Supplementary Information

Fully-physically crosslinked silk fibroin/ poly (hydroxyethyl acrylamide) hydrogel with high transparency and adhesive property for wireless sensing and low-temperature strain sensing

Xia Sun, [a] Shaoshuai He, [a] Mengmeng Yao, [a] Xiaojun Wu, [a] Haitao Zhang, [a] Fanglian Yao, [a, b, *] Junjie Li, [a, b *]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China

[b] Frontiers Science Center for Synthetic Biology and Key Laboratory of Systems Bioengineering (Ministry of Education), Tianjin University, Tianjin 300350, China

*Corresponding author:

Junjie Li, E-mail: li41308@tju.edu.cn

Fanglian Yao, E-mail: yaofanglian@tju.edu.cn

Experimental section

Materials

Protein hydrolyzates, silk (SF, 90%) was purchased from Yuanye Bio-Tech (Shanghai, China), hydroxyethyl acrylamide (HEAA, 98%) was purchased from D&B (Shanghai, China), lithium chloride (LiCl, 99%) and photo-initiator (I2959, 99%) was purchased from Aladdin (Shanghai, China). All reagents were used as received. Deionized water was used in all experiments.

PHEAA/SF-LiCl hydrogel preparation

Fully-physically crosslinked PHEAA/SF-LiCl hydrogel was prepared through a facile one-pot method. Briefly, HEAA, SF and LiCl were all added into deionized water in a bottle. Then, the precursor was heated at 60 ℃ for 10 min. Then, 0.7 mol% I2959 (compared to HEAA monomer) was added into the mixed solution under stirring. Finally, the mixed solution was injected into a homemade mold comprising a 1 mm silicone rubber spacer between two glass plates. The free radical polymerization was conducted under UV light (8 W, 365 nm) for 4 h. The obtained hydrogel was named as PHEAA/SF-Y hydrogel, where Y represented the concentration of LiCl.

For comparison, PHEAA hydrogel (hydrogel without SF and LiCl), and PHEAA/SF hydrogel (hydrogel without LiCl) were also prepared. The detailed information was shown in **Table S2**.

Characterization

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-LiCl hydrogel with different LiCl contents were recorded by Nicolet 6700 FT-IR spectrophotometer after lyophilizing the samples. UV-vis spectroscopy (Thermo EVOLUTION 201) was used to evaluate the transmittance of hydrogel (thickness: 1 mm) in the visible light range (400–800 nm). The rheological tests were performed on VISCOTESTER iQ. Before tests, the samples were cut into a cylinder of 20 mm in diameter and 1 mm in thickness. Frequency (ω) sweep tests were performed with ω=1-150 rad s^{-1} and strain (ν) = 0.1% at 25 ℃. Strain (ν) sweep tests were performed with ν =0.1%-1000% and frequency (ω)

= 10 rad s^{-1} at 25 ℃. Differential scanning calorimetry (DSC) tests were investigated in a temperature range of -70-20 ℃ at a rate of 2 °C min^{-1}.

Mechanical tests

At room temperature, all the mechanical tests were carried out on a universal electromechanical machine (WDW-05, Si Pai Inc, China). Samples were cut into dumbbell shapes with a length of 30 mm, a gauge length of 12 mm, a width of 2 mm, and a thickness of ca. 1 mm, and the crosshead speed was 50 mm min^{-1} with a load cell of 50 N. 20 successive loading-unloading cycles were performed with the same condition at a fixed strain of 100%. The tensile stress (σ), the tensile strain (ε), the elastic modulus (E), the toughness (W) and the dissipated energy (U_{hys}) of the hydrogels were calculated according to our previous reports.

At low temperature (-30 ℃), all the mechanical tests were carried out on an universal electromechanical machine (WDW-T05, Tianchen, CO., LTD) with an environmental chamber, in which the temperature could be adjusted by spraying liquid nitrogen. Notably, every specimen was held at testing temperature for about 30 min to ensure the complete cooling. Sample preparation and other test conditions were same as that at room temperature.

Adhesion tests

The adhesive strength of hydrogel on different substrates (metal, glass, paper, PET and porcine skin) was evaluated by lap shear tensile tests. The hydrogel was sandwiched by two identical substrates and pressed by 500 g weight for 10 min. After that, samples were tested at a speed of 10 mm min^{-1} to failure. The area of tested hydrogel was about 10 mm × 10 mm. The adhesive strength was calculated *via* dividing the maximum force load by the corresponding lap area.

