An environment-stable hydrogel with skin-matchable performance for human-machine interface

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ABSTRACT Ionic hydrogel-based sensors have shined a spotlight on wearable electronics. However, the sensitivity and reliability of hydrogel devices are significantly hampered by the weak adhesion of skin-sensor interface as well as inferior temperature tolerance. Here, inspired by the structure and composition of dermis, a novel skin-attachable and environment-stable hydrogel was designed by integrating collagen into the LiCl-containing chemically cross-linked polyacrylamide hydrogel. The hydrogel exhibited skin-like mechanical properties of low modulus, superior stretchability as well as excellent elasticity. Furthermore, the introduction of collagen endowed the hydrogel with robust and seamless interfaces with diverse materials, including the curved skin. As a result, the hydrogel is capable of serving as a human-machine interface for collecting reliable electrocardiography (ECG) signals and discerning various human motions, with high sensitivity (gauge factor = 10.7), fast response, negligible hysteresis as well as extensive monitoring range. Notably, the hydrogel that can mimic the temperature-tolerant mechanism of most organisms possesses persistent stabilization of adhesive, conductive, sensory and mechanical performances at subzero or ambient conditions. The skin-inspired strategy paves an effective way for the design of multifunctional materials with potential applications in next-generation electronics.

Keywords: hydrogel, human-machine interface, skin-matchable, self-adhesive, environment-stable

INTRODUCTION

Ionic hydrogels have been recognized as revolutionary candidates for wearable electronics based on the merits of stretchability, biocompatibility as well as organism-similar conductive way, which could achieve real-time electromechanical response in a broad sensing range, promoting the potential applications in personal health-

care diagnosis and human motion detection [1–7]. Despite the significant breakthroughs, most ionic hydrogel-based sensors still suffer from low sensitivity [8–10]. In addition, currently available hydrogel sensors generally secure the contact with skin by adhesive tapes, resulting in not only complicated operations and uncomfortable wearing experience, but also unstable signal detection due to the large interface resistance [11–13]. The robust self-adhesion of hydrogel is necessary for enabling the sensors to be seamlessly attached to curvilinear skin and move together with the dynamic human body without slippage and delamination, thus ensuring the accurate monitoring with high signal-to-noise ratio [14,15].

Besides, the hydrogel sensors usually struggle to maintain stable properties at subzero or ambient conditions due to the evaporation and freeze of water, severely hindering the reliability and application range [16–18]. Partially or entirely replacing the water with nonvolatile solvent is an effective method for developing environmentally stable electronics, however, significantly compromising the conductivity of ionic hydrogels [19,20]. Accordingly, some strategies are urgent to construct on-skin sensors with critical feature combinations, including self-adhesion, moisture retention, freeze-resistance, skin-similar mechanical properties, and high sensitivity.

Human skin with super sensitivity to multiple stimuli is mainly composed of collagen, elastic fiber and inorganic salt, in which collagen as a significant component can work together with elastic fibers to form a three-dimensional (3D) network for imparting softness and elasticity to the skin [21,22]. In recent years, collagen has attracted numerous concerns in the fields of artificial skin, tissue engineering and wound dressings, due to their water solubility, good biocompatibility and low antigenicity [23,24]. In particular, abundant amino acid groups in

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collagen open up the feasibility of generating diverse physical interactions for constructing an adhesive interface. Furthermore, in nature, ions are the basis of biological activities in organisms, contributing to the transmission of neural sensing signals and the suppression of water crystallization in cells [25–27]. It can be anticipated that the introduction of collagen into ionic hydrogel networks through the simulation of human skin would inspire the development of flexible sensors with expectable features such as remarkable sensitivity, skin-attachable ability and environmental adaption.

Herein, inspired by skin, a self-adhesive and temperature-tolerant hydrogel was presented for an environment-stable human-machine interface. Collagen was introduced into a network consisting of chemically cross-linked polyacrylamide (PAAm) and lithium chloride (LiCl), which mimicked the structure of dermis for endowing the hydrogel with ideal softness and stretchability desired for wearable sensors. Impressively, the hydrogel demonstrated repeatable adhesiveness on various substrate surfaces for seamless skin-sensor interface benefited from the molecular structure of collagen. Besides, remarkable stability of flexibility, conductivity and adhesion for the hydrogel were achieved as exposed to subzero or room temperature chronically. As a result, the hydrogel presented superior sensitivity toward mechanical deformation, which could be applied as a human-machine interface for monitoring electrocardiogram (ECG) signals and body motions with negligible hysteresis, rapid response, broad sensing range and durability.

