

Self-healing, Stretchable, Temperature-Sensitive and Strain-Sensitive Hydrogel-based Flexible Sensors

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Abstract Flexible hydrogels have shown promise as strain sensors in medical monitoring, human motion detection and intelligent robotics. For a hydrogel strain sensor, certain challenges need to be urgently addressed for practical applications, such as the damage caused by external effects, leading to equipment failure, and the inability to perceive ambient temperature, resulting in single functionality. Herein, a stretchable, self-healing and dual temperature-strain sensitive hydrogel, with a physically-crosslinked network, is designed by constructing multiple dynamic reversible bonds. Graphene oxide (GO) and iron ions (Fe^{3+}) act as dynamic bridges in the cross-linked network and are mediated by the covalent and hydrogen bonding, rendering excellent stretchability to the hydrogel. The reversible features of coordination interactions and hydrogen interactions endow excellent recoverability and self-healing properties. Moreover, the incorporated *N*-isopropyl acrylamide (NIPAM) provides excellent temperature responsiveness to the hydrogel, facilitating the detection of external temperature changes. Meanwhile, the hydrogels exhibited strain-sensitivity, with a wide working range of 1%–300%, fast response and electrical stability, which can be used as flexible sensors to monitor body motions, *e.g.*, speaking and the bending of finger, wrist, elbow and knee. Overall, the hydrogel possesses dual sensory capabilities, combining external temperature and strain, for potential applications in wearable multifunctional sensing devices.

Keywords Hydrogel sensor; Self-healing; Dual temperature-strain sensitive; Monitor body motions

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INTRODUCTION

Nowadays, many studies are devoted to develop high-performance materials for smart wearable devices,^[1–4] which can transduce external stimuli, such as temperature,^[5] pressure,^[6] strain,^[7] light^[8] and pH^[9] into electronic signals in real-time. Thus, wearable devices provide novel opportunities for personal healthcare, human motion detection, human-machine interactions and soft robotic applications.^[10–14] The materials for a wearable sensor should essentially possess flexibility, high stretchability and conductivity. Most of these sensors are usually fabricated by incorporating conductive materials, *e.g.*, nanofillers and conductive polymers,^[15–17] into flexible matrices, *e.g.*, PDMS, rubber or gel.^[18–20] Besides, ionic conductors are also widely applied in wearable electronics with excellent stretchability.^[21,22] Hydrogels are ideal ionic conductors with a high water content, which are capable of dissolving ions but exhibit inferior mechanical properties.^[23,24]

More recently, several nanofillers, such as nanocellulose,^[25] silica nanoparticles^[26] and graphene oxide,^[27,28] have been reported to improve the mechanical properties of hydrogels. These nanofillers are incorporated into the hydrogel network, interacting with the surrounding polymeric phase to efficiently dissipate energy and thereby improving the mechanical properties.

Self-healing is the ability to restore the initial structure after damage and maintain normal operations, which adds to the safety and reliability of wearable devices. Currently, the research on self-healing conductive hydrogels is divided into two types based on the healing mechanism: (1) chemically cross-linked hydrogels based on dynamic covalent bonds^[29,30] and (2) physical cross-linked hydrogels based on non-covalent interactions, such as hydrogen bonds, hydrophobic interactions, host-guest interactions, and metal coordination bonds.^[31–37] Of particular interest are non-covalent interactions, which allow the hydrogels to heal spontaneously without external stimuli, *e.g.*, pH, UV light or temperature.^[38] Meanwhile, conductive hydrogels exhibit relatively a high strain sensitivity due to the dynamically physical cross-linking effect. However, sensing temperature is an important function to provide information about the surrounding environment, which is still under exploration. Lin *et al.*^[39] pre-

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pared a flexible wearable sensor has good thermal response ($0.01636\text{ }^{\circ}\text{C}^{-1}$) and can monitor the temperature change from $30\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$. Therefore, it is imperative to achieve the dynamic capture of temperature signals under the premise of guaranteeing a stable sensing strain. According to the operational requirements, dual temperature-strain sensitive sensors have been designed by using the combination of temperature-sensitive materials and ionic gels.^[40,41] Moreover, *N*-isopropyl acrylamide is a temperature-sensitive material with a low critical dissolution temperature (LCST, $32\text{ }^{\circ}\text{C}$) close to the human body, which has been widely used as a monomer for temperature-sensitive hydrogels.^[42–44]

Herein, a highly stretchable and self-healing ionic hydrogel, with dual temperature-strain sensitivities, is designed *via* one-pot *in situ* polymerization without using a chemical cross-linker, exhibiting promise for wearable sensors. The P(AA-co-NIPAM)/GO hydrogel is prepared by constructing dynamic ion coordination bonds and hydrogen bonds among graphene oxide (GO), poly(acrylic acid) (PAA), poly(*N*-isopropyl acrylamide) (PNIPAM), and Fe^{3+} ions in a polymeric network, leading to reliable mechanical and self-healing properties of ionic hydrogels. Besides, the hydrogels possess excellent conductivity and strain sensitivity due to the existence of a large number of free ions and the electron transfer ability of GO. Moreover, the hydrogel exhibits a high-temperature sensitivity and rapid recovery without any external stimuli due to the incorporation of NIPAM and a dynamically cross-linked network. Thus, the as-fabricated hydrogel sensor realizes simultaneous monitoring of human joint motion and surrounding environments temperature, providing potential applications in multifunctional wearable sensing devices.

EXPERIMENTAL

Materials

N-isopropyl acrylamide (NIPAM), acrylic acid (AA), ammonium persulfate (APS) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Chengdu Kelong Chemical (Beijing InnoChem Science & Technology Co. Ltd., China and Shanghai Aladdin Biochemical Technology Co. Ltd., China. GO was prepared in our laboratory, as reported elsewhere.^[45]

Hydrogel Preparation

A GO suspension was prepared using the modified Hummers' method^[45] and sonicated for 10 min before usage. A one-step method was applied to synthesize nanocomposite hydrogels. NIPAM and AA were initially dissolved in the GO suspension with a certain proportion, stirred for 1 h and, then, 0.002 g of APS and 0.056 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the mixture, followed by stirring in an ice-water bath for 10 min to form a uniform mixture. Then, the reaction mixture was transferred to cylindrical glass bottles with an internal diameter of 8 mm and sealed for storage. The mixture was polymerized at $30\text{ }^{\circ}\text{C}$ for 8 h.

Characterization

Spectroscopic analyses

Fourier transform infrared (FTIR) spectroscopy was recorded using a Nicolet 6700 spectrophotometer in the wavelength range of 4500 cm^{-1} to 500 cm^{-1} at room temperature.

Morphological observations

The morphology of cross-linked hydrogel samples was

observed by scanning electron microscopy (SEM, ZEISS EVO MA15). The test specimens were placed at 25, 30, 35, 40 and $45\text{ }^{\circ}\text{C}$ for 15 min, followed by freezing in liquid nitrogen and freeze-drying for 24 h.

DSC analysis

Differential scanning calorimetry (DSC Q20, TA Instruments) was used to measure the low critical solution temperature (LCST) of the hydrogels. The temperature was increased from $10\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$ with a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$.

Mechanical characterization

The mechanical tests were performed using a microcomputer-controlled electronic universal testing machine (CMT4104, MTS Industrial Systems (China) Co., Ltd.) with a load cell of 20 N. Uniaxial tensile tests were performed using cylindrical hydrogel samples (8 mm internal diameter $\times$ 25 mm length) under the stretching rate of 20 mm/min at room temperature.

Self-healing experiments

The cylindrical hydrogel samples were cut into halves with a knife and, then, freshly cut surfaces of two separate halves were placed together and sealed properly to ensure minimal water evaporation. After self-healing, the healed hydrogels were subjected to the tensile test.