Electrical measurements

For conductivity tests, a cylinder hydrogel was sandwiched by two copper electrodes and tested by an electrochemical workstation (Vertex C, IVIUM Tech, Netherlands). The resistance of PHEAA/SF-LiCl hydrogels were determined by the intercepts of EIS curves with x axis. The conductivity (σ, S m^{-1}) was calculated by Equation (1):

$$\sigma = \frac{d}{R \times A} \qquad (1)$$

where d means the distance between the two fixed copper electrodes, R means the obtained resistance and A means the contact area between hydrogel and electrode.

For strain sensitivity measurements, the relative resistance changes ($\Delta R/R_0$) were measured by the same electrochemical workstation combined with universal electromechanical machine (WDW-05, Si Pai Inc for room temperature tests and WDW-T05, Tianchen, CO., LTD for low temperature tests). The strain sensitivity was defined as Gauge Factor (GF) according to Equation (2):

$$GF = \frac{(R - R_0)/R_0}{\varepsilon} = \frac{\Delta R/R_0}{\varepsilon} \qquad (2)$$

where R and R_0 are the resistances of the original and stretched hydrogels, respectively, and ε is the applied strain of the hydrogel. Notably, when the temperature was -30 ℃, the hydrogel was stored at testing temperature for 30 min before tests.

Human motion sensing, wireless sensing and low temperature strain sensing

For human motion sensing, the hydrogel with two copper electrodes and conductive wires on two edges was sealed by VHB tape and directly adhered on volunteer's skin with assistance of commercial tape. Silver paste was used to reduce contact resistance during all contact area. Signals were collected by electrochemical workstation.

For wireless sensing, a piece of PHEAA/SF-LiCl hydrogel was connected to Arduino UNO (processor with Bluetooth module) by conductive wires. Signals were sent to a cell phone through Bluetooth when the hydrogel was under deformation.

For low temperature sensing, a piece of PHEAA/SF-LiCl hydrogel with conductive wires was directly adhered on a prosthetic hand and fixed with conductive copper tape. Then, the whole prosthetic hand with hydrogel sensor was placed into an environmental chamber, in which the temperature could be adjusted by spraying liquid nitrogen. Before sensing, the sensor was placed for 30 min. Silver paste was used to reduce contact resistance during all contact area and signals were collected by electrochemical workstation.

All tests involving human volunteers were carried out in full compliance with all local laws and institutional ethical guidelines. Full and informed consent was given by each subject for these experiments.

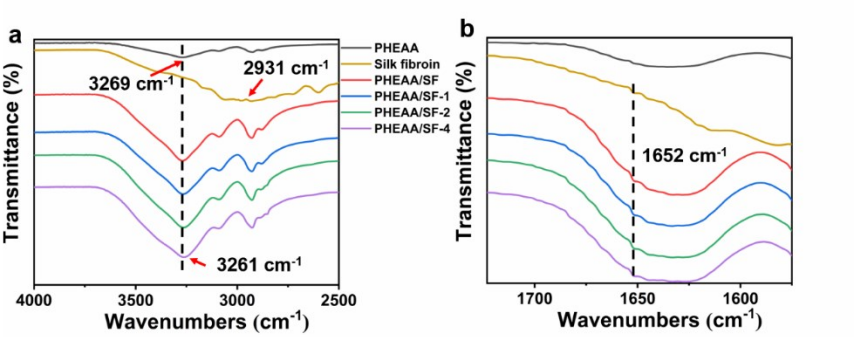

Figure S1. FTIR results of **(a)** PHEAA hydrogel, SF powder, PHEAA/SF hydrogel, PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel at 4000-2500 cm^{-1} and **(b)** at 1800-1400 cm^{-1}.

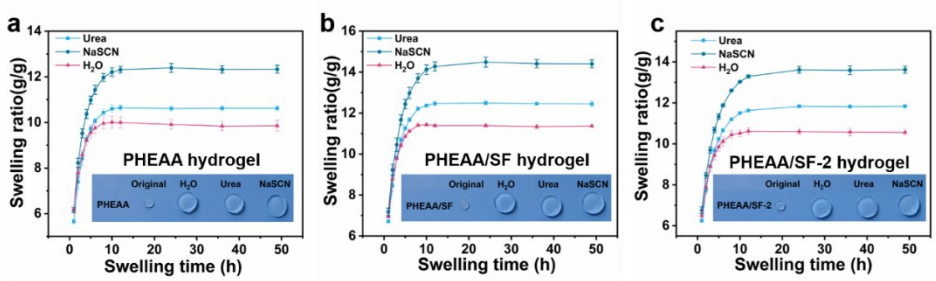

Figure S2. Swelling kinetics results of **(a)** PHEAA hydrogel, **(b)** PHEAA/SF hydrogel, **(c)** PHEAA/SF-2 hydrogel in urea, NaSCN and water, respectively.

