

# Supporting information

## Highly Stretchable Electrochromic Hydrogels for Wearable Electronic Devices

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## 1. Experimental details

### *Materials.*

The base and curer of polydimethylsiloxane (PDMS) were purchased from Dow Corning. The silver nanowires (L30, diameters-30 nm, length-100-200  $\mu\text{m}$ ) were bought from Nanjing XFNANO Materials Tech Co.,Ltd. 4-OH Tempo, potassium chloride (KCl), ammonium persulfate (AP), N,N-methylenebisacrylamide (MBAA), chloroauric acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), L-arginine were purchased from Energy Chemicals, China. P-benzoquinone (p-BQ), acrylamide (AAM), N, N, N', N'-tetramethylethylenediamine (TEMED), dopamine hydrochloride were purchased from Aladdin Chemicals, China. Thymol blue sodium salt (M-G) and phenol red sodium salt (M-R) were bought from TCI (Shanghai) Development Co., Ltd. The hydrochloric acid, nitric acid and hydrogen peroxide were purchased from the Beijing Chemical Works. The ITO and FTO were purchased from South China Xiang Science & Technology company. All the solvents were purchased in commercialized way and used without further purification.

### *Instrument.*

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. The electrochemical data were obtained from Bio-logic electrochemical work station. UV-Vis absorption spectra and optical transmittance spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer. The sheet resistances of stretchable electrodes were measured using a ST-2258C multifunction digital four-probe tester. The reflective spectra of electrochromic device and in situ kinetic measurement were recorded by Maya 2000PRO fiber optical spectrometer with Ocean DH-2000-BAL UV-Vis-NIR light source.

### *Synthesis of electrochromic hydrogels.*

The polyacrylamide (PAAM) hydrogel was synthesized as below: 2.2 mol/L AAM was dissolved in the deionized water, added MBAA  $6 \times 10^{-4}$  the weight of AAM, AP  $1.7 \times 10^{-3}$  the weight of AAM. After a clear precursor solution was produced, the system was bubbled with nitrogen to get rid of oxygen. And then the solution was degassed in a vacuum chamber. When the above treatments were finished, TEMED  $2.5 \times 10^{-3}$  the weight of AAM was added. The solution was put into a oven which was maintained the temperature of 60  $^{\circ}\text{C}$  with 12 hours. The gel was formed after the heat treatment. Then another solution with the same volume contained p-BQ ( $10^{-2}$  mol/L), 4-OH-Tempo ( $2 \times 10^{-2}$  mol/L), base-responsive molecule ( $2 \times 10^{-3}$  mol/L), KCl (1 mol/L) and 150  $\mu\text{L}$  hydrochloric acid (0.1 mol/L) were poured onto

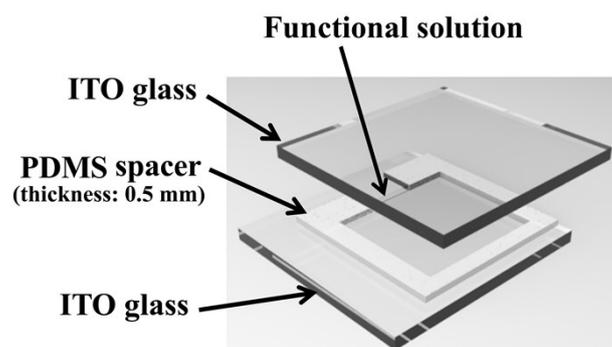
the hydrogel and heated at 60 °C with twelve hours again. After the above treatments, the hydrogel with electrochromic function was finally formed. Hereinto, 1,4-Dihydroxy-2,2,6,6-tetramethylpiperidine (4-OH-Tempo) could be used as an ideal ion storage material which had a good reversibility as revealed in **Figure S2g**.

#### ***The preparation of solid PDMS film and PDMS spacer***

Firstly, the base and curer of PDMS were mixed with the weight ratio of 10:1, then the mixture was degassed by a vacuum pump. After the above treatments, the mixture was poured onto a clean glass and heated at 60 °C for 12 h. Finally, the cured PDMS film with the thickness of 0.5 mm was prepared. And the PDMS spacer with various areas could be formed by a scissor.

#### ***Fabrication of the liquid electrochromic device.***

The structure of liquid electrochromic device was shown in **Scheme S1**. The functional solution contained  $1 \times 10^{-3}$  mol/L base-responsive molecule (M-R or M-G),  $5 \times 10^{-3}$  mol/L p-BQ,  $1 \times 10^{-2}$  mol/L 4-OH-Tempo, 0.5 mol/L KCl in 5 mL deionized water. The cured PDMS (thickness=0.5 mm) with a hole in center (area=2 cm\*2 cm=4 cm<sup>2</sup>) as the spacer was between two ITO glasses (each area=2.5 cm\* 2.5 cm=6.25 cm<sup>2</sup>). Then the functional solution was injected into the spacer and the liquid device was fabricated finally.

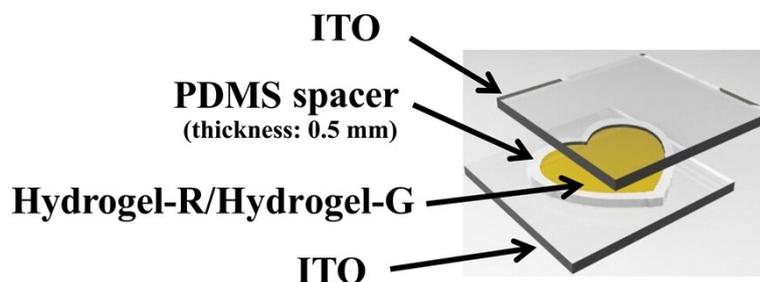


**Scheme S1.** The structure of liquid electrochromic device.

#### ***Fabrication of electrochromic hydrogel device.***

The structure of device containing electrochromic hydrogel could be shown in **Scheme S2**. ITO glass was used as electrode. The cured PDMS (thickness=0.5 mm) with a hole (area=2 cm\*2 cm=4 cm<sup>2</sup>) as the spacer was between two ITO glasses (each area=2.5 cm\* 2.5

cm=6.25 cm<sup>2</sup>). Finally, electrochromic hydrogel (hydrogel-G/hydrogel-R) was put into the spacer.



**Scheme S2.** The structure of the device containing electrochromic hydrogel.

#### ***Fabrication of stretchable gold electrodes.***

The process of the fabrication of stretchable gold electrode could be seen as **Figure S13**. And the detailed experimental operation was listed below.

The gold nanosheets were synthesized by a one-step hydrothermal synthesis: 1.7 mg of L-arginine was dissolved in 5 mL of water and the solution was heated to 95 °C. Meanwhile, 2 mL of aqueous solution containing 13.5 mg of hydrogen tetrachloroaurate trihydrate was rapidly injected into the reactor using a pipette. The reactor was kept at 95 °C for 2 h, and then cooled to room temperature in air.

Then the -SH function group was formed on the surface of PDMS (thickness=0.5 mm) by the reaction of MPTMS and PDMS after the hydrophilic treatment. Meanwhile, gold membrane was formed by the extraction filtration of solution of the gold nanosheets on a PC filter membrane. And the gold nanosheets was transferred to PDMS modified with MPTMS by the pressure. Finally, the stretchable gold electrode with high conductivity was fabricated.

#### ***Fabrication of stretchable transparent silver electrodes.***

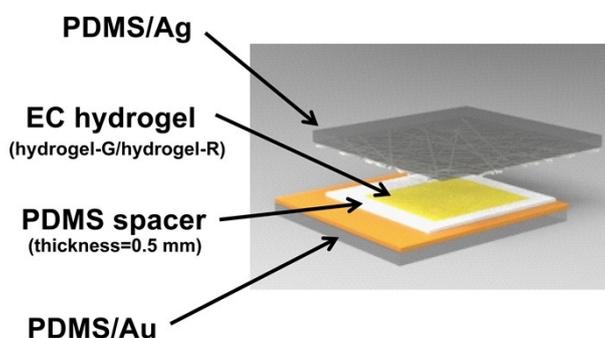
The process of the fabrication of stretchable silver electrode could be seen as **Figure 5a**. And the detailed experimental operation was listed below.

