Supporting Information

Highly Tough, Freezing-Tolerant, Healable and Thermoplastic

Starch/Poly(vinyl alcohol) Organohydrogels for Flexible Electronic

Devices

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Experimental

1. Preparation of starch/PVA/Glycerin/CaCl₂ (SPGC)organohydrogel

Soluble starch (AR, >99%) was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China), PVA (degree of polymerization was 1700, degree of alcoholysis was 99%) was purchased from Aladdin Biochemical Technology Co. Ltd. Glycerin (analytical purity, the specific gravity ranging from 1.263 to 1.303) and CaCl₂ were purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd (Tianjin). All chemicals were used without further purification. Deionized water was used throughout the experiment.

The organohydrogels were prepared by three repeated cycles of freezing and thawing at -30 °C and room temperature. The organohydrogels with different contents of glycerin and CaCl₂ were obtained by the following method. First, 2 g starch and 2 g PVA were added into 15 mL distilled water. To prevent water ingress and moisture evaporation at high temperatures, the beaker that containing the mixture was sealed with plastic wrap and heated in a water bath at 90 °C for 2 hours to ensure that all ingredients were completely dissolved. Then, 13 grams of glycerin was added into the beaker and continuously heated and stirred at 90 °C for 1 hour. Subsequently, a certain amount of CaCl₂ was added into starch/PVA/Glycerin solution. The stirrer was turned off after 15 minutes and the water bath was constantly heated to remove air bubbles. The mixture was gently transferred into a mold made by placing a rubber spacer with a height of 2.0 mm between two glass plates while it was hot. Finally, the mold with mixed solution was frozen in a refrigerator at -30 °C for 3 h, and then thawed at room temperature for 1 hour. The process was repeated three times to form organohydrogels. To verify the effect of glycerin, organohydrogels with different glycerol contents were prepared using the same method according to the ratio in Table S1. In this research, the starch/PVA hydrogel was denoted as SP. The SPGC organohydrogel with different CaCl₂ content were referred to as SPGC-0, SPGC-7.5%, SPGC-15%, SPGC-22.5%, SPGC-30%, SPGC-37.5%, contained respectively. The number the abbreviated name in of starch/PVA/Glycerin/CaCl₂ organohydrogel was the ratio of the mass of CaCl₂ to the mass of starch and PVA. The organohydrogels prepared by only changing the glycerin concentration were named by the ratio of glycerin to total solvent.

2. Preparation of organohydrogel strain sensor

Copper tape as an electrode was attached on both sides of the organohydrogel, and the conductive silver paste was applied to make the bond tighter and make the interface contact between the electrode and the organohydrogel electrolyte better.

3. Fabrication of all-solid-state supercapacitor

The activated carbon (AC, YP-50F) was purchased from Kuraray Co., Ltd (Japan). Acetylene black (F-900, AB) was purchased from Tianjin Ebory

Chemical Co., Ltd. (Tianjin, China). Polyvinylidene fluoride (PVDF) was provided by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China).

AC, acetylene black, and PVDF were mixed in a 5 ml reagent bottle at the weight ratio of 8:1:1 (active material: conductive agent: binder). $3\sim4$ ml ethanol was added into the mixture and under ultrasonic treatment for 20 min in an ultrasonic water bath. Then, the obtained slurry was baked in an oven at 80 °C overnight to ensure complete evaporation of ethanol. Subsequently, the dried powder was uniformly coated onto a porous nickel foam ($20 \times 10 \times 1$ mm) with an area of 10×10 mm as the current collector. Lastly, the working electrodes were obtained by overlapping two nickel foams coated with conductive material and extruding with an extruder with a force of 10 MPa.

4. Characterization

4.1 FTIR analysis

The chemical structures of SPGC organohydrogels were analyzed by using the Attenuated total reflection (ATR) method with the Fourier transform infrared spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA) in the wavenumber range of 4000-500 cm⁻¹ and a resolution of 4 cm⁻¹.

4.2 XRD analysis

The crystalline properties of SPGC organohydrogels were characterized by X-ray diffractometer (DY5261/Xpert3, CEM, America) with the Cu K α radiation (40 kV, 40 mA, λ =1.542 nm) at room temperature. The measurements were performed at the 2 θ range of 5-70°.

4.3 SEM analysis

Morphological details of SPGC organohydrogels were obtained by a filedemission scanning microscope (FE-SEM, FEI Nova Nano-SEM 230, America) with the primary electron energy of 10.0 kV. The samples of SP, SPG, and SPGC organohydrogels for SEM observation were made by soaking in deionized water and then treated by a freeze-dry method.

4.4 Optical microscope analysis

In order to visually describe the thermal repair process, the initial state, cutting, approaching and repaired state of the organohydrogels were photographed using an optical microscope (DVM6, LEICA).