Electrical characterization

The strain sensors were prepared using conductive hydrogels, equipped with electrodes at each end. The real-time electrical signals of sensors were recorded using Tektronix PWS4323 and Keithley 6485 instruments (Tektronix Inc.), which was based on the resistance variation in hydrogels under various strains and temperatures.

The resistance variation can be expressed as:

$$\Delta R/R_0 = R - R_0 \quad (1)$$

where R_0 and R refer to the original resistance and the resistance under stimulation, respectively. The strain sensitivity (S) of the hydrogel sensor can be further evaluated by the ratio of resistance change ($\Delta R/R_0$) to the strain (ϵ), as given below:

$$S = (\Delta R/R_0)/\epsilon \quad (2)$$

In addition, the sensitivity to temperature (S_T) was expressed by the ratio of resistance change ($\Delta R/R_0$) to temperature change (ΔT), as given below:

$$S_T = (\Delta R/R_0)/\Delta T \quad (3)$$

RESULTS AND DISCUSSION

Herein, a stretchable and self-healing ionic hydrogel with dual temperature-strain sensitivity features is prepared by a one-step polymerization. A schematic diagram of the P(AA-co-NIPAM)/GO hydrogel synthesis process is shown in Fig. 1(a). Briefly, GO and Fe^{3+} were used as physical cross-linking points to form a three-dimensional network structure with polymeric molecular chains, where Fe^{3+} forms ionic coordination with carboxyl groups and the oxygen-containing functional groups of GO forms hydrogen bonds with carboxyl and amide groups. The FTIR spectra of PAA/GO and P(AA-co-NIPAM)/GO are presented in Fig. 1(b). The C—N absorption band of the amide group can be observed at 1090 cm^{-1} in the hydrogel with NIPAM structural units. The intensity of the absorption band at 3410 cm^{-1} significantly increases after the increase of NIPAM content due to the overlapping absorption of O—H and N—H

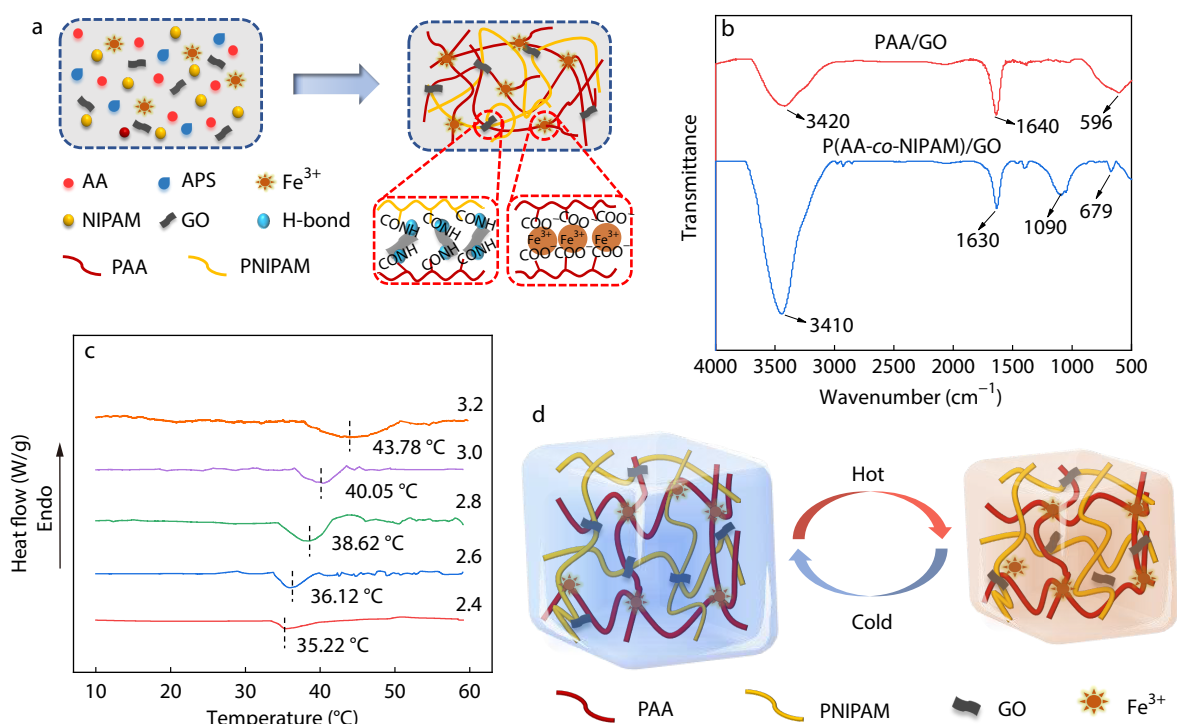


Fig. 1 (a) Schematic diagram of the synthesis process of P(AA-co-NIPAM)/GO hydrogel; (b) FTIR spectra of PAA/GO and P(AA-co-NIPAM)/GO; (c) DSC curves of hydrogels with different monomer ratios; (d) Schematic diagram of the structural changes of P(AA-co-NIPAM)/GO hydrogel in response to the temperature.

stretching vibration peaks.

Owing to the hydrophilic amide groups and hydrophobic isopropyl groups, the P(AA-co-NIPAM)/GO hydrogel exhibits a low critical solution temperature (LCST). Herein, DSC analysis was carried out to explore the influence of NIPAM on the LCST of hydrogels. As shown in Fig. 1(c), the LCST of the hydrogel gradually increases with the decrease of NIPAM content due to the reduced hydrophobic interaction in hydrogel, as well as the reduction of hydrogen bonding between H₂O and amide group, as well as. Fig. 1(d) shows a schematic diagram of the structural changes of the hydrogel in response to the temperature. When the temperature rises, the polymeric molecular chains shrink and the volume of hydrogel decreases. When the temperature drops, the polymeric molecular chains are stretched and the volume of hydrogel is increased. This is due to the presence of a temperature-sensitive NIPAM monomer with hydrophilic amide groups and hydrophobic isopropyl groups. Also, the formation efficiency of the hydrogen bonds between amide groups and water is temperature-dependent. The hydrogen bonds are gradually broken with the increase of temperature and the chains gradually aggregate, leading to the shrinkage of hydrogel. One should note that the hydrogen bonds are rebuilt when the temperature is lowered, effectively preventing the aggregation of molecular chains. Therefore, the hydrogel exhibits excellent responsiveness to the temperature, and its volume shrinks and recovers reversibly with the increase and decrease of temperature, respectively. Figs. 2(a)–2(e) present SEM images of the hydrogel at different temperatures. When the temperature is low, the structure is loose and the pores are evenly distributed. However, when the temperature is successively increased, the

structure of hydrogel gradually becomes dense and the pores gradually disappear.

Moreover, the hydrogel exhibited outstanding mechanical properties, which can be stretched, compressed and bent, as shown in Fig. 3(a). The hydrogels were subjected to tensile tests with different monomer ratios and GO contents to specifically probe the mechanical properties of the hydrogels. It can be seen that, as the content of AA increased, the fracture stress of the hydrogel increased successively and the elongation at breaking point is also increased (Fig. 3b). This is because the carboxyl groups of AA form dynamic ionic bonds with Fe³⁺, increasing the cross-linking density of the hydrogel. GO contains active functional groups such as hydroxyl (–OH) and carboxyl (–COOH), which can polymerize with polymer chains to form covalent bonds.^[46] The hydrogen bonds are formed between oxygen-containing functional groups on the surface of GO, carboxyl groups of PAA and amide groups of NIPAM. As the GO content increased from 0.7% to 2.0% (Fig. 3c), the fracture stress and elongation of the hydrogel increased due to the increasing hydrogen bonds and intermolecular force. Subsequently, the hydrogel was conducted to cyclic tensile loading-unloading at 50% strain. In Fig. 3(d), no significant drop in maximum strain was recorded under repeated cycles, confirming the excellent recovery performance due to the reversible dynamic cross-linking.

