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Ultra-stretchable hydrogel thermocouples for intelligent wearables

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ABSTRACT **Stretchable temperature sensors are necessary to enable tactile interaction and thermoregulation in the human body and soft robots. These sensors should be conformably adhered to a deformable surface and maintain temperature perception accuracy when stretched. However, current mainstream stretchable temperature sensors based on thermistors suffer from inherently unstable sensing during stretching due to the mutual interference of resistance changes caused by temperature and mechanical deformations. Herein, we propose an ultra-stretchable hydrogel thermocouple that provides unaltered temperature sensing upon stretching. The ultra-stretchability of this thermocouple is achieved by constructing thermogalvanic hydrogels with dynamic crosslinked double networks. By connecting P-type and N-type thermogalvanic hydrogels, the thermocouple exhibits a high equivalent Seebeck coefficient of 1.93 mV K^{-1} and a stable sensitivity even under a 100% tensile strain. The advantage of this ultra-stretchable thermocouple is demonstrated in a smart glove prototype, which enables haptic feedback. Our work provides a new strategy for stretchable temperature sensors and may promote the development of intelligent wearables.**

Keywords: ultra-stretchable thermocouple, thermogalvanic hydrogels, strain-insensitive perception, intelligent wearables

INTRODUCTION

Temperature perception is crucial for all soft tissues, from soft machines to the human skin, as it not only facilitates thermo-haptic interactions but is also a key element for intelligent thermoregulation [1–4]. Because soft tissues typically perform motions with inevitable deformations, thermometry devices should gain comparable stretchability and maintain measurement accuracy during stretching. These stretchable temperature sensing elements have great potential in artificial skin [5–9], soft robots [10–13], personal thermoregulation [2,14], and thermo-haptic feedback [15,16]. Currently, thermistors and thermocouples are the two most widely used devices in measuring temperatures in industry and academia. Some stretchable thermistors have been implemented either by employing ionic conductors or compounding electronic conductors with elastomers [17–21]. However, they suffer from unstable accuracy due to the changes in the internal resistance when stretched. This intrinsic drawback makes them incapable of resisting tensile disturbances. Although the temperature measurement accuracy can be partially improved through post-processing techniques and structural engineering [21–26], the data processing and manufacturing barriers are cumbersome. Thus, thermistors cannot easily meet the large-scale proliferation requirements of consumer electronics.

By contrast, thermocouples based on the Seebeck effect can generate a voltage that is linear with the temperature difference. The temperature measurement properties are not related to the internal resistance, indicating that stretching will not theoretically interfere with the temperature measurement. However, commercial thermocouples are generally made of solid thermoelectric materials, which are mostly electronic conductors and cannot be stretched due to their inherent brittleness. As an alternative, ionic hydrogel conductors with the thermogalvanic effect are promising for stretchable temperature sensing devices, and they can possess a high Seebeck coefficient and excellent tensile properties [27–33]. Therefore, intrinsically stretchable thermocouples with strain-insensitive sensing accuracy can be realized by integrating thermogalvanic hydrogels with different polarities.

In this work, we proposed an ultra-stretchable thermocouple based on thermogalvanic hydrogels, which were fabricated by introducing a redox couple into a polyacrylamide/chitosan (PAM/CS) double-network hydrogel. The enhanced mechanical properties of the hydrogels can be attributed to ionic coordination and interchain interactions. The abundant free ions in the thermogalvanic hydrogels endow them with high ionic conductivity. The thermocouple was assembled by connecting a P-type and an N-type thermogalvanic hydrogel with conductive grease to form a measurement junction at one end. The hydrogels were separated at the other end as a reference junction to measure the output voltage. These thermocouples exhibited excellent stretchability and temperature sensitivity and well-maintained temperature measurement accuracy even during stretching. Furthermore, we demonstrated a virtual reality (VR) glove prototype that utilizes thermal-driven artificial muscle for kinesthetic haptic feedback. The ultra-stretchable hydrogel

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thermocouple was successfully employed for accurate temperature sensing under various mechanical deformations, laying a solid foundation for the realization of virtual haptics. Through the real-time temperature feedback of the ultra-stretchable thermocouple, our VR glove prototype can precisely control the thermally driven actuator to give users a realistic tactile experience. This work paves the way for the design of future stretchable temperature sensors and demonstrates the promise of ultra-stretchable hydrogel thermocouples in VR and intelligent wearables.