4.5 Mechanical property

Tensile and compressing tests were conducted with an electrical universal material testing machine (MTS CMT4104). For both uniaxial and cyclic tensile tests, the organohydrogels specimens with a thickness of ca. 2 mm were cut into a dumbbell shape (length of 75 mm and width of 4 mm) and the stretching rate was fixed at 100 mm min⁻¹. The cylindrical organohydrogel samples with a diameter of 22 mm and a height of 15 mm were used for compression tests and

the loading rate was fixed at 5 mm min⁻¹. In order to explore the freezing resistance, the organohydrogel samples were frozen at -20 °C for 24 hours before the experiment and kept the cold conditions during the test.

4.6 Rheological measurement

Dynamic rheological measurements were carried out by Modular Compact Rheometer (Anton Paar, MCR 302). First, a dynamic oscillation amplitude scanning experiments were performed on the organohydrogel samples to determine the linear viscoelastic region. The dynamic amplitude scanning range was 0.01% to 100% at a constant frequency of ω =1 rad/s. Then, the frequency scanning tests were performed at a strain amplitude of γ =1% over a frequency range of 0.1-100 rad/s for the SPGC organohydrogel.

4.7 DSC analysis

The thermal characterization was tested by DSC214 (NETZSCH, German). 5-10 mg organohydrogel sample was sealed in an aluminium pan, followed by equilibrated at -60 °C for 3 min, rose to 200 °C at 10 °C min⁻¹ under nitrogen atmosphere.

4.8 Anti-drying property

The SP, SPG and SPGC organohydrogels were made into a cylinder with a diameter of 22 mm and a height of 15 mm as the testing samples and weighed as the initial weight. Then, all organohydrogel samples were placed in the atmosphere and weighed every 24 h. The quality retention rate (QRR) was calculated by the following formula:

$$QRR = \frac{W_i}{W_0} \tag{1}$$

where QRR was quality retention rate, W_i and W_0 were the weight of the organohydrogels after losing water and the initial weight of organohydrogels, respectively.

4.9 Conductive property

The ionic conductivity of the organohydrogel was measured by the impedance spectrum in a frequency range of 1 to 1×10^{6} Hz using the electrochemical workstation (CHI 660E, shanghai). The conductivity (σ) was calculated by the following formula:

$$\sigma = \frac{L}{AR} \tag{2}$$

where L (cm) was the distance between each two electrodes, A (cm²) was the cross-sectional area of organohydrogels, R (Ω) was the intercept through the horizontal axis in the EIS diagram.

4.10 Preparation of organohydrogel strain sensor

The organohydrogel was used as sensing material to fabricate a strain sensor using the two-electrode configuration. Two copper tapes were attached on both sides of the organohydrogel, and the conductive silver wires were connected with the instrument to investigate the sensing performance of the organohydrogels.

4.11 Fabrication of all-solid-state supercapacitor

The flexible all-solid-state supercapacitor was assembled in a symmetric two-electrode configuration by using the activated carbon electrodes, as well as the organohydrogel as the electrolyte and separator.

4.12 Electrical measurements

The electrical performances of the organohydrogel strain sensor were tested by a self-assembled intelligent data-acquisition-system, which contained a digital SourceMeter (Keithley 2450, Tektronix Co., USA) and a universal tensile tester (CMT 6503, MTS/SANS, China). To avoid delay between test instruments, the electrical and mechanical signals were simultaneously recorded. For measurement of the human-activity-related signals, hydrogel-based strain sensors were attached onto the corresponding epidermis parts and the electrodes were connected to Keithley 2450 to realize synchronous detection. The strain sensitivity of the organohydrogel was evaluated using the gauge factor (GF), which was defined according to the following equation:

$$GF = \frac{(R - R_0)/R_0}{\varepsilon}$$
(3)

where R_0 and R were the resistances of the original and stretched organohydrogels, respectively, and ε was the strain applied to the organohydrogels.

The electrochemical properties of the as-fabricated supercapacitors were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) through CHI660 electrochemical workstation. The voltage window for CV and GCD tests was set from 0 to 1.0 V. The specific capacitance (C, mF/cm²) of the supercapacitors was calculated from the GCD curves according to the following formula:

$$C = \frac{I \times \Delta t}{A \times \Delta V} \tag{4}$$

where I was the constant discharge current (mA), A was the electrode area (cm²), Δt was the discharge time (s) and ΔV was the voltage drop during discharge. The energy densities (E, mWh cm⁻²) and power densities (P, mW cm⁻²) were calculated by using the following formula:

$$E = \frac{C \times \Delta V^2}{2 \times 3600} \tag{5}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{6}$$

