Electronic Supplementary Information

Highly Skin-adhesive and Washable On-skin Electrodes Based on Polydopamine and Silk Fibroin for Ambulatory Electrocardiography Sensing

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1. Experimental Section

Materials: Anhydrous calcium chloride, formic acid, dopamine hydrochloride, Tris and toluene were purchased from Sigma-Aldrich and used as received. SEBS (H1221 with volume fraction of poly(ethylene-co-butylene) = 88%) was provided by Asahi Kasei company. The commercial electrodes were bought from Likang company.

Preparation of PDASF gels: Degumming of silk fibroin (SF) by the way reported of Sofia etc.[1] Firstly, Bombyx mori silk fibers were minced to a length of about 3 cm and the pieces were degummed by boiling in Na_2CO_3 solution (0.02 M) for 90 min, and washed with distilled water for three times to remove the residual sericin. Then, the degummed silk fibers were allowed to dry in the oven for 12 h at 60 ℃. SF gels were prepared by the way reported of Yue etc.[2] SF/$CaCl_2$ (ratio = 5:1) formic acid solution was prepared by dissolving $CaCl_2$ (0.3 g) in formic acid (10 mL) at 50 ℃, and then dried silk fibers (1.5 g) were added and mixed at 70 ℃ until a homogeneous solution was obtained. Then, the mixed solution was poured into a polystyrene petri dish to volatile formic acid at room temperature for 24 h to form SF gel. Dopamine hydrochloride (0.45 g) was added into the Tris buffer solution (pH = 8.5, 0.1 mol L^{-1}, 10 ml) and the mixed solution was directly dropped into SF gels. Then, dopamine polymerized in SF gels to form PDA (DA/SF = 30 wt%, DA represent dopamine hydrochloride). Finally, to volatile solvent at room temperaturen and form PDASF gels. PDASF gels with other DA/SF ratios were prepared through following the same process but changing the single variable, referring to the DA content which added into the Tris buffer solution.

Preparation of SEBS/Au films: The elastomer substrates were prepared by casting SEBS H1221 (200 mg ml^{-1} in toluene) onto glass slides to form elastic films (≈ 200 μm) and volatilizing solvent in a ventilated place at room temperature for 12 h. Then, the samples were annealed at 130 °C for 1 hour under nitrogen atmosphere. Finally, thermal evaporation of Au with different thicknesses on SEBS substrates was carried out to form SEBS/Au films. The evaporation rate was 0.02 Å s^{-1} at the beginning of the thermal evaporation process for a thickness of 5 nm. Then, the evaporation rate slowly increased to 0.3 Å s^{-1} to finish the progress.

Characterization of PDA: The surface morphology of the PDASF gel was observed by a Hitachi SEM SU8010 Field Emission Scanning Electron Microscope. The samples were prepared by the technique of freezing and freeze-drying in advance. Later, the freeze-dried samples were cut, gold-coated and applied to SEM observation. Fourier transform infrared

(FT-IR) spectra of dopamine and PDA were examined by a Bruker Vertex 70 spectrometer. The resolution setting was 4 cm^{-1} with 16 scans for the spectral region of 4500–500 cm^{-1}.

Tensile Testing: The mechanical properties of PDASF gels, SEBS/Au films and AWS electrodes were performed with an MTS CMT4000 electronic universal testing machine. The stretching experiments were carried out, with a loading rate of 0.2 mm s^{-1}, up to the point that samples (length = 4 cm, width = 1 cm) were broken, and which allowed us to measure the ultimate tensile strength.

Impedance testing: The interfacial impedance was measured by laminating pairs of AWS electrodes with a circle shape (diameter = 2 cm) and a centre-to-centre distance of 5 cm on the forearm skin of a volunteer. The impedance was measured through a CHI660D electrochemical workstation by the traditional three-electrode system, where Pt sheet as a counter electrode, two AWS electrodes as work electrodes. The measuring range was from 1 Hz to 1 MHz, and the voltage was 100 mV.