As shown in Fig. 3(e), the hydrogel was cut in half and two freshly-cut surfaces of both halves were combined together immediately to demonstrate the self-healing properties. The hydrogel maintains a high elongation during stretching after healing, confirming the excellent self-healing ability. Subsequently, tensile tests of the healed hydrogels with different

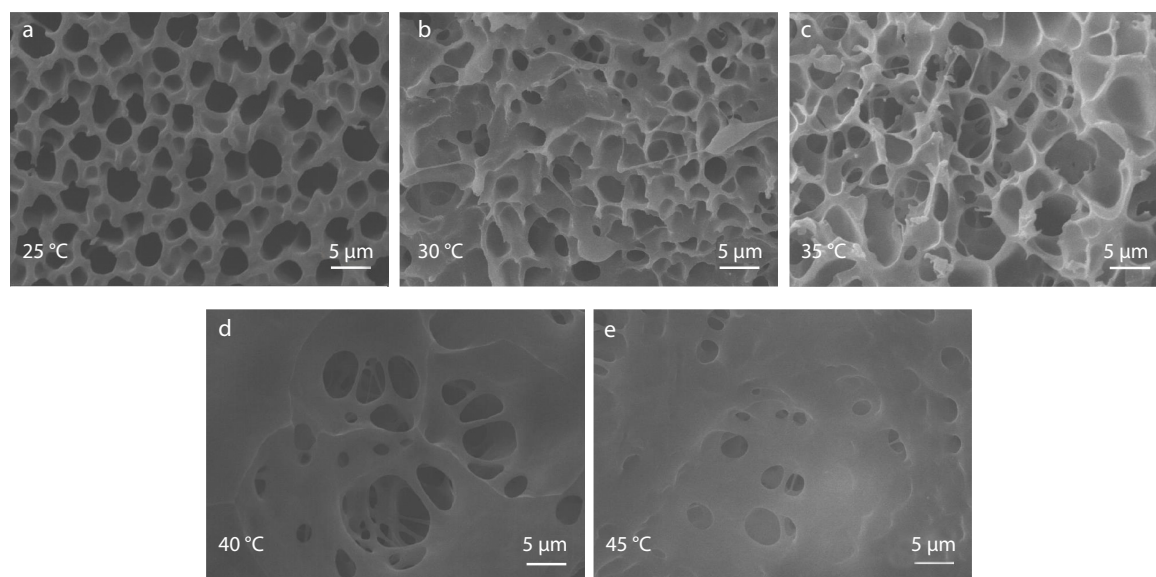


Fig. 2 SEM images of PNIPAM-PAA-GO at different temperatures.

healing times were carried out to further evaluate the self-healing ability. Fig. 3(f) demonstrates that the elongation at the breaking point of the hydrogel increased significantly with increasing healing time. The tendency of hydrogel healing efficiency with increased healing time is shown in Fig. 3(g), where healing efficiency is defined as the ratio of elongation at the breaking point between the healed and original hydrogels. The increased amplitude in healing efficiency gradually decreases with the increase of healing time until the self-healing process reaches equilibrium with a healing efficiency of up to 83.93%. The excellent self-healing properties of hydrogels can be ascribed to the reversible dynamic network, consisting of hydrogen bonds and ionic coordination bonds.

The hydrogels possess excellent conductivity due to the existence of Fe^{3+} and GO. The content of NIPAM affects the network structure of the hydrogel directly due to the hydrophilic amido groups and hydrophobic isopropyl groups in NIPAM molecular chains. Meanwhile, the carboxyl groups contained in AA units can be ionized under electric current. Therefore, monomer ratios and GO contents render a certain effect on the conductivity of the hydrogel. The conductivity of hydrogels with various monomer ratios is presented in Fig. 4(a). The conductivity of hydrogel initially decreases with the increase of AA content and decrease of NIPAM content, followed by a gradual increase. At the same temperature, as the NIPAM content decreases, the hydrophobic isopropyl content decreases and the hydrogen bonds linked by amide groups decrease, resulting in an increase in the degree of molecular chain relaxation, which reduces the contact conditions for electron conduction. Consequently, the conductivity decreases gradually. However, with the increasing of AA content, the hydrogen ions ionized caused by the increasing carboxyl groups, which increases the electrical conductivity. When the monomer ratio is below 3.0, the dominated NIPAM effects result in a decreasing of conductivity. Correspondingly, the resistance variation of hydrogels with various GO contents is presented in Fig. 4(b). Obviously, it can be seen that the elec-

trical conductivity increased with the increase of GO content. In order to investigate the effect of monomer ratio on the strain-sensitive behavior of hydrogel sensors, a series of hydrogels with different ratios of AA and NIPAM is prepared to measure the relative resistance variation at a strain of 50%. As shown in Fig. 4(c), the relative resistance variation of the hydrogel sensor is similar to the electrical conductivity, which initially decreases with the increase of monomers ratio, followed by a gradual increase. Similarly, Fig. 4(d) shows the relative changes in the resistance of hydrogels with different amounts of GO under the strain of 50%. It can be seen that the relative resistance variation increases with the increase of GO content. GO provides electrodes with large electrochemical surface area, and the delocalized π bonds are conducive to electron transport. The numerous hydrophilic functional groups in GO can facilitate its combination with AA and NIPAM to form more complex network-structured channels, which are more conducive to ion transport inside the hydrogel.^[47]

In addition, the response time to strain is an important indicator to measure the performance of hydrogel strain sensors. To explore the response time of hydrogel strain sensor, the loading-unloading process was analyzed under a strain of 50%. As shown in Fig. 4(e), when loading was applied to the hydrogel, the relative resistance variation of the sensor reached a stable value after 0.25 s. On the other hand, when the strain is removed, the relative resistance variation of the sensor immediately returns to the initial state after 0.13 s. These results confirm that the hydrogel strain sensor possesses a rapid strain response and recoverability.

Fig. 5(a) shows that the relative resistance changes significantly under different deformation conditions of 1%–5%. Similarly, the relative resistance variation can be observed at a medium strain of 10%–50% (Fig. 5b) and 50%–90% (Fig. 5c) and a large strain of 100%–300% (Fig. 5d). As the stress increases, the polymer chains are gradually elongated, and the change in ionic spacing leads to an increase in electrical resistance.^[36] Fig. 5(e) reveals that the relative resistance vari-

