Self-adhesive electronic skin for ultra-sensitive healthcare monitoring

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Experimental section

Material

Polyvinyl alcohol (PVA) is supplied by Sinopharm Chemical Reagent Co., Ltd. Glycerol (Gly), acrylamide (AM), acrylic acid (AA) and N, N'-Methylenebis (acrylamide) (MBA) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. The photo initiator was produced by BASF Chemical Trading Co., Ltd., and Triton X-100 was provided by Shanghai Yuanye Biotechnology Co., Ltd.

Preparation of CNTs/GO ink

1g of GO was added to the CNTs solution (The mass ratio of CNTs to GO was 1:1) and magnetically stirred at 25 °C for 10 min, the mixture was then put into a ball mill and ground at 300 rpm for 12 h to obtain a homogeneous mixed solution of CNTs and GO.

Preparation of hydrogels for adhesive and elastic Layers

The synthesis of PVA/PAMAA/Gly hydrogels (PPG) was carried out by a one-pot method as shown in **Fig.** S1. In the first step, 0.2 g of PVA was dissolved in 1 ml of water and stirred at 90 °C. After fully dissolved, 5 g of glycerol was instilled to the PVA dispersion solution, then 2 g of AM was slowly added after one hour, and finally 200 mg of AA, 1.5 mg of MBA and 100 mg of Irgacure 2959 were mixed into the solution and stirred until all components dissolve. A reflux device is used throughout the process to prevent evaporation of water during the dissolution process. The mixed solution was then slowly poured into a 1 mm high silicone mold composed of a gasket combined with two glass plates. Finally, the solution was placed under UV light (λ=365 nm wavelength, intensity of 8 W) for 1 h to form the PPG hydrogels adhesive layer. PPG hydrogels solutions with different ratios of water and glycerol were prepared by the same method for further experiments as elastic layers. The compositions and ratios of PPG hydrogels with different glycerol additions are shown in **Table** S1.

Fabrication of PPG/CNTs/GO Strain Sensor

First, a silver wire was attached to the adhesive layer of the PPG hydrogels, and then 1 ml of the CNTs/GO mixture was sprayed on the hydrogels. After the liquid is completely dry, the 1 mm thick silicone gasket was replaced with a 3 mm thick one. The solution of the elastic layer is then slowly poured into the silicone mold, which is formed by combining a 3 mm thick gasket with two glass plates. Finally, the solution was placed under ultraviolet light (λ=365 nm wavelength, intensity of 8 W) for 1 h, and finally the PPG/CNTs/GO hydrogels strain transducer was obtained by encapsulation

(as illustrated in Fig. S2) and represented as PPGCG for simplification.

Characterization and measurements

The infrared spectra were obtained by a Fourier-transform infrared (FT-IR) spectrometer (Vertex 70, Bruker), collecting at wavenumbers ranging from 4000 to 500 cm^{-1}at a resolution of 4 cm^{-1}. The crystalline properties of the hydrogels were characterized by X-ray diffraction (DY5261/Xpert3, CEM, America) with the Cu Kα radiation (40 kV, 40 mA, λ=1.542 nm) at room temperature and the 2 theta was ranging from 5° to 60°. The Raman spectra were acquired by utilizing a LabRAM HR Raman Spectrometer (HORIBA Jobin-Yvon, France) in a laser of 532 nm from 500 to 4000cm^{-1}. The samples were observed by scanning electron microscopy (FEI Nova Nano-SEM 230, America). The DSC scans were conducted on a differential scanning calorimeter instrument (DSC214, Nestzsch, GER) at a heating rate of 10 °Cmin^{-1}.

The tensile performances test was performed on a universal material tester (AG-X plus, SHIMADZU, Japan) with a 1kN load cell at 25 °C and the stretching speed was 100 mm min^{-1}. In order to simultaneously record the dynamical response signals of the current, potential and mechanics of the self-powered integrated system, a digital Source Meter (Keithley 2450, Tektronix Co., USA), and a universal material test machine (AG-X plus, SHIMADZU, Japan) was used.