Electrical Performance Testing: The resistance of SEBS/Au films (length = 4 cm, width = 1 cm) under stretching were recorded at room temperature in air by using a multimeter, and a KH-1 Stepper Motor Controller.

Control of the relative humidity: A constant temperature and humidity machine was used to control the humidity of the samples. Different samples were put inside the machine for 30 min to ensure them under certain humidity similar to that of the machine. Besides, the temperature of the machine was controlled to 25 ℃. The testing process of adhesion under different relative humidity was performed in a closed space and the testing time was very short (< 1 minute), so the water content of the sample remained unchanged. In this way, we got samples under certain relative humidity.

Adhesion strength between SEBS/Au films and PDASF gels: Adhesion strength between SEBS/Au films and PDASF gels was examined through the way proposed by Bao's group.[3] For the AWS electrode, the SEBS/Au layer was fixed on a glass slide (length =75 mm, width = 25 mm) by double-sided adhesive tape, and a hard stick (diameter =2 mm) was fixed on the PDASF gel by epoxy resin glue, which was allowed to cure for 10 min at room temperature. Then, the glass side hold with the sample was put into the constant temperature and humidity machine for 30 min to ensure them under the specific humidity. After that, the glass side was taken out. The hard stick was fixed with the jig, and the glass side was fixed on the sample stage for the test of adhesion strength between SEBS/Au film and PDASF gel by an MTS CMT4000 electronic universal testing machine (speed = 0.2 mm s^{-1}). The maximum adhesion force was read while peeling off the PDASF gel from the SEBS/Au film. The value of

adhesion strength was calculated by dividing the maximum load by the broken area of each sample. All these tests were repeated at least three times.

Adhesion energy of the PDASF gel: A custom-built setup consisting of a glass convex mirror (diameter = 20 mm) and a rigid stick, which was a□xed to the plane side of glass convex mirror using super glue, was used for adhesion energy test by an MTS CMT4000 electronic universal testing machine (speed = 0.2 mm s^{-1}). The custom-built setup was set to move downward to contact the PDASF gel, which was fixed on a glass side by double-side adhesive tape, until the sensor detected that the downward force reached 50 N, then changed the moving direction of the custom-built setup and moved upward for a distance of 1 cm. We needed to record the critical value F when the sphere suddenly broke contact with the PDASF gel. Then adhesion energy was calculated by the equation of J-K-R contact mechanics model theory:

$$F = -(3/2)\pi E_A R^*$$

ECG Monitoring: Ambulatory ECG signals were detected by using a three-electrode system. Two of them were working electrodes by using our AWS electrodes, and one of them was the reference electrode by using a commercial electrode. To acquire ECG signals, AWS electrodes were placed on the chest of volunteers. Then, we connected the AWS electrodes with a LiKang PC-80A ECG monitor together by lead wire to amplify and collect ambulatory ECG signals. To minimize the noise generated by the movement, the cables were fixed onto the volunteers' skin using a compression bandage.

Simulate of dry and wet condition in fig. 3a-c: The experiments of fig. 3a-c were performed on the same person's skin on the same day. The indoor relative humidity of our laboratory was 30%-40%. For fig. 3a and 3c (left), the wet skin and pig heart surface were simulated by spraying equal amount of water on the skin to make it moist. For fig. 3b and 3c (right), the dry skin was simulated by wiping the sweat off the skin with disposable tissues.

Informed consent statement of volunteers: The purpose and procedure of this study have been explained in detail to the volunteers. All volunteers agreed to participate in the study and agreed that their personal data would be collected, used, and made public for the purpose of experimental studies. In addition, they signed the consent form before participating in this study.