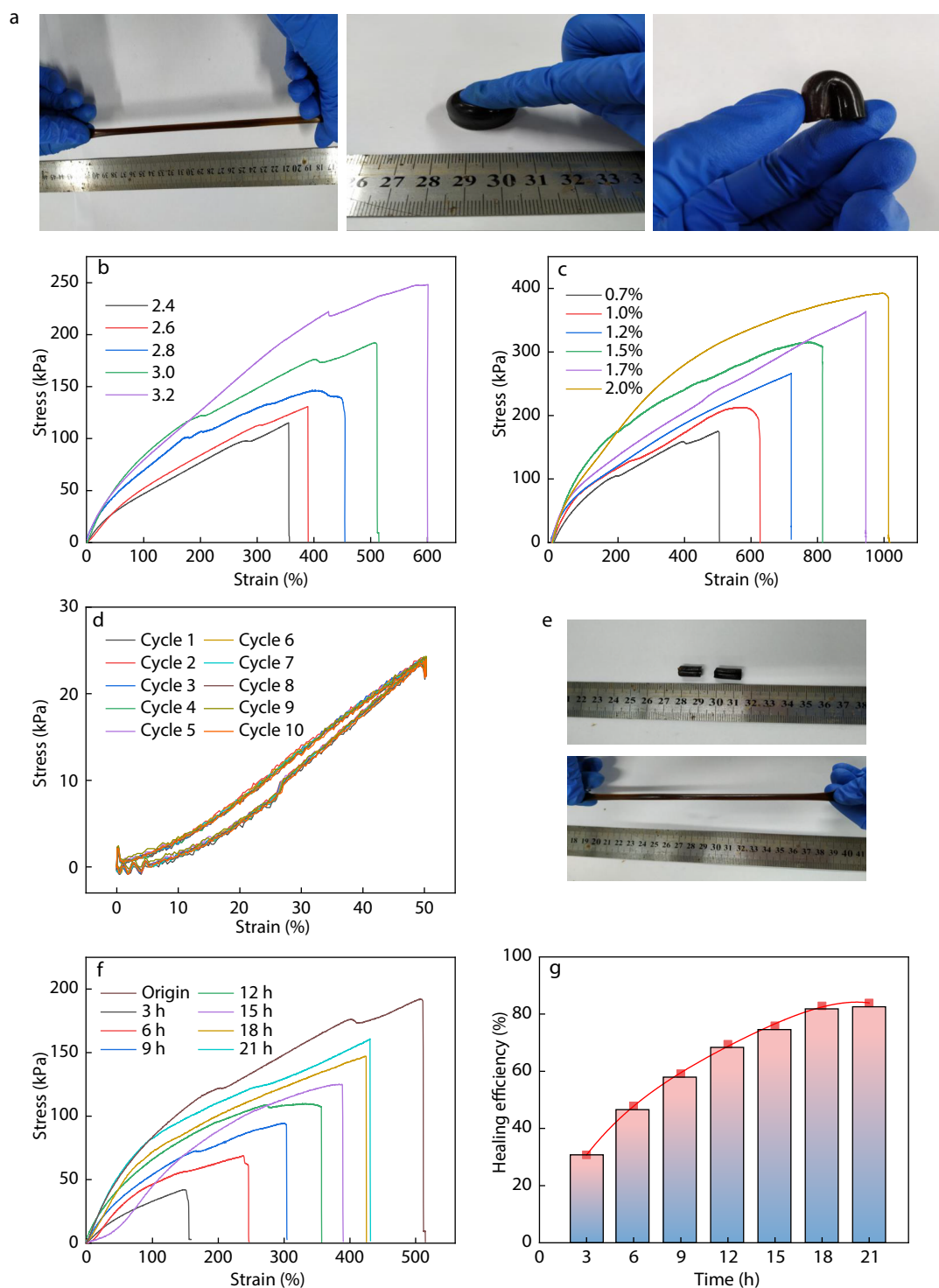


Fig. 3 (a) Digital photographs of hydrogels under stretching, compression and bending; Stress-strain curves of PNIPAM-PAA-GO hydrogels with different (b) monomer ratios and (c) GO contents; (d) Tensile loading-unloading tests of PNIPAM-PAA-GO hydrogel at 50% strain; (e) The cut gel can be stretched after self-healing; (f) stress-strain curves and (g) self-healing efficiency of the healed hydrogels with different healing times.

ation increased linearly at first when the strain sensitivity is increased from 25.3 ($\Delta\epsilon < 50\%$) to 58.9 ($50\% < \Delta\epsilon < 90\%$). Moreover, the inset also shows an approximately linear response with strain sensitivity of 45.6 at a large strain of 100%–300%. Thus, the hydrogel sensors display a high strain

sensitivity under deformations with different amplitudes of strains. Fig. 5(f) shows the 1000-cycle load-unload test of the hydrogel under a strain of 50%. The relative resistance change of the sensor fluctuated slightly, but the illustration shows that the value of relative resistance change remains

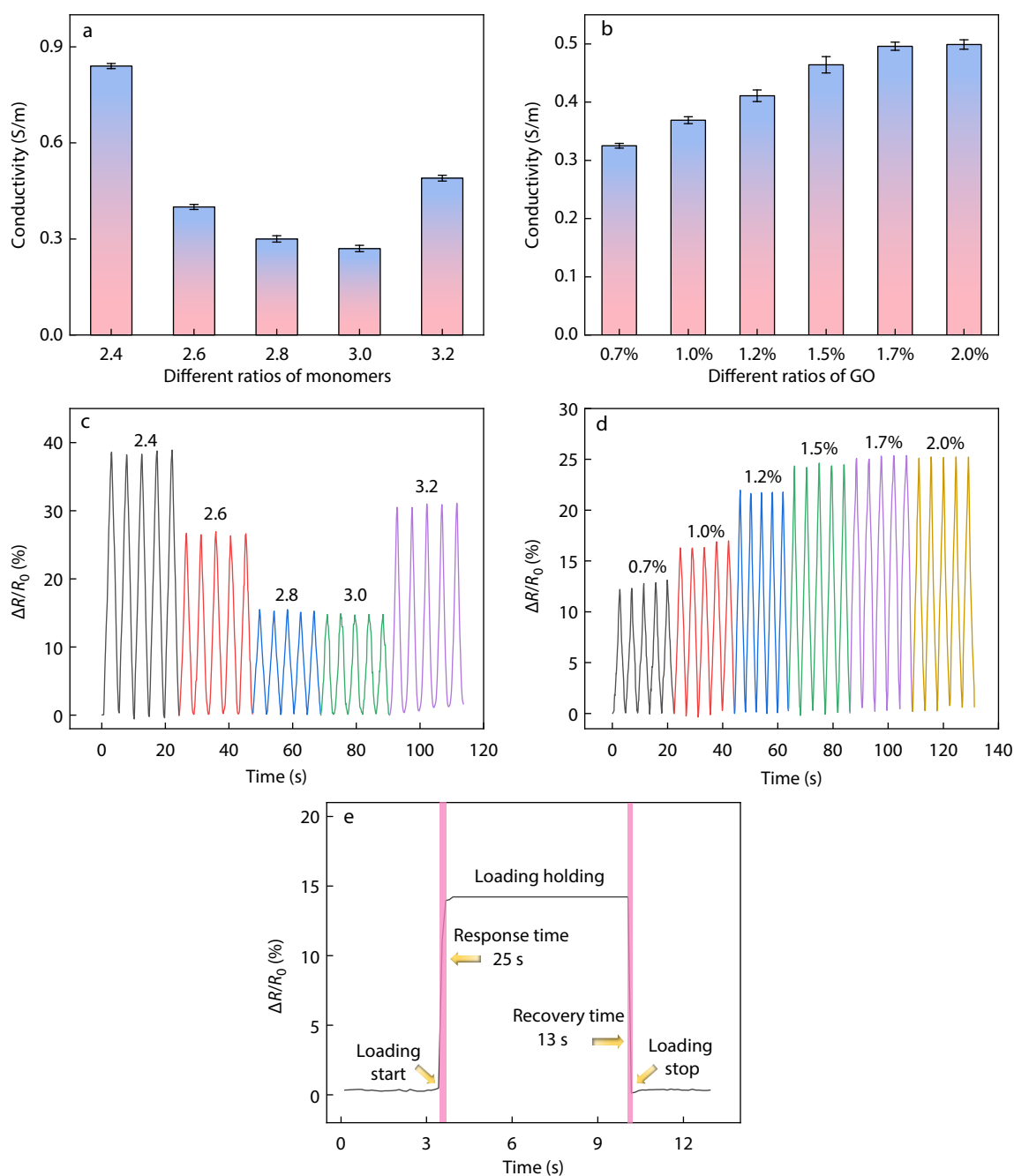


Fig. 4 The conductivity of P(AA/NIPAM) hydrogels with (a) different monomer ratios and (b) different GO contents; The relative changes in the resistance of gel sensor with (c) different monomer ratios and (d) different GO contents; (e) The response time of hydrogel strain sensor at a strain of 50%.

stable.

