

Utilizing Multilayer Design of Organic-Inorganic Hybrids to Enhance Wearable Strain Sensor in Humid Environment

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Electronic Supplementary Information

Abstract Flexible strain wearable sensors have attracted considerable attention due to their advantages of low cost, lightweight, high sensitivity and good flexibility. However, the strain sensors are easy to be damaged in an extreme humidity environment or by the wearer's sweat in the process of use, resulting in detection disorder or even a short circuit. Furthermore, preparation of sensors with stable properties under extreme environments is one of the most important research directions. To fill this gap, a flexible sensor was prepared by using polyurethane and carbon nanotubes, then modified by polydopamine and 1*H*,1*H*,2*H*,2*H*-perfluorodecane-mercaptan. A typical tunnel model was used to explain the working mechanism of the sensor, the sensitivity of the sensor is also explained and evaluated by the tunneling theory. The results show that the sensor has good sensitivity (the sensor has a stable sensing signal output under a strain range from 2% to 300%) and stability over 8500 cycles. At the same time, the sensor has good superhydrophobicity, the water contact angle reaches 152°, and it is still stable in a humid environment. Moreover, this sensor shows excellent performance in monitoring human joint motion (such as finger, elbow, wrist and knee) and physiological signals (such as speaking and drinking). This work provides an effective design method for the sensor which can be applied in a high humidity environment.

Keywords Wearable strain sensor; Polyurethane; Carbon nanotubes; Superhydrophobicity

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INTRODUCTION

Wearable strain sensors have been widely applied in health monitoring, medical tests and data analysis.^[1–6] However, the strain range of metal and semiconductor-based sensors is small, leading to poor wearable properties.^[7,8] Therefore, the strain sensor needs to have a large strain range to meet its application, which can be solved by adding conductive filler into flexible polymer materials.^[9–12] Currently, the conductive filler includes carbon nanomaterials (such as reduced graphene oxide (rGO),^[4,13,14] carbon nanotubes CNT^[15–23] and Mxenes^[24]) metal materials (for example, silver nanowires^[25]) and metallic oxide (like ZnO).^[26] Polymer materials generally include polyurethane (PU),^[10,13,15,21,27] polydimethylsiloxane,^[14,28,29] ecoflex[®],^[30] natural rubber,^[20,31,32] cellulose,^[33] polyamide,^[34,35] etc.

At present, many strain sensors have been reported to be

prepared by adding conductive fillers to polymers. Zhan *et al.* obtained a kind of highly stretchable thermoplastic PU pads by electrospinning, which were then modified by *in situ* polymerization and ultrasonic treatment with polyaniline nanoparticles and graphene oxide, and assembled into strain sensors.^[36] Seyedin *et al.* used scalable wet spinning technology to produce Ti₃C₂T_x MXene/PU composite fiber, which can be used as a strain sensor with both excellent sensitivity and high tensile properties.^[37] Although the sensors reported above have a larger strain range than the conventional sensor, in the process of use, those strain sensors are easily affected by extreme humidity and the wearer's sweat, which may lead to their properties being unstable, and even losing the ability to convert strain signals.^[38] To solve this problem, it is an effective method to construct superhydrophobic structures on the sensor surface.

In this work, we propose a simple method for preparing some flexible strain sensors that can be used in extremely humid environments. Firstly, CNT was anchored on the surface of PU electrospinning film with the assistance of ultrasonic. Then, it was modified by polydopamine (PDA) and

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1H,1H,2H,2H-perfluorodecane-mercaptan (PFDM). In this process, PDA was introduced as an insulating layer to improve the interface interaction between the film and CNT,^[38] PFDM has low surface energy, so it was grafted onto PDA to provide superhydrophobicity. The results showed that the superhydrophobic sensor has a water contact angle (WCA) of 152°, and has strong corrosion resistance (it can retain hydrophobicity in strong acid and alkali conditions). Regarding the sensing properties, the sensor is stable and sensitive (the sensing signal is stable in 8500 cycles, and the GF is about 3.43 at 0%–25% strain). In addition, as a wearable sensor, it showed excellent performance in monitoring the motion of the joints, such as fingers, elbows, wrists, and knees, as well as physiological signals, such as vocalization and drinking.