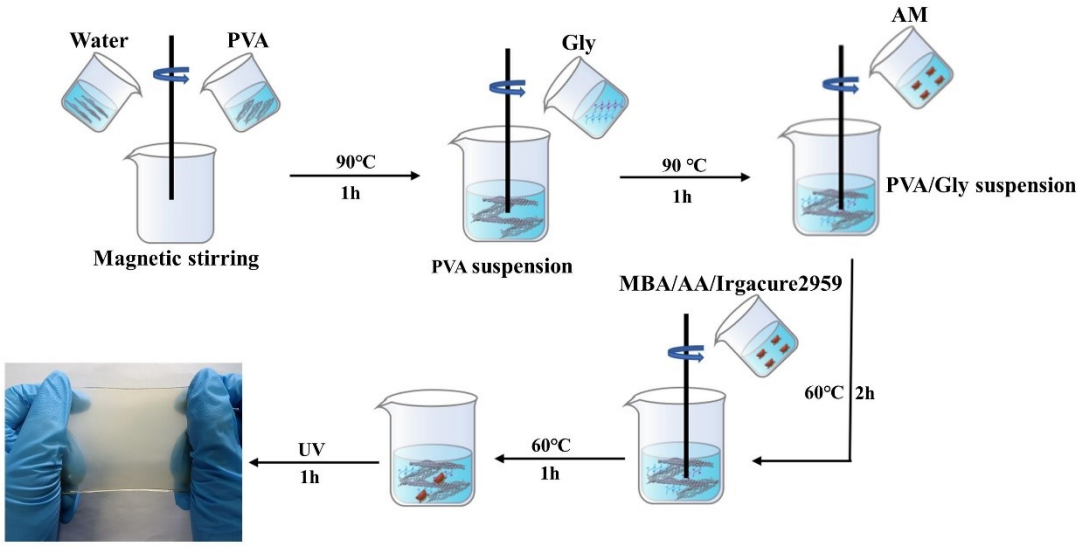


Fig. S1. Flow diagram of preparation of PPG hydrogels

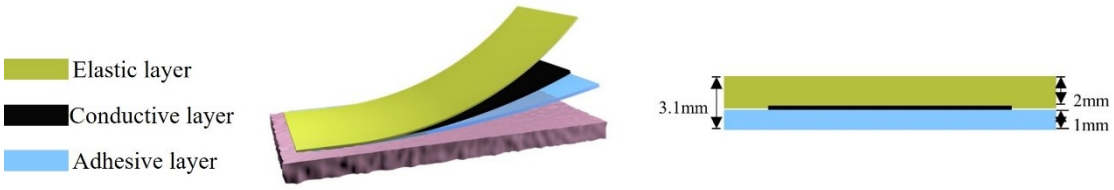


Fig. S2. the whole structure of the sensor and the size of each layer.

