Facile preparation and high performance of wearable strain sensors based on ionically cross-linked composite hydrogels

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ABSTRACT Flexible sensors that can respond to multiple mechanical excitation modes and have high sensitivity are of great significance in the fields of electronic skin and health monitoring. Simulating multiple signal responses to skin such as strain and temperature remains an important challenge. Therefore, new multifunctional ion-crosslinked hydrogels with toughness and conductivity were designed and prepared in this work. A chemical gel with high mechanical strength was prepared by cross-linking acrylamide with *N,N'*-methylene-bisacrylamide and ammonium persulfate. In addition, in order to enhance the conductive properties of the hydrogel, Ca^{2+} , Mg^{2+} and Al^{3+} ions were added to the hydrogel during cross-linking. The double-layer network makes this ionic hydrogel show excellent mechanical properties. Moreover, the composite hydrogel containing Ca^{2+} can reach a maximum stretch of 1100% and exhibits ultra-high sensitivity ($S_p = 10.690 \text{ MPa}^{-1}$). The obtained hydrogels can successfully prepare wearable strain sensors, as well as track and monitor human motion. The present prepared multifunctional hydrogels are expected to be further expanded to intelligent health sensor materials.

Keywords: hydrogel, ionic cross-linking, strain sensor, E-skin

INTRODUCTION

In recent years, the demand for flexible sensors has been increasing, especially for electronic skin, human health monitoring, and wearable devices [1–7]. Most of these flexible sensors rely on conductive materials such as doped carbon-based materials [8–12], metal nanowires [13,14], and metal nanoparticles to convert mechanical signals to electrical signals [15]. A flexible sensor material needs to have biocompatibility, excellent mechanical

properties, high sensitivity and linear response to stress and strain, high conductivity under large strain, good stability, repeatability and other characteristics [16–18]. However, the current flexible conductive materials usually cannot integrate multiple performances, which is a huge challenge for most flexible stress-strain sensors. Conductive hydrogels are ideal materials for flexible sensors due to their outstanding biocompatibility, flexibility and mechanical properties, as well as excellent electron and ion transmission capabilities [19]. The sensing mechanism of flexible sensors is mainly made up of four parts: transistors [20,21], piezoresistance [22], piezoelectric sensor [23] and capacitor [24]. Among them, the piezoresistive sensor is the most widely used electronic strain sensor due to the advantages of simple structure, low price, and fast data output. However, traditional piezoresistive sensors also have many problems. For example, their mechanical properties and electrical conductivity cannot be taken into account at the same time, and they have low biocompatibility and difficulty in measuring in low-voltage areas ($\leq 10 \text{ kPa}$).

To solve the above problems, various types of flexible sensors have been studied. Inspired by the properties of mussels in nature, Jing *et al.* [25] mixed protein polydopamine (PDA) into the hydrogel to obtain chitosan (CS)/graphene oxide (GO) composite hydrogels with good biocompatibility, ultra-long tensile properties, self-adhesive properties and self-healing properties. During the process of dopamine (DA) oxidation, GO was reduced by PDA and dispersed into the hydrogel network to form an electrical pathway to achieve the purpose of signal transduction. Zhang *et al.* [26] achieved the effec-

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tive combination of a carbon tube/graphene two-dimensional (2D) film with elastomers such as polydimethylsiloxane (PDMS)/Ecoflex; they endowed the device with multiple features, including ultra-high sensitivity, wide detection range, low detection limit and self-adhesion, and made a preliminary attempt at the large-scale production of the device. Peng *et al.* [27] reported on an ultra-tensile hydrogel sensor of liquid metal (LM) filler, that is, a hydrogel sensitive to ultra-tensile force using LM as soft filler in the hydrophilic polymer network. The liquid properties of LMs toughen the hydrogel matrix and make the network significantly malleable (tensile strain ~1500%). Pang *et al.* [28] coated platinum on urethane nanofibers with high aspect ratio to prepare layered strain sensors with nano-level mechanical interlocks. Under the action of external forces, nanofibers with a high aspect ratio can produce different nanoscale deformations and cause changes in resistance, which will achieve the purpose of detecting stress such as pressure, shear and torsion. Amjadi *et al.* [29] prepared silver nanowires into thin films and embedded them in a sandwich structure between two layers of PDMS to prepare sensors with excellent sensitivity and tensile properties.