EXPERIMENTAL

Materials and Chemicals

CNT, PFDM and dopamine hydrochloride (DA-HCl, 98%) were supplied by Aladdin Reagent (Shanghai) Co., LTD., China. *N,N*-dimethylformamide (DMF), acetone, Tris (hydroxymethyl), aminomethane hydrochloride Tris HCl (99%), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Sinopharm Chemical Reagents Co., LTD. PU (Estane 2103-90AE) was obtained by Lubrizol Inc., USA.

Preparation of PU Film

PU particles were dissolved in a mixed solvent ($V_{\text{DMF}}/V_{\text{Acetone}}=3/2$) to prepare the spinning solution. Then the spinning solution was loaded into a 10 mL syringe. PU film was obtained by electrospinning. The working parameters of electrospinning follow the previous research results of our laboratory.^[4]

Preparation of PU-CNT

The CNT was dispersed in a solution of ethanol and ultrapure water ($V/V=7/3$) to prepare a 1 mg/mL solution assisted by ultrasonic (20 kHz, 142.5 W), CNT was completely dispersed in the ethanol and water solution for half an hour. PU films (5 cm × 2 cm × 120 μm) were placed into the CNT suspension, and ultrasonic treatment (20 kHz, 380 W) was carried out for 20 min. The obtained film was labeled as PU-CNT film (label it as PU-CNT). The treated film was taken out and the remaining CNT particles on the surface were washed by ultrapure water. The film was laid on a polytetrafluoroethylene (PTFE) plate and dried in an air-blast drying oven at 50 °C for 30 min.

Preparation of PU-CNT-PDA

A Tris-HCl buffer solution with a pH of 8.5 was prepared with Tris-HCl (7.88 g/L) and Tris (121.14 g/L) solutions, quickly weighing a certain amount of dopamine (dopamine is easily oxidized when exposed to light in the air). The buffer solution was used as the solvent to prepare a 2 mg/mL dopamine solution. The PU-CNT-PDA film was obtained by immersing PU-CNT in the above-configured dopamine solution (label it as PU-CNT-PDA), after processing, the film was washed with ultrapure water to wipe off undeposited dopamine. Finally, the film was also laid on the PTFE plate and dried in an air-blast drying oven at 50 °C for 30 min.

Preparation of PU-CNT-PDA-PFDM

PU-CNT-PDA was placed in a hydrothermal reactor

supplemented with 20 μL of PFDM. The autoclave was heated to 120 °C, and then the reactor was placed in the autoclave to react for a while at 120 °C to ensure that the PFDM vapor can fully contact the surface of the PU-CNT-PDA. Finally, PU-CNT-PDA-PFDM film (label it as PU-CNT-PDA-PFDM) was obtained. It should be emphasized that, in addition to the experiment of exploring the effects of PDA and PFDM treatment time on the WCA of film, the dopamine polymerization time and fluorination time of other films used in the test were 6 h and 12 h, respectively.

Characterization of Sample Properties

Scanning electron microscopy (SEM) was used to observe the surface morphology of PU film and modified conductive film at different stages. Fourier transform infrared spectroscopy (FTIR) was used to determine the absorption bands of the films at different modification stages. The resolution of the test was set as 4 cm⁻¹, in scan range of 500–4000 cm⁻¹, and the attenuated total reflection (ATR) mode was adopted. The graphitization degree of CNT was determined by Raman spectroscopy with a 532 nm laser, 5% intensity, and 900 Gr/mm grating. The crystal structures of the films at different stages of modification were analyzed using X-ray diffraction (XRD, SmartLab, Rigaku), which was performed using Cu Kα radiation with 2θ values of 10°–80° and a scan speed of 0.05 (°)·min⁻¹. X-ray photoelectron spectrometer (XPS) was used for the test, the operating voltage was 12 kV, the scanning range was 0–1200 eV, and the fine spectrum of C, N, O, F and S elements was scanned. The mechanical properties of the materials were tested by a universal tensile testing machine (Intersilon). Five-point random sampling was conducted on the samples by an electronic thickness meter to obtain the average thickness. The tensile mode was selected to complete the test, and the test rate was set at 20 mm·min⁻¹. The tensile strength, Young's modulus and elongation at break of each sample were measured for 5 times and averaged. The WCA of each sample was determined by a Lux contact angle analyzer (3 μL/drop). The WCA was measured at three different points on the positive and negative sides of each sample. Thermogravimetric analysis (TG) was performed on the materials, and the test temperature was set as 20–800 °C with the heating rate of 10 °C·min⁻¹. The test was carried out in a nitrogen atmosphere with an airflow rate of 20 mL·min⁻¹.