2. Supplementary Figures

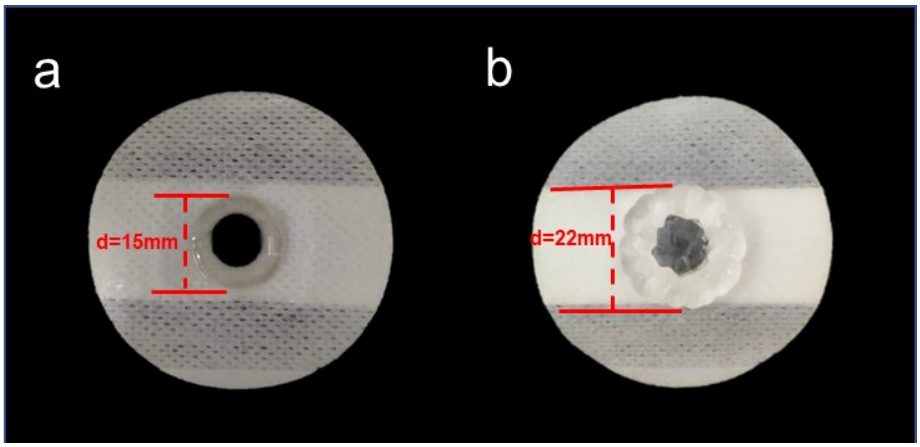

Fig. S1 Swelling characteristics of the gel of Ag/AgCl electrodes. (a) the original state of the Ag/AgCl electrode. (b) after swelling in water for 1 hour.

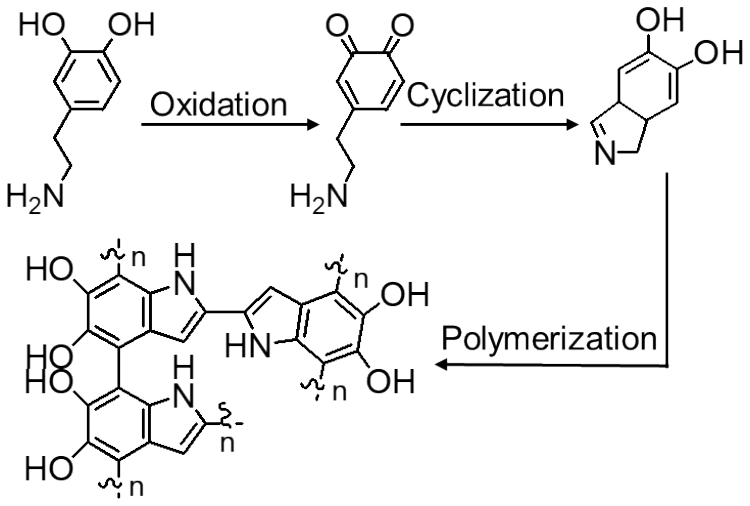

Fig. S2 Self-polymerization of dopamine to form polydopamine.

