Fruit battery-inspired self-powered stretchable hydrogel-based ionic skin that works effectively under extreme environments

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Supplementary Figures

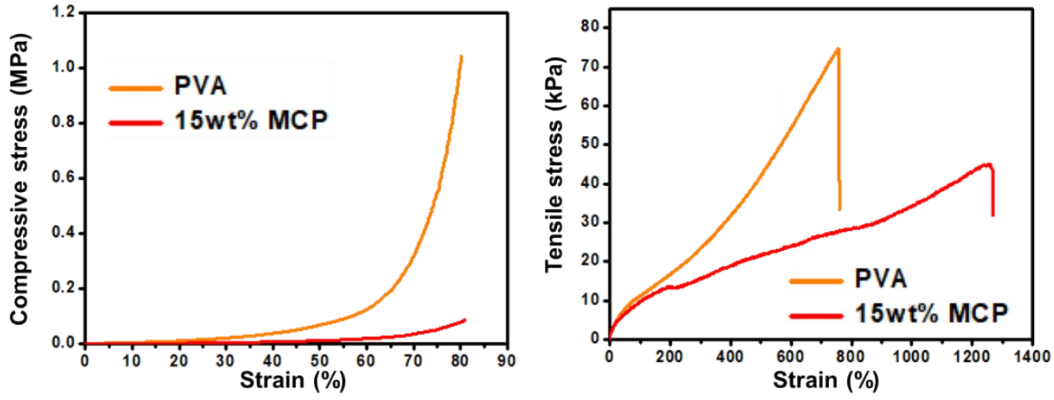

Figure S1. Compressive stress and tensile stress of PVA and 15 wt% MCP hydrogels.

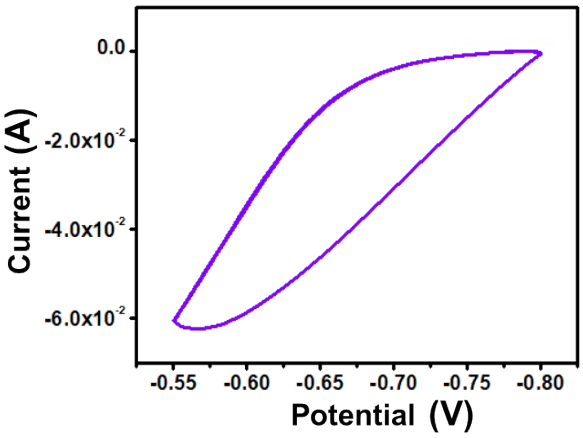

Figure S2. Cyclic voltammetry (CV) curves of the Zn electrode in electrolyte solution.

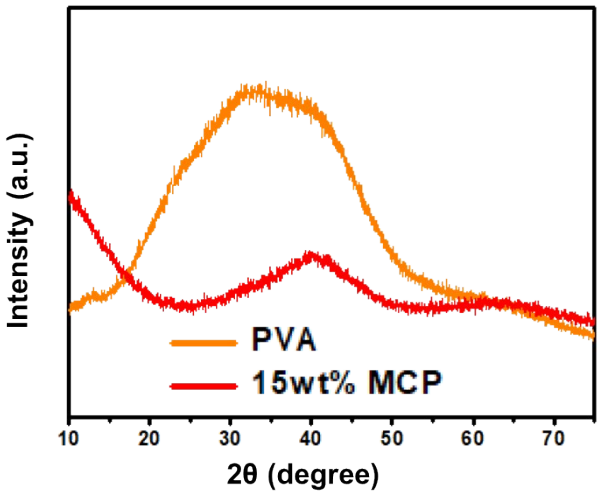

Figure S3. X-Ray Diffraction (XRD) patterns of PVA and 15 wt% MCP hydrogels.