Measurement of Sensing Properties

A rectangular PU-CNT-PDA-PFDM film with a thickness of about 160 μm was selected. Copper strips were connected at both ends of the film, the sample was installed on the universal material testing machine (Intersilon), and the positive and negative electrodes of the electrochemical workstation were respectively connected to the copper strips on the film with crocodile wire. The time-current test mode was selected, the voltage was set at 10 V, the collection interval was 0.1 s, and the frequency was set at 10 Hz. The 100 cycles of tests were carried out under the conditions of 2%, 20%, 50%, 100% and 300% strain, respectively, and the 10 cycles of them were captured and plotted. Ohm's law $R=U/I$ was used to calculate the instantaneous resistance of the film, and the responsivity of the sensor was defined as $\Delta R/R_0$ to describe the relationship between the sensor properties and the applied tension (ΔR is the difference between the real-time resistance and the initial

resistance R_0). At the same time, PU-CNT-PDA-PFDM films were connected to the fingers, elbows, wrists, knees or throat, and the electrical current changes caused by joint motion or physiological signals were recorded via an electrochemical workstation.

RESULTS AND DISCUSSION

Preparation and Characterization of Superhydrophobic Flexible Strain Sensor

Fig. 1 shows the design idea of the superhydrophobic flexible strain sensor in this work. Figs. 2(a)–2(d) are the SEM images of PU film, PU-CNT, PU-CNT-PDA and PU-CNT-PDA-PFDM and the corresponding WCA, respectively. Firstly, PU film is prepared by electrospinning (Fig. 2a). Secondly, the PU is immersed in the CNT dispersion, and with the help of ultrasonic, the CNT is anchored on the surface of the PU fiber (Fig. 2b). Then, PU-CNT is immersed in a dopamine solution with a pH of 8.5. Dopamine polymerization occur in an alkaline environment, and PDA formed, PDA is deposited on the surface of the PU-CNT (Fig. 2c). Finally, PU-CNT-PDA and PFDM are put into the reactor, the fluorination reaction occur under high temperature and pressure, and the PU-CNT-PDA-PFDM is obtained (Fig. 2d). In Fig. 2(a), the surface of the PU fiber looks smooth, but the whole PU film is rough and shows hydrophobicity with a WCA of 120° . In the dispersed medium (such as water and ethanol solution), CNT can hit the fiber surface under ultrasonic. In this process, CNT can interact with the fibers, and the PU fibers may soften or even partially melt, so the CNT is tightly anchored to the fiber surface.^[39,40] In addition, the roughness of the surface is further improved, so the WCA increases to about 136° , as shown in Fig. 2(b). PDA deposited on the surface of PU-CNT (Fig. 2c) can not only form an insulating layer but also be regarded as an anchoring platform, which can trigger a series of secondary reactions.^[41] Because the PDA contains more hydrophilic groups, the WCA value of PU-CNT-PDA decreases to 110° . In Fig. 2(d), after fluoride treatment, the surface morphology of PU-CNT-PDA-PFDM shows no obvious change compared with PU-CNT-PDA. Furthermore, due to the PFDM's low surface

energy, the final WCA value of PU-CNT-PDA-PFDM can reach about 152° . The EDS mapping results of the corresponding elements on the PU-CNT-PDA-PFDM membrane (Figs. 2e–2j) prove that C, N, O, S and F are uniformly distributed on the fiber.