However, the flexibility and mechanical properties of the hydrogel are affected due to the inelasticity of the carbon material. There is a high degree of incompatibility between the LM and the hydrogel. In addition, the weak interfacial interaction between the LM and the polymer network will also lead to poor mechanical properties of the hydrogel. Metal nanowires have high mechanical strength and good electrical conductivity, but their firing process is complicated and environmental requirements are high. After comprehensive consideration, metal ions were chosen as the active material of the sensor. In the selection of flexible materials, Yang *et al.* [30] reported a CS/polyacrylamide (PAAM) hydrogel with a mixed ion covalently crosslinked double network, and Sun *et al.* [31] reported on a sodium alginate (SA)/PAAM hydrogel formed by the formation of ions and a covalently cross-linked network composite. Therefore, we chose PAAM hydrogel as the flexible substrate of the sensor. In this work, a method of rapidly synthesizing *N,N*-dimethacrylamide-PAAM/Ca hydrogel (MBAA-PAAM/Ca gel) sensors using the “one-pot method” is reported. PAAM hydrogels have low raw material costs, uniform polymerization, good transparency, non-toxicity and other characteristics. At the same time, different metal ions such as Al^{3+} , Mg^{2+} , and Ca^{2+} were added to each other as the control group. The results showed that the addition of these metal ions could not only form an ion crosslink

with the polymer chain to enhance the toughness of the hydrogel, but also could be used as an active material to transform the resistance signal. It has been proven that the MBAA-PAAM/Ca gel composite hydrogel could monitor various human movements (such as air blowing and wrist movements). In addition, the prepared MBAA-PAAM/Ca gel composite hydrogel could be used as a hydrogel electronic pen. In short, the prepared composite hydrogels provide a broad opportunity for high-performance wearable electronic devices.

EXPERIMENTAL SECTION

Materials

In the experiments, ultrapure water was prepared using a Milli-Q Millipore filtration system (Millipore Co., Bedford, Massachusetts, USA). Acrylamide (AAM, 99.0%), MBAA (99.0%), ammonium persulfate (APS, 99.0%), aluminum nitrate ($\text{Al}(\text{NO}_3)_3$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), and calcium chloride (CaCl_2) were purchased from Aladdin (China). In addition, all chemicals were used as received without any further purification.

Preparation of the hydrogel sensor

Ionically cross-linked composite hydrogels were prepared by a one-pot method. The deionized water (10 mL) and MBAA (1 mL) were mixed, and then AAM (1.42 g), APS (0.06 g) and $\text{Al}(\text{NO}_3)_3/\text{Mg}(\text{NO}_3)_2/\text{CaCl}_2$ (0.2 mol L^{-1}) were added and mixed evenly. The solution was kept still for 3 min, and then moved into the mold. The mixed solution was irradiated for 100 min by ultraviolet light (365 nm) and then formed into a hydrogel. The water content of the hydrogel was about 79% calculated by the formula. The obtained hydrogels were named as MBAA-PAAM/Al gel, MBAA-PAAM/Mg gel, MBAA-PAAM/Ca gel, and MBAA-PAAM gel, where MBAA-PAAM gel was a hydrogel without adding metal salt ions.

Testing of strain sensors

The sensitivity of a strain sensor can be reflected by changes in resistance. Two shapes of the strain sensor were used in the tests. For the strain sensor to sense strain, the hydrogels were made into a rectangular sample with a length of 40 mm (with an effective length of 20 mm), a width of 15 mm, and a thickness of 2 mm. For the sensor to sense changes in breathing, the hydrogels were made into a circular sample with a diameter of 26 mm and a thickness of about 2 mm. When assembling the sensor and the test instrument, we connected copper wires to the wires at both ends of the sample.