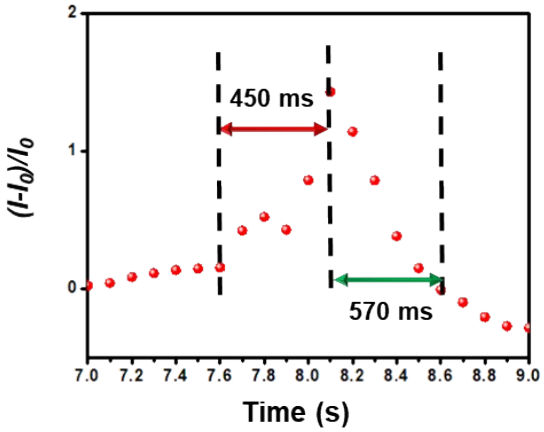

Figure S4. Response and recovery speed of the self-powered hydrogel sensor.

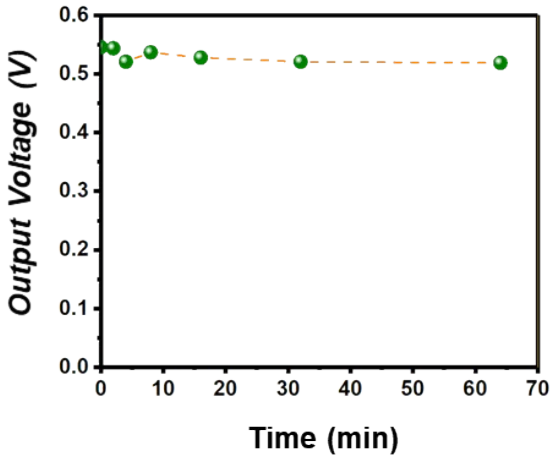

Figure S5. Changes in the voltage output of the self-powered hydrogel sensor with time.

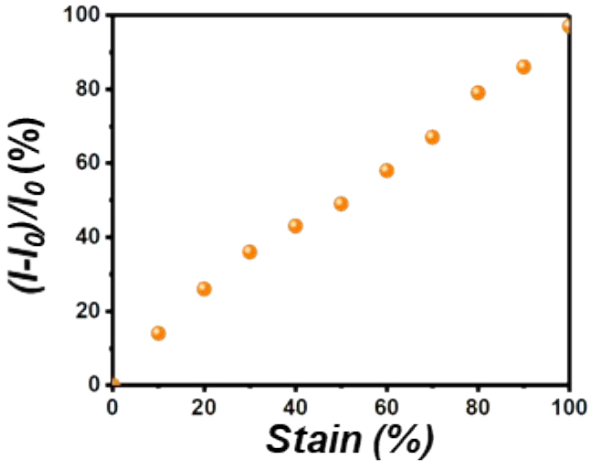

Figure S6. Strain sensitivity of self-powered sensors

Experimental section

Materials

Malic acid (MA), tannic acid (TA), acrylic acid (AA), polyvinyl alcohol-1799 (PVA), and calcium chloride ($CaCl_2$) were purchased from Aladdin Industrial Corporation (Shanghai, China). Citric acid (CA) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Eucalyptus lignin (local pulp and paper mill) was sulfonated to obtain water-soluble lignosulfonic acid (LA, sulfonation degree: ~1.2 mmol/g).

Preparation of the MA-Ca-PVA(MCP) hydrogels

First, 0.1 g MA and 2.525 g $CaCl_2$ were dissolved in 10 mL deionized water and stirred at room temperature for approximately 10 min to obtain a homogeneous solution. Second, PVA powders were added to the above solution, and the mixture was heated to 95℃ for about 12 h for a complete dissolution of PVA. Then, the mixture solution was sonicated for 1 hour to remove excess bubbles. Finally, the solution was rapidly frozen at -24℃ for 24 h. The frozen hydrogel was thawed at room temperature for 6 h to obtain the MA-Ca-PVA(MCP) hydrogel. The detailed compositions of the hydrogel are shown in TableS1.