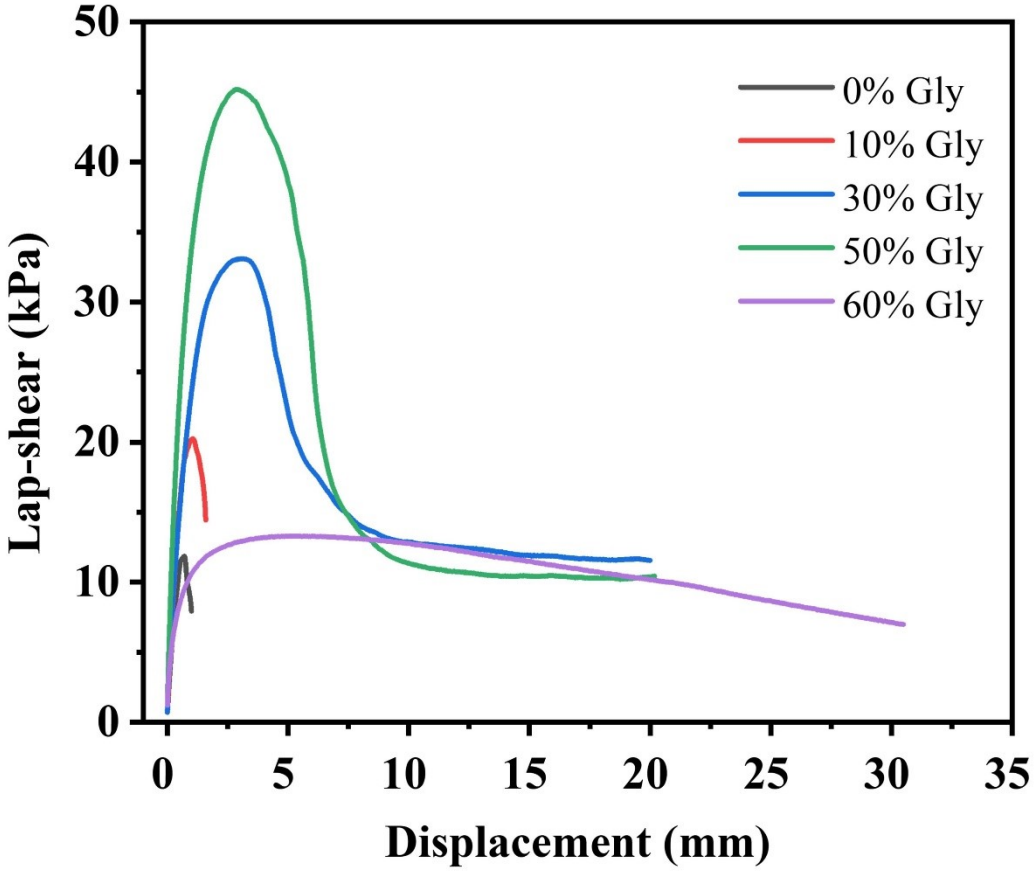


Fig. S3. Shear strength curve of PPG hydrogels on pigskin

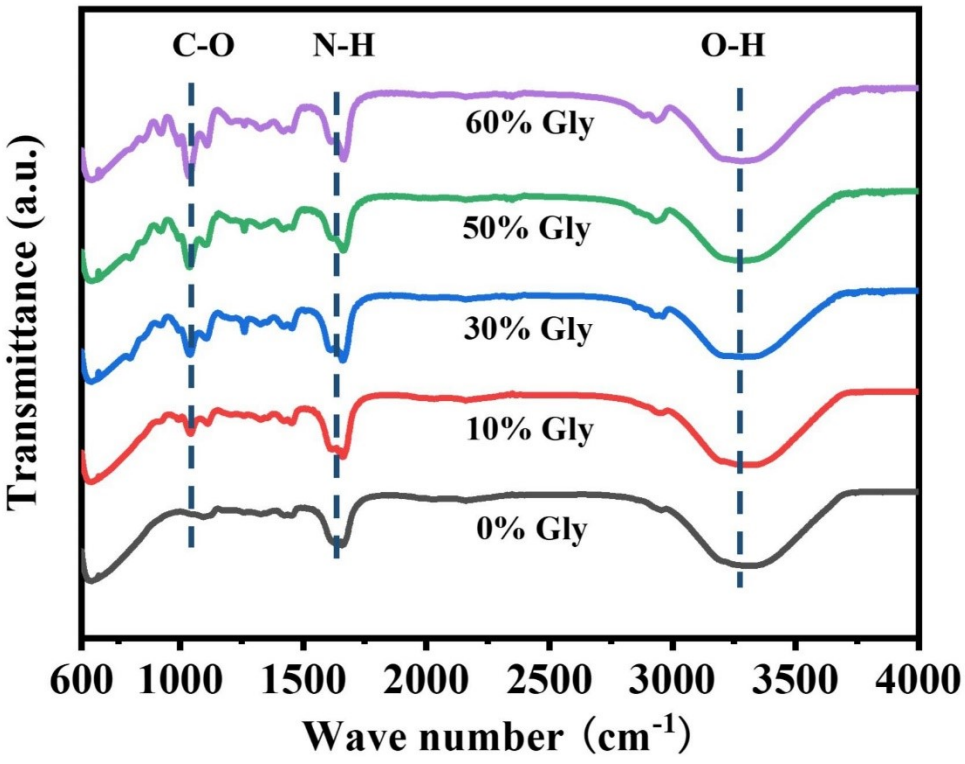


Fig. S4. (a) FTIR spectra of PPG hydrogels with different glycerol contents in the spectral range of 600-4000 cm^{-1}.