The electrode was fabricated by the combination of PDMS and silver nanowires. First, 10 mM Tris buffer solution was prepared using water and the pH was maintained at 8.5 by adding HCl. 5 mg dopamine hydrochloride was dissolved in 10 mL of Tris-HCl solution. Then, the PDMS films were then modified by simply soaking them in the dopamine solution for 24 h.

The Ag nanowires (3 mg/mL) dispersed in ethanol was spin-coated on the surface of the hydrophilic PDMS. And then the PDMS was at a pretrain state (40 %) to be deposited silver nanowires. The spin-coating condition was optimized in **Figure S2**. After the spin-coating, the PDMS with silver nanowires was heated at 60 °C to remove the residual solvent. Then the stretchable transparent silver electrode with high conductivity and transmittance was fabricated.

### ***Fabrication of the stretchable electrochromic device.***

The structure of the stretchable device containing electrochromic hydrogel was shown in **Scheme S3**. It contained a stretchable transparent silver electrode on the top and a stretchable gold electrode on the bottom. Then, the electrochromic hydrogel (hydrogel-G or hydrogel-R) was put into the device containing PDMS (thickness=0.5 mm) spacer.



**Scheme S3.** The structure of the stretchable device based on electrochromic hydrogel.

### ***The definitions of various switching times***

**Response time:** The time for device which it could reach the 90% of the total change of maximum absorbance/transmittance (increase for coloring and decrease for bleaching) between the colored state and bleached state.

**Open time:** The shortest time for device which has a detectable optical change.

### ***The measurements of electrochemistry***

Cyclic voltammetry (CV) experiments were measured using a Bio-logic electrochemical work station. Electrochemical experiments were conducted using three-electrode system in deionized water containing KCl (0.1 mol/L) as supporting electrolyte. The three-electrode cell consisted of a glass-carbon working electrode (3 mm dia., Chenhua, China), a Pt wire counter electrode (ida, China) and an Ag wire reference electrode (ida, China). The surface of the

working electrode was polished with 0.3 and 0.05  $\mu\text{m}$  alumina (ida, China) followed by ultrasonic cleaning in deionized water for three times.

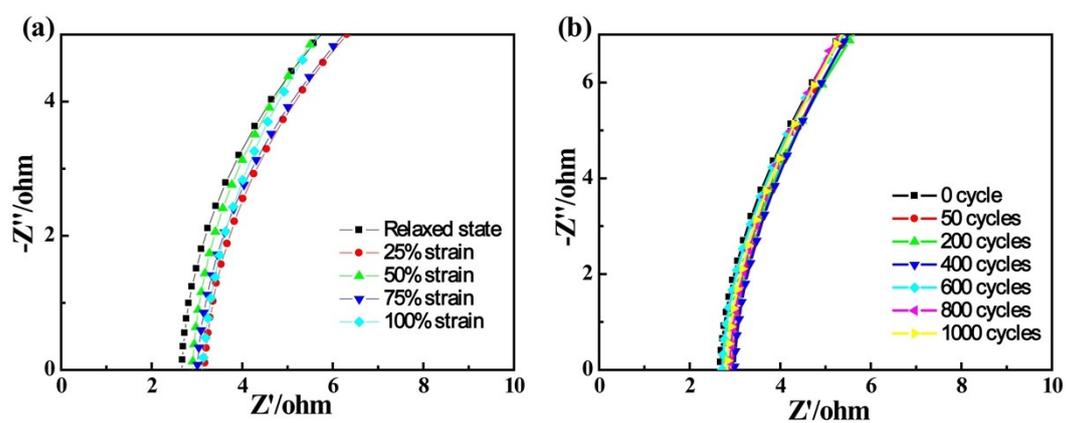
**Water solutions:** The three electrodes were inserted in measured solutions (1 mM molecule soluted in 0.1 mol/L KCl/H<sub>2</sub>O).

**Hydrogel matrix:** The prepared solution (1 mM molecule soluted in 0.1 mol/L KCl/H<sub>2</sub>O) were first combined with PAAM hydrogel by one-step swelling. And then three electrodes were inserted into hydrogel to get the electrochemical data.

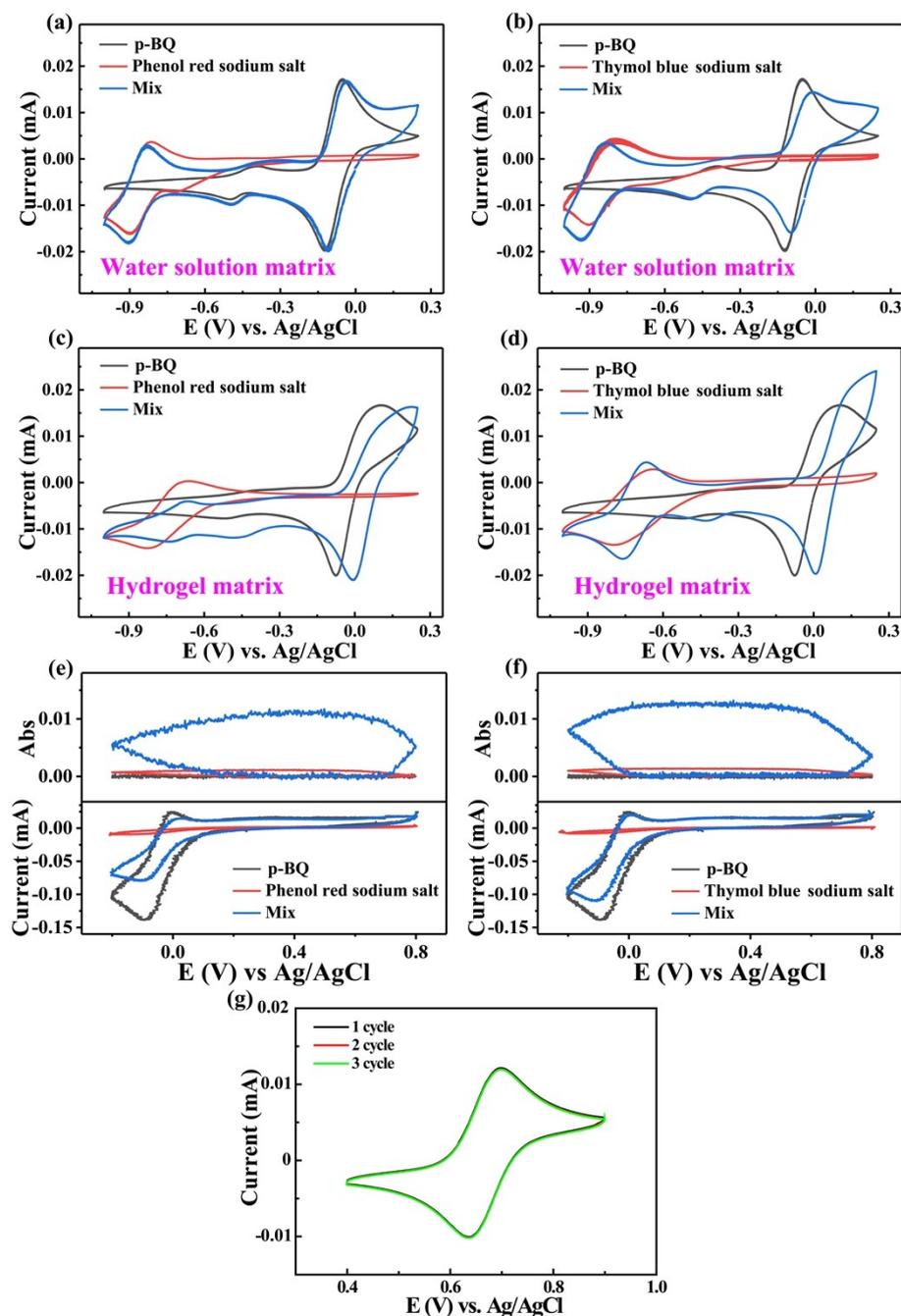
### ***The calculation of the coloration efficiency***