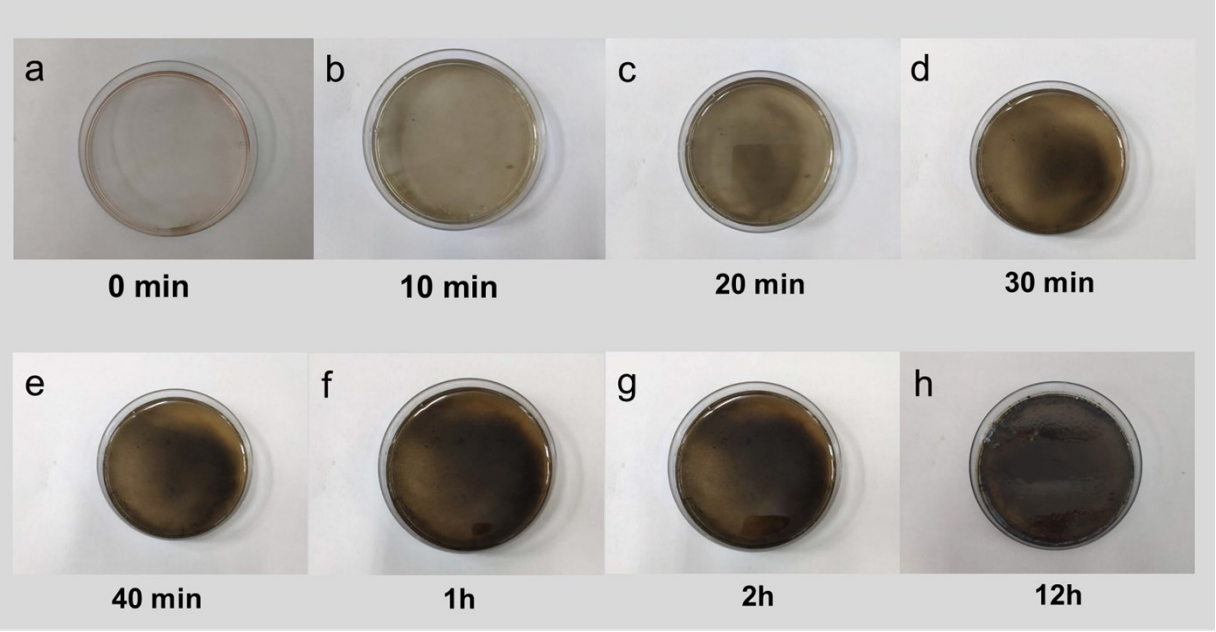

Fig. S3 Color change of the SF gel dropped with the Tris buffer solution (pH = 8.5) of dopamine for 12 h.

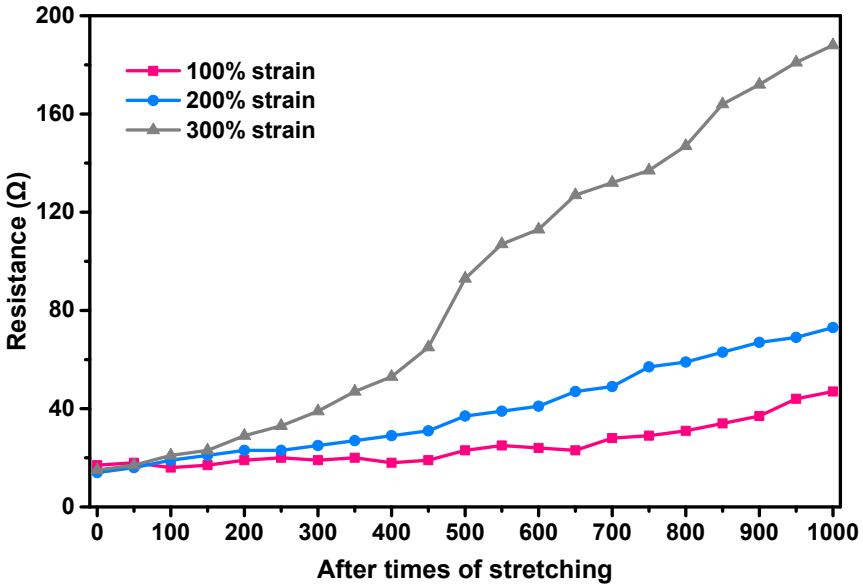

Fig. S4 The conductivity of SEBS/Au films after stretching and releasing to the initial state.

The testing method of 1000 cycles of stretching and releasing: The resistance value of the samples under unstretched states were recorded after every 50 cycles of stretching and releasing. Each sample was performed a total of 1000 cycles of stretching and releasing.