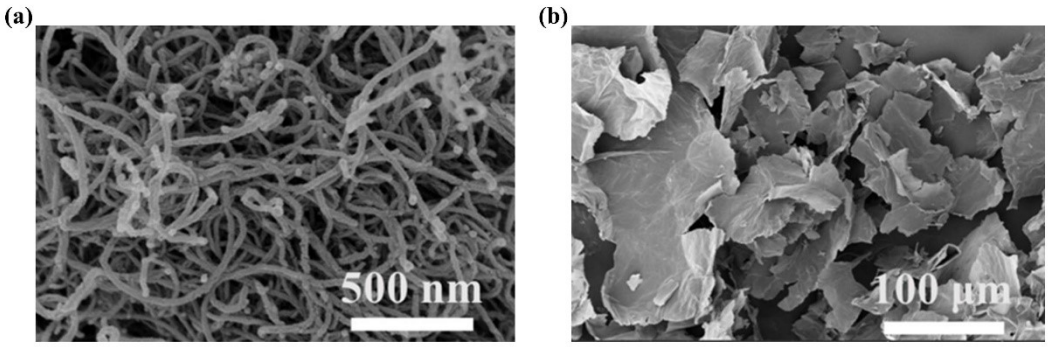


Fig. S5. (a) SEM image of CNTs. (b) SEM image of GO.

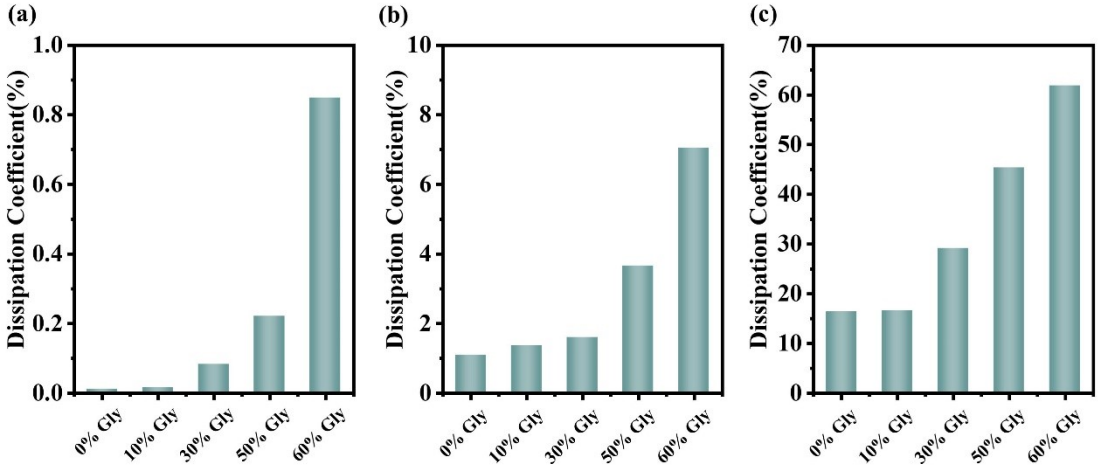


Fig. S6. Energy dissipation efficiency of hydrogels with different glycerol contents at (a) 50% strain (b) 100 strain (c) 200 strain

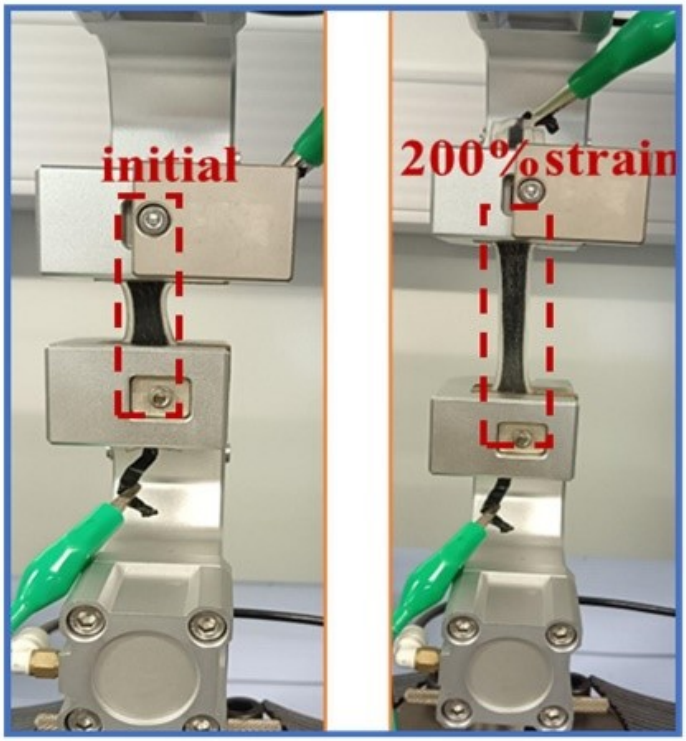


Fig. S7. The digital image of sensor stretching to 200% tensile strain.