The coloration efficiency (CE) is defined as the change in absorbance or reflectance ( $\Delta A$  or  $\Delta R$ ) obtained for a specific amount of injected charge per unit area (Q/S). And Q/S is defined as charge density with the unit of mC/cm<sup>2</sup>. In this way, the coloration efficiency (CE) was calculated from the formula:  $CE = \Delta A/(Q/S)$  or  $\Delta R/(Q/S)$ . The area of device was 4 cm<sup>2</sup>. The change of absorption (or reflectance) with the injection of charge was measured by the combination of UV-vis spectrophotometer and electrochemical work station. The voltage parameter was added with -1.0 V for 60 s to reach the maximum colored state. So the CE plots could be shown as the increasement of absorption intensity with the injection of charge per unit. The tangent lines were corresponding to the CE of the device.

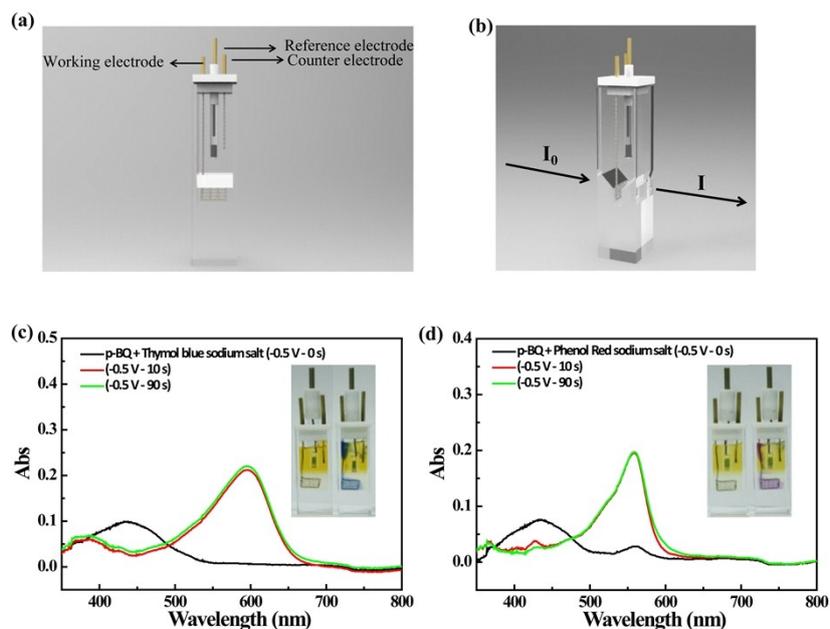
## 2. Characterization of stretchable electrochromic hydrogels



**Figure S1.** The Nyquist plots of KCl/PAAM gel electrolyte (a) at different strain applied and (b) after different stretching-relaxation cycles (strain=50%).

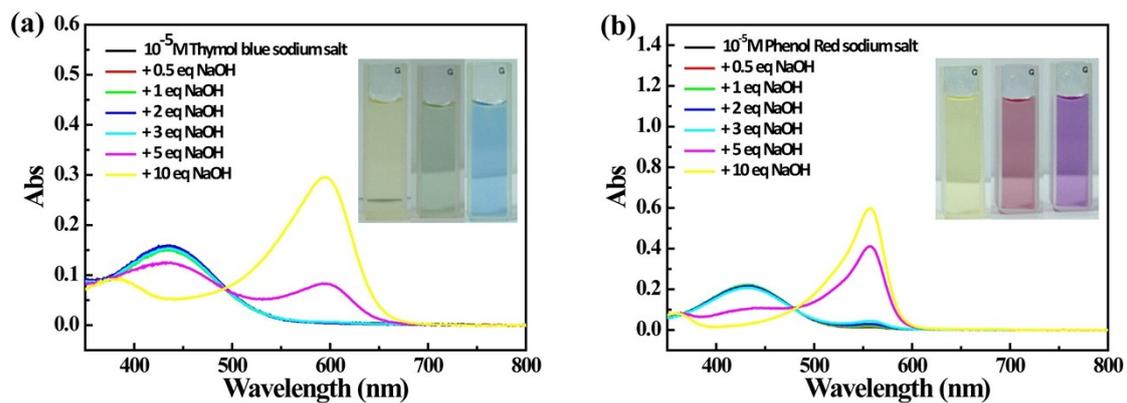


**Figure S2.** Cyclic voltammograms of 1 mM p-benzoquinone (p-BQ), 1 mM phenol red sodium salt (M-R) and the mixture of 1 mM p-BQ & 1 mM M-R in water (a) and in hydrogel matrix (c) with 0.1 M KCl. Cyclic voltammograms of 1 mM p-BQ, 1 mM thymol blue sodium salt (M-G) and the mixture of 1 mM p-BQ & 1 mM M-G in water (b) and in hydrogel matrix (d) with 0.1 M KCl. (e) Changes in absorption at 559 nm (top) and cyclic voltammograms (bottom) ‘in situ’ of p-BQ (0.5 mM), M-R (0.1 mM) and p-BQ & M-R (0.5 mM & 0.1 mM) in 0.1 M KCl/H<sub>2</sub>O. (f) Changes in absorption at 595 nm (top) and cyclic voltammograms (bottom) ‘in situ’ of p-BQ (0.5 mM), M-G (0.1 mM) and p-BQ & M-G (0.5 mM & 0.1 mM) in 0.1 M KCl/H<sub>2</sub>O. (g) Cyclic voltammograms of 1 mM 4-OH-Tempo in 0.1 M KCl/H<sub>2</sub>O for three cycles.

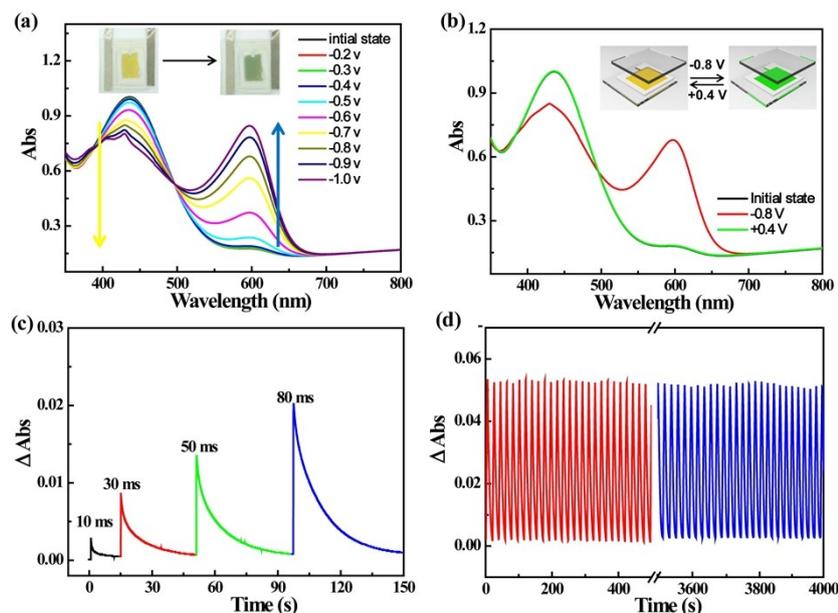


**Figure S3.** (a) The structure of a thin-layer quartz electrochemical cell for measuring in-situ the UV-Vis spectra of redox state in solution. (b) The route of ultraviolet and visible lights. UV-Vis spectra of the mixture of 0.5 mmol p-BQ with (c) 0.1 mmol thymol blue sodium salt, (d) 0.1 mmol phenol red sodium salt when the -0.5 V voltage is applied in 0.1 M KCl/H<sub>2</sub>O.