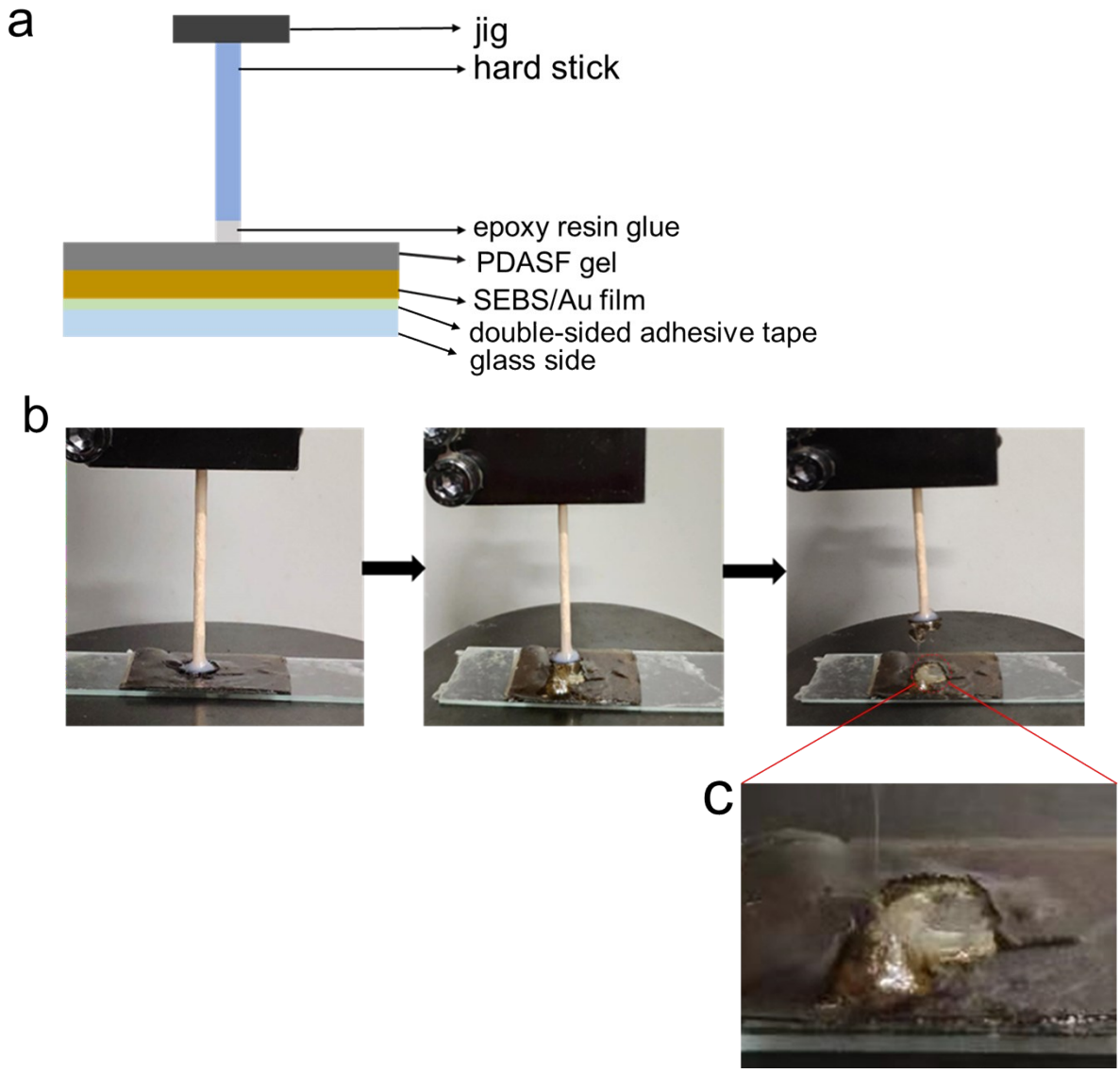

Fig. S5 Adhesion strength between the PDASF gel and the SEBS/Au film. (a) Schematic drawing of the device. (b) Photographs of the testing process. (c) A photograph to show the broken area in the PDASF gel.