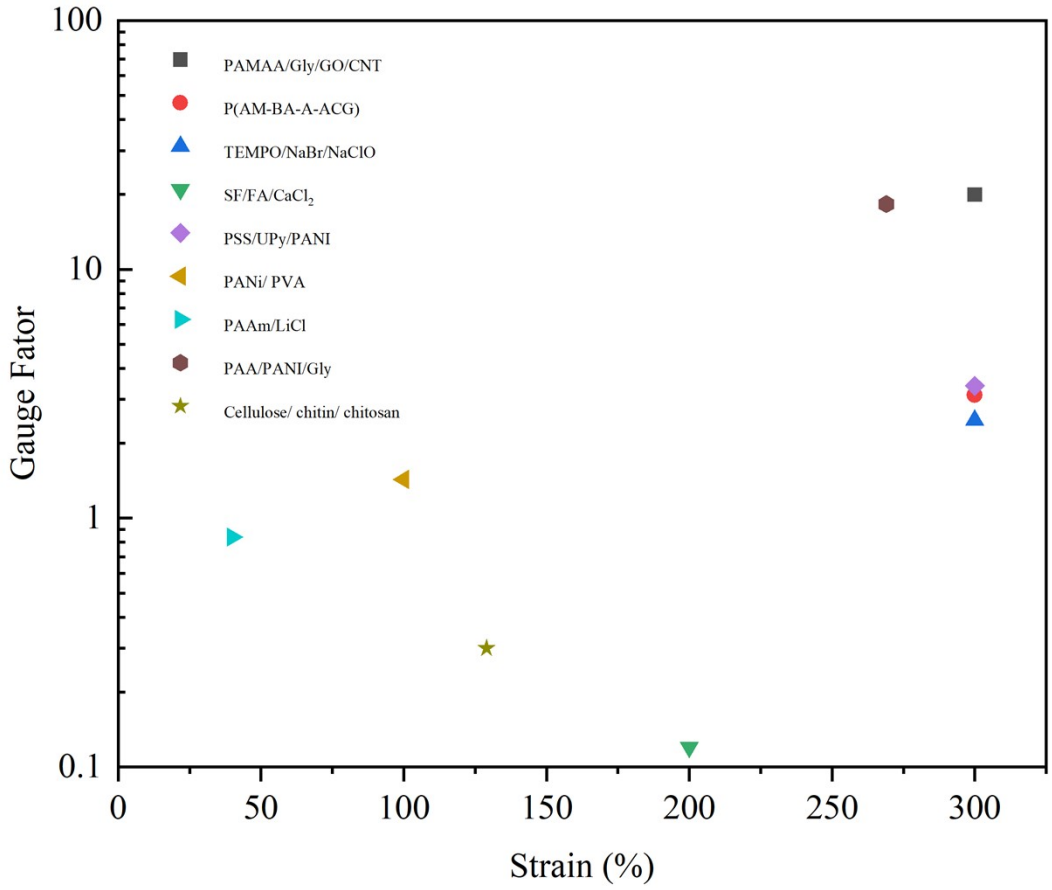
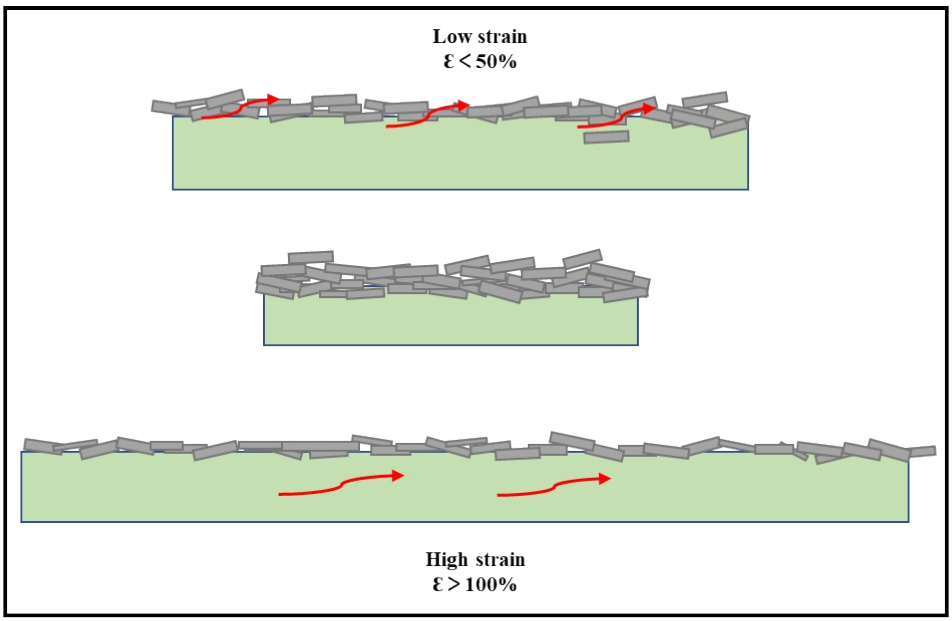