Table S1

| The experimental | ingredients | and | nomenclatures | of | the | as-prepared | hydrogel | and |
|------------------|-------------|-----|---------------|----|-----|-------------|----------|-----|
| organohydrogels. | | | | | | | | |

| Sample | Starch (g) | PVA (g) | Gly (g) | Water (g) | CaCl ₂ (g) |
|------------|------------|---------|---------|-----------|-----------------------|
| SP | 2 | 2 | 0 | 28 | 0 |
| SPG | 2 | 2 | 13 | 15 | 0 |
| SPGC-7.5% | 2 | 2 | 13 | 15 | 0.3 |
| SPGC-15% | 2 | 2 | 13 | 15 | 0.6 |
| SPGC-22.5% | 2 | 2 | 13 | 15 | 0.9 |
| SPGC-30% | 2 | 2 | 13 | 15 | 1.2 |
| SPGC-37.5% | 2 | 2 | 13 | 15 | 1.5 |

Table S2

Comparison of our work with other reported starch-based hydrogels.

| Hydrogel | Tensile strength (kPa) | Strain (%) | Ref | |
|---|------------------------|------------|----------|--|
| Starch/PVA/Glycerin/CaCl ₂ | 533.3 | 793 | Our work | |
| Starch/alginate/gelatin | 39.8 | 71 | [1] | |
| Starch/PVA/borax | 2.1 | 1550 | [2] | |
| Starch/gluten/NaCl/K ₂ CO ₃ | 65.1 | 225 | [3] | |
| Starch/SA/CaCl ₂ | 47.6 | 176 | [4] | |
| Starch/PAM | 305 | 1300 | [5] | |
| Amylopectin/NaCl | 0.5 | 260 | [6] | |

Table S3

Comparison of our work with other reported flexible supercapacitors.

| Electrolyte | Electrode | Areal capacitance (mF cm ⁻²) | Ref |
|---------------------------------------|-------------------------|---|----------|
| Starch/PVA/Glycerin/CaCl ₂ | AC | 107.2@1 mA cm ⁻² | Our work |
| PVA-KOH-KSCN-EG | PPy/GO-RuO ₂ | 32.4@100 mV s ⁻¹ | [7] |
| PVA/PAMAA/Gly/NaCl | CNT | 75.8@0.5 mA cm ⁻² | [8] |
| PVA/Gly/LiCl | CNT | ~17@0.5 mA cm ⁻² | [9] |
| PVA/H ₂ SO ₄ | PVA/PEDOT:PSS/EG | 128.9@0.5 mA cm ⁻² | [10] |
| PVA/LiCl | MnO ₂ /CFC | 54.0@0.2 mA cm ⁻² | [11] |
| PVA/H ₃ PO ₄ | CNT | 72.9@0.5 mA cm ⁻² | [12] |
| PVA/SA/PEG/NaCl | AC | 103.6@2 mA cm ⁻² | [13] |



Fig. S1. (a) Typical stress-strain curves and (b) corresponding stress and strain values of organohydrogels formed at different freezing temperatures.



Fig. S2. (a) Typical tensile stress-strain curves of organohydrogels with different CaCl₂ contents and fixed glycerin content of 40 wt%; (b) Tensile strength, (c) elongation at break, (d) toughness, and (e) Young's modulus of organohydrogels with different CaCl₂ contents.



Fig. S3. (a) Typical tensile stress-strain curves of organohydrogels with different glycerin contents and fixed CaCl₂ content of 20 wt%; (b) Tensile strength, (c) elongation at break, (d) toughness, and (e) Young's modulus of organohydrogels with different glycerin contents.



Fig. S4. The XRD curves of the SP hydrogel as well as the SPG and SPGC organohydrogels.



Fig. S5. The FTIR spectra of the SP hydrogel, SPG and SPGC organohydrogels.



Fig. S6. Photos showing the degradation process of the SPGC organohydrogel under immersion conditions of DI water at 90 °C.



Fig. S7. (a) The quality retention ratio of SP hydrogel, SPG and SPGC organohydrogels with different days of water loss at 25 °C and 57% (RH); (b) Morphology changes of the SP hydrogel, SPG and SPGC organohydrogels within 30 days.



Fig. S8. (a) Changes of G' and G'' of the SPGC organohydrogel before and after thermoplastic process with the increasing strain; (b) The variations of G' and G'' of the SPGC organohydrogel before and after thermoplastic process with the reduction of scanning frequency.



Fig. S9. The time of healing process for the organohydrogel by the real-time resistance measurement.



Fig. S10. (a) The conductivity changes and (b) Nyquist plots of organohydrogels at room temperature.



Fig. S11. (a) The GCD curves and (b) CV curves of supercapacitors assembled with untreated electrolytes.



Fig. S12. Areal capacitance at different densities calculated from GCD curves.



Fig. S13. The luminance change images of the small red bulb are obtained during the process of stretching the SPGC organohydrogel.



Fig. S14. The resistance response of the thermoplastic organohydrogel based sensor by applied tensile strain between 0 and 25% for 200 cycles at 150 mm/min.



Fig. S15. The relative resistance changes of the thermoplastic organohydrogel based sensors for different strain (25%-100%).

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