EXPERIMENTAL SECTION

Materials

Acrylamide (AM) and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). *N*,*N*′-methylenebis (acrylamide) (MBAA), acrylic acid (AA), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), ethanol, methanol, benzophenone, calcium acetate ($Ca(Ac)_2$), α-ketoglutaric acid (α-KGA), potassium ferricyanide ($K_3Fe(CN)_6$), potassium ferrocyanide ($K_4Fe(CN)_6$), iron chloride ($FeCl_3$), and iron(II) chloride ($FeCl_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Short-chain CS (degree of deacetylation > 90%, viscosity 45 mPa s for 1% (*w*/*v*) solution) was purchased from Shandong Jinhu Company (China). Ecoflex 00-20 (Smooth-On) was purchased from Beijing Angelcrete Art Landscape Technology Co., Ltd. (China). The graphite conductive grease was purchased from JUNE Special Lubrication Technology (Japan). All the chemicals were used without further purification.

Preparation of the thermogalvanic hydrogel

The thermogalvanic hydrogel was prepared by the following steps: First, 1.7770 g of AM, 250 mg of short-chain CS, 2.57 mg of MBAA, and 56.02 mg of Irgacure 2959 were added into 10 mL of deionized water to obtain a pre-gel solution. After complete degassing, the solution was poured into a mold and irradiated with ultraviolet light (365 nm) with a power density of ~4 mW cm^{-2} for 4 h under the protection of nitrogen, obtaining a PAM/CS composite hydrogel. Then, the composite hydrogel was immersed in a 2 mol L^{-1} Na_2SO_4 solution for 10 min to convert it into a PAM/CS double-network hydrogel *via* ionic coordination. Finally, the double-network hydrogel was soaked in $K_4Fe(CN)_6/K_3Fe(CN)_6$/NaCl or $FeCl_3/FeCl_2$/NaCl aqueous electrolytes for 2 h. The concentrations of the redox couple and NaCl in the electrolyte solution were 0.2 and 3.8 mol L^{-1}, respectively. The hydrogel containing $K_4Fe(CN)_6/K_3Fe(CN)_6$ is a P-type hydrogel, whereas the other one containing $FeCl_3/FeCl_2$ is an N-type hydrogel, according to a previous definition [34].

Preparation of the ultra-stretchable thermocouple

Fig. S1 illustrates the fabrication process of the ultra-stretchable thermocouple. First, an Ecoflex film (~100-μm thick) was treated with a 10 wt.% benzophenone alcohol solution for 2 min to absorb benzophenone that can graft monomers to the films under ultraviolet radiation. Then, 10 mL completely degassed pre-gel solution was poured into the mold on the Ecoflex film. Subsequently, two parallel PAM/CS composite hydrogels adhered to the Ecoflex film were obtained *via* ultraviolet (UV) irradiation (365 nm UV light with a power density of ~4 mW cm^{-2}) under nitrogen protection for 4 h. Thereafter, the two PAM/CS composite hydrogels were soaked in 2 mol L^{-1} Na_2SO_4 for 10 min and respectively drip-coated with $K_4Fe(CN)_6/K_3Fe(CN)_6$/NaCl and $FeCl_3/FeCl_2$/NaCl aqueous electrolytes for 2 h. Thus, P-type and N-type thermogalvanic hydrogels adhering to Ecoflex were obtained. Finally, the P-type and N-type hydrogels were connected with conductive grease to form a thermocouple and encapsulated with the Ecoflex film *via in-situ* spin coating.