EXPERIMENTAL SECTION

Materials

Acrylamide (AAm, 99.0%), LiCl (99%), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 99.5%), *N,N'*-methylene bisacrylamide (MBA, 99.0%) and potassium persulfate (KPS, 99.5%) were obtained from Shanghai Aladdin (China). Collagen (90%, from fish) was supplied by Shanghai Macklin (China).

Preparation of PAAm-collagen composite hydrogels

Briefly, AAm monomer, collagen, LiCl and MBA were firstly dissolved in deionized water (5 mL) and stirred for 1 h. Then, KPS (0.03 g) and TMEDA (15 μ L) as initiators were added with stirring for 5 min. Finally, the polymerization proceeded at 45°C for 6 h, obtaining the PAAm_x-collagen_y hydrogel, where the *x* represented the MBA content and *y* was the mass ratio of AAm and collagen. The weight ratio of AAm monomer and col-

lagen was fixed at 4:0, 4:1, 4:2 and 4:3. The molar content of LiCl was 0.6, 1.2, 1.8 and 2.4 mol L⁻¹. The mole ratios of MBA/AAm were 0.025%, 0.05%, 0.075% and 0.1%, respectively. For comparison, pure PAAm hydrogel without collagen and PAAm-collagen hydrogel without LiCl were synthesized using the same method. The compositions of PAAm-collagen hydrogels were displayed in Table S1.

Peeling measurement

The adhesive strength of PAAm-collagen hydrogel (thickness of 6 mm, width of 20 mm) for diverse substrates was surveyed through 90° peeling tests with a CT3-1000 texture analyzer (made in Brookfield of USA). Silica rubber, aluminum, glass, titanium and polytetrafluoroethylene (PTFE) were selected as typical testing surfaces, and the test speed was maintained at 5 mm s⁻¹. Before measurement, to prevent the deformation of hydrogel in peeling direction, the upper surface of hydrogel was bonded with polyethylene terephthalate film. At least five samples for each component were tested for determining the final bonding strength. Unless otherwise specified, the LiCl concentration of PAAm-collagen hydrogel in the peeling test was 1.8 mol L⁻¹.

Mechanic contact test

Mechanic contact test was conducted on the PAAm-collagen hydrogel to investigate the adhesive property by the texture analyzer (CT3-1000, made by Brookfield in USA) with a Spherical Nylon probe of 25.44 mm in diameter. The loading force, dwell time and test velocity were preset as 100 mN, 60 s, and 0.5 mm s⁻¹, respectively. The adhesion energy (W_{adh}) of hydrogel could be obtained using the formula below:

$$W_{adh} = \frac{\int F dx}{A_{max}}, \quad (1)$$

where *F*, *x*, and *A*_{max} represent the force, displacement and maximum contact area, respectively. *A*_{max} is defined as *A*_{max}=2 π *r**h*, in which *r* is the representative of radii for probe and *h* is the distance at the maximum compressive force. Unless otherwise specified, the LiCl concentration of PAAm-collagen hydrogel in the mechanic contact test was 1.8 mol L⁻¹.

Mechanical measurement

The tensile measurements of PAAm-collagen hydrogels were executed by a universal testing machine with a load of 100 N (AGX-X, SHIMADZU, Japan). Dumbbell-shaped hydrogel samples of 4 mm width and 3 mm

thickness were measured with a constant speed (100 mm min^{-1}). The elastic modulus and toughness were obtained by calculating the slope at 0%–20% strain and integral area of stress-strain curves, respectively. For the cyclic loading-unloading tests, the hydrogels were stretched to the preset strain and the dissipated energy was obtained from the integral area of tension-relaxation curves. Unless otherwise specified, the LiCl concentration of PAAm-collagen hydrogel in mechanical measurement was 1.8 mol L^{-1} .

Rheological measurement

The rheological measurements were performed on the PAAm_{0.075}-collagen_{4:1} hydrogel with 1.8 mol L^{-1} LiCl by Modular Compact Rheometer of MCR 302 (Anton Paar) with parallel plate in 25 mm diameter. The shear strain tests ranging from 0.01% to 1000% were carried out with a stationary frequency of 10 rad s^{-1} . The frequency sweep measurements (0.1 – 100 rad s^{-1}) were implemented at the strain of 0.1%. Temperature sweep tests were used to determine the freeze tolerance of PAAm_{0.075}-collagen_{4:1} hydrogel with 2.4 mol L^{-1} LiCl. The temperature was changed from 50 to -20°C with a cooling rate of 5°C min^{-1} .

