Electronic Supplementary Information

Experimental Section

Materials

The leather is a 2 mm thick American bull double wet blue leather and it was purchased from Xinghao Leather Co., LTD., China. Pyrrole (PPy, 99.7%), ethylene glycol methyl ether (99.5%) and p-dimethylaminobenzaldehyde (99.5%) were obtained from Shanghai Macklin Biochemical Technology Co., LTD., China. Sodium hydroxide (NaOH, 99.7%) was obtained from Shanghai Yien Chemical Technology Co., LTD., China. Sulphuric acid (H_2SO_4, 99.7%), potassium chloride (KCl, 99.7%), perchloric acid ($HClO_4$, 70%) and hydrochloric acid (HCl, 99.7%) were purchased from Yonghua Chemical Co., LTD., China. p-Toluenesulfonic acid (PTSA, 99.7%) is purchased from Energy Chemical Co., LTD., China. Acetic acid (CH_3COOH, 99.5%) was obtained from Aladdin Co., LTD., China. Chloramine T (98%) and citric acid (99.5%) were purchased from Shanghai yuanye Bio-Technology Co., LTD., China. All Chemicals and reagents were of analytical grade and used without further purification.

Preparation of Leather Based Hydrogel Electrolyte (LHE)

The leather was cut into 2 cm × 2 cm square and 1 cm × 2 cm rectangular shapes. The two shapes of leather were soaked in NaOH solution of different concentration and different temperature for different time. After swelling, the leather was repeatedly washed with deionized water to remove the residual alkali, and then each group of leather was separately placed in a 3 mol L^{-1} KCl solution for use. The LHE was soaked in 0.5 M H_2SO_4 and 0.3 M NaOH solution respectively, to measure the degradable property of LHE.

Fabrication of Leather-Based Hydrogel Supercapacitor (LHSC)

Suspended the leather-based hydrogel in a beaker containing a well-stirred py/p-Toluenesulfonic acid (PTSA) solution. The concentration of py is 0.1 mol L^{-1}, PTSA is 0.125 mol L^{-1}. Subsequently, 30 mL of $FeCl_3$/PTSA solution was added within 30 minutes, and the reaction was stirred for 6 h in an ice-water bath. The concentration of $FeCl_3$ was 0.12 mol L^{-1}, PTSA was 0.125 mol L^{-1}. After reaction, the device was taken out, and washed repeatedly with ethanol and deionized water to remove residual $FeCl_3$ and pyrrole monomer. After soaking in 0.125 mol L^{-1} PTSA solution for 10 minutes, the device was rinsed with deionized water. Finally, cut off the edge part around the device and put it in the electrolyte (3 mol L^{-1} KCl solution) for use. Carbon cloth was used as the current collector and stainless steel was used as the wire to assemble a supercapacitor with all-in-one configured structure. The supercapacitor was packaged with polyimide tape for testing.

Material Characterization

The LHE was characterized by scanning electron microscope (SEM, Hitachi S4800).

The LHSC was characterized by the fourier transform infrared spectrometer (FTIR, FTIR 460 plus).

The absorbance of solution is tested by UV spectrophotometer (UV-1750).

Ionic Conductivity Testing

Two 2 cm × 2 cm stainless steel sheets were used as blocking electrodes, and electrochemical impedance spectroscopy (EIS) was performed on the LHE with the same size at room temperature. The EIS was tested by Biologic VMP-300 and the range was from 10 mHz to 100 kHz. The ionic conductivity of LHE was calculated according

to the formula $\delta = \frac{d}{R \times S}$. δ is the ionic conductivity of the LHE, d is the thickness of the LHE, R is the impedance of the LHE and S is the area of the LHE.

Determination of Dissolved Collagen Content

Collagen contains a large number of specific amino acids and the content of both is relatively stable, such as hydroxyproline (Hyp) and hydroxylysine. After the dissolved collagen is completely hydrolyzed, the Hyp content is measured and then the collagen content is calculated, that is a common method for quantitative detection of collagen. Hyp reacts with chloramine T to obtain pyrrole oxide, which can undergo condensation reaction with the color developing agent dimethylaminobenzaldehyde to make the solution appear red. Then measure the absorbance of the solution at 560 nm. Based on the pre-measured standard curve to determine the Hyp concentration and calculate the dissolved collagen concentration by the following formulas. Hyp=(Hyp(μg)×dilution rate×1000)/sample's mass, collagen%=Hyp%×7.46(constant).