Preparation of the thermohardening artificial muscle

The artificial muscle used for the kinesthetic haptic feedback demonstration was prepared by the following steps: First, 10 mL pre-gel solution was prepared with 2.1618 g of AA, 250 mg of short-chain CS, 6.16 mg of MBAA, and 29.22 mg of α-KGA. The mixture was heated at 80°C and stirred to form a transparent precursor solution. Then, the solution was placed in a vacuum kettle for 30 min to remove oxygen. Thereafter, the oxygen-free solution was poured into a mold and irradiated with ultraviolet light (365 nm) with a power density of ~4 mW cm^{-2} for 6 h under the protection of nitrogen, obtaining a polyacrylic acid/CS (PAA/CS) hydrogel. Finally, a thermal stiffening hydrogel was prepared by soaking the PAA/CS hydrogel in a 0.2 mol L^{-1} $Ca(Ac)_2$ solution for 7 d.

Characterizations and measurements

The mechanical property of the thermogalvanic hydrogel was performed on an electronic universal tensile testing machine (UTM2503). The temperature sensing performance of the thermocouple was characterized by measuring the output voltage under a certain temperature difference. The temperature difference was created by a Peltier element and ceramic heater, whereas the output voltage was measured by a Keithley 2000 meter. The temperature sensing performance during the stretching process was tested on an electric linear slide table.

RESULTS AND DISCUSSION

Fig. 1 illustrates the structure and working mechanism of the ultra-stretchable thermocouple. Different from the thermocouples based on electronic conductors, the main components of our ultra-stretchable thermocouple are two strips of thermogalvanic hydrogel adhered to a stretchable Ecoflex elastomer substrate. The two thermogalvanic hydrogels contain Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couples, which are named N-type and P-type hydrogels, respectively. The P-type and N-type hydrogels were connected using conductive grease at one end to form the measurement junction, whereas the other end served as a reference junction. When there is a temperature gradient (ΔT) across the ultra-stretchable thermocouple, the Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple in the hydrogels generated an output voltage $V = (S_p - S_n)\Delta T$ through the thermogalvanic effect, where S_p and S_n represent the P-type and N-type ionic Seebeck coefficients, respectively. The temperature can then be read by measuring the output voltage of the ultra-stretchable thermocouple. As the thermogalvanic effect is mainly dominated by the solvent-structure entropy difference and the concentration ratio difference between redox couples [34–36], the stretching of the thermocouple does not affect the ionic Seebeck coefficient. Thus, the tensile deformation does not interfere with the sensing performance of the ultra-stretchable thermocouple.

To improve the stretchability of the thermocouple, the mechanical properties of thermogalvanic hydrogels can be tuned