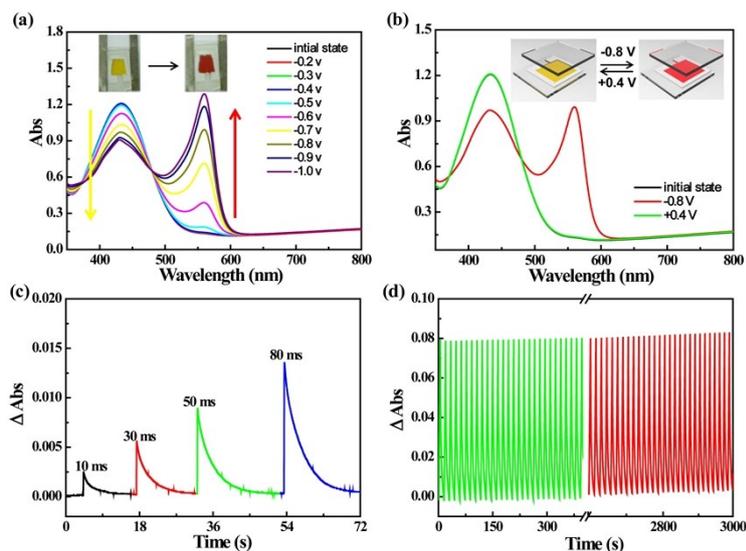
(The three electrodes contained a Pt network working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode.)



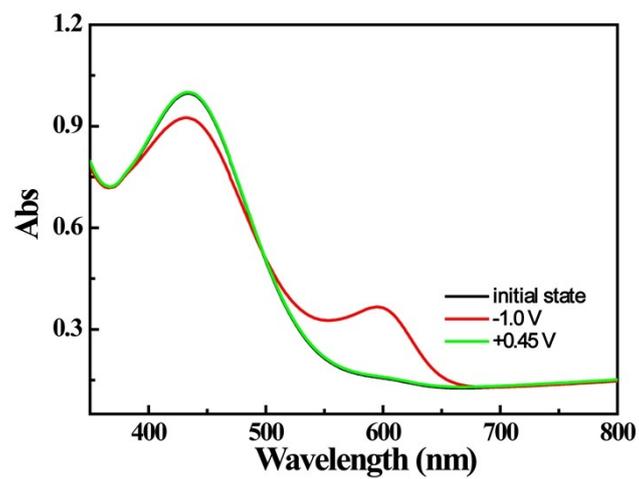
**Figure S4.** UV-Vis spectra and corresponding photographs of solution containing by adding different equivalent NaOH in H<sub>2</sub>O. (a)  $1 \times 10^{-5}$  mol/L Thymol blue sodium salt; (b)  $1 \times 10^{-5}$  mol/L Phenol red sodium salt.



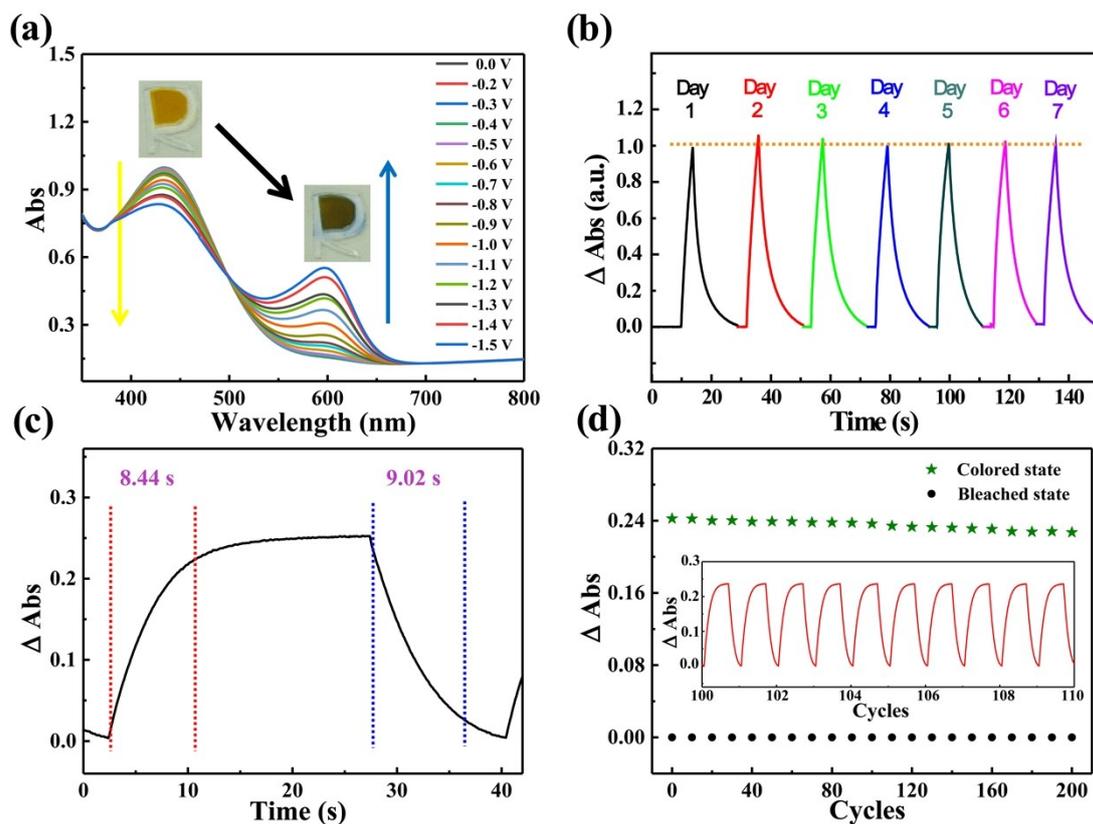
**Figure S5.** The basic properties of liquid device with thymol blue sodium salt. (a) The UV-Vis spectra of device at different voltage. (b) The change of the color by adding voltage reversibly. (c) The change of absorbance at 595 nm when added -0.8 V with different time (d) The change of absorbance (595 nm) variation with the switch cycles by alternative -0.6 V (5 s) and +0.3 V (14 s).