In order to explore the sensing behavior of hydrogel sensors to different temperatures, the sensor was sequentially placed in an environment of 25, 30, 35, 40 and 45 °C. As shown in Figs. 6(a) and 6(c), the relative resistance change was negative and the amplitude of change increased with the increase of temperature. This was because the molecular chains of the hydrogel shrank with the increase of temperature, reducing the distance between conductive particles. At the same time, the increase of temperature leads to hydro-

gen bond fracture, molecular chain shrinkage, and the distance between conductive particles decreases. Furthermore, the magnitude of relative resistance variation with increased temperature reflected the temperature sensitivity of the sensor. The temperature sensitivity of the hydrogel sensor is displayed in Fig. 6(b), and it can be clearly observed that the relative resistance variation showed an almost linear response with a temperature sensitivity of $-1.582\text{ }^{\circ}\text{C}^{-1}$. Then, the hydrogel sensors were quickly placed in a water bath (35 °C) and quickly taken out (Fig. 6c). The average response time

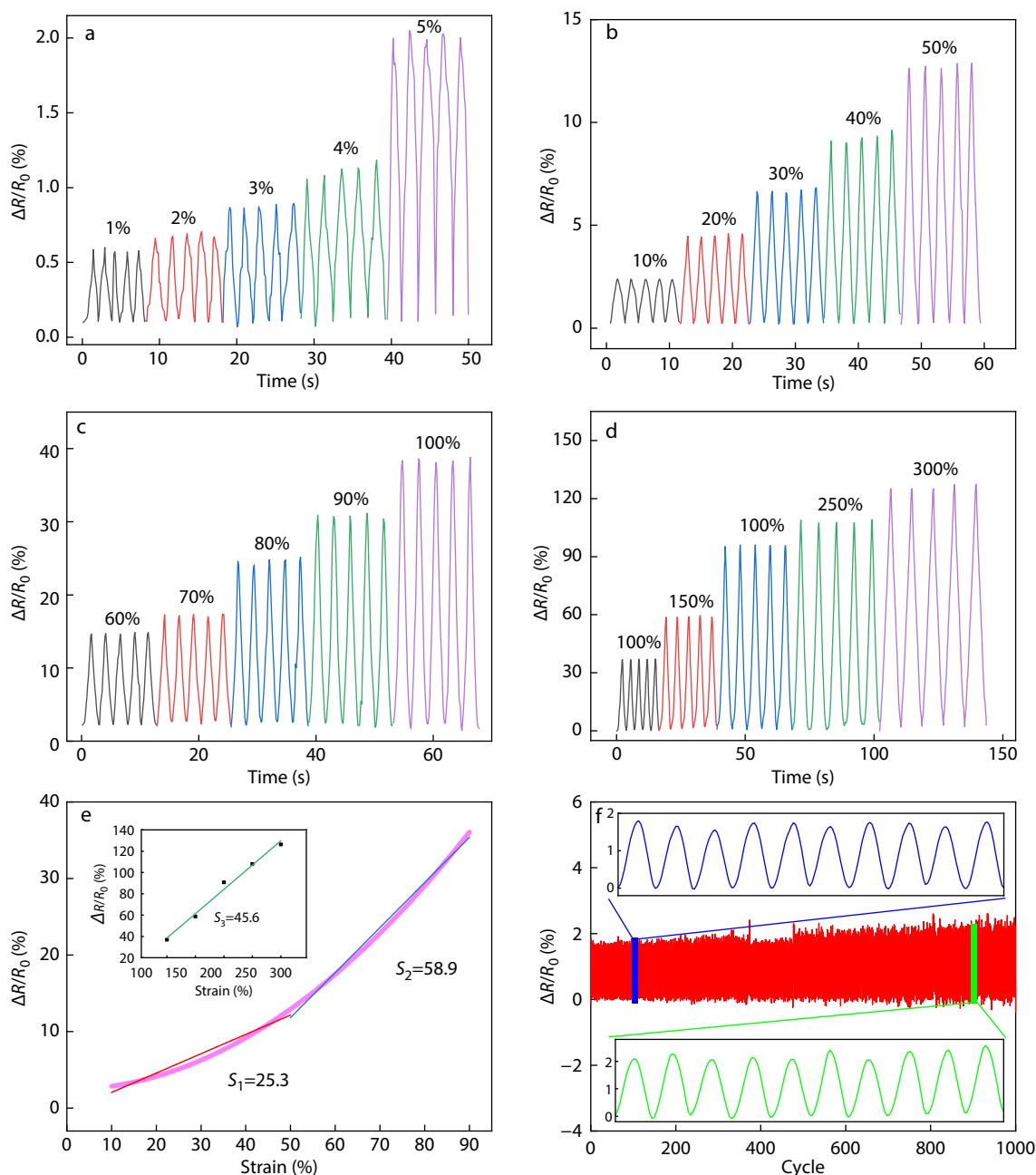


Fig. 5 (a–d) Electrical signal response curve under strains of 1%–300%; (e) The strain sensitivity of the hydrogel sensor with different amplitudes of strains; (f) The stability of hydrogel sensor under repeated strain of 50% for 1000 cycles.

of the hydrogel sensor to the temperature was about 0.25 s, and the average recovery time was about 0.15 s after being removed from the water bath, indicating that the sensor can respond quickly to the external temperature and exhibits a rapid recoverability. In addition, the hydrogel sensor can repeatedly and stably respond to the temperature. As demonstrated in Fig. 6(d), the value of relative resistance change remained stable when repeatedly placed at 35 °C, confirming excellent repeatability and stability of the temperature sensor. One should note that the *N*-isopropyl acrylamide is a temperature-sensitive monomer of the hydrogel sensor and its content affects the sensing performance. As shown in Fig.

6(e), the relative resistance variation of the hydrogel sensor increased significantly with the increase of the NIPAM monomer ratio, and the thermal response time of the sensor decreased when the sensor was placed in water at 35 °C. During the cyclical stretch process, the hydrogel sensor was initially maintained at room temperature (25 °C), an increased sensor resistance was observed clearly when the sensor was suddenly transferred to an environment with a little higher temperature (30 °C) (Fig. 6f). The higher temperature under the same strain resulted in a greater increase in the relative resistance change due to the break of hydrogen bonds and the shrink of hydrogel molecular chains.