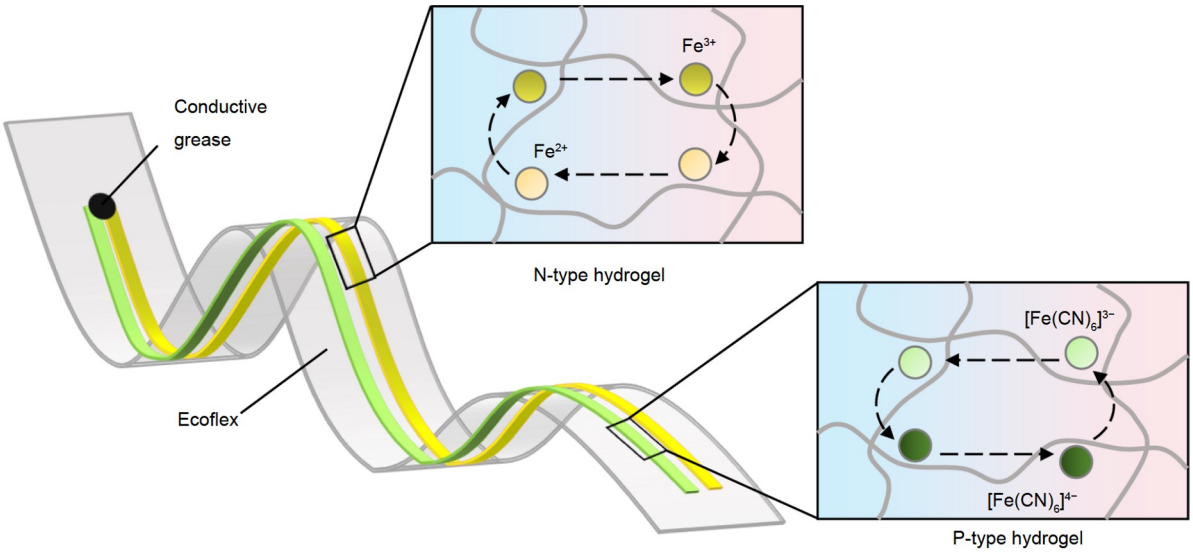

Figure 1 Schematic of the ultra-stretchable thermocouple based on thermogalvanic hydrogels. The N-type and P-type hydrogels are bonded to a stretchable elastic substrate (Ecoflex) and connected at one side by conductive grease. The magnified insets illustrate the working mechanism of the hydrogel thermocouple. At a certain temperature difference, the N-type and P-type hydrogels generate opposite voltages through the thermogalvanic effect, converting the temperature signal into a voltage signal.

during fabrication. We converted the PAM/CS composite hydrogels into dynamic crosslinked thermogalvanic hydrogels with excellent mechanical properties. As shown in Fig. 2a, the short CS chains uniformly penetrate the PAM network due to hydrogen bonding interactions and form a physically crosslinked network through a continuous immersion in the Na_2SO_4 solution and NaCl/redox couple solution. After treatment with the 2 mol L^{-1} Na_2SO_4 solution, the CS chains generated an ionic-crosslinked network *via* the *N*-glucosamine-anion coordination interaction. Subsequently, through the secondary treatment of the NaCl/redox couple solution, the combination of the salting-out effect, shielded electrostatic repulsion and enhanced interchain hydrophobic interactions facilitated the formation of the intermolecular aggregation of CS chains [37], which became the connection points of the chain entanglement network. The hydrogen bonding, ionic coordination, and chain entanglement of the CS chains are all dynamic crosslinking sites, which can play a reversible energy dissipation role during the stretching process of the hydrogel and synergistically toughen the double-network hydrogel with the soft PAM network (Fig. 2a). The hydrogels for the ultra-stretchable thermocouple can be designed into arbitrary shapes due to the facile method of bonding elastomers with hydrogels (Fig. 2b). The obtained P-type and N-type thermogalvanic hydrogels exhibit improved mechanical properties after being treated with the Na_2SO_4 solution and NaCl/redox couple solutions (Fig. 2c). The P-type and N-type hydrogels possess excellent mechanical deformability and durability (Fig. S2). Furthermore, the abundant free Na^+ and Cl^- in the thermogalvanic hydrogels not only improved the mechanical properties but also provided a high ionic conductivity. Fig. 2d shows that as the NaCl concentration increases from 1 to 3 mol L^{-1}, the ionic conductivity of the P-type and N-type hydrogels increases accordingly. However, further increasing the NaCl concentration did not continue to promote the ionic conductivity, because the intermolecular aggregation of the chains would make the hydrogel denser and hinder the diffusion of ions.

The P-type and N-type hydrogels can be bonded to an ultrathin elastomer to realize a thin-film thermocouple with excellent flexibility and stretchability (Fig. 3a). To characterize the temperature sensing performance of the ultra-stretchable thermocouple, we first demonstrated the response of the ultra-stretchable thermocouple to temperature in the non-stretched state. The output voltage was measured under different temperature gradients (Fig. S3a). As shown in Fig. 3b, the equivalent Seebeck coefficients of the N-type and P-type thermogalvanic hydrogels are −0.73 and 1.29 mV K^{-1}, respectively, which is consistent with previous reports on the thermogalvanic effect [38–41]. As the ultra-stretchable thermocouple is composed of P-type and N-type hydrogels in series, it exhibits a high Seebeck coefficient of 1.93 mV K^{-1}, which is much higher than the microvolt-level temperature sensitivity of thermocouples based on semiconductors [42,43]. With the reference junction fixed at 25°C, the output voltage of an ultra-stretchable thermocouple caused by the temperature gradient was monitored in real-time (Fig. 3c). The output voltage linearly increased as the temperature gradient increased from 0 to 20 K in steps, indicating the excellent response of the thermocouple to temperature. In addition, the thermocouple can still work well, even if the temperature gradient increases from 0 to 80 K (Fig. S4), which shows its wide temperature sensing range.