Table S1. The compositions of PVA and MCP hydrogels

Hydrogel samples	*MA (g)*	*$CaCl_2$ (g)*	*PVA (g)*	*Deionized water(g)*
PVA	0	0	2.2279	10
15 wt% MCP	0.1	2.525	2.2279	10
20 wt% MCP	0.1	2.525	3.156	10

25 wt% MCP	0.1	2.525	4.208	10

Preparation and application of the self-powered hydrogel sensor

The thin pure copper and zinc sheets were inserted into strip and block 20 wt% MCP hydrogels to assemble self-powered hydrogel-based strain and pressure sensors, respectively. The electrochemical workstation (CHI 630E, Shanghai) was used to collect the output current of the hydrogel sensor (working voltage: 0 V).

Characterization of the electrolyte

The concentration of H^+, conductivity, and oxidation-reduction potential (ORP) of various MA and MA-Ca^{2+} solutions were measured using a PH meter (Thermo Fisher Scientific Co., Ltd.).

$$PH = -\lg\left[H^+\right] \quad \textbf{(Equation S1)}$$

Zn coated on Ti foil was used as the working electrode, Ag/AgCl (KCl sat.) as the reference electrode. Cyclic voltammetry (CV, CHI 630E, Shanghai) curves of the Zn electrode in MA-Ca^{2+} solution were recorded.

Characterizations of MA-Ca-PVA(MCP) hydrogels

The X-ray diffraction (XRD) patterns of wet PVA and 15wt% MCP hydrogels were measured on a Rigaku Ultima IV (Japan) diffractometer, using Cu Kα radiation.

Output voltage and current capability

The output voltage and current of MCP hydrogels with different PVA contents were recorded using a multimeter (UT890D+, UNI-T CHINA). The electrodes of hydrogels are thin pure copper sheets and pure zinc sheets.

Conductivity tests

The conductivity of hydrogels was measured by an LCR meter (TH 2832), the applied voltage is 1 V and the measuring frequency is 1 kHz. The conductivity (σ) is calculated using the following equation,

$$\sigma = L/RA \quad \textbf{(Equation S2)}$$

in which R is the resistance, L and A are the materials' length and cross-sectional area, respectively.

Swelling property

The swelling ratio of the wet MCP hydrogels with various PVA contents were also determined. The swelling ratio was calculated as follows:

$$Swelling\ ratio = \frac{M_x - M_0}{M_0}(\frac{g}{g}) \quad \textbf{(Equation S3)}$$

where M_x is the weight of the swollen hydrogel and M_0 is the initial weight of the wet hydrogel.

Tensile tests

Tensile tests were performed on a digital tensile machine (KJ-1065B, Kejian Instrument Co. Ltd, Dongguan, China), with a loading rate of 30 mm/min. The tensile stress (T)

was calculated as

$$T = F/S \quad \textbf{(Equation S4)}$$

where F is the tensile load and S is the cross-sectional area. Four parallel samples were tested for each group and the average of the test results was recorded.

Young's modulus of the hydrogel was calculated from the slope of the 5-20% strain region in the tensile stress-strain curve.

Compression tests

Cylindrical hydrogel specimens were used for the compression tests. The compressive stress (t) was calculated as

$$t = f/s \quad \textbf{(Equation S5)}$$

where f is the compressive load and s is the original area of the sample. The crosshead speed during compression was maintained at 10 mm/min. Four parallel samples were tested for each group and the average of the test results was recorded.

Differential scanning calorimetry (DSC) analysis

The freezing temperature of the PVA and MCP hydrogels were investigated using a differential scanning calorimetry (DSC 214, Netsch). The cooling cycle was carried out from 20 °C to −80 °C at a rate of 5 °C/min.

Light management property

The light transmittance of the PVA and 20 wt% MCP hydrogels (thickness:3 mm) were

measured by using a UV–Vis spectrometer (Lambda 750, Perkin Elmer) from 400 to 750 nm.