Characterization

The morphologies of the prepared hydrogel samples were observed using a Hitachi S-4800II (Japan) field emission scanning electron microscope (SEM) at an acceleration voltage of 5–15 kV. Fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet Corporation, USA) was used to obtain the FT-IR spectra after the hydrogels and KBr were thoroughly ground and compressed. Thermogravimetric (TG) analysis was finished in an argon atmosphere using a Netzsch STA 409 PC Luxx simultaneous thermal analyzer. The specific surface area and pore size distribution of the hydrogel were measured by using a Brunauer-Emmett-Teller (BET) measurement (MicroActive for ASAP 2460 version 2.01). The microcomputer controlled electronic universal testing machine LGS50N obtained by Kunshan Lugong Precision Instrument Co., Ltd. was used to analyze the tensile properties of the hydrogels. The benchtop digital bridge 4091A produced by Shenzhen Yisheng Shengli Technology Co., Ltd. was used to characterize the resistance change of the sensor. It is worth noting that, except for the tensile test and resistance change, the hydrogels used for characterization were lyophilized at -50°C using a FD-1C-50 lyophilizer purchased from Boykang Experimental Instrument Co., Ltd. (Beijing, China).

RESULTS AND DISCUSSION

Ionic composite hydrogels were prepared by the ultraviolet photogel-forming method. As shown in Fig. 1,

MBAA cross-linked PAAM was used as a chemical covalent network to maintain the shape of the hydrogels. The prepared hydrogels can stretch up to a dozen times. In this process, the ionic coordination bond will be broken as a reversible bond, which will destroy the energy dissipation under the external force and increase the length of the hydrogel without breaking. In addition, the ionic bonds will quickly reconstruct without stimulation after the load is removed, indicating that the hydrogel has good elasticity and cyclic stretchability.

As is known to all, the preparation of a hydrogel into a strain sensor needs to meet conditions such as high transparency, adhesion, conductivity, and toughness. Fig. 2a, b show that the hydrogel has good transparency and can adhere to the skin. There is no residue on the skin after tearing the gel, and the secondary adhesion effect is still good. Fig. 2c is a schematic diagram of blowing nitrogen into a 2-mm-thick composite gel. As shown in Video S1, it could be found that the composite hydrogel would be formed into an ultra-thin film under gas pressure. The results show that hydrogels are very tough and offer the possibility to make miniature sensors in the future. From Fig. 2d, it shows that the hydrogel can act as a wire to connect the circuit, and the stretching and release of the composite hydrogel can effectively control the light-emitting diode (LED) bulb to become brighter and darker, indicating that the composite hydrogel shows great potential as an ideal strain sensor.

Four kinds of ionically cross-linked composite hydro-

Figure 1 Schematic preparation process of ion-crosslinked composite hydrogel and the sensing application of strain sensors.

Figure 2 (a) Optical photo of a transparent hydrogel covering the Yanshan University emblem. (b) Hydrogel could adhere to the skin. (c) Hydrogel bubble blown with gas. (d) Hydrogel could conduct electricity to brighten the bulb, and the bulb would become darker when the hydrogel was stretched.

gels were freeze-dried to obtain aerogels, and the morphologies of the aerogels were systematically characterized. As shown in Fig. 3a–d, the inside of Fig. 3a is a large protrusion, and the protrusion is uneven. The sizes of the inside protrusions of Fig. 3b, c are small, while the protrusion of Fig. 3c is dense. And the inside of the gel is relatively smooth and flat as shown in Fig. 3d. It can be found that compared with acrylamide hydrogels, the in-

ternal structure of the composite hydrogels doped with Al^{3+} , Mg^{2+} and Ca^{2+} ions have protrusions. When the hydrogel is deformed, the protrusions are first stretched to protect the overall structure of the hydrogel, which is not easy to break and enhance the mechanical properties of the prepared hydrogels. Fig. 3e is the FT-IR of the four hydrogels and acrylamide. The double peaks at 3179 and 3349 cm^{-1} correspond to the stretching vibration of N–H,

Figure 3 SEM images of (a) MBAA-PAAM/Al gel, (b) MBAA-PAAM/Mg gel, (c) MBAA-PAAM/Ca gel, and (d) MBAA-PAAM gel. (e) The FT-IR spectra, and (f) TG curves of the four hydrogels.