To further illustrate that stretching does not affect the temperature measurement, we characterized the temperature sensing performance of the hydrogel thermocouple under stretching on an electric linear slide table (Fig. S3b). When there was no temperature gradient, the P-type and N-type hydrogels exhibited a tiny initial voltage, which did not change much even if the tensile strain increased from 0% to 100% (Fig. S5a). During the periodic stretching-releasing process, their initial voltages periodically fluctuated with small variations (Fig. S5b). This result reveals the effect of stretching on the initial voltage of the ultra-stretchable thermocouple is almost negligible. The equivalent

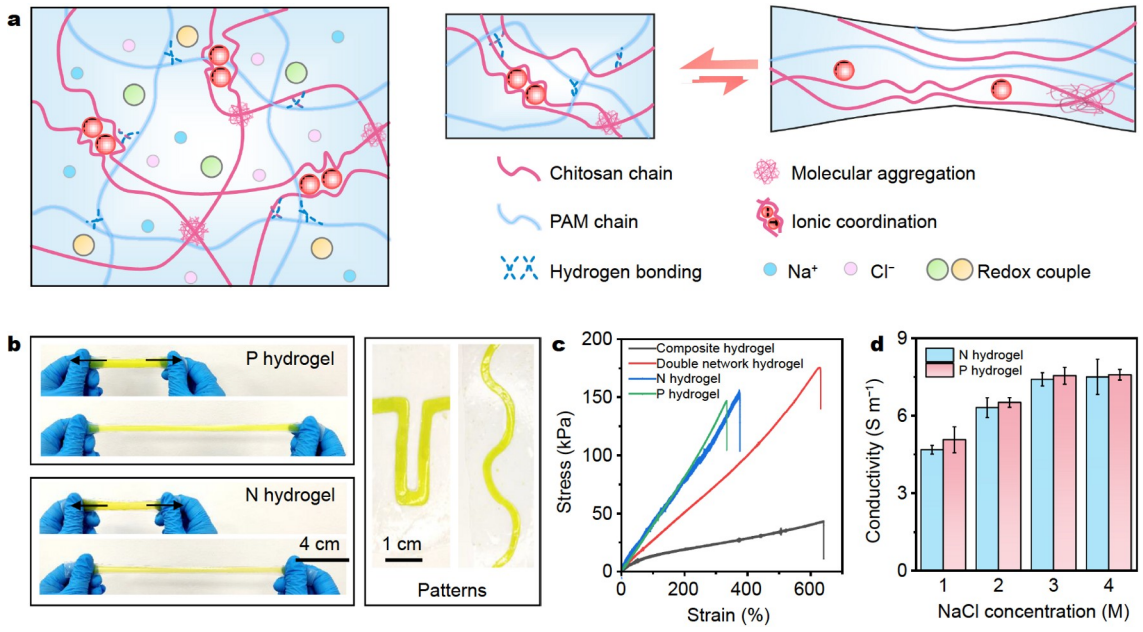

Figure 2 Design and properties of the thermogalvanic hydrogels. (a) PAM/CS double-network hydrogel with a reversible dynamic crosslinking; (b) photograph of the P-type and N-type hydrogels under tensile deformation and pattern design; (c) tensile stress-strain curves of the PAM/CS composite hydrogel, PAM/CS double-network hydrogel, P-type hydrogel, and N-type hydrogel; (d) conductivity of the hydrogels with different NaCl concentrations.