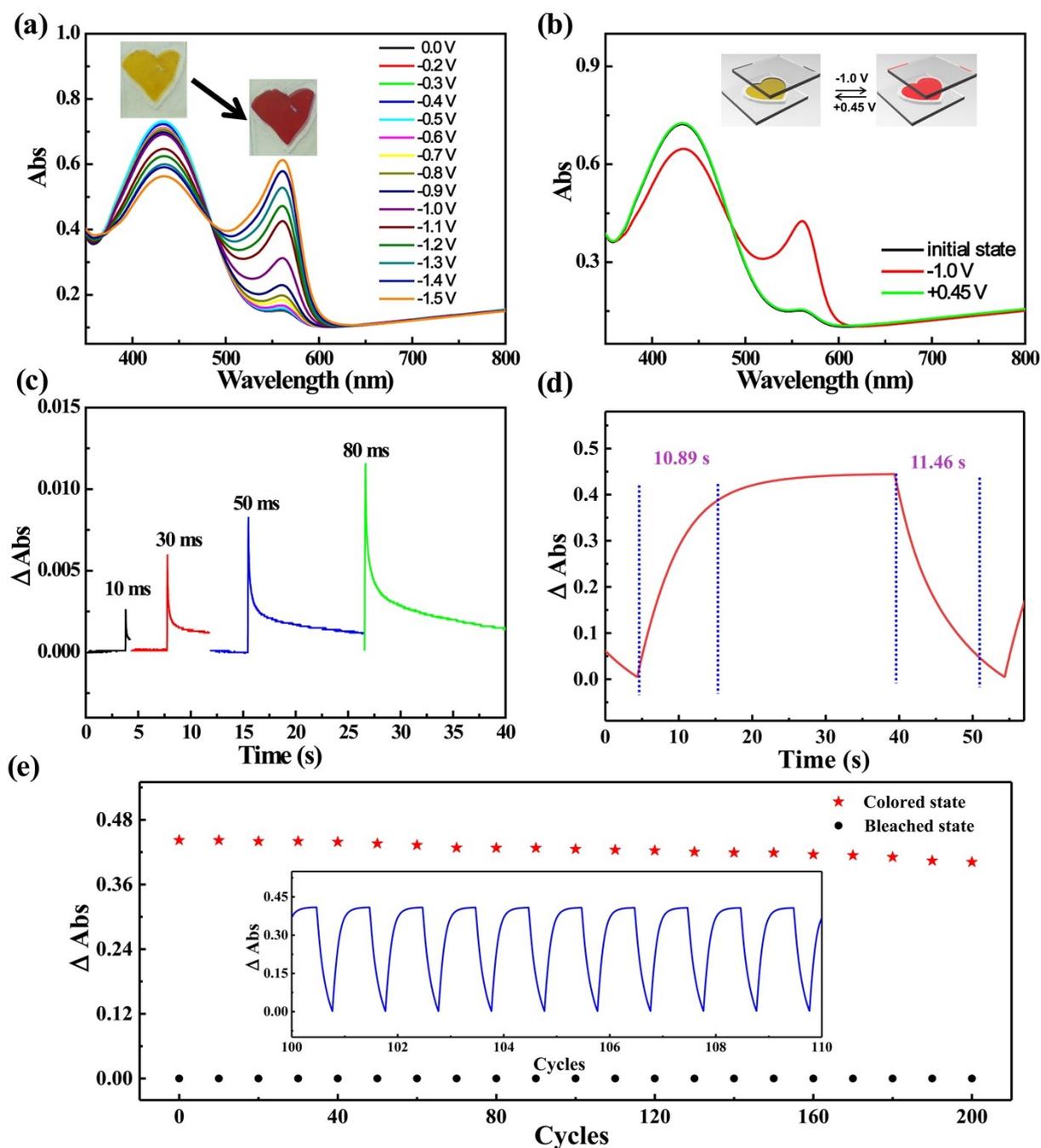
**Figure S6.** The basic properties of liquid device with phenol red sodium salt. (a) The UV-vis spectra of device at different voltage. (b) The change of the color by adding voltage reversibly. (c) The change of absorbance at 559 nm when added -0.8 V with different time (d) The change of absorbance (559 nm) variation with the switch cycles by alternative -0.65 V (4 s) and +0.35 V (10 s).



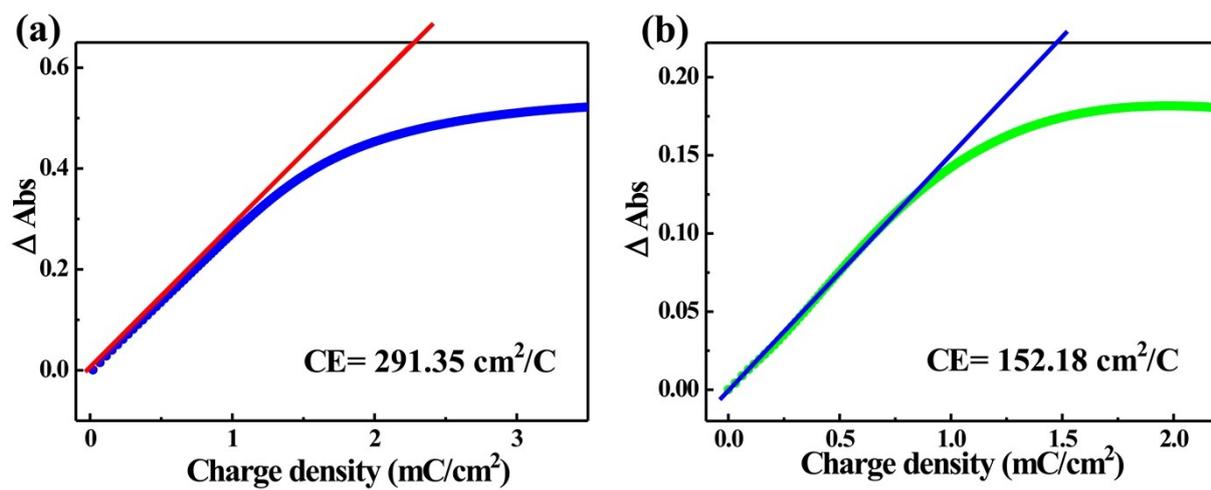
**Figure S7.** The change of the color by adding voltage reversibly (ITO device containing hydrogel-G).



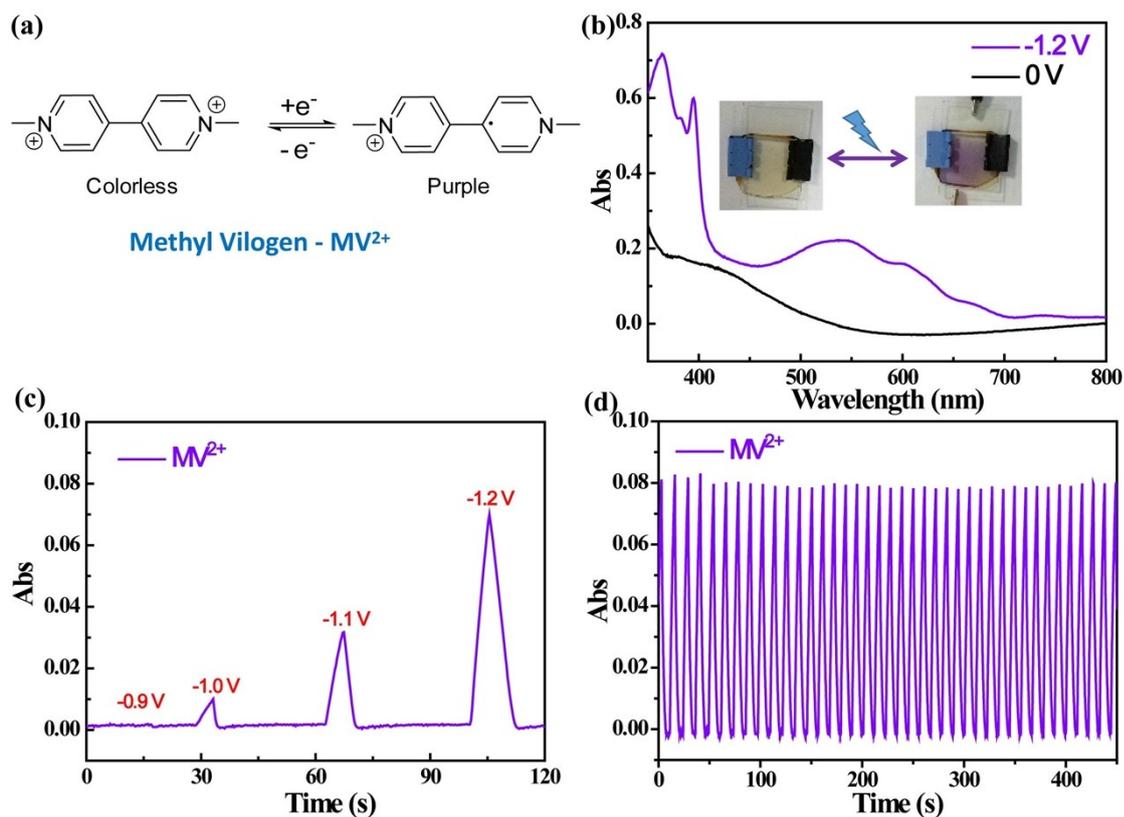
**Figure S8.** (a) The absorption spectra of hydrogel-G device with different voltages. (b) The stability of hydrogel-G device which was put for a week (normalized absorption graph). (c) The response time of hydrogel-G device during the coloring and bleaching process. (d) The change of absorption (595 nm) variation with the switch cycles by alternative -1.1 V (25 s) and +0.45 V (13 s).



