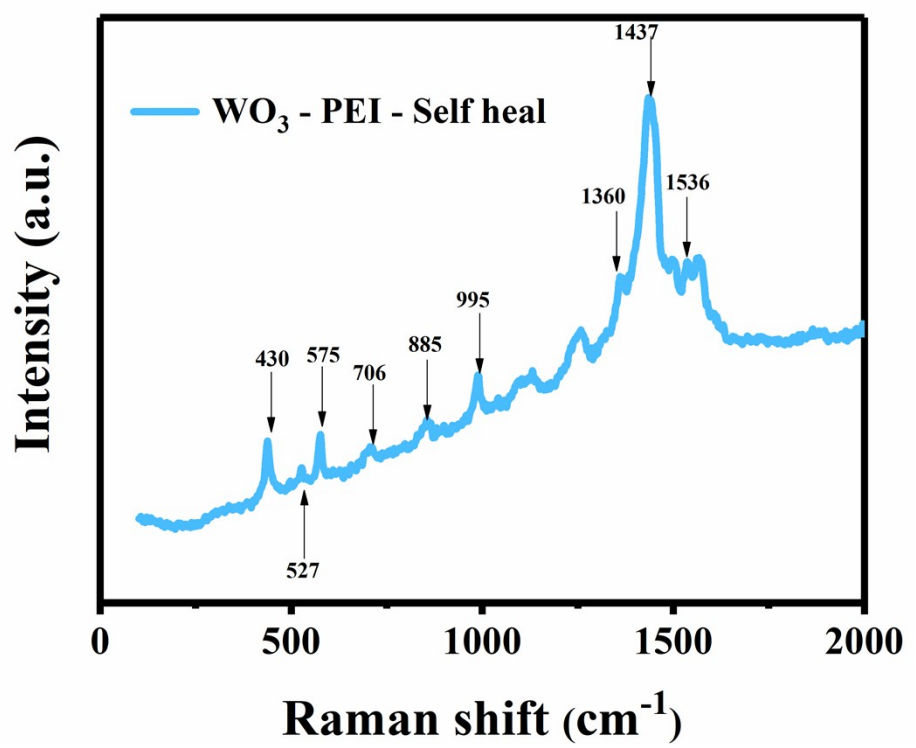

Fig. S5. Raman Spectrogram of WPSH film.

Self-healing experiment

Cutting experiment

In the self-healing experiment under optical microscope, a mixed organic solution was dropped on a 1.5 cm×2.5 cm glass, dried and tested under an optical microscope.

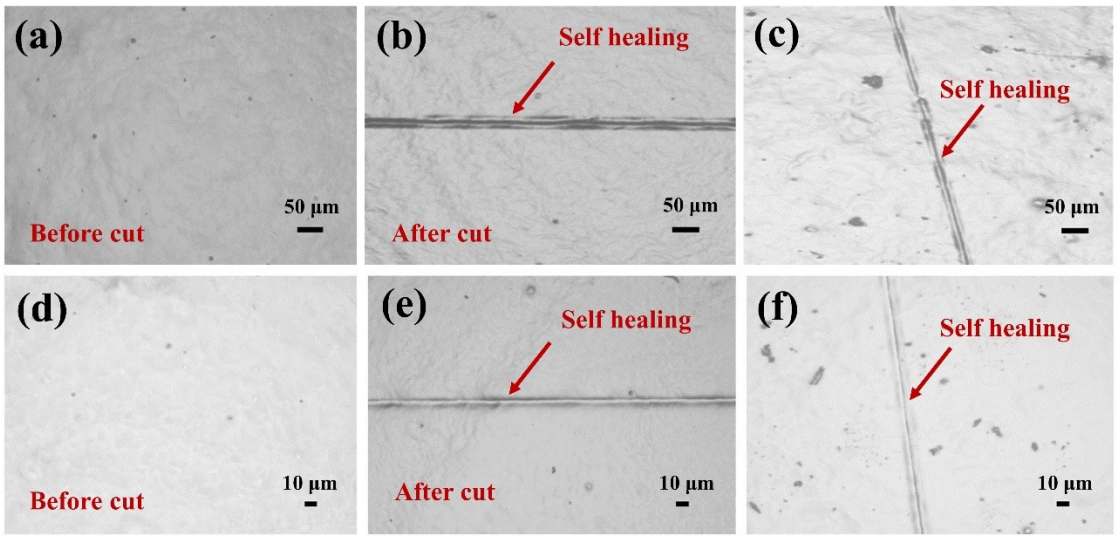

Fig. S6. (a) 50x optical microscope images of film surface and (b-c) self-healing after cutting. (b) 100x optical microscope images of film surface and (e-f) self-healing after cutting.

As shown in Fig. S7, when the incision is greater than 20μm, the film cannot achieve self-healing.