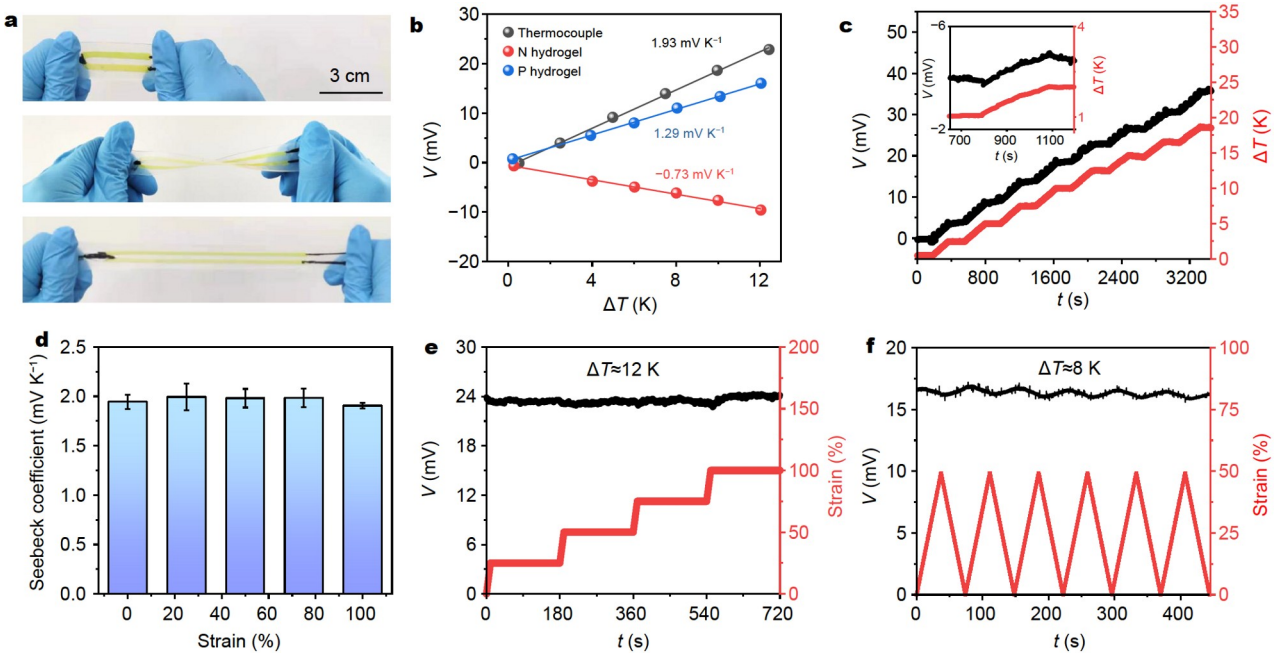

Figure 3 Temperature sensing performance of the ultra-stretchable thermocouple. (a) Photographs of an ultra-stretchable thermocouple in original, twisting, and stretching states. (b) Equivalent Seebeck coefficient fitting of the P-type and N-type thermogalvanic hydrogels and ultra-stretchable thermocouple. (c) The output voltage of a thermocouple with an increasing temperature gradient. The inset shows the response voltage of the thermocouple to a temperature gradient of 1 K. (d) Equivalent Seebeck coefficients of a thermocouple under different tensile strains. Statistical analysis is based on three similar samples. (e) The output voltage of a thermocouple varies with tensile strain when the temperature gradient is 12 K. (f) The output voltage of a thermocouple under periodic tensile strain when the temperature gradient is fixed at 8 K.

Seebeck coefficient almost kept constant when the tensile strain was increased from 0% to 100% (Fig. 3d). Meanwhile, the output voltage of the ultra-stretchable thermocouple could be well maintained during stretching from 0% to 100% under a temperature gradient of 12 K (Fig. 3e). The stable voltage output indicates that the stretched state of the thermocouple does not affect its temperature sensing. Furthermore, the output voltage of the ultra-stretchable thermocouple remained stable under a cyclic tensile strain when the temperature gradient was 8 K (Fig. 3f), further confirming that even a dynamic strain does not

interfere with temperature sensing. The small periodic fluctuations of the output voltage may be caused by temperature fluctuations due to stretching. Compared with the reported thermocouples, our hydrogel thermocouples combine high temperature sensitivity and excellent strain-insensitive performance (Table S1) [33,42,44–49].