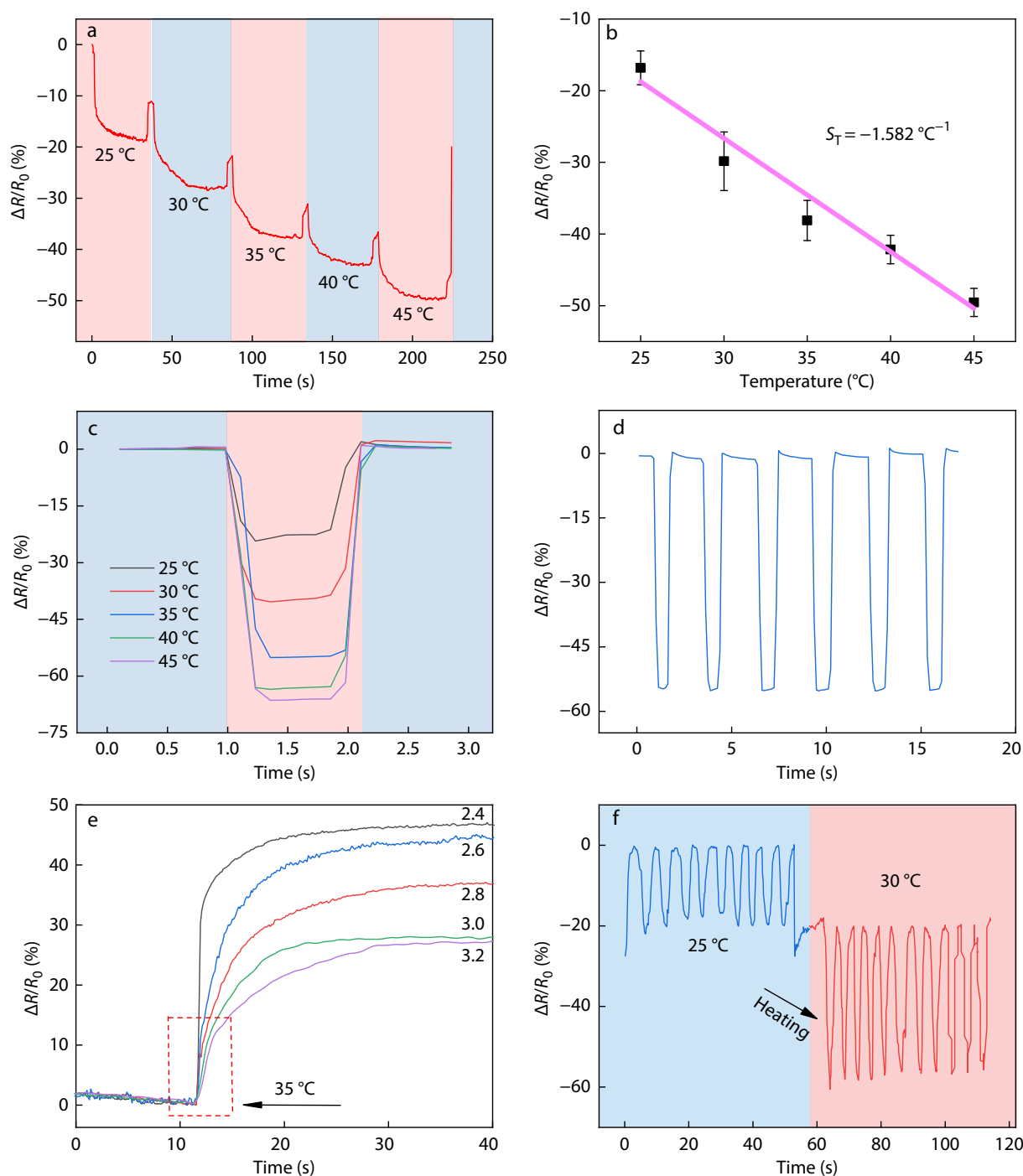


Fig. 6 (a, b) Relative resistance change and temperature sensitivity of hydrogel sensors at various temperatures; (c) The rapid response of hydrogel sensor to the external temperature; (d) The relative resistance change of the hydrogel sensor when it was repeatedly placed at 35 °C; (e) The relative resistance changes of hydrogel sensor with different monomer ratios; (f) The hydrogel sensor stretched at 25 and 30 °C.

In order to verify that the hydrogel sensor can detect human movement as a flexible wearable device, the hydrogel was attached to the human joint with tape and the relative resistance changes of the hydrogel sensor were transmitted and recorded in real-time. Notably, the hydrogel sensor not only detects large motions but is also capable of recording subtle motions. Vocalization is related to the subtle vibration of the vocal cords, and the hydrogel sensor can sensitively

perceive the signals when attached to protruding parts in the throat and the surrounding skin. Fig. 7(a) shows the relative resistance changes of different voice signals, and it is displayed as a single peak when the pronunciation was “hi” and a double peak when the pronunciation was “hello”. Fig. 7(b) shows the sensor signals of the finger bending process. The different angles of finger bending were converted into resistance changes of the hydrogel sensor. It can be observed that

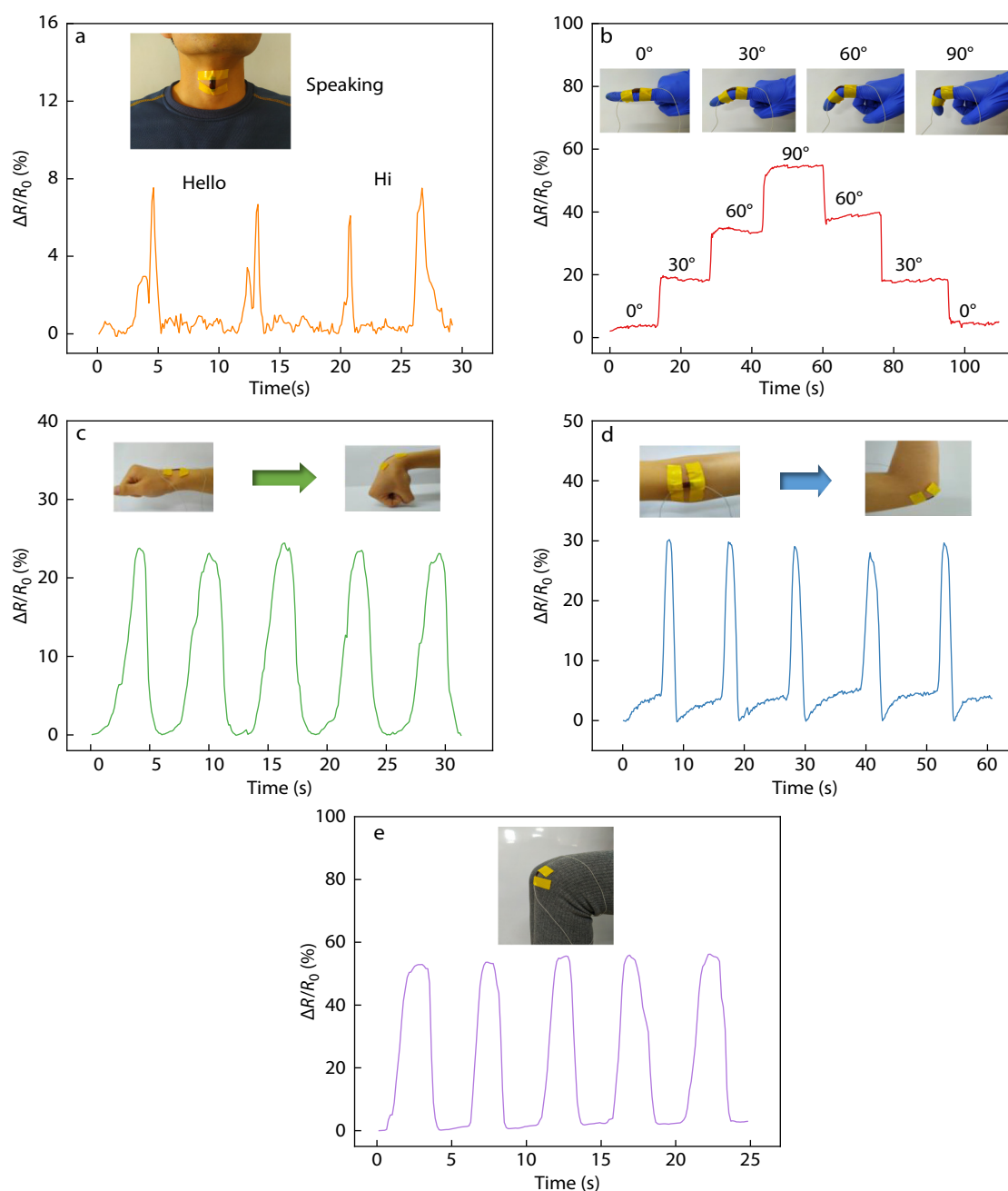


Fig. 7 The relative resistance changes of the hydrogel sensor during (a) speaking, (b) forefinger bending at different angles, (c) wrist joint bending, (d) elbow joint bending and (e) knee joint bending.

the finger bending to different angles of 0°, 30°, 60° and 90° resulted in a stepwise increase in the resistance of hydrogel sensor.