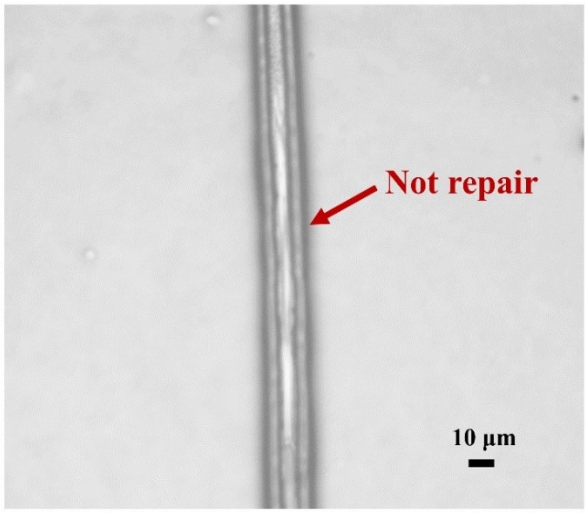

Fig.S7. Cutting unrepaired images under a 100x optical microscope

Experiments corresponding to Fig. 4a-b in the main text. The glass slide was coated with 150 μL organic mixed solution. After drying, the film was connected to the electrochemical workstation, and a constant voltage of 5 V was input. After the current was stable, the film was cut with a stainless steel blade. During each cutting, the film has an incision, and the current will decrease briefly. However, due to the good repairability of the film, the current will rise rapidly and return to normal. The stainless steel blade is conductive, which will have some influence on the cutting experiment. In order to eliminate the influence, the self-healing of the film is more fully proved. We also used a non-conductive ceramic blade to re-experiment under the same conditions. The current decreases more obviously during cutting, but it will return to normal soon. This reflects the reason behind the current recovery, the influence of stainless steel blade is not large, mainly due to the good repair performance of the film.

A 150 μL organic mixed solution is dropped on the slide, dried and filmed, and then connected to the circuit with the LED bulb. The film was cut with a stainless steel blade and a ceramic blade to observe the LED bulb.

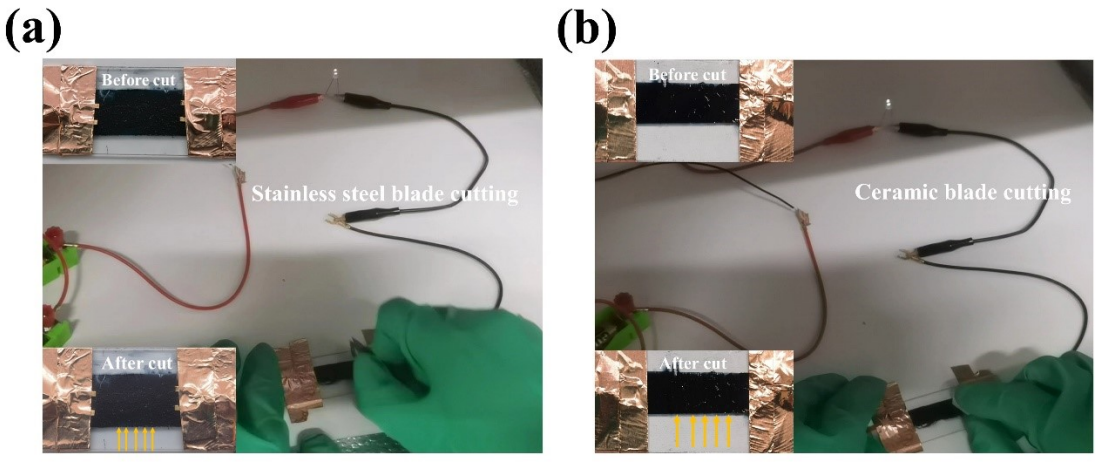

Fig.S8. The state diagram of the LED bulb during the cutting / repairing process of the mixed organic film. (a) stainless steel blade cutting (b) ceramic blade cutting. The arrow refers to the location of the scratch.

Pressing experiment

200 μL of mixed organic solution was dropped on the slide, dried and connected to the electrochemical workstation. Input constant voltage 1.5 V. The glass slide is covered on the film (the size of the glass slide should not be pressed against the electrode), and the film is pressed by a uniform circulating reciprocating electric machine. Using different gears, the speed of the motor can be changed, so that the film can undergo different degrees of deformation when subjected to compression, which can be seen from the degree of current change. The film is pressed first and deformed, so that the resistance increases and the current decreases. When the motor is lifted, the pressure disappears, the film quickly returns to its original state, and the current returns to normal. In the cyclic pressing experiment. In the early stage of pressing, the film deforms greatly, making the overall current decrease more obvious. After 400 s, the film reached the deformation balance and the change of current tended to be stable. At the end of the pressing, the current drop is not large. Before and after pressing, we use the current through the film to determine its self-healing performance. Compared with the current at the balance of deformation (400s), there is a retention rate of 74%, compared with the current at the beginning of pressing (0s), there is a retention rate of 57 %. In Fig. S10, we performed 1660 cycles of nine-stage cyclic pressing experiments on the film after a period of pressing. Before the cyclic pressing experiment, each film will be pressed for 1000 s in random mode with different gears.

The plastic sheet was cut into the same size as the slide, and 200 μL of mixed organic solution was dropped on it. After drying, it was connected to the electrochemical workstation. Input a constant voltage of 1.5 V. Cover the film with a plastic sheet, and the sheet cannot also compress the electrode. The same test method is used for testing.