and the peak at 2813 cm^{-1} corresponds to the stretching vibration of C–H. The peak at 1673 cm^{-1} can be attributed to the stretching vibration of C=O connected to $-\text{NH}_2$, and it overlaps with the characteristic peak of C=C, which is the characteristic peak of acrylamide. In addition, the peak at 1611 cm^{-1} corresponds to the bending vibration of N–H, which verifies the existence of primary amines in AAM. The peak located at 1428 cm^{-1} may be derived from the C–N stretching vibration of aromatic amines. For four different hydrogels, medium-intensity multiple compound bands appeared at 2360 cm^{-1} . It is believed that the peak at 2918 cm^{-1} corresponds to the stretching vibration peaks of $-\text{CH}_2-$ and $-\text{CH}-$, indicating that a carbon chain structure was generated. Fig. 3f is a TG analysis of the four hydrogels. For the MBAA-PAAM gel, there is a small mass loss in the TG curve from room temperature to 220°C due to the volatilization of residual moisture in the xerogel. For the MBAA-PAAM/Al hydrogel, MBAA-PAAM/Mg hydrogel and MBAA-PAAM/Ca gel, water loss occurs between room temperature and 260°C , and the curve shifts to the right as a whole, which may be due to the hydrogen bonding in these three gels. The second mass losses of the four gels are concentrated in $250\text{--}350^\circ\text{C}$. This mass loss is due to the condensation of adjacent amide groups on the PAAM polymer chain. The amino group is removed to form an imide group. The third mass loss is about 50%, which is due to the dehydrogenation of the PAAM long chain at $350\text{--}500^\circ\text{C}$ and the formation of CO_2 . Compared with the other three hydrogels, the MBAA-PAAM/Ca gel loses the most mass, probably due to that the bonds close to the tertiary and quarterly carbon atoms in the main chain are prone to break. When the temperature is higher than 550°C , further weight loss occurs, and the PAAM oxidizes and exotherms. The above data show that the addition of metal ions is beneficial to the formation of hydrogen bonds in the hydrogel and can improve the thermal stability of the hydrogel. In addition, Table S1 summarizes the same results for the cumulative surface area of pores adsorbed-desorbed by Barrett-Joyner-Halenda (BJH) and other parameters obtained at 77.3 K . The MBAA-PAAM/Ca gel has a larger BET surface area, as shown in Fig. 3c. SEM comparison shows that the surface of the MBAA-PAAM/Ca gel has small protrusions, which may be the reason for the large BET surface area of this hydrogel. In addition, it can be found by comparing related hydrogels reported by the average adsorption pore size and the cumulative volume of the adsorption pores of the four hydrogels that are small, which also confirms that this material has a pleated structure with few pores.

The mechanical properties of the four composite hydrogels are shown in Fig. 4a, b, which present the stress-strain curve at a tensile rate of 100 mm min^{-1} , and the corresponding elastic modulus. It can be found that the elastic modulus of the MBAA-PAAM gel is 4.308 kPa , which is significantly higher than that of the other three types of ion-crosslinked composite hydrogels. The results indicate that MBAA-PAAM gels that rely on covalent and hydrogen bonding crosslinking have large stresses when elastic deformation occurs, and their stiffness is also very large. Therefore, the MBAA-PAAM gel is not prone to deformation and has poor flexibility. The maximum strain of the MBAA-PAAM/Al gel is 750%, the maximum stress is 37.513 kPa and the elastic modulus is about 3.732 kPa . These data show that the stress and strain have been improved after the addition of Al^{3+} ions into the hydrogel, but the elastic modulus is still large, so it is not suitable for the flexible sensor. On this basis, we improved the hydrogel by adding Mg^{2+} and Ca^{2+} ions, and it was observed that the maximum strain of the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel increased to about 1100%, and the elastic modulus of the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel were 2.648 kPa and 2.339 kPa , respectively. The strain increased and the elastic modulus decreased, indicating that the mechanical properties of hydrogels were greatly improved. This phenomenon may be because the polymer chain segments in pure hydrogels are cross-linked by strong covalent bonds. Ionic hydrogels have ionic bonds formed by adding Ca^{2+} salts to the polymer electrolyte and covalent bonds. Single chemically cross-linked hydrogels will reach a certain degree of equilibrium swelling due to different crosslinking densities, a cluster structure will be formed in the high crosslinking and low swelling regions, and the hydrogel will be easily scattered. In the low crosslinking region, due to the high swelling and high crosslinking density caused by the hydrophobic aggregation, the addition of aggregates leads to greater rigidity and brittleness of the pure hydrogel, so the high-purity hydrogel exhibits a higher elastic modulus. This conclusion is also consistent with the results of SEM. The hydrogels with folds inside have better flexibility, because these folds will strain first when they are stretched, so they can withstand more stress and protect the whole structure of the hydrogel from fracture. From the above studies, it can be seen that the introduction of ion coordination interaction is of great significance to the formation of ductile hydrogels, and the strength of ion crosslinking is far greater than that of oxygen bonding. The amount of energy dissipated can be calculated by the area of the