Preparing 1 μg mL^{-1}~5 μg mL^{-1} Hyp standard solutions with different concentrations, as well as relevant solutions that will be used in the experiment, such as chloramine T solution, p-dimethylaminobenzaldehyde solution, perchloric acid solution, etc (Table S1).

Table S1 Preparation of Dissolved Collagen Test Related Solutions.

Reagent	Preparation method
HCl solution	200 mL, 0.001 mol L^{-1} HCl and 200 mL, 6 mol L^{-1} HCl
buffer solution	12 mL CH_3COOH, 50 g citric acid, 34 g NaOH, constant volume to 1000 mL with DI water
chloramine T solution	1.4 g chloramine T, 20 mL DI water, 30 mL ethylene glycol methyl ether and 50 mL buffer solution
$HClO_4$ solution	27 mL $HClO_4$ (70%), constant volume to 100 mL with DI water
p-dimethylaminobenzaldehyde solution	20 g p-dimethylaminobenzaldehyde and 100 mL ethylene glycol methyl ether
Hyp standard solution	1 μg mL^{-1}~5 μg mL^{-1} Hyp standard solutions prepared with 0.001 mol L^{-1} HCl

Taking 5 mL of alkaline solution in each group, adding 5 ml of 6 mol L^{-1} hydrochloric acid and place it at 110℃ for 24 h to completely hydrolyze collagen into amino acids. After hydrolysis, adjust the pH of the solution to 7 and dilute it to 30 mL. Taking 1 mL of diluent from each group and standard solution, respectively, add 7.5 mL of 0.001 mol L^{-1} hydrochloric acid and 0.5 mL of chloramine T solution into it, and let it stand for 20 minutes. Add 0.5 mL of perchloric acid solution and let it stand for 5 minutes, then add 0.5 mL of p-dimethylaminobenzaldehyde solution and let it stand at 60℃ for 20 minutes for color development. Finally, the absorbance of the solution at 560 nm was measured by UV spectrophotometer (Table S2). Among them, the dilution ratios

of group 7 and group 9 were 2 and 3, respectively.

Table S2 The absorbance of the solution at 560 nm

Solution	Absorbance
1 μg mL^{-1} Hyp standard solution	0.130
2 μg mL^{-1} Hyp standard solution	0.251
3 μg mL^{-1} Hyp standard solution	0.381
4 μg mL^{-1} Hyp standard solution	0.501
5 μg mL^{-1} Hyp standard solution	0.578
group 1	0.014
group 2	0.063
group 3	0.216
group 4	0.554
group 5	0.872
group 6	1.132
group 7	0.819
group 9	0.623

The Hyp standard curve was obtained according to the absorbance of the standard solution at 560 nm (Fig. S1). The concentration of the Hyp can be calculated by following regression equation (S1) and variance (R^2):

$$y = 0.1143x + 0.0257 (S1)$$

$$R^2 = 0.9905$$

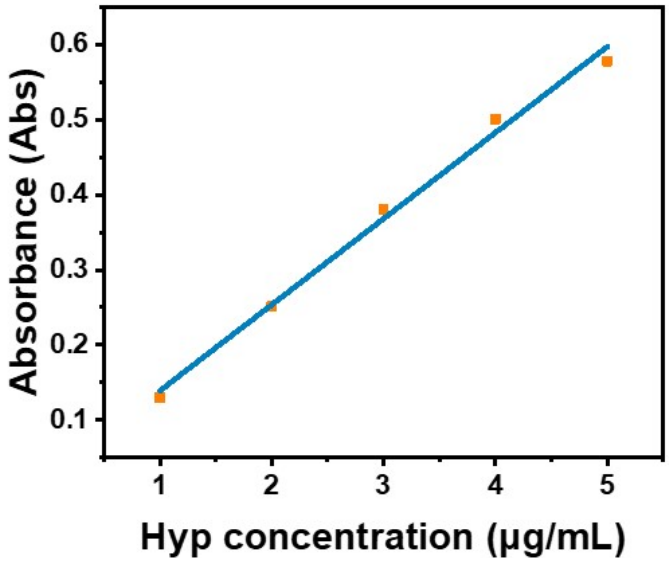

Fig. S1 The hydroxyproline standard curve.