Considering the excellent temperature sensing performance and insensitivity to tensile strain, our ultra-stretchable thermocouples are ideal for measuring the temperature of stretchable electronics. Thermally driven actuators are devices that convert thermal energy into mechanical energy and enable important applications in artificial muscles, soft robotics, and haptic feedback [16,50,51]. They achieve actuation by changing their stiffness through a temperature-induced phase transition. To ensure the success of the actuators, a more precise and controllable actuation process must have temperature feedback from sensors. Here, we proposed a VR glove prototype, which is driven by a thermal actuator integrated with an ultra-stretchable thermocouple to enable kinesthetic haptic feedback in VR. As shown in Fig. 4a, the thermally driven actuator is attached to the back of the VR glove with one side fixed on the wrist and the other side connected to the finger using a flexible yarn. Its main components include an ultra-stretchable thermocouple, a thermally driven artificial muscle, and a stretchable heater. When a tester tries to grasp an object in the virtual world, the VR glove restricts finger bending by controlling the thermally driven actuator to generate kinesthetic haptic feedback. The detailed process of the kinesthetic haptic feedback is shown in Fig. S6. Based on the modulus of the grasped object in the virtual world, the VR glove controls the stretchable heater to heat the thermally driven artificial muscle through the temperature feedback by the ultra-stretchable thermocouple. As the stiffness of the artificial muscle is temperature dependent, different damping resistances can be applied to the finger motion by regulating the temperature, giving the user an immersive experience of grasping objects with different moduli.

To achieve the above goal, a thermally driven artificial muscle and stretchable heater need to be prepared first. Drawing on the reported thermohardening hydrogels [52], we fabricated thermally driven artificial muscles with excellent stretchability by introducing CS into a PAA hydrogel as a second network. Fig. 4b demonstrates that the stiffness of thermally driven artificial muscles increases with the temperature, resulting in a decrease in stretchability. The decreased transparency of the hydrogel in Fig. 4c is attributed to the phase separation caused by the enhanced interaction between polymer chains. In addition, the stretchable heater was obtained by embedding a serpentine nichrome wire into an Ecoflex elastomer (Fig. S7a). As the input voltage increased from 6 to 21 V, the equilibrium temperature increased from 29 to 70°C (Fig. S7b), which is sufficient for the regulation of artificial muscle stiffness.

We selected three elastic balls with different moduli as grasping objects to demonstrate the kinesthetic feedback function of the VR glove prototype. To quantitatively describe the tactile sensations during grasping, the bending angle of the finger and the grasping force on the fingertip were measured by a flex sensor and a press sensor, respectively (Fig. S8). In reality, the free motion of the human finger does not generate a grasping force (first column of Fig. 4d). This scenario corresponds to the feeling that the fingers are not touching any virtual objects in the virtual world. In fact, because the thermally driven actuators remain soft at room temperature (24°C), it does not constrain finger movements, and the pressure sensor does not detect any gripping force (first column of Fig. 4e). In the real world, when the glove grips an elastic ball, the bending angle of the fingers decreases with an increasing modulus at the same