**Figure S9.** The basic properties of ITO device containing the hydrogel with phenol red sodium salt. (a) The UV-vis spectra of device at different voltages. (b) The change of the color by adding voltage reversibly. (c) The change of absorbance at 559 nm when added -1.2 V with different time. (d) The response time of hydrogel-R device during the coloring and bleaching process. (e) The change of absorbance (559 nm) variation with the switch cycles by alternative -1.0 V (35 s) and +0.35 V (15 s).

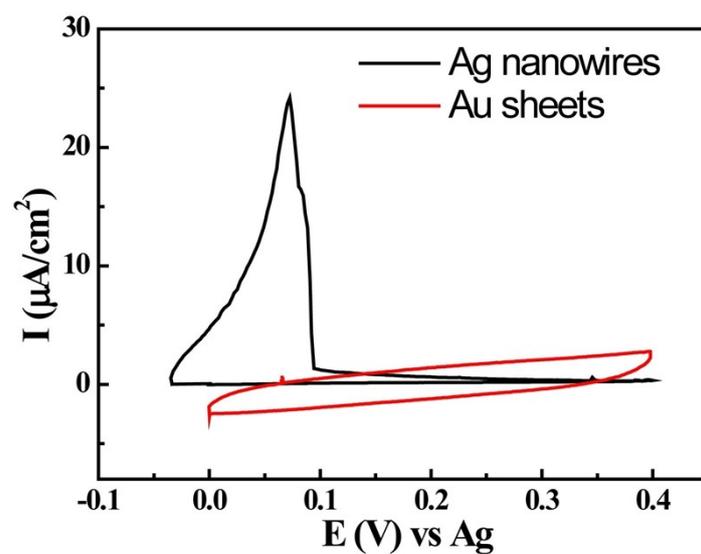


**Figure S10.** Coloration efficiency (CE) of ITO device containing hydrogel-R (a) and hydrogel-G (b).

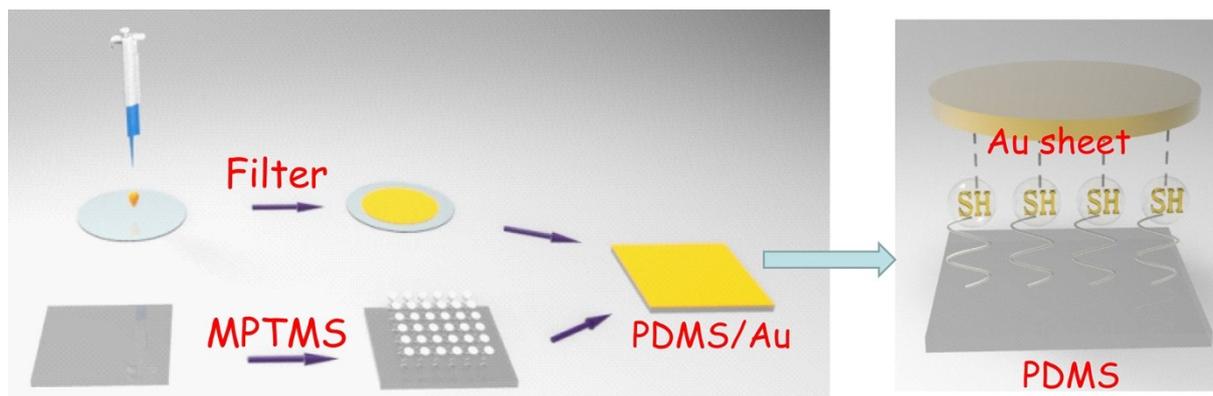


**Figure S11.** (a) Coloring mechanism of methyl viologen. (b) The physical display of the hydrogel device when added -1.2V and its corresponding UV-vis absorption spectra. (c) The open voltage of the hydrogel device. (measuring wavelength-550 nm). (d) The cycle stability of the device. (-1.15v-5s, 0V-6s).

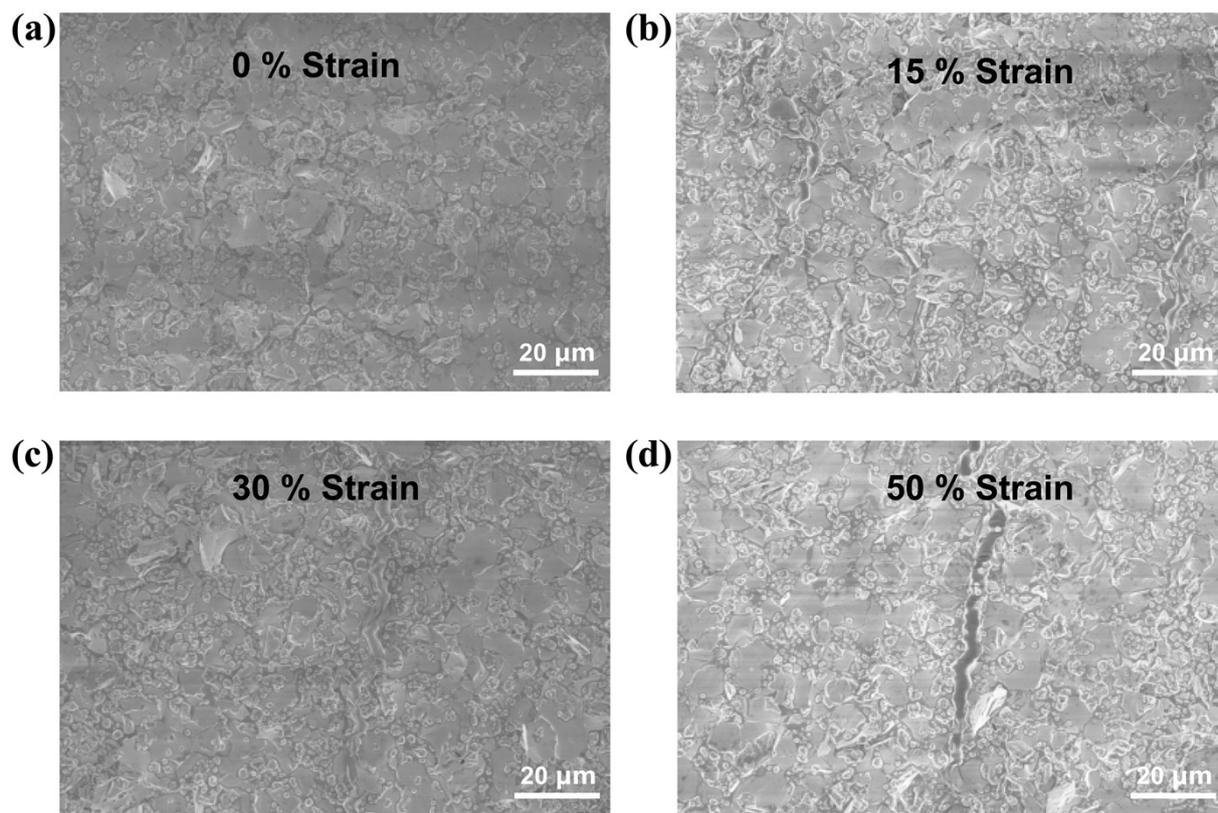
### 3. Characterization of stretchable electrodes