Moreover, the resistance value remained constant when the finger was bent to maintain a certain angle, proving the excellent electrical stability of the hydrogel sensor. Furthermore, the hydrogel was applied to detect multiple large limb activities, where the hydrogel sensor was attached to the wrist to detect the bending and stretching of the joint. The real-time resistance changes are recorded and presented in Fig. 7(c). When the wrist was bent, the hydrogel sensor was stretched and the resistance increased, and the resistance re-

turned to its original value when the wrist was straightened. Fig. 7(d) presents the relative resistance changes of hydrogel sensor after being integrated into the elbow. Clearly, the hydrogel sensor was in natural relaxation state with a minimum resistance value when the arm was straightened. The resistance of hydrogel sensor increased to a maximum value when the arm was bent to about 90°, and the resistance gradually recovered to the initial value when the bending angle of the arm decreased to 0°. Fig. 7(e) illustrates that the hydrogel sensor was stretched when the knee joint resulted in bending motion, which increased the resistance of hydrogel sensor. It is worth noting that the resistance peak re-

mained stable when the knee repeated its action. These results confirm that the hydrogel sensor possesses a high strain sensitivity, rapid response, electrical stability and repeatability.

CONCLUSIONS

In summary, a conductive nanocomposite hydrogel with high stretchability, self-healing ability and dual temperature-strain sensitivity is synthesized *via* one-pot *in situ* polymerization. The P(AA-co-NIPAM)/GO hydrogel was facilitated by dual cross-linking effects, including ionic coordination cross-linking and hydrogen-bonding interactions, contributing to the high stretchability with a strain of up to 509.48%. The reversible features of coordination bonds and hydrogen bonds resulted in excellent recoverability and self-healing properties by dynamical breakage and reformation. Additionally, the hydrogels exhibited excellent strain sensitivity in a large elongation range (1%–300%), as well as rapid response and recoverability. Meanwhile, the hydrogels demonstrated superior temperature sensitivity, converting the external temperature changes into electrical signals in real-time due to the introduction of NIPAM. Moreover, the hydrogel sensor can be applied to monitor body motions, involving speaking and bending of finger, wrist, elbow and knee. The current work presents an efficient route to fabricate stretchable and self-healing hydrogels with excellent strain and temperature sensitivities for potential applications in multifunctional wearable sensing devices.

NOTES

The authors declare no competing financial interest.

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REFERENCES

- Guo, M. L.; Yan, J.; Yang, X.; Lai, J. J.; An, P.; Wu, Y. P.; Li, Z. Y.; Lei, W. W.; Smith, A. T.; Sun, L. Y. A transparent glycerol-hydrogel with stimuli-responsive actuation induced unexpectedly at subzero temperatures. *J. Mater. Chem. A* **2021**, 9, 7935–7945.
- Cao, Z.; Wang, R.; He, T.; Xu, F.; Sun, J. Interface-controlled conductive fibers for wearable strain sensors and stretchable conducting wires. *ACS Appl. Mater. Interfaces* **2018**, 10, 14087–14096.
- Zuo, X. L.; Wang, S. F.; Le, X. X.; Lu, W.; Chen, T. Self-healing polymeric hydrogels: toward multifunctional soft smart materials. *Chinese J. Polym. Sci.* **2021**, 39, 1262–1280.
- Li, X. K.; Liu, J. Z.; Guo, Q. Q.; Zhang, X. X.; Tian, M. Polymerizable deep eutectic solvent-based skin-like elastomers with dynamic schemochrome and self-healing ability. *Small* **2022**, 18, 2201012.
- Trung, T. Q.; Ramasundaram, S.; Hwang, B. U.; Lee, N. E. An all-elastomeric transparent and stretchable temperature sensor for body-attachable wearable electronics. *Adv. Mater.* **2016**, 28, 502–509.
- Park, S. J.; Kim, J.; Chu, M.; Khine, M. Flexible piezoresistive pressure sensor using wrinkled carbon nanotube thin films for human physiological signals. *Adv. Mater. Technol.* **2018**, 3, 1700158.
- Liu, Q.; Zhang, M.; Huang, L.; Li, Y.; Chen, J.; Li, C.; Shi, G. High-quality graphene ribbons prepared from graphene oxide hydrogels and their application for strain sensors. *ACS Nano* **2015**, 9, 12320–12326.
- Wang, E.; Desai, M. S.; Lee, S. W. Light-controlled graphene-elastin composite hydrogel actuators. *Nano Lett.* **2013**, 13, 2826–2830.
- Li, X.; Fu, M.; Wu, J.; Zhang, C.; Deng, X.; Dhinakar, A.; Huang, W.; Qian, H.; Ge, L. pH-sensitive peptide hydrogel for glucose-responsive insulin delivery. *Acta Biomater.* **2017**, 51, 294–303.
- Li, Z.; Ye, L.; Shen, J.; Xie, K.; Li, Y. Strain-gauge sensing composite films with self-restoring water-repellent properties for monitoring human movements. *Compos. Commun.* **2018**, 7, 23–29.
- Rus, D.; Tolley, M.; Design, T. Fabrication and control of soft robots. *Nature* **2015**, 521, 467–475.
- Agua, I. d.; Mantione, D.; Ismailov, U.; Sanchez-Sanchez, A.; Aramburu, N.; Malliaras, G. G.; Mecerreyes, D.; Ismailova, E. DVS-crosslinked PEDOT:PSS free-standing and textile electrodes toward wearable health monitoring. *Adv. Mater. Technol.* **2018**, 3, 1700322.
- Amjadi, M.; Kyung, K. U.; Park, I.; Sitti, M. Stretchable, skin-mountable, and wearable strain sensors and their potential applications: a review. *Adv. Funct. Mater.* **2016**, 26, 1678–1698.
- Yu, X. G.; Li, Y. Q.; Zhu, W. B.; Huang, P.; Wang, T. T.; Hu, N.; Fu, S. Y. A wearable strain sensor based on a carbonized nanosponge/silicone composite for human motion detection. *Nanoscale* **2017**, 9, 6680–6685.
- Sang, S. B.; Liu, L. H.; Jian, A. Q.; Duan, Q. Q.; Ji, J. L.; Zhang, Q.; Zhang, W. D. Highly sensitive wearable strain sensor based on silver nanowires and nanoparticles. *Nanotechnol.* **2018**, 29, 255202.
- Li, Q.; Li, J.; Tran, D. Engineering of carbon nanotube/polydimethylsiloxane nanocomposites with enhanced sensitivity for wearable motion sensors. *J. Mater. Chem. C* **2017**, 5, 11092–11099.
- Wang, Y. L.; Hao, J.; Huang, Z. Q.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Shen, C. Y. Flexible electrically resistive-type strain sensors based on reduced graphene oxide-decorated electrospun polymer fibrous mats for human motion monitoring. *Carbon* **2018**, 126, 360–371.
- Kim, H. J.; Sim, K.; Thukral, A. Rubbery electronics and sensors from intrinsically stretchable elastomeric composites of semiconductors and conductors. *Sci. Adv.* **2017**, 3, 1701114.
- Xin, X. G.; Fei, G. T.; Wen, B. F.; Ming, F.; Xu, D. G.; Zhong, B. N.; Li, D. Z. Flexible strain sensor with high performance based on PANI/PDMS films. *Org. Electron.* **2017**, 47, 51–56.
- Li, J.; Geng, L.; Wang, G.; Chu, H.; Wei, H. Self-healable gels for use in wearable devices. *Chem. Mater.* **2017**, 29, 8932–8952.
- Kim, C.; Kim, H. C.; Lee, H.; Oh, K. H.; Sun, J. Highly stretchable, transparent ionic touch panel. *Science* **2016**, 353, 682–687.
- Mao, J.; Zhao, C. X.; Li, Y. T.; Xiang, D.; Wang, Z. X. Highly stretchable, self-healing, and strain-sensitive based on double-crosslinked nanocomposite hydrogel. *Compos. Commun.* **2020**, 17, 22–27.
- Dai, T.; Qing, X.; Lu, Y.; Xia, Y. Conducting hydrogels with enhanced mechanical strength. *Polymer* **2009**, 50, 5236–5241.
- Sun, J. Y.; Keplinger, C.; Whitesides, G. M. Ionic skin. *Adv. Mater.* **2014**, 26, 7608–7614.