Fig. S8. Compared with the parameters of various flexible sensors reported in the literature.

(a)



(b)

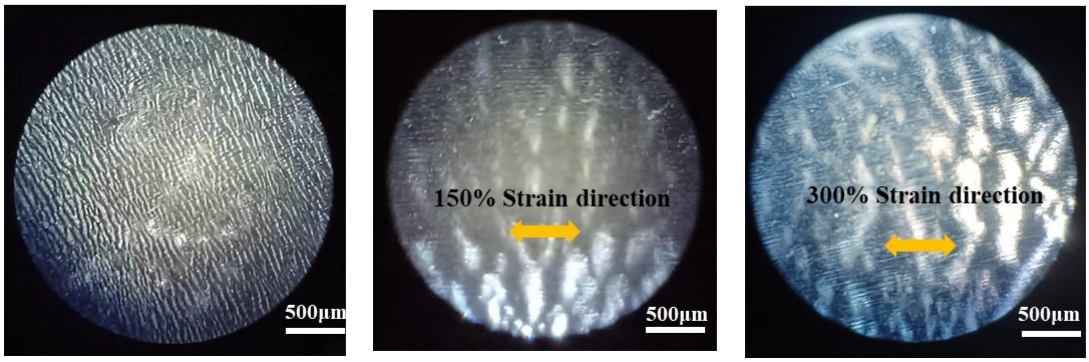


Fig. S9. (a) Schematic diagram of the close-packed conditions of the conductive layer (CNTs/GO) under large and small strain. (b) Crack propagation of conductive layer at 150% and 300% strain stretching.

Fig. S10. Detection of sequential single-step ultralow strains (1%) under a large base strain of 100%.