Electrical measurement

The conductive performance of PAAm-collagen hydrogel was measured through the four-probe AC impedance spectrum on an electrochemical workstation (PGSTAT302N, Metrohm). The conductivity (σ , S cm^{-1}) of hydrogels was defined as

$$\sigma = D / (R \times S), \quad (2)$$

where D (cm) is the spacing distance between every two probes, R (Ω) is the expression of resistance of hydrogel, S (cm^2) refers to the area of hydrogel cross-section.

The resistance changes of PAAm_{0.075}-collagen_{4:1} hydrogel with 1.8 mol L^{-1} LiCl under strain or pressure were recorded by the tensile machine associated with B35T digital multimeter (OWON, China). Besides, the hydrogel was applied as a wearable sensor for the real-time detection of whole-body movements through connecting with a digital multimeter by wires. The relative resistance variations of hydrogel were obtained by the equation below:

$$\Delta R / R_0 = (R - R_0) / R_0 \times 100\%, \quad (3)$$

where R_0 and R are the initial resistance and resistance after deformation.

The gauge factor (GF), which could indicate the sensitivity of the hydrogel sensor to applied strain (ϵ), was

acquired by the formula as follows: $\text{GF} = [\Delta R / R_0] / \epsilon$.

The electrocardiography (ECG) signals were recorded by an Easy ECG Monitor (Prince 180B, Heal Force) through using the adhesive PAAm-collagen hydrogel as electrodes. The signals were transmitted to the smartphone in real-time via Bluetooth.

DSC measurement

The differential scanning calorimetry (DSC) using DSC-1 (Mettler Toledo, USA) was devoted to evaluating the anti-icing ability of PAAm_{0.075}-collagen_{4:1} hydrogel with different concentrations of LiCl. The testing temperature varied from 10 to -50°C with a constant speed of 5°C min^{-1} .

Water retention test

The PAAm_{0.075}-collagen_{4:1} hydrogels with varied concentrations of LiCl were placed at an oven with a constant temperature of 25°C to investigate the anti-drying capacity. The residual mass and resistance change of hydrogels were recorded at regular intervals. The residual mass was obtained from the following equation:

$$\text{Residual mass (\%)} = W_t / W_0 \times 100\%, \quad (4)$$

where W_t and W_0 are the weight of hydrogel after and before measurement.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed on Q500 (TA, USA) in a nitrogen environment to analyze the moisture retention performance of PAAm_{0.075}-collagen_{4:1} hydrogel. The temperature increased from 30 to 70°C with a heating rate of 5°C min^{-1} .

RESULTS AND DISCUSSION

In present work, a self-adhesive and temperature-tolerant hydrogel was fabricated by a one-step polymerization of AAm monomer in the presence of collagen and lithium chloride with the MBA as chemical cross-linkers, as schemed in Fig. 1. Collagen could form inter-molecular hydrogen bonds, thereby constructing a PAAm-collagen hydrogel network similar to the structure of dermis in which collagen and elastin form 3D networks to impart skin with softness and elasticity. The PAAm-collagen hydrogel exhibited surprising self-adhesiveness, excellent stretchability and low modulus under the effect of collagen. In addition, from the inspiration of organisms, LiCl was introduced to effectively improve the water retention and anti-icing capacity of the hydrogel, overcoming the problem that the traditional hydrogel can

Figure 1 Schematic illustration for preparing skin-inspired PAAm-collagen hydrogel.

hardly maintain stable properties for a long time in cold or normal temperature. The brilliant comprehensive features enabled the PAAm-collagen hydrogel as an ideal human-machine interface for real-time ECG signals recordation and motion detection.