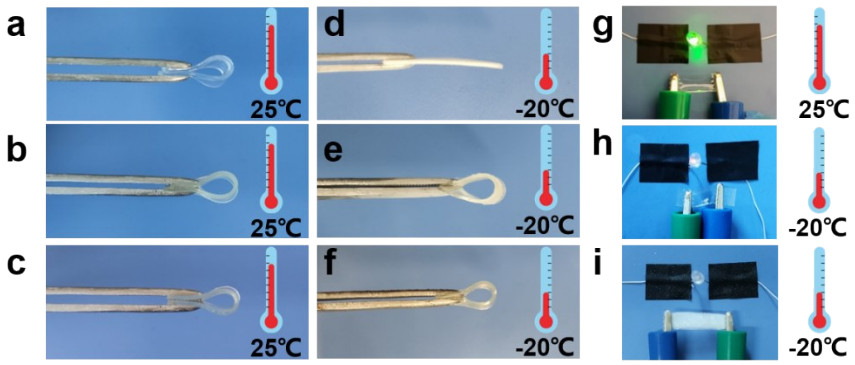

Figure S3. Digital photos of **(a)** PHEAA hydrogel, **(b)** PHEAA/SF hydrogel, and **(c)** PHEAA/SF-2 hydrogel at room temperature; **(d)** PHEAA hydrogel, **(e)** PHEAA/SF hydrogel and **(f)** PHEAA/SF-2 hydrogel at low temperature. Digital photos of lighting a LED of **(g)** PHEAA/SF-2 hydrogel at room temperature and **(h)** PHEAA/SF-2 hydrogel at low temperature. **(i)** Digital photos of PHEAA hydrogel connected with a circuit at low temperature.

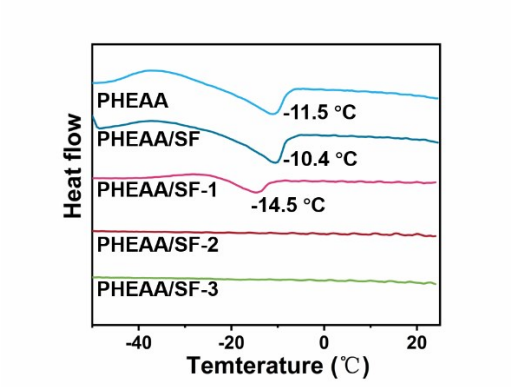

Figure S4. DSC curves of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel from 25 °C to -50 °C.

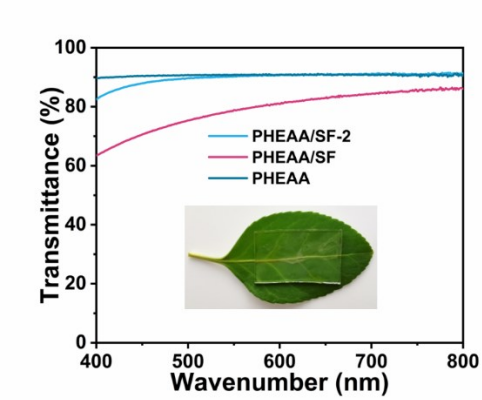

Figure S5. Transparency of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-2 hydrogel at 400-800 nm.