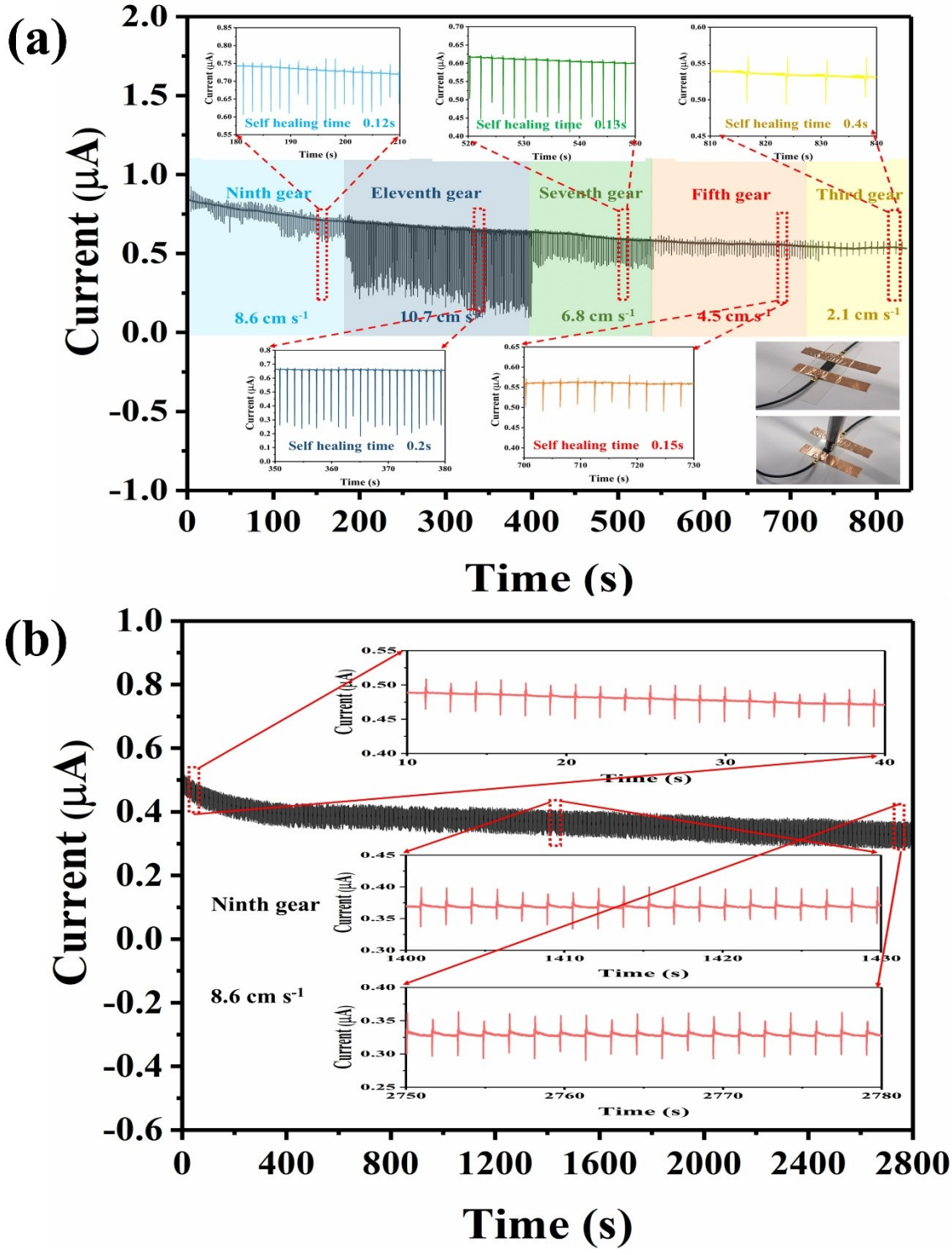

Fig.S9. The film drop-coated on the plastic sheet was subjected to (a) compression experiments at different gears and (b) cyclic compression experiments at nine gears.