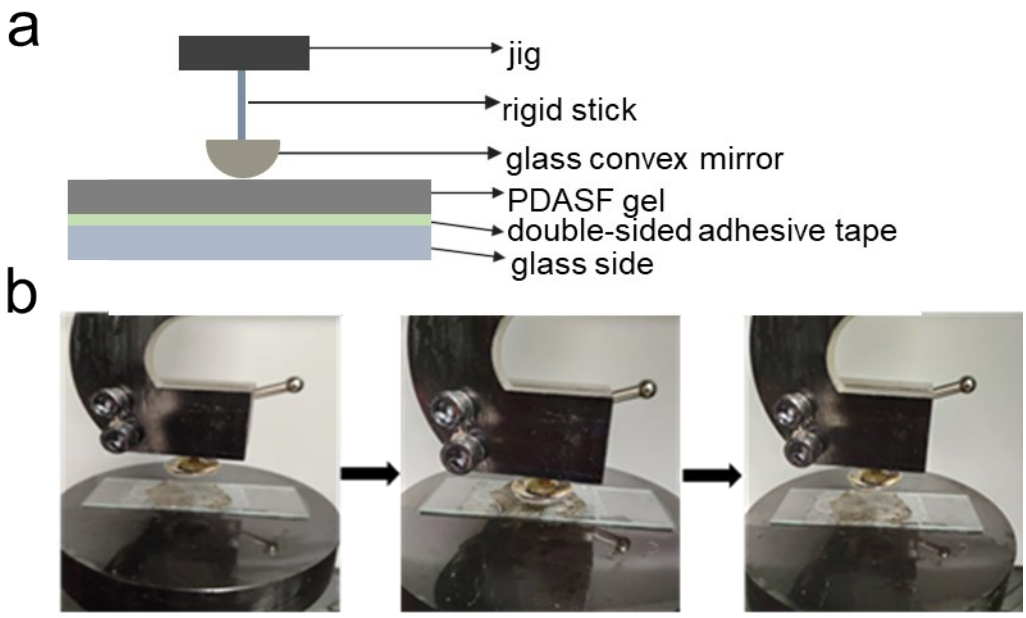

Fig. S6 Adhesion energy of the PDASF gel. (a) Schematic drawing of the device. (b) Photographs of the testing process.