- 25 Kevin, J.; De, F.; Todd, H.; Emily, D. C. Review of hydrogels and aerogels containing nanocellulose. *Chem. Mater.* **2017**, *29*, 4609–4631.
- 26 Abbas, Z. M.; Tawfilas, M.; Khani, M. M.; Golian, K.; Marsh, Z. M.; Jhalaria, M.; Benicewicz, B. C. Reinforcement of polychloroprene by grafted silica nanoparticles. *Polymer* **2019**, *171*, 96–105.
- 27 Huang, Y.; Zeng, M.; Chen, J.; Wang, Y.; Xu, Q. Multi-structural network design and mechanical properties of graphene oxide filled chitosan-based hydrogel nanocomposites. *Mater. Des.* **2018**, *148*, 104–114.
- 28 Ioniță, M.; Vlăsceanu, G. M.; Watzlawek, A. A.; Voicu, S. I.; Burns, J. S.; Iovu, H. Graphene and functionalized graphene: extraordinary prospects for nanobiocomposite materials. *Compos. Part B: Eng.* **2017**, *121*, 34–57.
- 29 Ye, B. H.; Zhang, S. Y.; Li, R. W.; Li, L. H.; Lu, L.; Zhou, C. R. An *in-situ* formable and fibrils-reinforced polysaccharide composite hydrogel by self-crosslinking with dual healing ability. *Compos. Sci. Technol.* **2018**, *156*, 238–246.
- 30 Andersen, A.; Krogsgaard, M.; Birkedal, H. Mussel-inspired self-healing double-crosslinked hydrogels by controlled combination of metal coordination and covalent cross-linking. *Biomacromolecules* **2018**, *19*, 1402–1409.
- 31 Lei, Z.; Wang, Q.; Sun, S.; Zhu, W.; Wu, P. A bioinspired mineral hydrogel as a self-healable, mechanically adaptable ionic skin for highly sensitive pressure sensing. *Adv. Mater.* **2017**, *29*, 1700321.
- 32 Taylor, D. L. Self-healing hydrogels. *Adv. Mater.* **2016**, *28*, 9060–9093.
- 33 Shao, C.; Chang, H.; Wang, M.; Xu, F.; Yang, J. High-strength, tough, and self-healing nanocomposite physical hydrogels based on the synergistic effects of dynamic hydrogen bond and dual coordination bonds. *ACS Appl. Mater. Interfaces* **2017**, *9*, 28305–28318.
- 34 Hu, Y.; Du, Z.; Deng, X.; Wang, T.; Yang, Z.; Zhou, W.; Wang, C. Dual physically cross-linked hydrogels with high stretchability, toughness, and good self-recoverability. *Macromolecules* **2016**, *49*, 5660–5668.
- 35 Deng, Z.; Guo, Y.; Zhao, X.; Ma, P. X.; Guo, B. Multifunctional stimuli-responsive hydrogels with self-healing, high conductivity, and rapid recovery through host-guest interactions. *Chem. Mater.* **2018**, *30*, 1729–1742.
- 36 Mao, J.; Zhao, C. X.; Liu, L.; Li, Y. T.; Xiang, D.; Wu, Y. P.; Li, H. Adhesive, transparent, stretchable, and strain-sensitive hydrogel as flexible strain sensor. *Compos. Commun.* **2021**, *25*, 100733.
- 37 Xue, S. H.; Wu, Y. P.; Liu, G. F.; Guo, M. L.; Liu, Y. H.; Zhang, T.; Wang, Z. H. Hierarchically reversible crosslinking polymeric hydrogels with highly efficient self-healing, robust mechanical properties, and double-driven shape memory behavior. *J. Mater. Chem. A* **2021**, *9*, 5730–5739.
- 38 Cai, G.; Wang, J.; Qian, J. Extremely stretchable strain sensors based on conductive self-healing dynamic cross-links hydrogels for human-motion detection. *Adv. Sci.* **2017**, *4*, 1600190.
- 39 Lin, M. Z.; Zheng, Z. J.; Yang, L.; Luo, M. S.; Fu, L. H.; Lin, B. F.; Xu, C. H. A high-performance, sensitive, wearable multifunctional sensor based on rubber/CNT for human motion and skin temperature detection. *Adv. Mater.* **2022**, *34*, 2107309.
- 40 Wang, Z.; Zhou, H.; Chen, W.; Li, Q.; Yan, B.; Jin, X.; Ma, A.; Liu, H.; Zhao, W. Dually synergetic network hydrogels with integrated mechanical stretchability, thermal responsiveness and electrical conductivity for strain sensors and temperature alertors. *ACS Appl. Mater. Interfaces* **2018**, *10*, 14045–14054.
- 41 Lei, Z.; Wang, Q.; Wu, P. A multifunctional skin-like sensor based on a 3D printed thermo-responsive hydrogel. *Mater. Horiz.* **2017**, *4*, 694–700.
- 42 Shi, Y.; Ma, C.; Peng, L.; Yu, G. Conductive “Smart” hybrid hydrogels with PNIPAM and nanostructured conductive polymers. *Adv. Funct. Mater.* **2015**, *25*, 1219–1225.
- 43 Belali, S.; Savoie, H.; O’Brien, J. M.; Cafolla, A. A.; O’Connell, B.; Karimi, A. R.; Boyle, R. W.; Senge, M. O. Synthesis and characterization of temperature-sensitive and chemically cross-linked poly(*N*-isopropylacrylamide)/photosensitizer hydrogels for applications in photodynamic therapy. *Biomacromolecules* **2018**, *19*, 1592–1601.
- 44 Li, Y.; Qin, J.; Bao, H.; Yan, H.; Zeng, X.; Hua, Z.; Huang, Y.; Xia, X.; Dong, Z. Controlled tuning of LCST based on poly(*N*-isopropylacrylamide)/hydroxypropyl cellulose temperature-sensitive hydrogel by electron beam pre-radiation method. *J. Polym. Res.* **2018**, *25*, 19.
- 45 Ding, J.; Zhao, C. X.; Zhao, L.; Li, Y. T.; Xiang, D. Synergistic effect of α -ZrP and graphene oxide nanofillers on the gas barrier properties of PVA films. *J. Appl. Polym. Sci.* **2018**, *135*, 46455.
- 46 Kong, W. Q.; Chang, M. M.; Zhang, C. H.; Liu, X. X.; He, B.; Ren, J. L. Preparation of xylan-g-P(AA-co-AM)/GO nanocomposite hydrogel and its adsorption for heavy metal ions. *Polymers* **2019**, *11*, 621.
- 47 Wei, J. J.; Wang, R. J.; Pan, F.; Fu, Z. Y. Polyvinyl alcohol/graphene oxide conductive hydrogels via the synergy of freezing and salting out for strain sensors. *Sensors* **2022**, *22*, 3015.