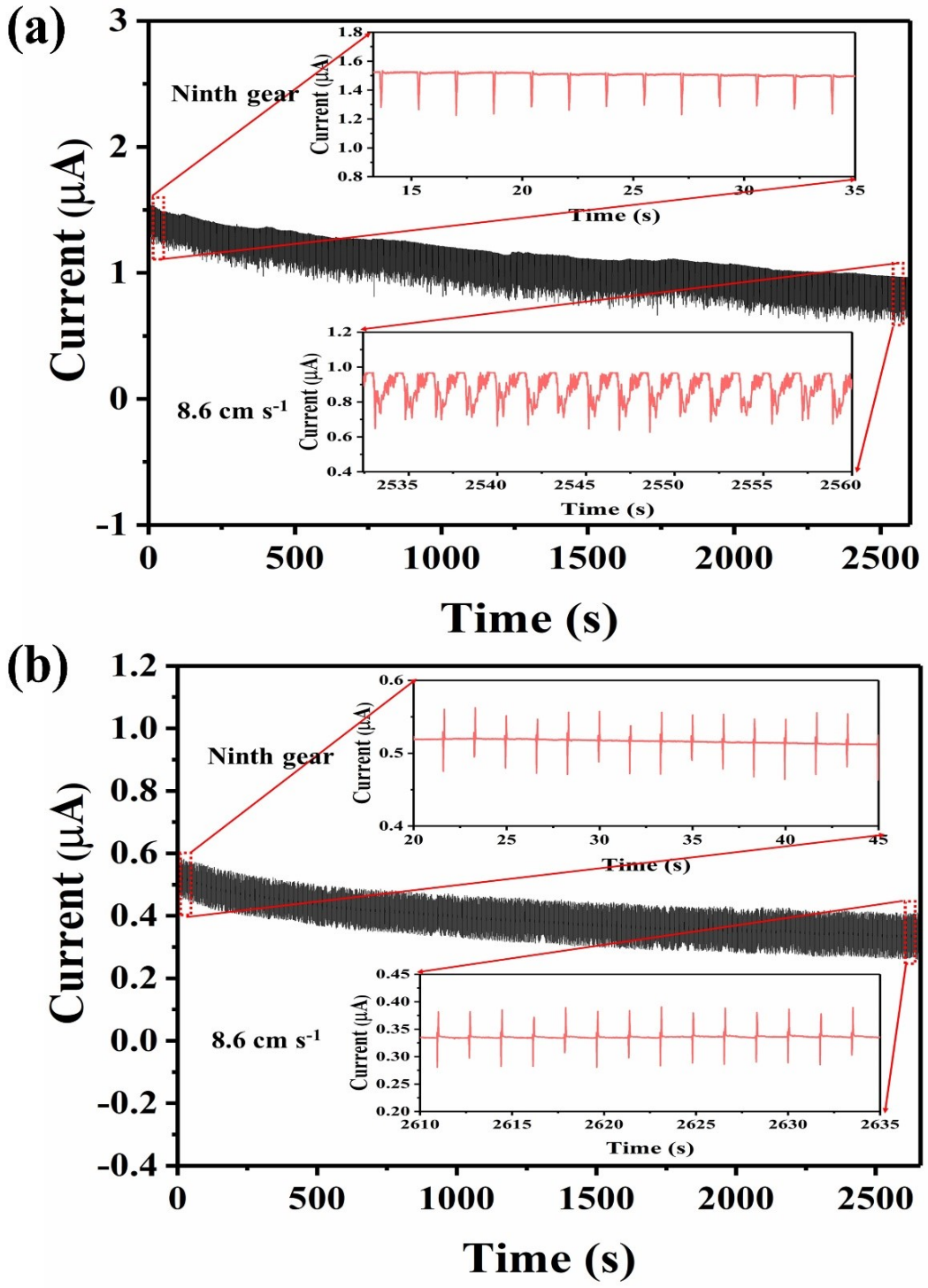

Fig.S10. After a period of pressing, (a) the film dropped on the glass slide and (b) the film dropped on the plastic sheet are pressed again.

Both PEDOT : PSS and WO_3 have suitable structures for the transport of H^+, and therefore also have certain energy storage properties. The introduction of modified PEDOT : PSS provides sufficient charge transfer pathways for WPSH composite electrodes, lowering the charge transfer potential barrier and providing more active sites for H^+ ion interactions, while also accelerating charge insertion/extraction between the WO_3 layer and electrolyte ions, thereby improving charge transfer efficiency and electrochemical performance [1]. PEDOT chains and PSS chains can fill the pores between the WO_3 nanosheets to form a dense surface layer, which in turn facilitates the formation of hybrid electrodes.

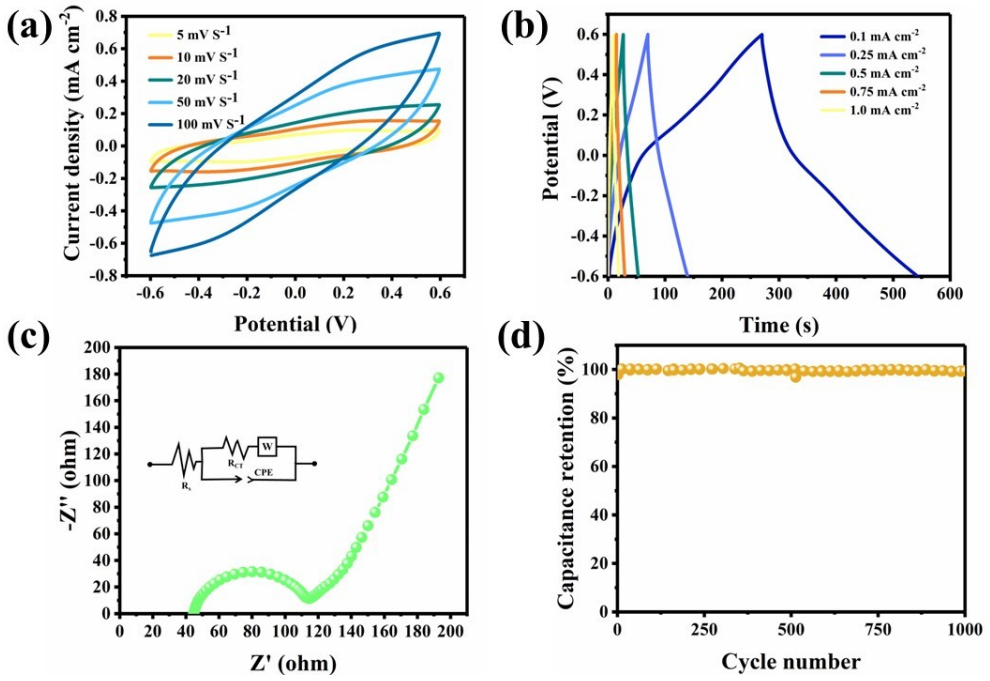

Fig. S11. (a) CV curves, (b) GCD curves, (c) EIS curve and (d) the capacitance retention rate of PSH device.