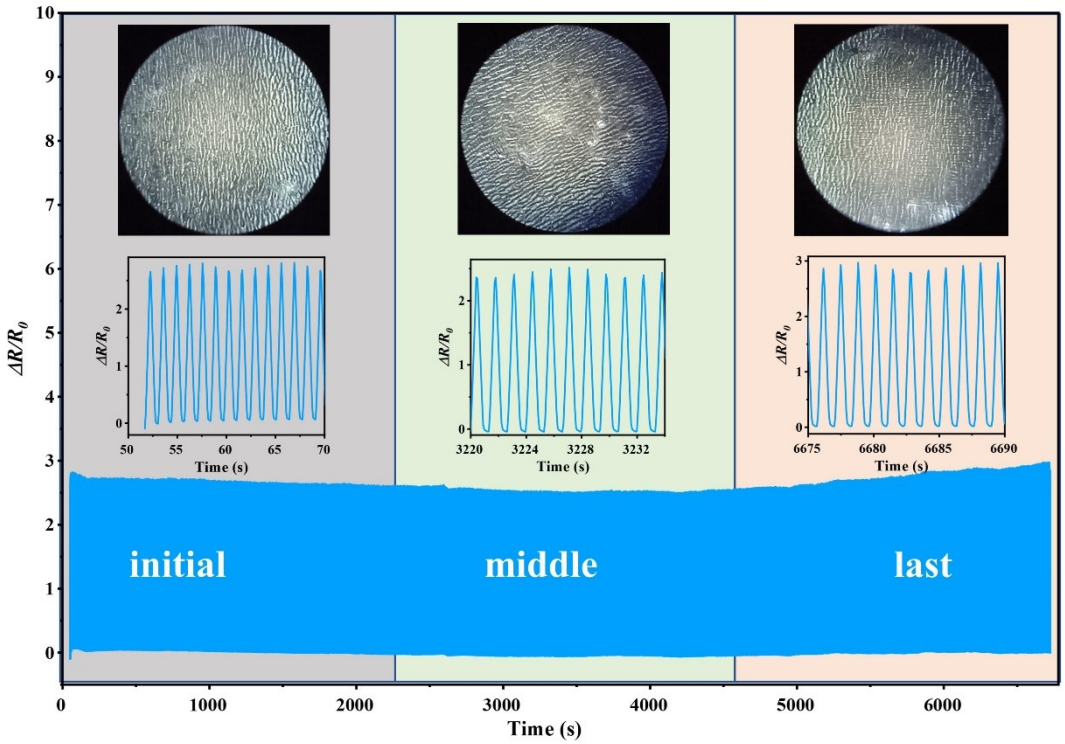


Fig. S11. The electrical signals of the sensor and the conductive layer under the microscope were displayed in 5000 durability experiments.

Table S1. Composition and ratio of hydrogel with different glycerol additions

Gly content	PVA (g)	AM (g)	AA (g)	Irgacure 2959 (g)	MBA (mg)	Water (g)	Gly (g)
0	0.2	2	0.2	0.1	1.5	6.0	0.0
10%	0.2	2	0.2	0.1	1.5	5.0	1.0
30%	0.2	2	0.2	0.1	1.5	3.0	3.0
50%	0.2	2	0.2	0.1	1.5	1.0	5.0
60%	0.2	2	0.2	0.1	1.5	0.0	6.0

Table S2. Compared with the parameters of various flexible sensors reported in the literature.

Base gel	Gauge factor (tensile)	Sensing range (%)	Reference
PAMAA/GLY/GO/CNT	19.97	300	Our work
P(AM-BA-A-ACG)	3.12	300	*J. Mater. Chem. A* [1]
PVA-CNF	1.5	300	*Adv. Funct. Mater.*[2]
SF/FA/$CaCl_2$	0.12	200	*ACS Mater. Lett.*[3]
PSS/UPy/PANI	3.4	300	*Chem. Mater.*[4]
PANi/PVA	1.43	100	*Matter* [5]
PAAm/LiCl	0.84	40	*Adv. Mater.*[6]
PAA/PANI/Gly	18.28	269	*ACS Nano* [7]
Cellulose/ chitin/ chitosan	0.3	129	*Biomacromolecules* [8]

Reference:

1. X. Di, J. Li, M. Yang, Q. Zhao, G. Wu and P. Sun, *J. Mater. Chem. A*, 2021, **9**, 20703-20713.
2. Y. Ye, Y. Zhang, Y. Chen, X. Han and F. Jiang, *Adv. Funct. Mater.*, 2020, **30**, 2003430.
3. Q. Liu, S. Yang, J. Ren and S. Ling, *ACS Mater. Lett.*, 2020, **2**, 712-720.
4. J. Chen, Q. Peng, T. Thundat and H. Zeng, *Chem. Mater.*, 2019, **31**, 4553-4563.
5. Y. Zhao, B. Zhang, B. Yao, Y. Qiu, Z. Peng, Y. Zhang, Y. Alsaid, I. Frenkel, K. Youssef, Q. Pei and X. He, *Matter*, 2020, **3**, 1196-1210.
6. K. Tian, J. Bae, S. E. Bakarich, C. Yang, R. D. Gately, G. M. Spinks, M. In Het Panhuis, Z. Suo and J. J. Vlassak, *Adv. Mater.*, 2017, **29**, 1604827.
7. G. Ge, Y. Lu, X. Qu, W. Zhao, Y. Ren, W. Wang, Q. Wang, W. Huang and X. Dong, *ACS Nano*, 2020, **14**, 218-228.
8. R. Tong, G. Chen, D. Pan, H. Qi, R. Li, J. Tian, F. Lu and M. He, *Biomacromolecules*, 2019, **20**, 2096-2104.