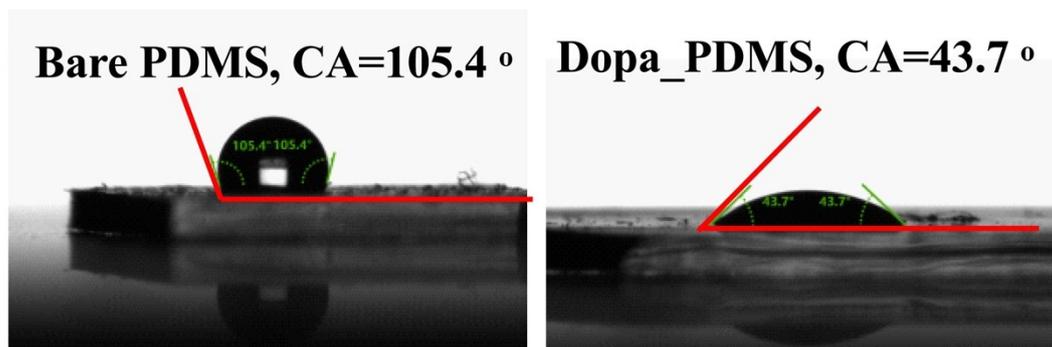
**Figure S12.** Cyclic voltammograms of Ag nanowires and Au nanosheets deposited on PDMS in 1 M KCl/H<sub>2</sub>O. (Counter electrode: Pt wire, Reference electrode: silver wire)



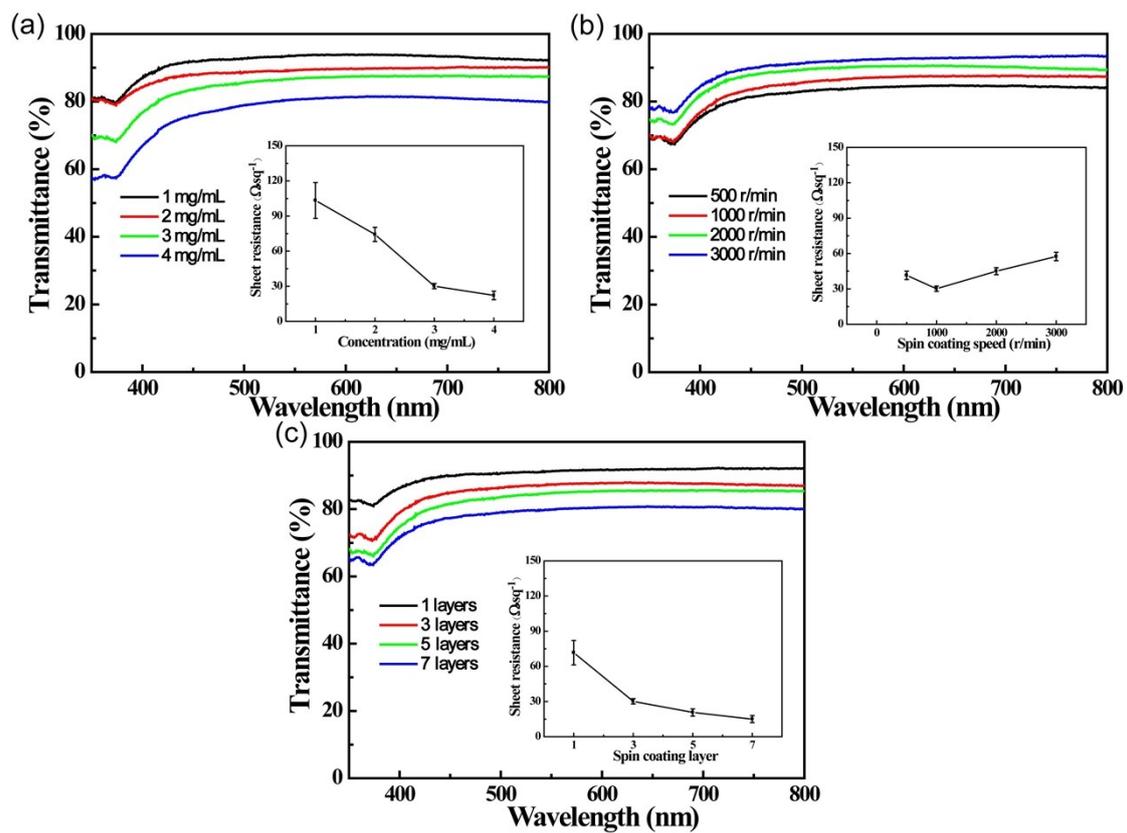
**Figure S13.** The schematic diagram of preparing stretchable Au-nanosheets electrode.



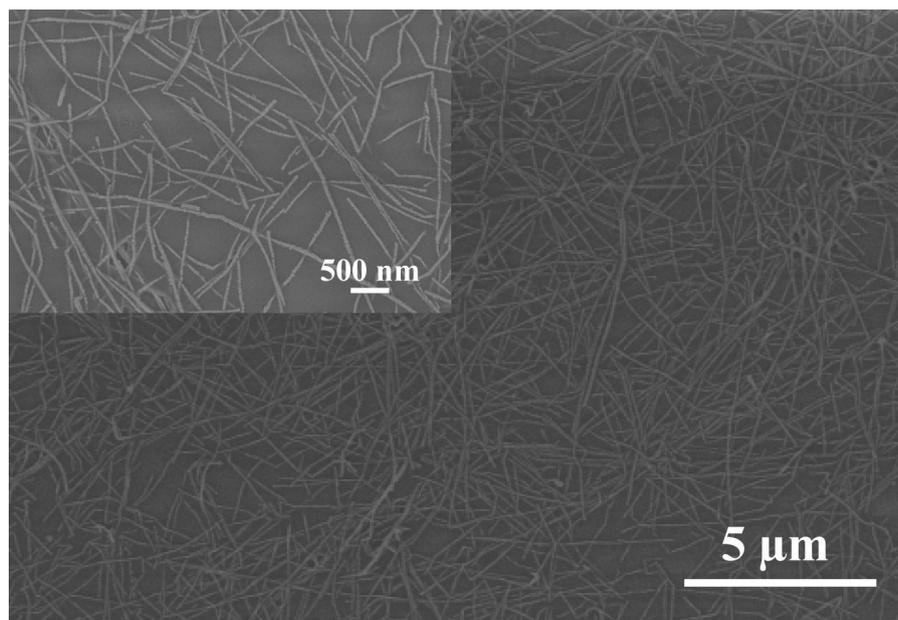
**Figure S14.** The SEM images of the stretchable gold electrode after various strains: (a) 0% strain; (b) 15% strain; (c) 30% strain; (d) 50% strain.



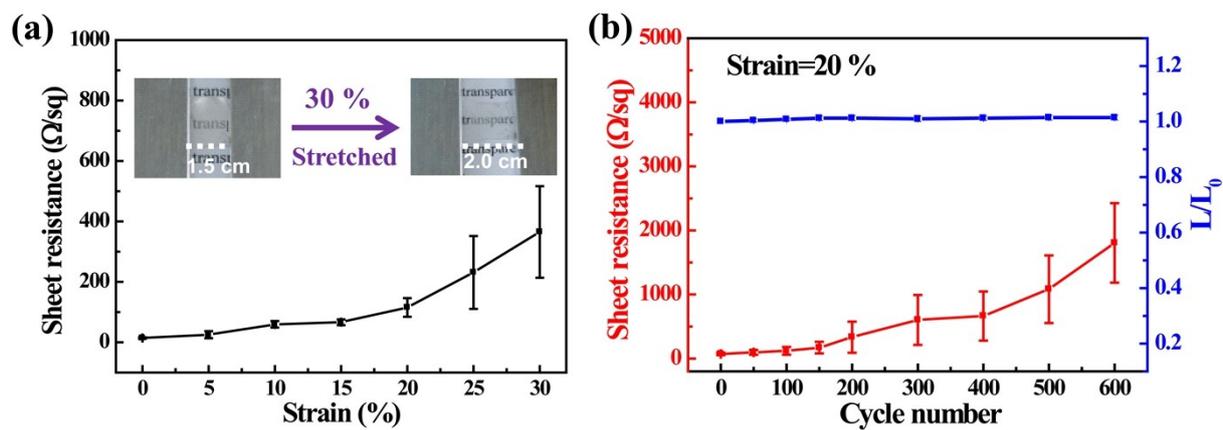
**Figure S15.** Water contact angle measurements for bare and polydopamine-coated PDMS (Dopa\_PDMS) surface.