Break Tensile Test

Using universal testing machine (ESM303 Mark 10 and M5-10 Mark-10) to test 1 cm × 4 cm swelled leather. Both ends of the leather were wrapped with stainless steel sheets and clamped on the fixture of the testing machine. Start the testing machine to pull until the leather breaks, and the maximum value of the tension value automatically recorded by the computer was the tension applied when the leather breaks. Took the average of three experiments for each group.

Electrochemical Performance Test

All the electrochemical performance tests were measured by the French Biologic multi-channel electrochemical workstation. The frequency range of electrochemical impedance spectroscopy (EIS) test was 10 mHz-100 kHz. The scan rates of cyclic voltammetry (CV) were 100 mV s^{-1}, 50 mV s^{-1}, 20 mV s^{-1}, 10 mV s^{-1}, 5 mV s^{-1} and the scan range was 0-0.6 V. The current densities of galvanostatic charge-discharge (GCD) test were 1 mA cm^{-2}, 2 mA cm^{-2}, 3 mA cm^{-2}, 4 mA cm^{-2} and the voltage range was 0-0.6 V. For the charge and discharge cycle stability test, the current density was 3 mA cm^{-2}. The specific capacitance (C_s, mF cm^{-2}) of the electrode material was calculated by following equation:

$$C_s = \frac{it}{su} (S2)$$

where i (mA), t (s), u (V) and s (cm^2) were the discharging current, discharging time, potential window for the charge-discharge process and area of supercapacitor, respectively.

Mechanical Stability Test

Tested the device's electrochemical performance according to the above electrochemical performance test when device under bent and fixed. Used a universal testing machine to bend the device and the electrochemical performance of the device before and after bending was carried out respectively.

Destructive Stability Test

Tested the device's electrochemical performance after packaged. Subsequently, a part of the device was cut off, the remaining part was repackaged and tested the electrochemical performance again.

Table S3 Orthogonal experiment table of swelling conditions.

Number	Orthogonal experiment	Swelling conditions		
		Temperature (℃)	Time (h)	Alkali concentration (mol/L)
1	A1 B1 C3	35	4	0.4
2	A1 B2 C1	35	5	0.2
3	A1 B3 C2	35	6	0.3
4	A2 B1 C1	40	4	0.2
5	A2 B2 C2	40	5	0.3
6	A2 B3 C3	40	6	0.4
7	A3 B1 C2	45	4	0.3
8	A3 B2 C3	45	5	0.4
9	A3 B3 C1	45	6	0.2

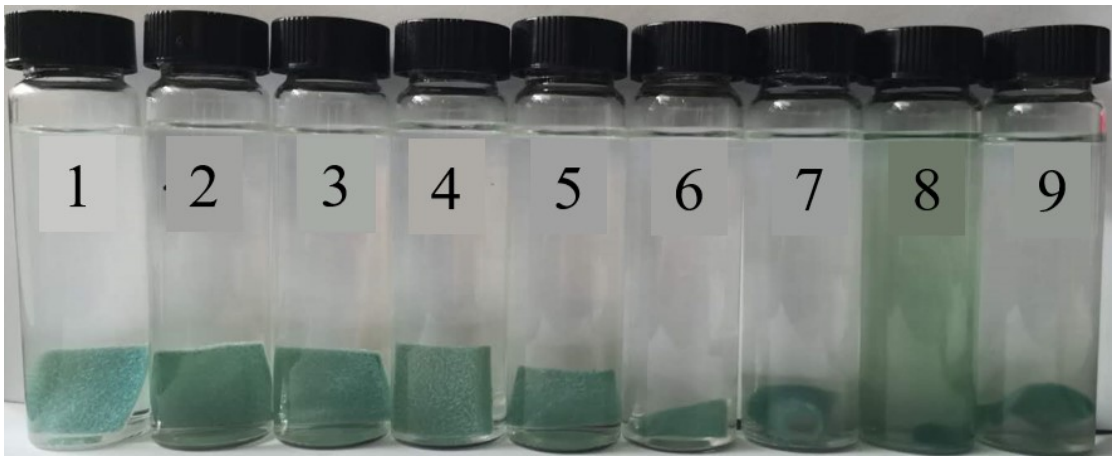

Fig. S2 Hydrolyzed leather under different conditions.