Benefitting from the massive amine acid groups (carboxyl, amino and hydroxyl groups, etc.) in collagen, the obtained PAAm-collagen hydrogel exhibited unique self-adhesive characteristic. As depicted in Fig. 2a, the PAAm-collagen hydrogel adhered to latex glove and finger could be stretched without detachment. Fig. 2b further presents that the PAAm-collagen hydrogel could be attached onto a human skin with excellent conformability and good adaptability, which is vital for providing conformal contact and stable integration of hydrogel-skin interface to pledge the motion-sensing accuracy. A series of highly sensitive JKR mechanical contact tests were performed to assess the adhesive performances of the hydrogel assisted by collagen. The force-displacement curves of hydrogels were plotted in Fig. 2c. The PAAm-collagen hydrogel showed a significantly enhanced adhesion force (280 mN) compared with the PAAm hydrogel, attributing to the multiple physical interactions with materials induced by collagen. Furthermore, the contribution of various PAAm/collagen mass ratios on the adhesion was also tested with the same contact force (0.1 N). As displayed in

Fig. 2d–e, the adhesion force and adhesion energy of the hydrogels gradually increased as the collagen content increased, indicating that the addition of collagen significantly improved the adhesive capability of hydrogels. To further estimate the adhesive behaviors of PAAm-collagen hydrogel, 90° peeling tests were performed to measure the adhesion on an aluminum alloy substrate (Fig. 2f). The PAAm-collagen hydrogel obtained the maximum adhesive strength (300 N m^{-1}) when the mass ratio of AAm and collagen was 4:3, which was 10 times that of pure PAAm (30 N m^{-1}). And the effect of MBA content on the adhesive performance of hydrogel was also explored, as shown in Fig. S1. The increase of MBA reduced the peeling strength of hydrogel, which may be ascribed to the destroyed balance between adhesion and cohesion. In addition, the collagen-assisted hydrogel exhibited a universal and robust bonding strength for different substrates. Fig. 2g shows the admirable peel strengths of PAAm-collagen hydrogel on silica rubber, glass, titanium, aluminum and PTFE, respectively. Besides, the PAAm-collagen hydrogel exhibited excellent adhesion behavior without any loss in peel strength during 20 times of repeated peeling tests (Fig. 2h), indicating the durable and reusable adhesion behavior of hydrogels for long-time usage.

Good softness and excellent stretchability are essential

Figure 2 The PAAm_{0.05}-collagen_{4.2} hydrogel adhered to (a) latex gloves and finger with stretchability and (b) the back of hand without interface delamination under squeezing (the hydrogel was dyed by methylene blue). (c) Mechanical contact tests of PAAm_{0.05}-collagen_{4.2} and PAAm_{0.05} hydrogel. (d) Adhesive force, (e) adhesion energy and (f) 90° peeling strength of PAAm_{0.05}-collagen hydrogel with varied AAm and collagen mass ratios. 90° Peeling strength of PAAm_{0.05}-collagen_{4.2} (g) on various materials and (h) for 20 times peeling cycles.

features for hydrogel-based sensors to mimic the sensing performance of human skin [28]. According to the dynamic rheology measurement (Fig. S2), the PAAm-collagen hydrogel exhibited a strain and frequency-dependent viscoelastic behavior, indicating that the hydrogel possessed the solid elasticity of a viscoelastic material ($G' > G''$). Fig. 3a vividly demonstrates the stretchability, softness and puncture resistance of PAAm-collagen hydrogel. As displayed in Fig. 3b–c, tensile tests were performed on the PAAm-collagen hydrogel to assess the contribution of collagen on mechanical properties. The increase of collagen weakened the tensile strength of hydrogel, but the tensile strain increased step-by-step for well matching with the stretchability of skin (65%) [12]. The main reason was that collagen interacted with PAAm networks *via* weak hydrogen bonds and played a role of lubricant in the hydrogel network during stretching [29]. Besides, the PAAm-collagen hydrogel exhibited a low elastic modulus of 10–15 kPa, which was comparable to the Young's modulus of human skin, thus ensuring the

mechanical compatibility between the hydrogel sensor and human skin as well as improving the wearing comfort [5,30]. The mechanical properties of the resultant hydrogel could also be adjusted by varying the content of MBA (Fig. S3). To be specific, the strength and fracture energy of hydrogel tended to increase first and then decrease, while the elastic modulus stepwise increased with the increment of MBA content. Subsequently, a series of tensile cycling measurements were performed. The results in Fig. 3d demonstrate that the hysteresis loop of PAAm-collagen hydrogel increased with varying strain from 100% to 500%, due to the increased level of destruction in the hydrogel network. Nevertheless, less energy dissipation was exhibited even at the strain of 500%, proving the hydrogel owned excellent resilience. In addition, as shown in Fig. 3e, a large hysteresis loop occurred in the first loading-unloading cycle, which could be attributed to the breakage of physical hydrogen bond cross-links in the network. After the first cycle, the hydrogel showed good fatigue resistance, the dissipated energy was almost