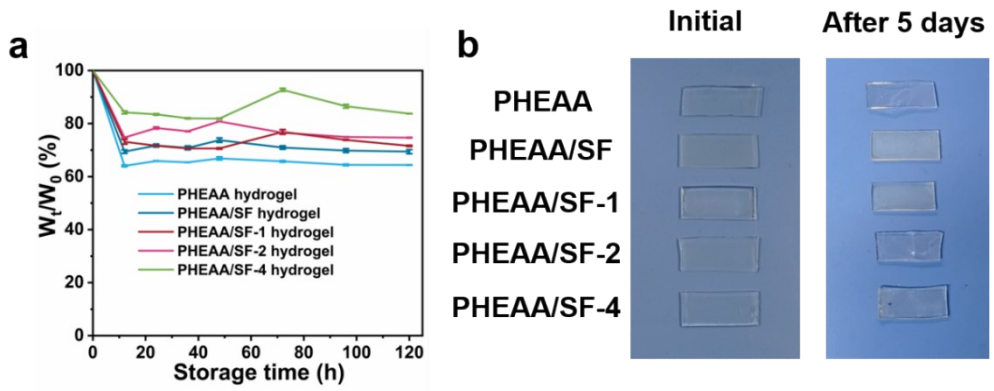

Figure S6. Stability of PHEAA/SF-LiCl hydrogel. **(a)** Weight change versus time of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel for 5 days, and **(b)** their photographs of initial states and 5-days-later states.

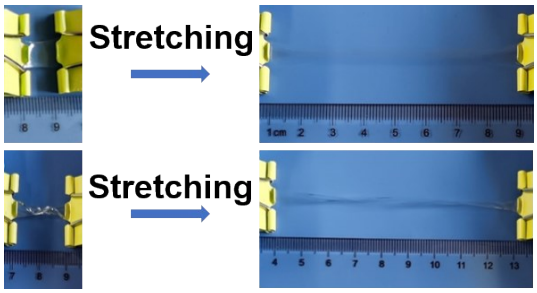

Figure S7. Digital photos of PHEAA/SF-2 hydrogel under stretching and curly stretching.

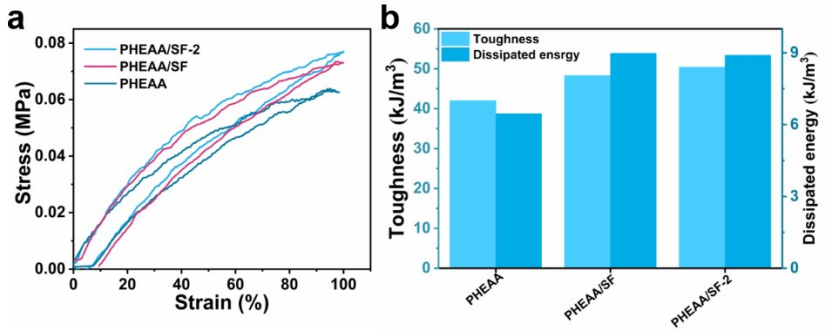

Figure S8. (a) Energy dissipation results of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-2 hydrogel at 100% strain, and **(b)** their corresponding toughness and dissipated energy.

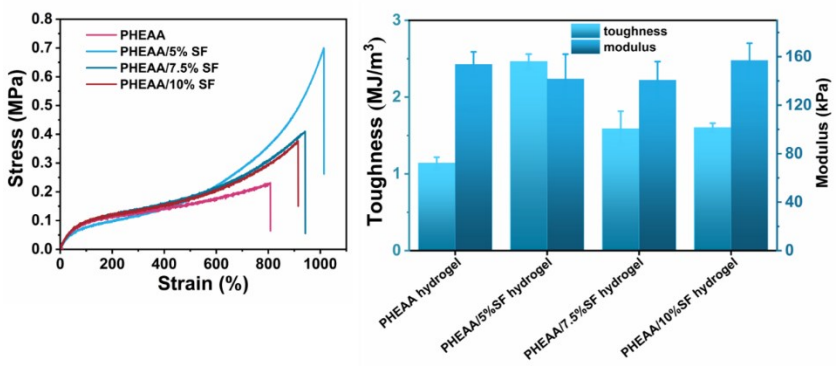

Figure S9. Stress-strain curves under different SF contents, and the corresponding toughness and modulus.

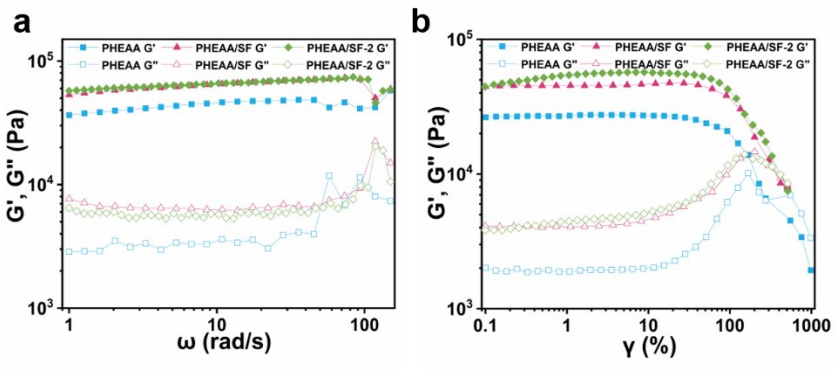

Figure S10. Rheology results of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-2 hydrogel at **(a)** frequency sweep and **(b)** strain sweep.