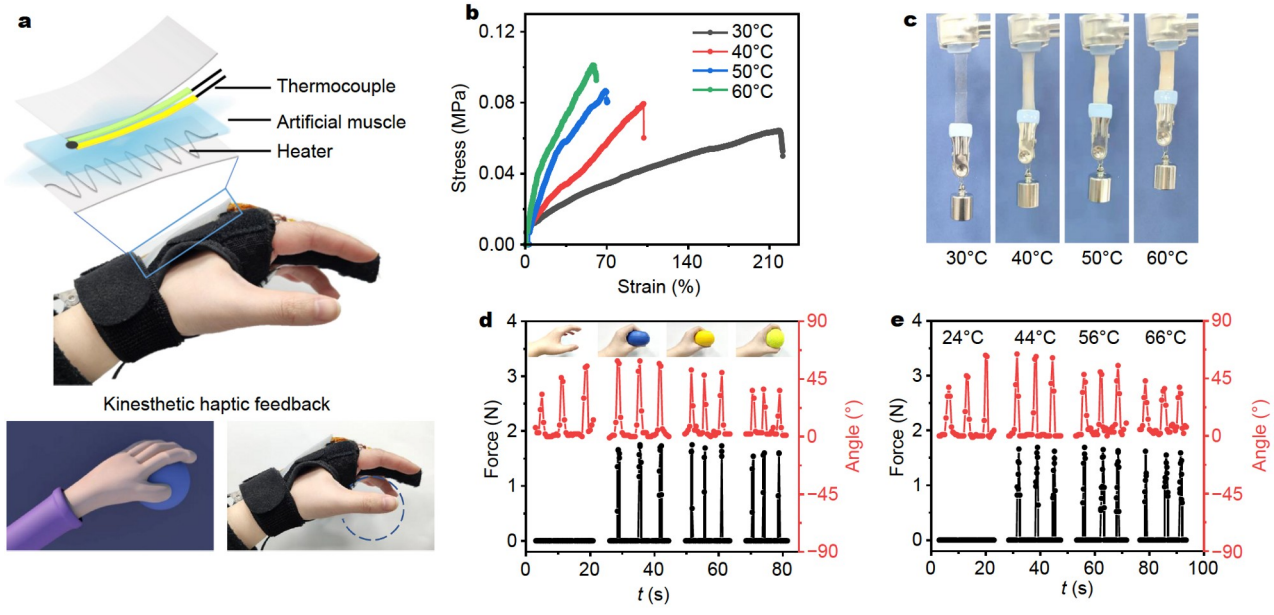

Figure 4 Demonstration of the ultra-stretchable thermocouple applied in a kinesthetic haptic feedback system. (a) Illustration of a VR glove prototype based on an ultra-stretchable thermocouple and thermally driven actuator. The VR glove produces kinesthetic haptic feedback by restricting finger motion. (b) Tensile test of the thermally driven artificial muscles at different temperatures. (c) Photographs of thermally driven artificial muscles under 200 g load at different temperatures. (d) Tactile sensations in reality. The first column shows the free bending of the finger, while the other three columns show the bending angles of the finger when grasping elastic balls of different moduli with the same grasping force. (e) Kinesthetic haptic feedback from the VR glove prototype. The VR glove exerts different tactile feedback on the fingers by controlling the temperature at 24, 44, 56, and 66°C.

grasping force (Fig. 4d). To mimic these tactile sensations, the thermally driven artificial muscle was heated and maintained at 44, 56, and 66°C through a feedback regulation by an ultra-stretchable thermocouple (Fig. S9). The thermally driven actuator produced different resistances to restrict the motion of the finger at the three temperatures. As shown in Fig. 4e, the VR glove almost restores the tactile sensations of grasping elastic balls with three different moduli in reality. The bending angle of the finger and the grasping force are nearly the same as those in Fig. 4e. These results confirm that our VR glove prototype can precisely control the kinesthetic feedback through the temperature feedback of the ultra-stretchable thermocouple. Aside from giving testers the feeling of grasping objects, it can also further mimic the mechanical properties of objects, creating the most realistic and immersive tactile experience.

CONCLUSIONS

In summary, we designed and realized an ultra-stretchable thermocouple based on thermogalvanic hydrogels. The excellent tensile properties of the thermocouple were achieved by combining ionic coordination and interchain interactions to construct dynamically crosslinked double-network hydrogels. Due to the thermogalvanic effect, the ultra-stretchable thermocouples exhibit high temperature sensitivity and unaltered sensing performance during stretching. As a vivid demonstration, a VR glove prototype was presented and driven by a thermally responsive actuator, which was integrated with an ultra-stretchable thermocouple for kinesthetic haptic feedback. Such a VR glove prototype can give users a realistic and immersive tactile experience. The presented stretchable hydrogel thermocouples may also provide an ideal solution to address the critical issues of temperature sensing with mechanical deformations and to advance the progress of next-generation haptic feedback technologies and VR.

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

Supplementary information Supporting data are available in the online version of the paper.

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超拉伸水凝胶热电偶

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摘要 可拉伸温度传感对实现人机触觉交互和温度调节至关重要，这些传感元件需要贴合特异性表面，且在拉伸条件下保持温度感知的精度．现有可拉伸温度传感器由于温度和形变引起电阻变化的相互干扰，在拉伸过程中存在固有的传感不稳定问题．本文提出了一种超可拉伸水凝胶热电偶，通过构建具有动态交联双网络的热电水凝胶，实现水凝胶热电偶的超拉伸性．通过设计的P型和N型热电水凝胶，构建热电偶单元．热电偶表现出1.93 mV K^{-1}的高塞贝克系数，即使在100%的拉伸应变下，灵敏度依然保持稳定．本文的研究结果为可拉伸温度传感器提供了一种新的策略，并有望广泛应用于智能可穿戴设备．