Figure 3 (a) The exhibitions of stretchability, softness and puncture resistance for PAAm-collagen hydrogel. (b) Stress-strain curves of PAAm_{0.075}-collagen hydrogel with varied contents of collagen, and (c) corresponding strain and elastic modulus. (d) Cyclic tensile tests of PAAm_{0.075}-collagen_{4:1} hydrogel at the strains of 100%, 200%, 300%, 400% and 500% (inset: corresponding stress and hysteresis energy). (e) Five loading-unloading cycles of PAAm_{0.075}-collagen_{4:1} hydrogel without dwell time, and (f) corresponding stress and hysteresis energy.

constant during the subsequent consecutive loading-unloading cycles (Fig. 3f). When a hydrogel was connected to the human body as a wearable device, this excellent energy dissipation ability and elastomer-like anti-fatigue could effectively prevent external forces from being transferred to human tissues, thereby protecting the human body from injury. The PAAm-collagen hydrogel could be assembled as a thin layer of on-skin sensor considering the skin-similar mechanical properties. Furthermore, the PAAm-collagen hydrogel demonstrated excellent self-adhesion and moderate mechanical properties compared with other hydrogels in Table S2 [15,31–35].

The PAAm-collagen hydrogel possessed excellent conductivity due to the incorporation of LiCl. Here, the hydrogel was applied as an ionic conductor in a circuit for lighting the light-emitting diode (LED) bulb (Fig. 4a). The luminance of LED was weakened by stretching the hydrogel, confirming the increased resistance at larger strain because of the prolonged ion transport channel [36]. It had been proved that the hydrogels were suitable for the application as strain sensors because of the rapid resistance-deformation responsiveness (Fig. 4b). The GF, an indicator of the sensitivity for hydrogel-based sensors, was divided into three stages. The GF was 3.2 in the applied strain range of 0%–100%, and then improved gradually to 7.6 in the interval from 100% to 300%. A

high GF of 10.7 was reached at strain above 300%, verifying the superior sensitivity of the PAAm-collagen hydrogel. Fig. 4c, d show that the hydrogel sensor exhibited outstanding stability and replicability for the detection of both tiny (0.25%–0.75%) and relatively large strain (1%–5%). As shown in Fig. 4e, the signal intensity was invariable under different tensile speed from 50 to 200 mm min^{−1}, signifying that the hydrogel sensor had excellent independence to the test speed. Furthermore, in Fig. 4f, the hydrogel sensor could provide real-time feedback to strain within a short response time (89 ms) and recovery time (97 ms). Fig. 4g illustrates that the variation of resistance had nearly kept pace with the applied strain without evident sensing delay. Furthermore, 200 tension-relaxation cycles at the strain of 10% were performed on the hydrogel sensor for investigating the electrical stability (Fig. 4h). Apparently, the relative resistance changes were almost constant after the repeated cycles, highlighting the stability and durability for long-term service life of the hydrogel sensor. As a result, the PAAm-collagen hydrogel exhibited higher sensitivity and quicker response in comparison with previously reported sensors [9,37–44] (Fig. 4i).

Apart from tensile strain, the hydrogels could also be applied as on-skin sensors for monitoring pressure deformation. Fig. 4j illustrates that the hydrogel sensor was acutely sensitive to a wide pressure range from 2 to

Figure 4 (a) The change of LED brightness with the increase of tensile strain. (b) The variation in relative resistance of hydrogel sensor *versus* applied strain. $\Delta R/R_0$ of the hydrogel sensor under (c) the small-strain range of 0.25%–0.75%, (d) the large-strain range of 1%–5%, and (e) the tensile speeds of 50–200 mm min^{-1} . (f) The response and recovery time of the hydrogel sensor. (g) The hysteresis behavior of the hydrogel sensor. (h) $\Delta R/R_0$ of the hydrogel sensor at the strain of 10% for 200 tensile cycles and the enlarged detail of a designated area. (i) Gauge factor and response time of this work compared with other reported sensors. (j) The PAAm-collagen hydrogel as a pressure sensor for monitoring pressure in the range of 2–17 kPa. (k) The variations in relative resistance of the PAAm-collagen hydrogel under different compression frequencies. (l) The response and recovery time of the PAAm-collagen hydrogel pressure sensor. (m) The relative resistance changes of the PAAm-collagen hydrogel at the pressure of 7 kPa for 250 cycles. (n) The $\Delta R/R_0$ of the PAAm-collagen hydrogel with the consecutively released pressure from finger.