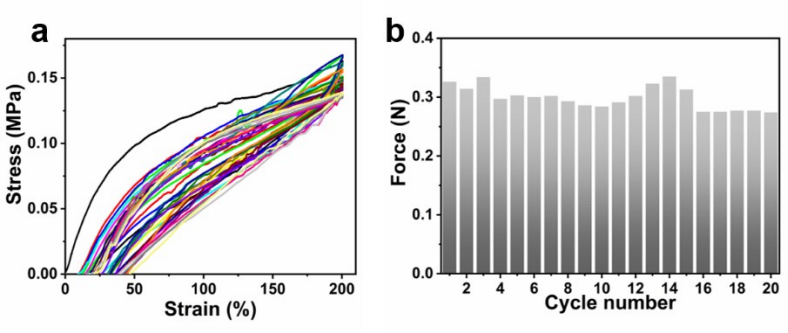

Figure S11. (a) 20 loading-unloading cycles of PHEAA/SF-2 hydrogel at 200% strain under -30 ℃ and **(b)** the corresponding stretching force.

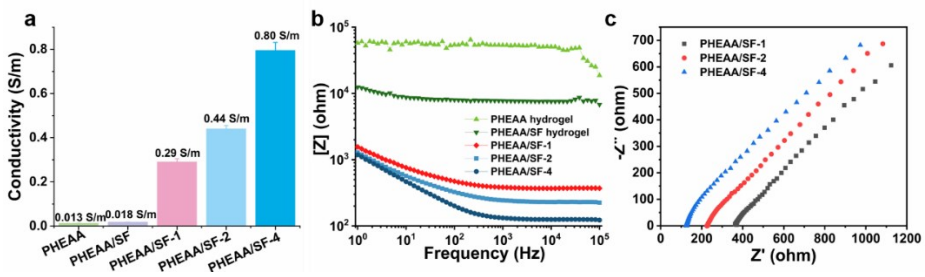

Figure S12. (a) Conductivity of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel. **(b)** Bode plots of PHEAA hydrogel, PHEAA/SF hydrogel, PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel. **(c)** Nyquist plots of PHEAA/SF-1 hydrogel, PHEAA/SF-2 hydrogel and PHEAA/SF-4 hydrogel.

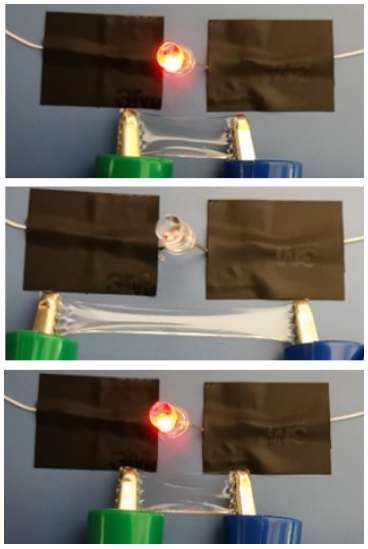

Figure S13. Photographs of the changes for LED brightness during stretching.