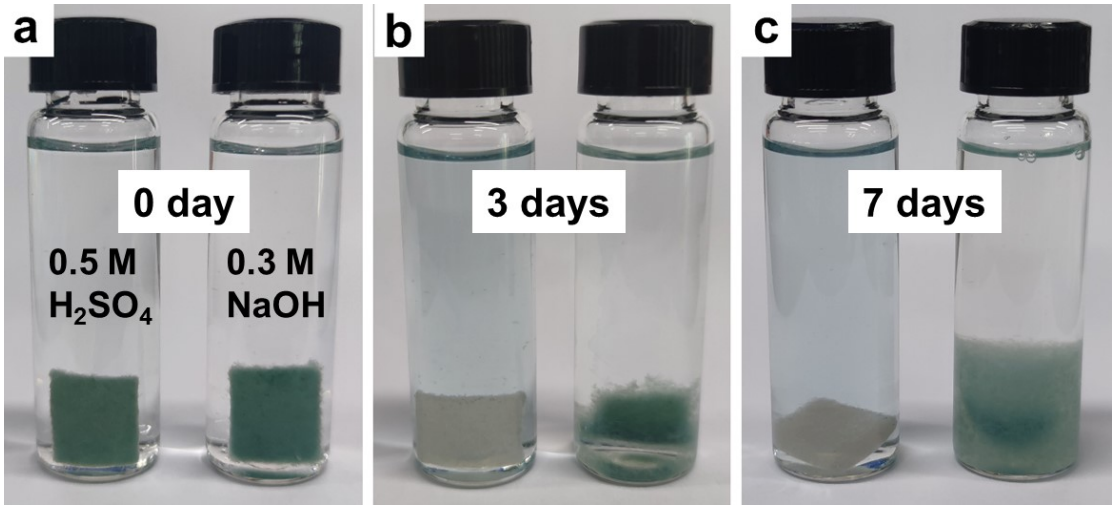

Fig. S3 Degradability of leather-based hydrogel in 0.5 M H_2SO_4 and 0.3 M NaOH solutions, respectively. (a) 0 day, (b) 3 days, (c) 7 days.

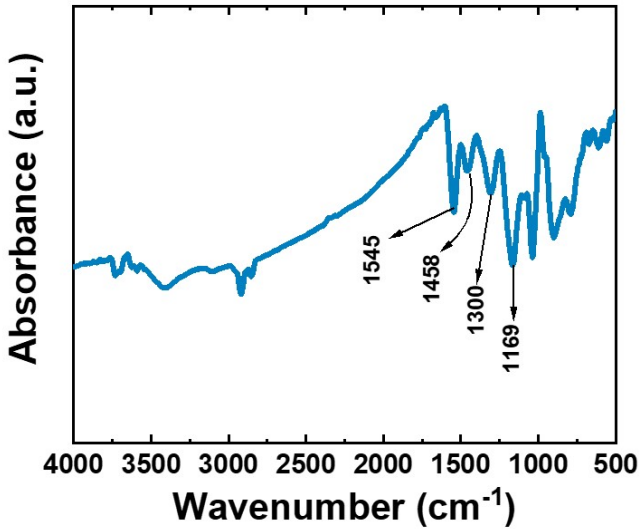

Fig. S4 FTIR spectrum of the LHSC in KBr.

The FTIR spectrum of the LHSC in KBr is shown in Fig. S4. The broad band from 3800 cm^{-1} to 3000 cm^{-1} could be attributed to N-H and C-H stretching vibrations of PPy. The peaks at 1545 cm^{-1} and 1458 cm^{-1} correspond to the stretching vibration of C-C and C-N bonds on the pyrrole ring, respectively. The absorption band from 1400 cm^{-1} to 1250 cm^{-1} can be attributed to the plane deformation of C-H or C-N bond, which has a maximum absorption peak at 1300 cm^{-1}. The region from 1250 cm^{-1} to 1000 cm^{-1} corresponds to the plane stretching vibration of C-H and N-H bonds, and its maximum absorption peak is 1169 cm^{-1}, which is consistent with previous reports.[1]