**Figure S16.** The optimization of spin coating condition. The transmittance and sheet resistance of PDMS/Ag electrode with different (a) concentration of Ag nanowires, (b) spin speed, (c) spin layers.

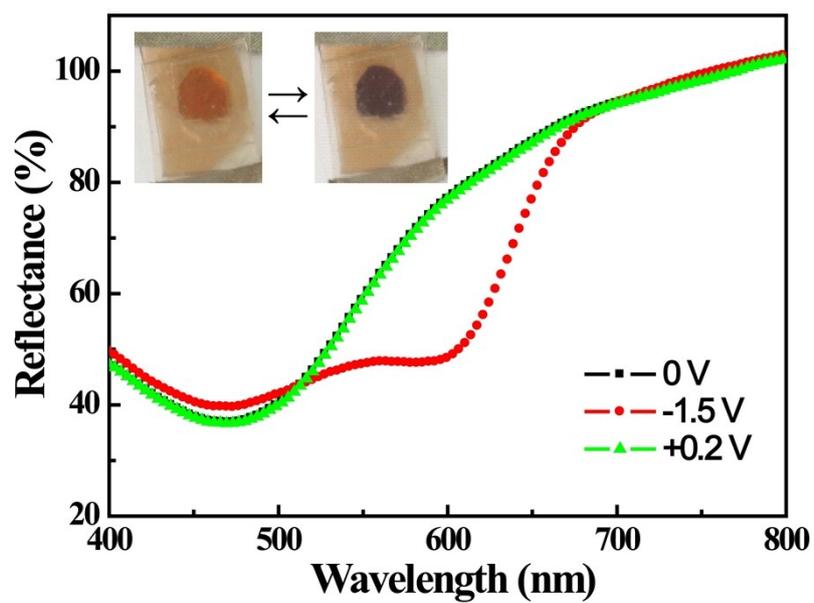


**Figure S17.** The SEM picture of Ag-nanowires electrode (inset picture: magnified pattern).

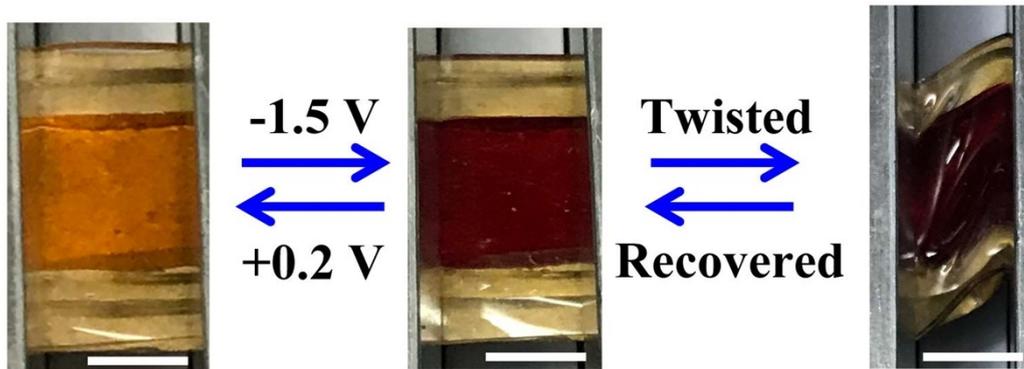


**Figure S18.** (a) The sheet resistances of the silver electrode at different strains. (b) The cycle performance of the conductivity and the length of the silver electrode when stretched at 20 % strain for 600 cycles.

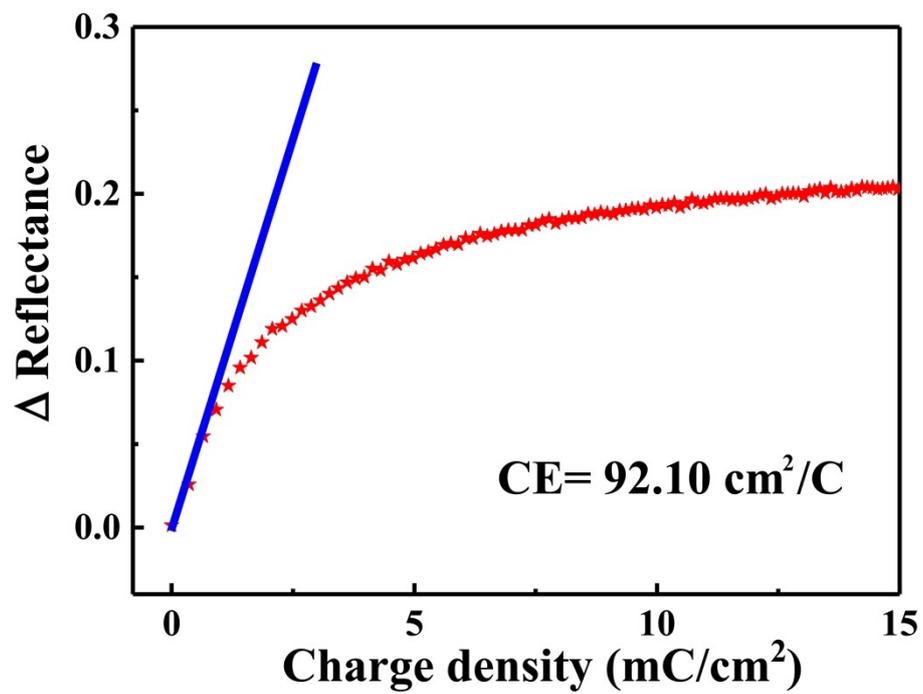
#### 4. The performance of the stretchable electrochromic devices



**Figure S19.** The UV-vis spectra and pictures of hydrogel-G device when different voltages was added.



**Figure S20.** The twisted performance of stretchable hydrogel-R device (scale bar = 1 cm).



**Figure S21.** The coloration efficiency of the stretchable hydrogel-R device.

Material	Color change	Coloration efficiency	Switching time	Reversibility	Environment & health issues
WO <sub>3</sub> <sup>[10]</sup>	white to blue	12.6 cm <sup>2</sup> /C	coloration (1 s)/bleaching (4 s)	81% retention after 100 cycles (relaxed state)	harmful
Poly(3-hexylthiophene-2,5-diyl) (P3HT) <sup>[11]</sup>	dark red to pale blue	-	coloration (1.4 s)/bleaching (1.2 s)	excellent efficacy after 1800 cycles (relaxed state / 20% strain)	harmful
Heptyl viologen tetrafluoroborate <sup>[12]</sup> HV(BF <sub>4</sub> ) <sub>2</sub>	colorless to blue	31.82 cm <sup>2</sup> /C	coloration (32 s)/bleaching (43 s)	excellent efficacy after 100 cycles (relaxed state)	toxic
Poly(3,4-ethylenedioxythiophene):p-toluene sulfonic acid (PEDOT:PTS) and polyurethane (PU) <sup>[13]</sup> (PEDOT/PU)	dark blue to pale blue	-	coloration (20 s)/bleaching (20 s)	excellent efficacy after 100 cycles (relaxed state)	harmful
Ethyl viologen <sup>[16]</sup>	colorless to blue	-	coloration (5 s)/bleaching (22 s)	excellent efficacy after 100 cycles (relaxed state/ 20% strain)	toxic
p-BQ and base-responsive molecules (This work)	yellow to red or brown or purple (multicolor-tunable)	92.10 cm <sup>2</sup> /C	coloration (9 s)/bleaching (25 s)	excellent efficacy after 100 cycles (relaxed state/ 20% strain)	Environmental friendly, non-toxic

**Table S1.** The comparison of electrochromic properties of stretchable electrochromic devices in recent years.