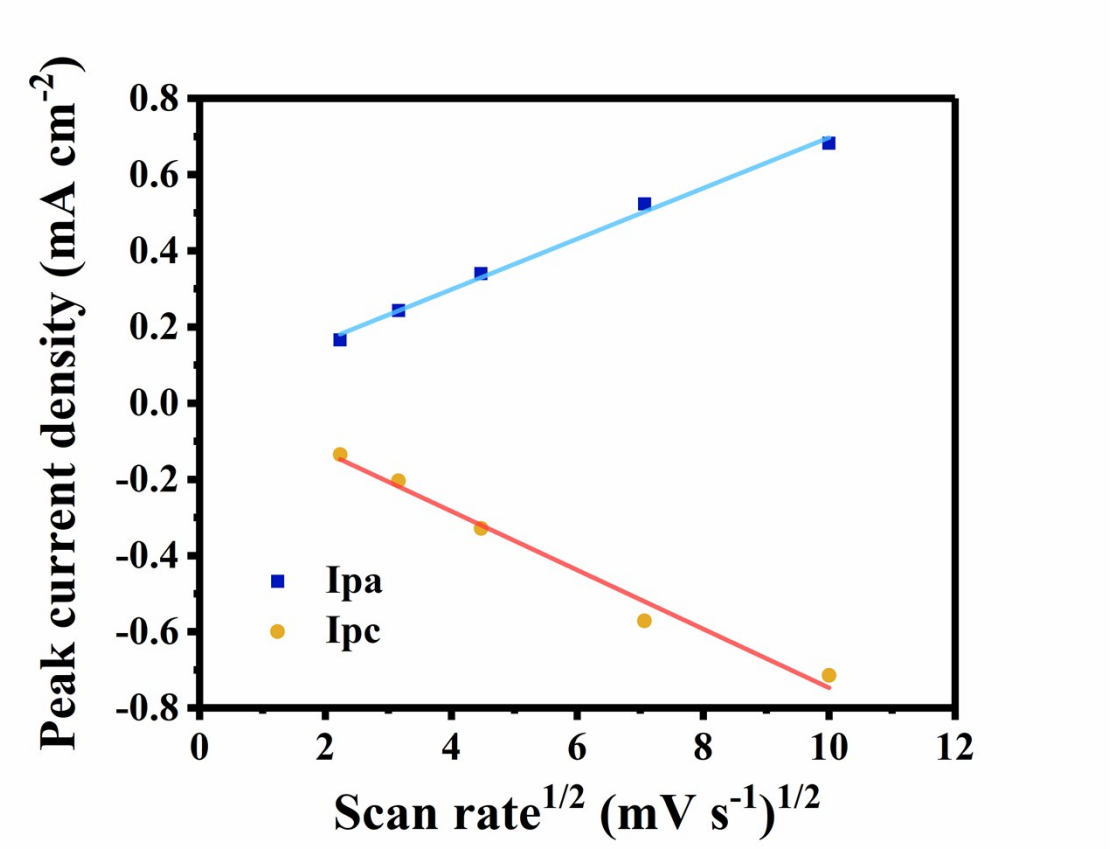

Fig. S12. Peak current density and sweep rate square root curve of WPSH device.

As shown in Fig. S12b, the EIS curves of the three, the PSH device has the smallest semi-arc radius in the high frequency region and the largest linear slope in the low frequency region, indicating that it has a low charge transfer resistance. Therefore, the combination of WO_3 and mixed organic films can effectively improve the performance.

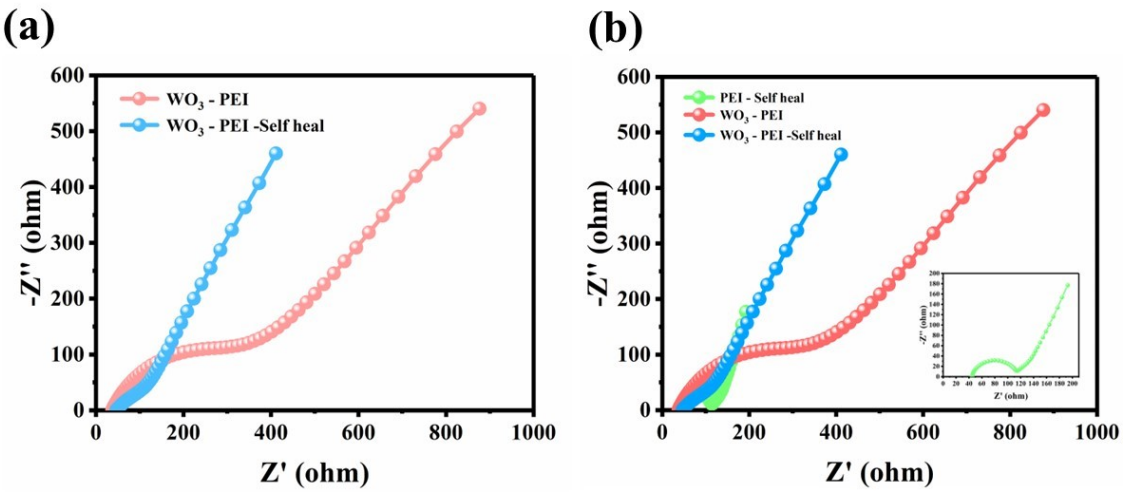

Fig. S13. (a) Comparison of EIS curves of WP film and WPSH film. (b) Comparison of EIS curves of the three films.