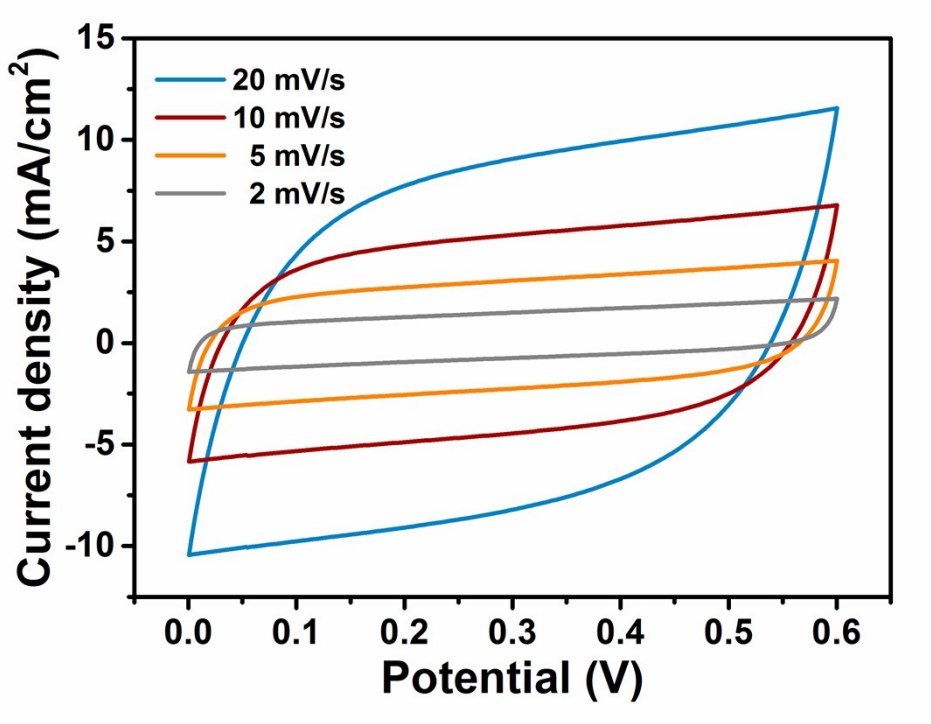

Fig. S5 CV profiles of LHSC at scan rates ranging from 2 mV s^{-1} to 20 mV s^{-1}.

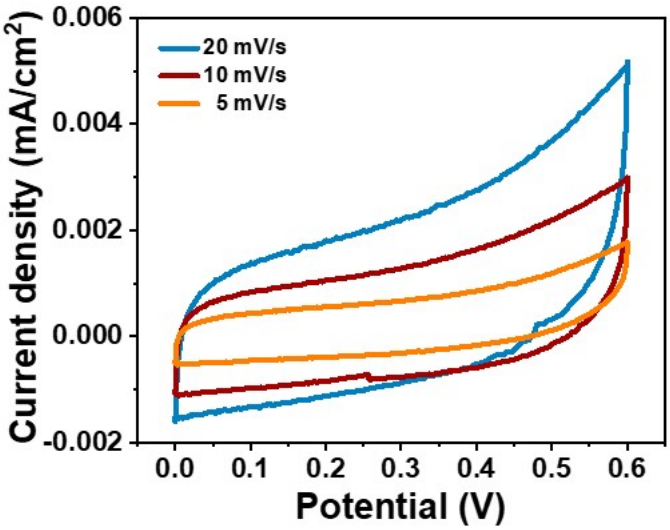

Fig. S6 CV profiles of supercapacitors for comparison at scan rates ranging from 5 mV s^{-1} to 20 mV s^{-1}.