17 kPa, note that the slight pressure of 2 kPa was also the minimum limit that the skin could perceive [45]. Ob-

viously, a higher amplitude of signal waveforms with repeatability was demonstrated by the hydrogel sensor at

increasing pressure. The hydrogel could also recognize the pressure under different frequencies without the apparent change of $\Delta R/R_0$ (Fig. 4k). In addition, the hydrogel sensor could respond to the compressing process in a short time of 107 ms (Fig. 4l). More importantly, the pressure sensor was sensitive and stable enough to withstand 250 compressive cycles at 7 kPa in Fig. 4m, illustrating the reliability and endurance of the hydrogel sensor. Furthermore, decreased relative resistance changes were observed with a consecutive decrease in pressure from the finger (Fig. 4n).

The stability under the external environment is highly desirable for the practical application of hydrogel sensors, because the water-rich hydrogels are easy to be freeze-dried at subzero temperatures and dehydrated even at ambient

conditions, causing the failure of their functions [16]. Freezing tolerance must be implemented by hydrogel sensor for the application in a subzero environment, such as skiing. From the illustration in Fig. 5a, the PAAm-collagen hydrogel without LiCl turned into white color after being placed at -20°C for 6 h, ascribed to the growth of ice crystals in the hydrogel. However, the LiCl-incorporated hydrogel still remained its initial state, indicating that LiCl reduced the freezing point of water. DSC test was carried out to investigate the anti-icing ability of the PAAm-collagen hydrogel. Obviously, a stepwise decrease in the crystallization temperature of the hydrogel was achieved by increasing the concentration of LiCl, as a result of the colligative property of ionic compounds [46]. Dynamic temperature-sweep measure-

Figure 5 (a) DSC tests of PAAm_{0.075}-collagen_{4.1} hydrogel with different concentrations of LiCl (inset: the states of hydrogel before and after storage at -20°C for 6 h). (b) Temperature sweep measurements of PAAm_{0.075}-collagen_{4.1} hydrogel without and with LiCl. (c) The exhibitions of adhesion and flexibility for PAAm_{0.075}-collagen_{4.1} hydrogel with 2.4 mol L⁻¹ LiCl at -20°C for 6 h. (d) The mechanical properties of PAAm_{0.075}-collagen_{4.1} hydrogel with 2.4 mol L⁻¹ LiCl under -20°C for 6 h and 12 h. (e) The conductivity of PAAm_{0.075}-collagen_{4.1} hydrogel with 2.4 mol L⁻¹ LiCl at 20°C and -20°C for 4 cycles. (f) The relative resistance changes of PAAm_{0.075}-collagen_{4.1} hydrogel with 2.4 mol L⁻¹ LiCl at the tensile strain of 10% after storage at -20°C for 0, 6, 8 and 12 h. (g) The TGA curves of PAAm_{0.075}-collagen_{4.1} hydrogel with and without LiCl in the temperature range of 30–70°C. (h) The residual mass of PAAm_{0.075}-collagen_{4.1} hydrogel with and without LiCl at 25°C for 24 h (inset: the exhibitions of adhesion and flexibility). (i) The resistance change of PAAm_{0.075}-collagen_{4.1} hydrogel with and without LiCl.

ment in Fig. 5b also verified the anti-icing behavior and outstanding flexibility of LiCl-assisted hydrogel with the constant moduli in a wide temperature range (50 to -20°C) [25]. It could be visually observed from Fig. 5c and Fig. S4 that the LiCl-free PAAm-collagen hydrogel became non-adhesive, rigid, and nonconducting at -20°C , while the hydrogel with LiCl was still adhesive, flexible and conductive invariably. As shown in Fig. 5d, the stretchability and tensile strength of the PAAm-collagen hydrogel with LiCl at -20°C for varying times almost maintained constant, manifesting the brilliant anti-freezing property of the hydrogel. Although the conductivity of the PAAm-collagen hydrogel decreased from 0.021 S cm^{-1} (at 20°C) to 0.017 S cm^{-1} (at -20°C) due to the constrained ion movement caused by unavoidable freezing of partial water, the hydrogel still exhibited excellent electrical conductivity and cycling stability with negligible deviation at each temperature in Fig. 5e. After the hydrogel was placed at -20°C for different storage times, the relative resistance variations of the hydrogel conductor at the tensile strain of 10% were recorded in Fig. 5f. The $\Delta R/R_0$ of the hydrogel always kept the constant values, indicating that the hydrogel possessed outstanding anti-icing performance. Beyond all that, as shown in Fig. S5, the PAAm-collagen hydrogel frozen at -20°C for 24 h could still respond to different tensile strains of 5%, 10% and 20% accurately.