The amount of PEDOT : PSS will have an impact on the overall performance of the device [2]. The modified PEDOT : PSS solution is more viscous, and the spin coating method not only wastes reagents, but also results in uneven solution distribution, poor energy storage performance and self-healing performance. Therefore, we chose the drop coating method to ensure the energy storage and self-healing properties of the hybrid organic film by uniformly applying the modified PEDOT : PSS solution dropwise on the FTO glass with WO_3 grown hydrothermally. Hybrid organic films can rely on the movement of molecular chains of organic polymers for self-healing and do not require the use of water for induced repair as in the case of PEDOT : PSS alone. Of course, mixed organic films can be repaired in the presence of aqueous solutions [3].

During the preparation of hybrid organic films, sufficient drying is required to evaporate as much water as possible to ensure that their excellent self-healing properties are not related to aqueous solutions [3]. However, the molecular chains of organic polymers have a limited ability to recombine and cannot flow polymerize beyond a certain limit. In the reactive environment of aqueous solution, an electric field is applied and the polymer molecular chains undergo doping and de-doping of electrolyte ions and the material energy band gap is changed to achieve electrochromic effect [4]. At the same time, because of the addition of water, the fluidity between polymer molecular chains is enhanced, which makes the transmittance slightly improved after the coloring fades. In the macroscopic view, the effect is not significant.

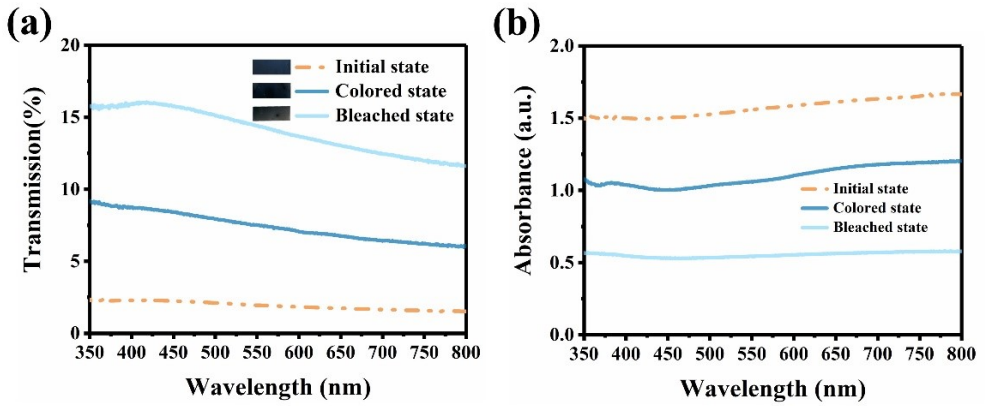

Fig. S14. (a) UV-VIS-NIR transmission spectra and (b) absorption spectra of PEI-Self healing films in initial state, coloring state and fading state. The illustrations from top to bottom are the images of initial state, coloring state and fading state.

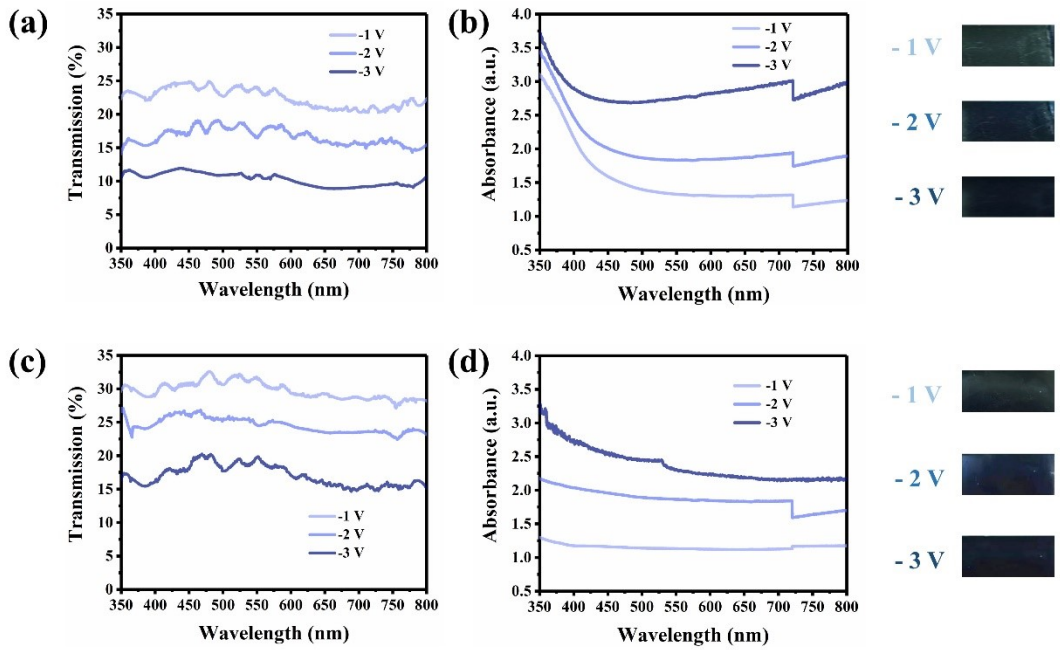

Fig. S15. (a) UV-VIS-NIR transmission spectra and (b) absorption spectra of WPSH device at different voltages. (c) UV-VIS-NIR transmission spectra and (d) absorption spectra of WPSH film at different voltages. The illustration shows colors of device and film at different voltages.