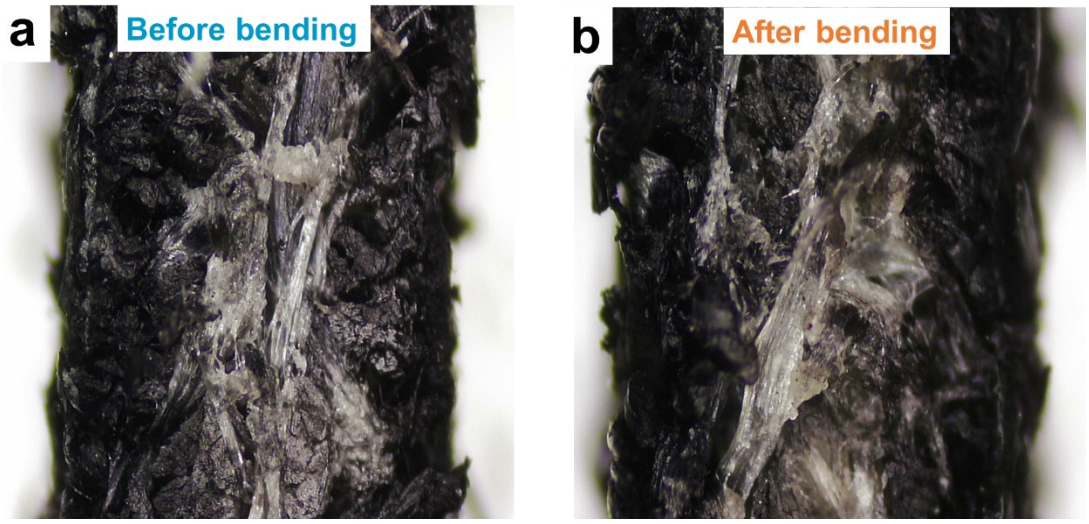

Fig. S7 Photographs of LHSC before and after repeated bending 3000 times.

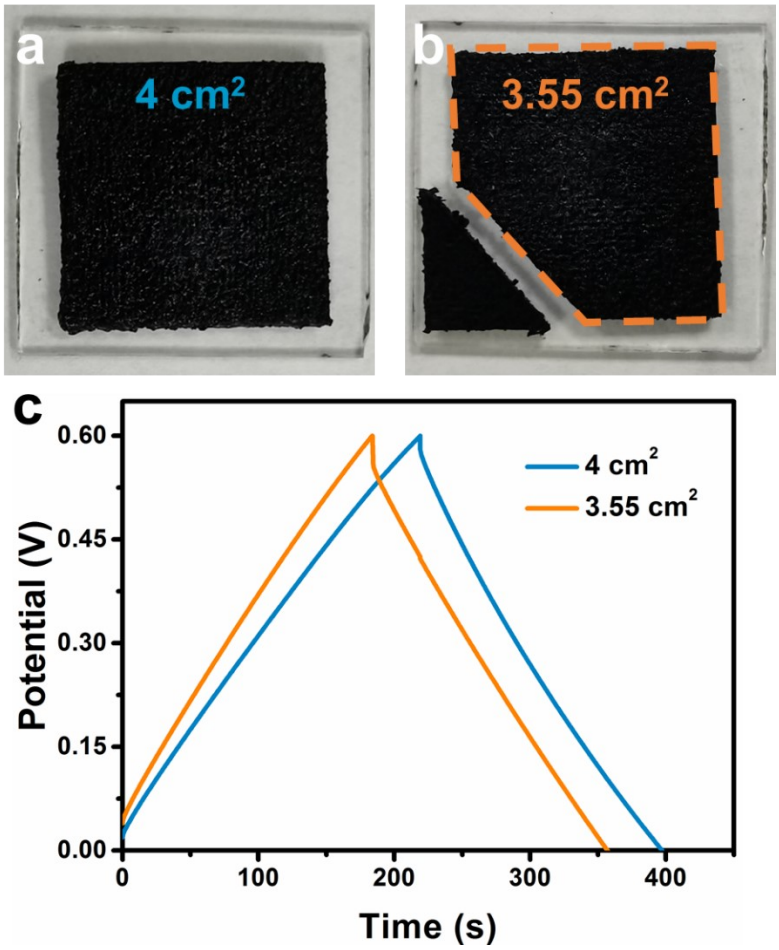

Fig. S8 Photographs and GCD curves before and after cutting leather-based hydrogel supercapacitor (current density: 2 mA cm^{-2}).

References

1 M. Li and L. Yang, *J. Mater. Sci. Mater. Electron.*, 2015, **26**, 4875-4879.