Figure 4 (a) Tensile fracture stress-strain curves of four different hydrogels. (b) Young's modulus. (c) Load-and-unload curves. (d) Area of the hysteresis loop. (e) Optical photographs of the stretching of the hydrogel.

load-unload curve. Fig. 4c shows the loading-unloading curves of the four hydrogels at 500% strain. Fig. 4d shows the area of the hysteresis loops of the four hydrogels. The maximum value indicates that energy is dissipated during the stretching process and a large hysteresis is caused. Covalent bonds and hydrogen bonds in the MBAA-PAAM gel are broken during the stretching process to dissipate energy. The relatively elastic hysteresis areas of the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel are relatively small. These data indicate that ionic bonds will change the network structure formed by the original chemical bonds and hydrogen bonds, and the gels exhibit more flexibility. In addition, the ionic bonds are broken during stretching, and then the bonds will be automatically formed in a short time after stretching. Therefore, the ion-crosslinked composite hydrogels have good recoverability and can quickly return to the original state. The above experiments indicate that the toughness of the hydrogels is due to the synergy of two mechanisms: the bridging of cracks formed by the covalently cross-linked network, and the hysteresis caused by dissociating the ion-crosslinked network.

According to a previous method of measuring fracture energy, pure shear tests were used to characterize the

toughness of the hydrogels [27]. In this experiment, the MBAA-PAAM/Ca gel was chosen as a typical sample. The process of measuring the fracture energy in pure shear experiments was as follows: the same sample was prepared into two rectangular samples of the same size, one of which was recorded as an unnotched sample, the other with a 5-mm gap in the middle of the hydrogel under vertical conditions, as shown in Fig. 5a. The two hydrogels were sandwiched between two clamps of a universal testing machine, and the elongation rate was set to 100 mm min^{-1} . When the crack of the notched sample began to expand, the critical tensile distance between the two clamps was recorded as L_0 . Then the integral of the stress-strain curve obtained from the unnotched sample stretch was calculated with a distance of $0-L_0$, and recorded as U_0 , as shown in Fig. 5b and Fig. S1. Therefore, the fracture energy (E_0) of the hydrogel (Fig. 5c) is calculated by the following formula:

$$E_0 = \frac{U_0}{a_0 \times b_0},$$

where a_0 and b_0 represent the width and thickness of the hydrogel sample, respectively.

By comparing the fracture energies of the four hydrogels, it can be found that $E_{\text{MBAA-PAAM/Mg gel}} >$

Figure 5 (a) Schematic diagram of two samples when testing the fracture energy. (b) The stress-strain curve integral of MBAA-PAAM/Ca gel. (c) The fracture energy of four composite hydrogels. (d) $\Delta R/R_0$ curves of the MBAA-PAAM/Ca gel under different tensile strains. (e) $\Delta R/R_0$ curves of the MBAA-PAAM/Ca gel during the stretching-recovery cycle when the tensile strain is 50%. (f) The $\Delta R/R_0$ curve of the hydrogel under 300 cycles of load-unload.