The coloring time of the film is calculated by the current-time curve, which is defined as the time taken for the current to decay to 20% of the absolute value of the maximum coloring (fading) current.

The film to be tested was used as the working electrode, the FTO conductive glass was used as the counter electrode, and the glass fiber (GF/D) diaphragm was placed between the two film electrodes. The size of the diaphragm was 1 cm × 1 cm. Sulphuric acid solution was dripped into the diaphragm and fixed with a swallowtail clip. The coloring process keeps constant pressure -1 V, -2 V, -3V 70 s; the fading was maintained at +1 V, +2 V, +3 V for 70 s. The WPSH device consists of two WPSH films.

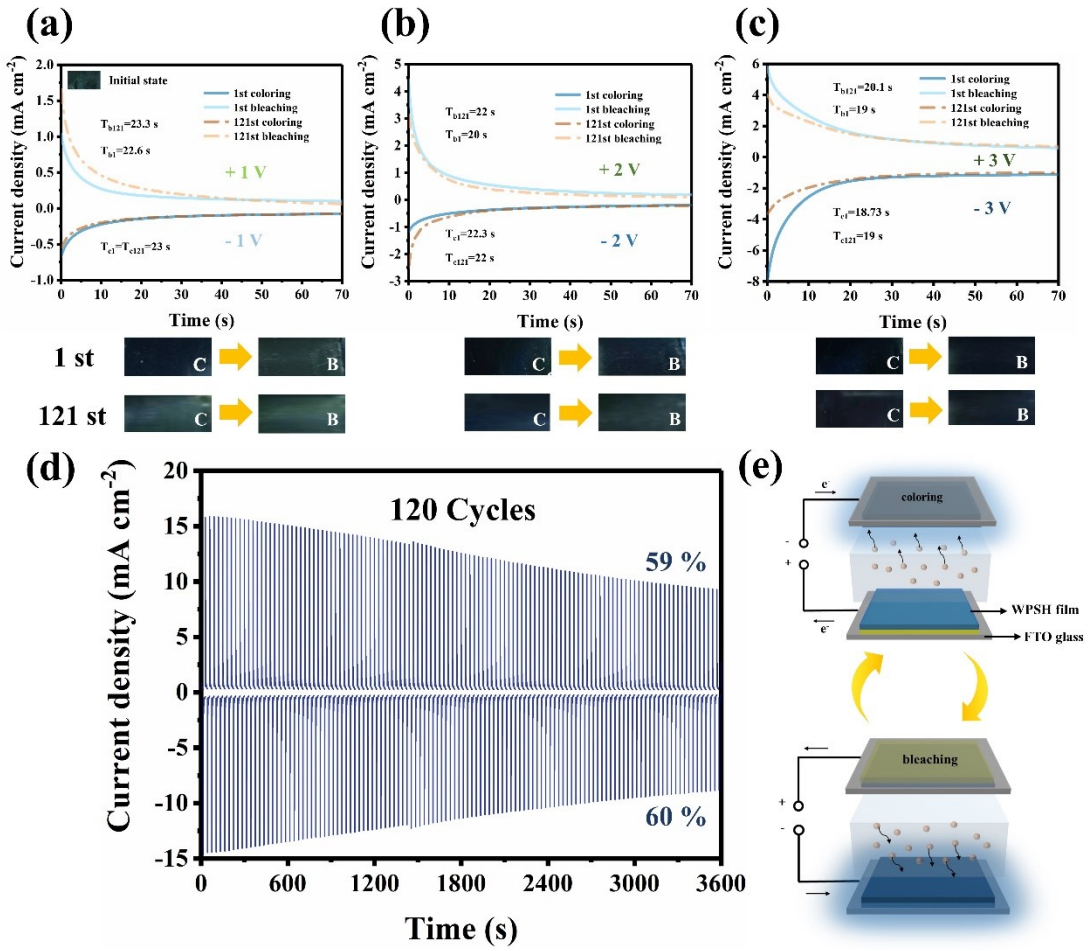

Fig. S16. (a-c) Coloring and fading time curves of WPSH device at ±1V, ±2V, ±3V, the inset below shows the color change of the WPSH device from coloring to fading at different voltages before and after the CA cycle. (d) CA Cycle Testing of WPSH device. (e) Schematic diagram of WPSH device color change.