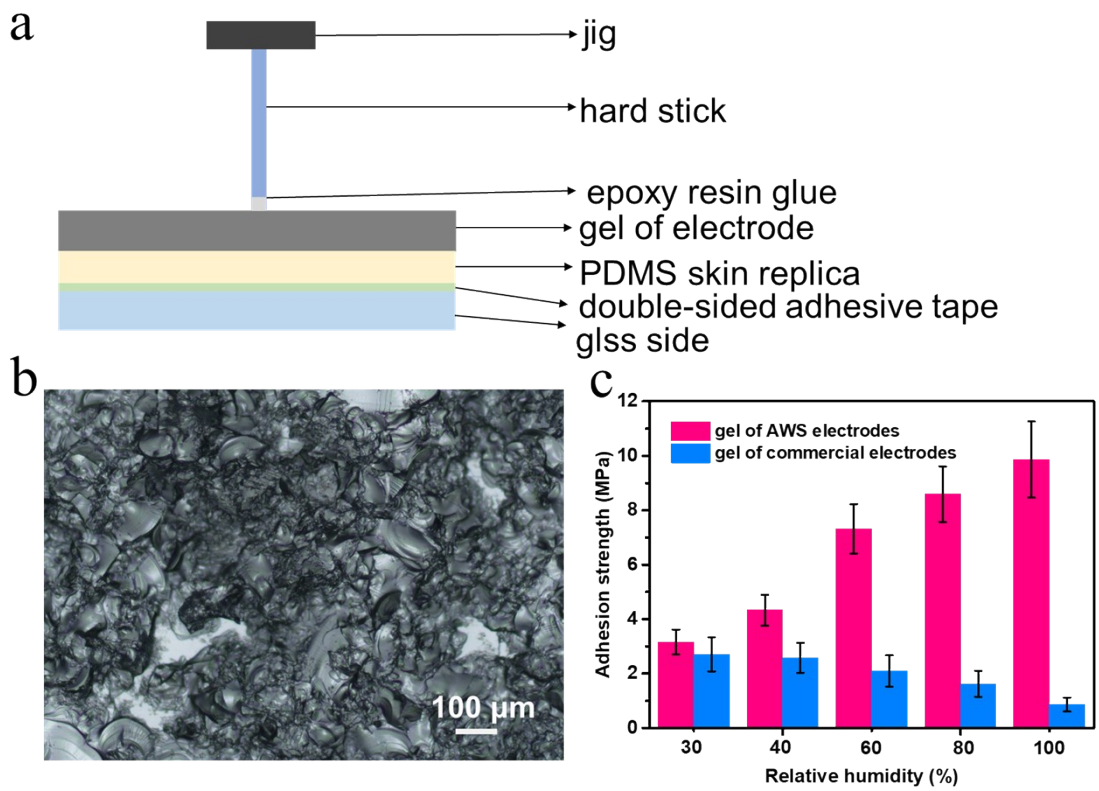

Fig. S7 Adhesion strength on the PDMS skin replica. (a) Schematic drawing of the device. (b) The optical microscope photograph of the PDMS skin replica. (c) Adhesion strength of the gel of AWS electrodes and commercial electrodes measured on the PDMS skin replica, respectively.

The fabrication of PDMS skin replica: Sylgard 184 prepolymer and curing agent were mixed at a weight ratio of 10:1, degassed, and cast on the ground glass. The samples were cured in a vacuum oven at 90 °C for 1 hour and then demolded. The skin replica was formed with a thickness of about 200 μm.

Adhesion between the gel of electrodes and the PDMS skin replica: The gels of AWS electrodes and commercial electrodes were attached to the skin replica, respectively. The skin replica was fixed on a glass slide (length =75 mm, width = 25 mm) by double-sided adhesive tape, and a hard stick (diameter =2 mm) was fixed on the gel by epoxy resin glue, which was allowed to cure for 10 min at room temperature. Then, the glass side hold with the sample was put into the constant temperature and humidity machine for 30 min to ensure them under the specific humidity. After that, the glass side was taken out. The hard stick was fixed with the jig, and the glass side was fixed on the sample stage for the test of adhesion strength between

the gel of electrodes and the skin replica by an MTS CMT4000 electronic universal testing machine (speed = 0.2 mm s^{-1}). The maximum adhesion force was read while peeling off the electrode from the skin replica. The value of adhesion strength was calculated by dividing the maximum load by the broken area of each sample. All these tests were repeated at least three times.

3. Supplementary Table

Table S1 Physical parameters of five volunteers, including gender, age, height, BW and BMI.

Volunteers' number	1	2	3	4	5
Gender	female	female	female	male	male
Age (years)	23	23	24	24	24
Height (cm)	160	156	165	167	189
BW (kg)	60	43	55	57	70
BMI	23.44	17.67	20.20	20.43	21.60

References:
1 S. Sofia, M. B. Mccarthy, G. Gronowicz and D. L. Kaplan, *J. Biomed. Mater. Res.* 2001, **54,** 139-148.
2 X. Yue, F. Zhang, H. Wu, J. Ming, Z. Fan and B. Zuo, *Mater. Lett.* 2014, **128,** 175-178.
3 X. Yan, Z. Liu, Q. Zhang, J. Lopez, H.Wang, H. Wu, S. Niu, H. Yan, S. Wang, T. Lei, J. Li, D. Qi, P. Huang, J. Huang, Y. Zhang, Y. Wang, G. Li, J. B. H. Tok, X.Chen and Z. Bao , *J. Am. Chem. Soc.* 2018, **140,** 5280-5289.