$E_{\text{MBAA-PAAM/Ca gel}} \gg E_{\text{MBAA-PAAM/Al gel}} > E_{\text{MBAA-PAAM gel}}$. The greater the fracture energy of the material, the more difficult the material is to fracture, and the higher the tensile strength and ductility. The breaking energy of the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel is about 10 times that of the other hydrogels, indicating that the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel are far superior to other hydrogels in terms of mechanical properties. When the gel is applied to a sensor, the excellent ductility allows the sensor to measure the movement of the human body in a larger range, and the hydrogel sensor is not easy to break and has better fatigue resistance. In order to investigate the stability of the sensor, we tested the resistance change (ΔR) of the MBAA-PAAM/Ca gel under the conditions of gradually increasing strain (10%–100%) and constant strain (50%), as shown in Fig. 5d, e. It can be clearly seen that the overall stability of the MBAA-PAAM/Ca gel is good, there are obvious steps in Fig. 5d, and the change of $\Delta R/R_0$ (%) in 11 exercise cycles is small. The overall fluctuation range of other three sensors shown in Fig. S2 is also small, indicating that the acrylamide hydrogel can better reflect the state of action when the amplitude of the action is large. In Fig. 5f, after 300 cycles at 0–25% tensile

strain, the strain sensor also showed good stability, indicating that the hydrogel still maintained intact structure and electrical sensitivity. The introduction of the chemically cross-linked network preserves the overall morphology of the hydrogel. The ion-crosslinked network can effectively disperse the energy generated by stretching and make the resistance of the hydrogel sensor change regularly when the strain occurs.

In order to better apply the sensor to human activities, we pressed a bottle with a weight of 40 g onto the sensor and left it for a period of time. This method simulates the squeeze force that may be generated during joint activities, as shown in Video S2. Through long-term simulation experiments, it can be observed that the data of the MBAA-PAAM/Al gel and MBAA-PAAM gel fluctuated by more than 25% in compression experiments, which has a greater impact on the accuracy of the experiment. According to Fig. 6a and Fig. S3a, the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel are relatively stable, and the peaks are stronger and smooth, indicating that the MBAA-PAAM/Mg gel and MBAA-PAAM/Ca gel sensors are more sensitive and stable when used in long-term actual sports. Fig. 6b and Video S3 show the change of $\Delta R/R_0$ (%) of the MBAA-PAAM/Ca gel sensor during

wrist movement. It can be found that when the sensor is connected to the elbow joint, the degree of wrist bending can be identified. Obviously, the resistance change will increase when the wrist is bent, and $\Delta R/R_0$ (%) will increase as the bending angle increases, and when returning to the original position, the change of resistance will be completely reduced to its initial value. This result highlights the superiority of the MBAA-PAAM/Ca gel as a human motion detection device. Compared with the data in Fig. S3b, it can be seen that the $\Delta R/R_0$ (%) of the hydrogel sensor containing Ca^{2+} ion changes more drastically when the wrist moves from 0° to 90° , indicating that the prepared MBAA-PAAM/Ca gel sensor is more suitable for testing human joints. Due to the high stability and wide strain sensing range of the MBAA-PAAM/Ca gel, a series of tests were performed to reveal its application prospects. The hydrogel sensor was installed on a smooth platform and kept at a distance of 5 cm to record the change in sensor resistance as the hydrogel was exhaled. When the room temperature is $19\text{--}25^\circ\text{C}$ and the humidity is 30%–60%, the temperature of the exhaled gas is about 32.3°C , which is higher than the surface temperature of the gel [32]. As shown in Fig. 6c, when the MBAA-PAAM/Ca gel sensor is affected by the exhaled gas, the resistance decreases rapidly and then returns to

the initial value. It is worth noting that the signal strength also changes with the strength of the airflow and can be quickly restored to the initial state. In Fig. S3c, the MBAA-PAAM gel sensor obviously cannot be used to test the expiratory movement, because the exhalation will cause the sensor to have a double parameter change, namely a small temperature change and deformation. The temperature difference between the exhaled gas and the air will accelerate the ion migration in the hydrogel. In addition, ion migration is a process of thermal excitation. The directional migration of ions in the hydrogel needs to cross the barrier of the polymer chain. As the temperature increases, the ion mobility increases, and the partially bound ions dissociate or release, resulting in an increase in ion concentration. Eventually, the resistance of the hydrogel decreases with the increase of temperature. Secondly, the compressed strain on the surface of the hydrogel will be generated when the gas is blown out. This micro-strain will also increase the ion transport channel of the hydrogel and the efficiency of ion passage, resulting in a reduction in resistance. $E_{\text{MBAA-PAAM/Ca gel}}$ can be used to monitor small non-contact physiological signals from the human body. Sensitivity (S_p) is defined as the trajectory slope as shown in Fig. 6d [33]. Like most sensors, the sensitivity diagram consists of multiple re-