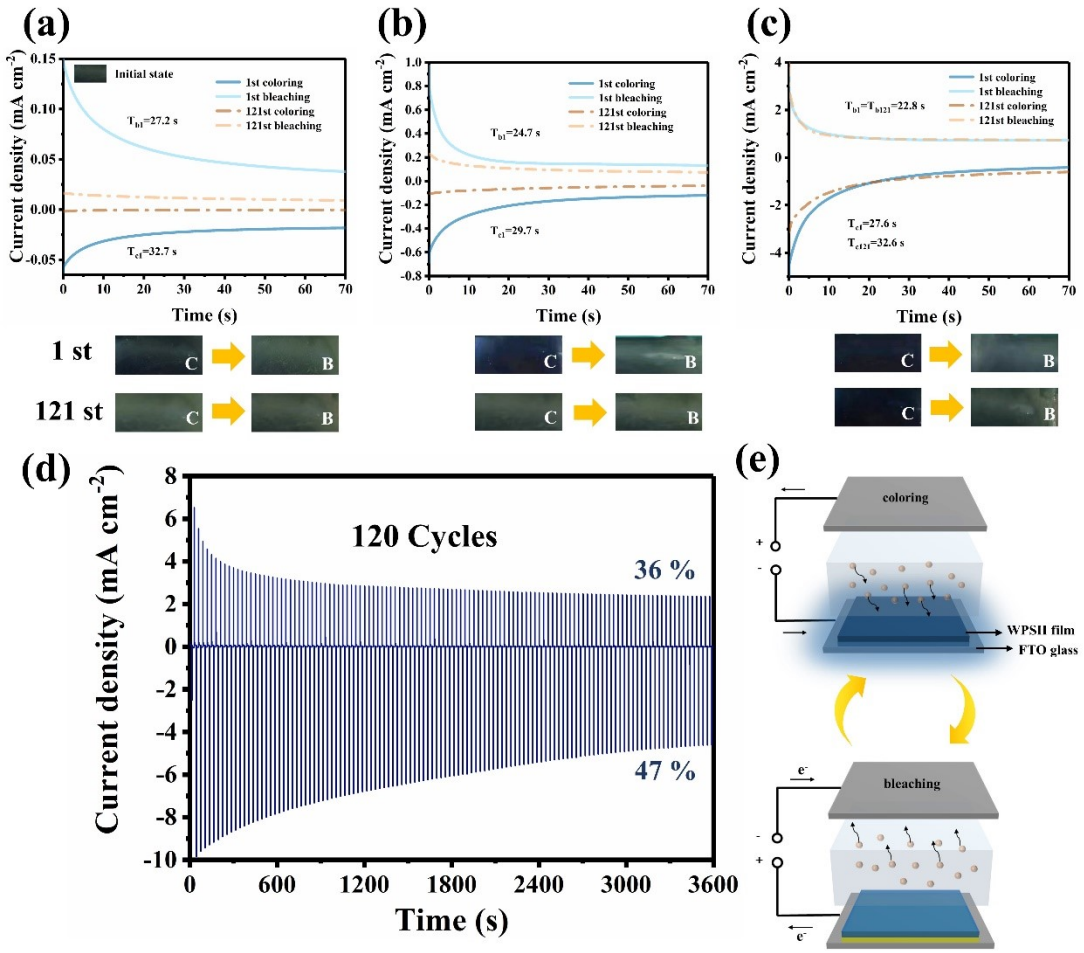

Fig. S17. (a-c) Coloring and fading time curves of WPSH film at ±1V, ±2V, ±3V, the inset below shows the color change of the WPSH film from coloring to fading at different voltages before and after the CA cycle. (d) CA Cycle Testing of WPSH film. (e) Schematic diagram of WPSH film color change.

1st	-1 V (C)	-2 V	-3 V	+1 V (B)	+2 V	+3 V
WO_3/PEDOT:PSS Device	23 s	22.3 s	18.73 s	22.6 s	20 s	19 s
WO_3/PEDOT:PSS Film	32.7 s	29.7 s	27.6 s	27.2 s	24.7 s	22.8 s

Table. S1. 1st Coloring and fading time curves of WO_3 /PEDOT : PSS device and film at ±1V, ±2V, ±3V.

121st	-1 V (C)	-2 V	-3 V	+1 V (B)	+2 V	+3 V
WO_3/PEDOT:PSS Device	23 s	22 s	19 s	23.3 s	22 s	20.1 s
WO_3/PEDOT:PSS Film	——	——	32.6 s	——	——	22.8 s

Table. S2. 121st Coloring and fading time curves of WO_3 /PEDOT : PSS device and film at ±1V, ±2V, ±3V.

Preparation Techniques	Transmittance	Capacitance	Number of Cycles	Cycle Retention	Self-healing Ability	Ref.
PPF/MA	ΔT = 42.7 %	——	——	——	Yes (4 min 110°C)	[7]
WO_3	——	69.9 mF cm^{-2} at 5 mV s^{-1}	2000	91.89 %	——	[39]
WO_3/NiO	ΔT = 76 %	2.57 mF cm^{-2} at 0.02 mA cm^{-2}	1000	93.8 %	——	[42]
Cu-doped NiO/WO_3	ΔT = 85 %	14.9 mF cm^{-2} at 0.1 mA cm^{-2}	10000	82 %	——	[43]
WO_3/Ppy/MnO_2	——	11.38 mF cm^{-2} at 20 mV s^{-1}	——	——	——	[44]
WO_3/Prussian white	ΔT = 53.6 %	1.97 mF cm^{-2} at 0.1 mA cm^{-2}	1000	99%	——	[45]
WO_3 BNW/FTO	ΔT = 45.81 %	22.7 mF cm^{-2} at 1.5 mA cm^{-2}	10000	90%	——	[46]
Bpy/Fc	ΔT = 12.5 %	——	——	——	Yes (20 min)	[47]
WO_3/PEDOT : PSS	ΔT = 5 %	105.35 mF cm^{-2} at 0.1 mA cm^{-2}	1000	98.2%	Yes (1.44 s)	**This work**

Table.S3. The comparison table between this work and other similar work.

References

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