Apart from the freezing-tolerance, moisture retention is vital for pledging the stability of hydrogel at ambient conditions. The original shape of PAAm-collagen hydrogel could be basically considered to maintain invariable after storage at 25°C for 24 h, in comparison with the LiCl-free PAAm-collagen hydrogel with contracted volume (Fig. S6). TGA curves in Fig. 5g verified that the weight loss of LiCl-assisted PAAm-collagen hydrogel was significantly lower than that of LiCl-free hydrogel, with the temperature increasing from 30 to 70°C , indicating the contribution of LiCl for moisture holding of the hydrogel. The possible reason was that the salt ions (Li^+ or Cl^-) could strongly bond with water molecule pairs to suppress the evaporation of water [47]. As shown in Fig. 5h, the residual mass of LiCl-free PAAm-collagen hydrogel was only 80% after exposure to 25°C for 24 h. Conversely, the hydrogel with LiCl possessed a residual mass of 95% in the condition of equivalence. Thus, in the illustration, the hydrogel without LiCl lost adhesion and flexibility, while the hydrogel with LiCl was always able to adhere to skin and stretch. Amazingly, the hydrogel with LiCl had a residual mass of 81% even after being placed at 25°C for 7 days (Fig. S7). In contrast, the residual mass of

the hydrogel without LiCl reduced to only 40%. The water-retention capacity of PAAm-collagen hydrogel in comparison with other hydrogels was shown in Table S3 [41,48–51]. Due to the excellent water retention ability, the PAAm-collagen hydrogel still possessed high mechanical property and conductivity after being stored at 25°C for 7 days (Fig. S8). Besides, a huge increase in resistance of hydrogel without LiCl was observed in Fig. 5i when exposed to 25°C for 24 h; however, the resistance change of LiCl-contained hydrogel was lower. Fig. S9 shows the resistance changes of the hydrogel with varying LiCl concentrations after 7 days, further corroborating the contribution of LiCl to the water retention ability of PAAm-collagen hydrogel. The impressive anti-icing and water-retention ability of PAAm-collagen hydrogel hold great promise for working at a wide range of temperatures. However, the high concentration of LiCl in hydrogel may cause the dehydration of skin, which is a noticeable problem in the applications. Furthermore, the mechanical property and conductivity of PAAm-collagen hydrogel were influenced by relative humidity due to the hygroscopicity of LiCl, as shown in Fig. S10.

Owing to the excellent mechanical compliance, high conductivity, remarkable self-adhesiveness, superior sensing sensitivity and durability, the PAAm-collagen hydrogel demonstrated excellent prospects as an on-skin sensor for detecting subtle physiological signals. As shown in Fig. S11, the hydrogels with self-adhesiveness and low modulus were installed on the electrodes to enhance the bonding force with skin for collecting the ECG signals, greatly reducing the imperfect contact due to the human activity. It could be seen that the ECG waveforms of a volunteer displayed evident separated and negligible fluctuated P, QRS, and T curves in Fig. 6a, b, supplying valuable medical informatics on cardiovascular problems. In addition, the subtle changes in pulse at the wrist were clearly presented and 79 beats per min in a relaxed state were detected by the hydrogel sensor (Fig. 6c). In Fig. 6d, the physiological breathing signals of volunteer were readily tracked *via* attaching the hydrogel on the chest, whether regular or rapid respiration modes. The hydrogel sensor also possessed the capacity of sensing throat movement during speech, as depicted in Fig. 6e, the phonation of “hydrogel” and “very good” could be recognized by the sensor attributed to the different syllables. And peaks and valleys in the characteristic curves were similar when each word was repeated three times.