Figure 6 (a) $\Delta R/R_0$ of the prepared sensor under a pressure of 0.4 N. (b) Real-time signal of the wrist movement. (c) Real-time signal when the sensor is blown. (d) Sensitivity of the prepared MBAA-PAAM/Ca sensor under different tensions. (e) Sensitivity and work range of the four prepared sensors. (f) Image of the phone controlled by the conductive hydrogels.

gions. The sensitivity of the ionic gel was 10.690 MPa^{-1} when the applied pressure was lower than 1.2 kPa, 0.420 MPa^{-1} when the applied pressure was higher than 1.2 kPa. Fig. 6e compares the sensitivity and sensor working range of the MBAA-PAAM/Ca gel sensor and the other three kinds of hydrogel sensors. It can be seen that the performance of the MBAA-PAAM/Ca gel as a sensor is significantly better than that of the other three kinds of hydrogels.

As we all know, the manipulation of electronic products such as mobile phones works through the human body's current induction. Certain materials can become obstacles between human-computer interactions, so the skin covered by these materials cannot control the capacitive screen through electronic transfer. Inspired by this, we tested whether the hydrogel strain sensor can be applied to the control of electronic screens. Although it is not a function of the strain sensor, it is one of the important attributes of human-computer interactions. As shown in Fig. 6e and Video S4, we can use a hydrogel like "Apple Pencil" to touch the screen and control the phone without any obstacles. In addition, because of the soft and smooth surface of hydrogels, they can prevent the formation of scratches. Present research work demonstrated new clue for the design and preparation of new self-assembled nanocomposites [34–38] and hydrogel materials [39–43].

CONCLUSIONS

In short, the ion-crosslinked composite hydrogels with high elasticity and high sensitivity were successfully prepared through a simple and environmentally friendly "one-pot" method. The results of FI-IR proved that the strong chemical interaction between AAM and MBAA is beneficial to the construction of strong chemical bonds. In addition, the sensing performance of the composite hydrogel can be effectively adjusted to meet different application requirements after adding salts containing Al^{3+} , Ca^{2+} and Mg^{2+} . The MBAA-PAAM/Ca gel composite hydrogel can withstand a maximum strain of 1100% and a stress of 36.056 kPa and its fracture energy can reach 2.72 MJ m^{-2} , indicating that the MBAA-PAAM/Ca gel has a tough structure. In addition, the MBAA-PAAM/Ca gel composite hydrogel shows excellent sensing performance under external pressure, including a wide sensing range (100% strain, 320% resistance change), ultra-high sensitivity ($S_p = 10.690 \text{ MPa}^{-1}$), low voltage area detection ($\leq 120 \text{ kPa}$), and excellent stability and sensing function under multiple parameter changes. It is worth noting that this composite hydrogel can be applied to

traditional strain sensors and electronic pens in combination with screens. The MBAA-PAAM/Ca gel strain sensor has a wide sensing range, high sensitivity, and low detection limit, which demonstrate a bright future in high-performance wearable strain sensors.

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

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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基于离子交联复合水凝胶的易制备、高性能的可穿戴应变传感器

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摘要 可响应多种机械激励模式且具有较高灵敏度的柔性传感器在电子皮肤、健康监测等领域具有重要意义。而模仿皮肤的多信号响应,如应变和温度,仍然是一个重要的挑战。因此,本文设计了具有韧性与导电性的多功能离子交联水凝胶。通过将丙烯酰胺与N,N'-亚甲基双丙烯酰胺、过硫酸铵交联,可制备出具有高力学强度特性的化学凝胶,交联时加入Ca²⁺, Mg²⁺, Al³⁺等盐类物质赋予水凝胶双层网络,使这种离子型双网络水凝胶具有优良的导电特性。这种双层网络结构使离子水凝胶表现出优异的力学性能。此外,含有Ca²⁺离子的复合水凝胶最大拉伸可以达到1100%,并表现出超高的灵敏度($S_p = 10.690 \text{ MPa}^{-1}$)。所获得的水凝胶能够实现可穿戴应力传感器的制备并跟踪监测人体运动,有希望进一步拓展到人机交互以及智能人体健康检测等领域。