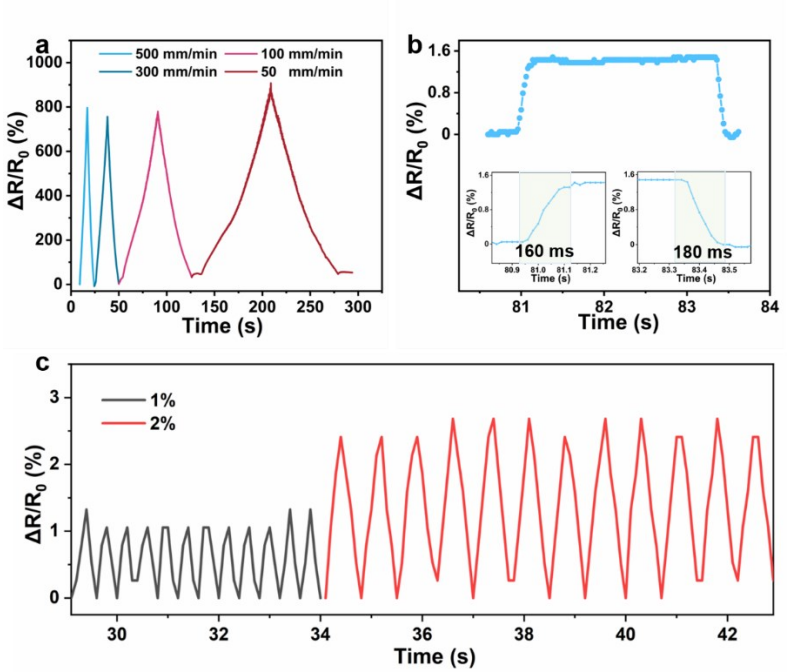

Figure S14. (a) $\Delta R/R_0$ versus the applied strains up to 500% at different displacement rates (50, 100, 300, and 500 mm min^{-1}) **(b)** Response time of PHEAA/SF-2 hydrogel under 1.5% strain. **(c)** $\Delta R/R_0$ at 1% strain and 2% strain of PHEAA/SF-2 hydrogel.

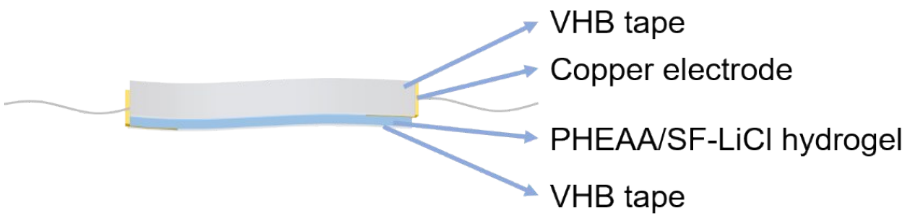

Figure S15. Scheme of hydrogel strain sensor

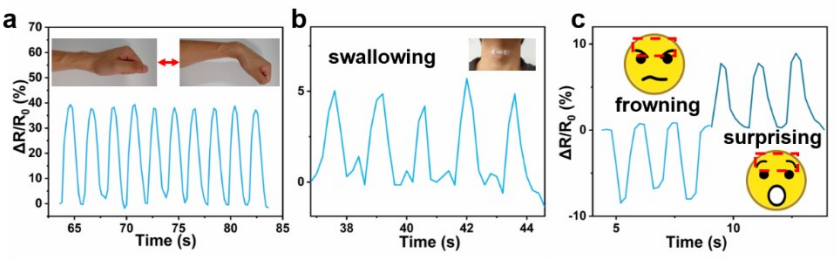

Figure S16. Applications of PHEAA/SF-2 hydrogel for monitoring **(a)** wrist bending, **(b)** swallowing, and **(c)** human expressions.

Table S1. Comparisons with Previous Studies

	Room temperature		Low temperature			
Hydrogel	Working range (%)	GF	Temperature	Working range	GF	Ref.
PAAM-carrageenan	400	-	-18	400	6	1
PVA-PEDOT	-	-	-40	20	1.5	2
cellulose	220	0.297	-24	50	-	3
PVA-Gly-NaCl	300	4.01	-20	30	2	4
PAA-PAAM-CS	400	6.6	-20	280	3.9	5
PAAM-SA-CNTs	-	-	-20	700	3	6
PHEAA-CS-CIT	400	6.9	-25	300	2.88	7
PAAM-PAA-Fe	500	1.96	-14	200	0.8	8
PHEAA-SF-LiCl	**900**	**3.6**	**-30**	**450**	**12.9**	**This work**

Reference:

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Table S2. Preparation of Different Hydrogels

Sample	PHEAA	SF wt%	LiCl mol/L	Water content wt%
PHEAA hydrogel	50	0	0	50%
PHEAA/SF hydrogel	50	5	0	45%
PHEAA/SF-1 hydrogel	50	5	1	44.2%
PHEAA/SF-2 hydrogel	50	5	2	43.3%
PHEAA/SF-4 hydrogel	50	5	4	41.8%
PHEAA/5%SF hydrogel	50	5	0	45%
PHEAA/7.5%SF hydrogel	50	7.5	0	42.5%
PHEAA/10%SF hydrogel	50	10	0	40%