In addition to subtle signals, the hydrogel sensor was sensitive enough for detecting complex motions in real-time. It could be seen from Fig. 6f that a gradual increase

Figure 6 (a) Pairs of hydrogel electrode were attached on the left and right chest of a volunteer with the reference electrode adhered on the left abdomen for detecting ECG signals. (b) Pairs of hydrogel electrodes were attached on the left and right forearms of a volunteer with the reference electrode adhered on left forearm for detecting ECG signals. (c–e) Detecting tiny muscle movements of pulsing, breathing, and speaking. (f) Bending of the finger at different angles (30°, 60° and 90°). (g) Detection of standing and walking with the hydrogel sensor mounted on the sole. (h) Monitoring of the walking speed with the hydrogel sensor.

in $\Delta R/R_0$ could be perceived by the sensor when enhancing the bending angles of finger from 30° to 90°, attributed to the stretching of hydrogel. Moreover, the $\Delta R/R_0$ maintained a similar value at the same bending angle, indicating the stability and accuracy of the sensor. Besides, the hydrogel-based sensor was also capable of monitoring the dynamic nodding behavior (Fig. S12). Impressively, the hydrogel could be attached on the cheek directly for the detection of laughing in Fig. S13, showing increased magnitude due to the deformation caused by muscle movement. In addition, the on-skin sensor could sense different exercise states, such as standing and walking, when being mounted on the sole. As shown in Fig. 6g, the relative resistance was almost constant when the volunteer remained stationary, and rapidly increased under the motion of walking due to the excellent sensitivity. In addition, the hydrogel-based sensor could respond quickly and accurately to walking speed (Fig. 6h), demonstrating a change from sparse to dense in curves

with the acceleration of walking from 1.5 to 3.6 km h⁻¹.

CONCLUSION

In summary, inspired by the structure and composition of human skin, a self-adhesive and temperature-tolerant hydrogel was fabricated by chemically crosslinking acrylamide in the presence of collagen and lithium chloride. With the synergistic effect of collagen and PAAM network, the hydrogel exhibited large stretchability, low modulus, elasticity, fatigue resistance as well as robust self-adhesion to diverse material surfaces, which could move with the dynamic skin without delamination. It was worth noting that the hydrogel could maintain stable mechanical properties, conductivity and self-adhesion in a subzero or room temperature for a long time. Furthermore, the hydrogel showed superior sensitivity ($GF = 10.7$) to mechanical deformation, which was capable of serving as human-machine interface for reliably recording ECG signals and monitoring whole-body movements

with low hysteresis, broad operating range, fast response and high durability. It is envisioned that the skin-inspired strategy would revolutionize multiple fields, including ionic skin, human-machine interface and wearable sensors.

Received 7 November 2020; accepted 22 January 2021;
published online 8 April 2021

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Acknowledgements This work was supported by the National Natural Science Foundation of China (51873024), and the Science and Technology Department of Jilin Province (20200708102YY and 20190201234JC).

Author contributions Gao Y designed and performed the experiments, and wrote the paper; Wang Y analyzed the data and prepared the figures; Xia S and Gao G revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of

interest.

Supplementary Information Supporting data are available in the online version of the paper.

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用于人机界面的具有类皮肤性质的环境稳定水凝胶

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摘要 离子水凝胶基传感器已经成为制备可穿戴电子产品的热点。然而, 皮肤与传感器之间弱的界面粘合力以及水凝胶较差的耐温性严重影响了传感器的灵敏度和可靠性。受皮肤结构和功能的启发, 我们将胶原蛋白整合到化学交联的水凝胶中, 设计出一种新型的可皮肤附着的且环境稳定的水凝胶。该水凝胶具有较低的模量、良好的拉伸性能和良好的弹性。此外, 胶原蛋白的引入使水凝胶与包括皮肤在内的多种材料具有牢固的和紧密贴合的界面。因此, 该水凝胶具有极高的灵敏度(GF=10.7)、快速响应性、可忽略的迟滞行为以及广泛的监测范围, 可作为人机界面以采集可靠的心电图(ECG)信号和辨别各种人体动作。值得注意的是, 模仿大多数生物体的耐温机制的水凝胶在零下或常温条件下具有持久的粘合性、导电性、传感性能和机械稳定性。这种以皮肤为灵感的策略为多功能材料的设计提供了一条有效途径, 并有望应用于新一代电子产品中。