Fig. 3(a) is the FTIR spectra. For PU film, the band at 3318 cm^{-1} is attributed to the absorption vibration of N—H, and the band at 1064 cm^{-1} is attributed to the C—O—C stretching vibration.^[42] In addition, the band at 1526 cm^{-1} is related to the N—H bending and the C—H stretching.^[15] When CNT is anchored on the PU, several absorption bands of the PU can be found to shift. For example, the bands at 3318, 2938, 1729 and 1064 cm^{-1} decrease to 3307, 2935, 1726 and 1061 cm^{-1} , respectively. These changes indicate that the interaction between PU and CNT. Compared with PU-CNT, those characteristic absorption bands of PU-CNT-PDA and PU-CNT-PDA-PFDM also change. It is worth noting that the band of PU-CNT-PDA-PFDM at 1145 cm^{-1} belongs to the C—F bond, representing the PMDM that is successfully grafted onto the PDA surface.^[41]

Fig. 3(c) shows the Raman spectra of the films and CNT used in this work. For the CNT, there are three typical bands, D, G and 2D, at 1346, 1584 and 2695 cm^{-1} , respectively, as shown in Fig. 3(c), reflecting the graphitized structure of CNT.^[43] When CNT is anchored on PU fibers, the D, G and 2D bands of PU-CNT shift to 1343, 1595 and 2689 cm^{-1} , respectively, which may be attributed to the interfacial stress transfer between CNT and PU fibers. For common carbon materials, the D band is related to the disordered graphite structure, the 2D band is related to the second-order overtone of a different vibration mode in a graphene-like structure, and the G peak represents the stretching mode of the C—C bonds.^[44] The defect density in CNT is represented by the intensity ratio of D band to G band (I_D/I_G). The higher the defect density of CNT is, the higher the I_D/I_G value will be. Fig. 3(c) shows that the I_D/I_G value of PU-CNT increases from 1.004 to 1.015, compared to the CNT, due to the increases defects of the CNT under the action of ultrasonic.^[40] After depositing PDA and PFDM on CNT, the I_D/I_G value decreases, indicating that the graphitization degree of CNT is improved during the modifi-

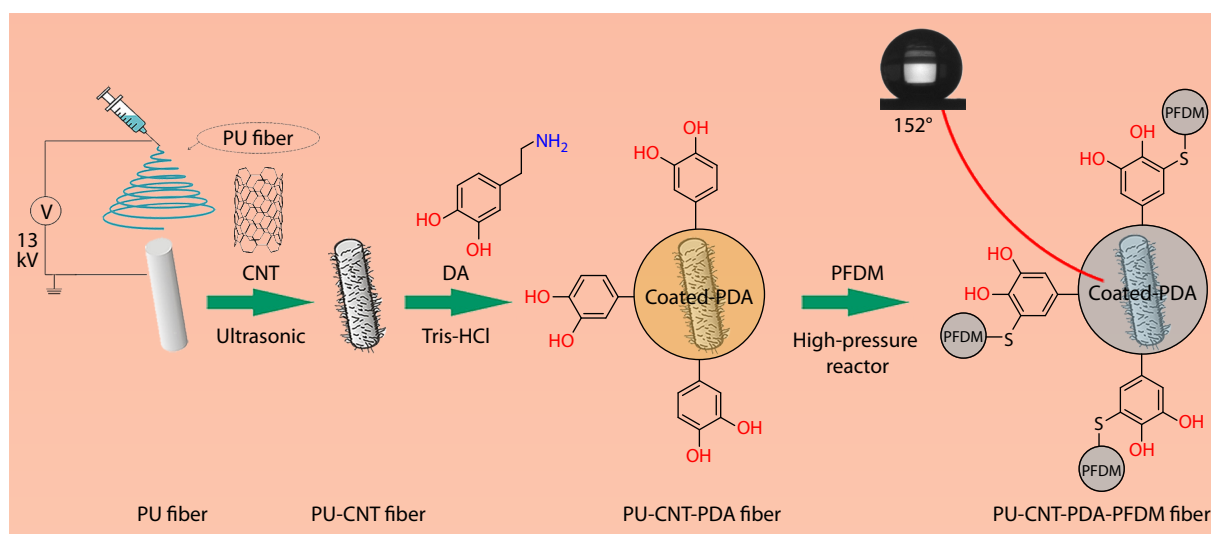


Fig. 1 Design idea of the superhydrophobic flexible strain sensor.

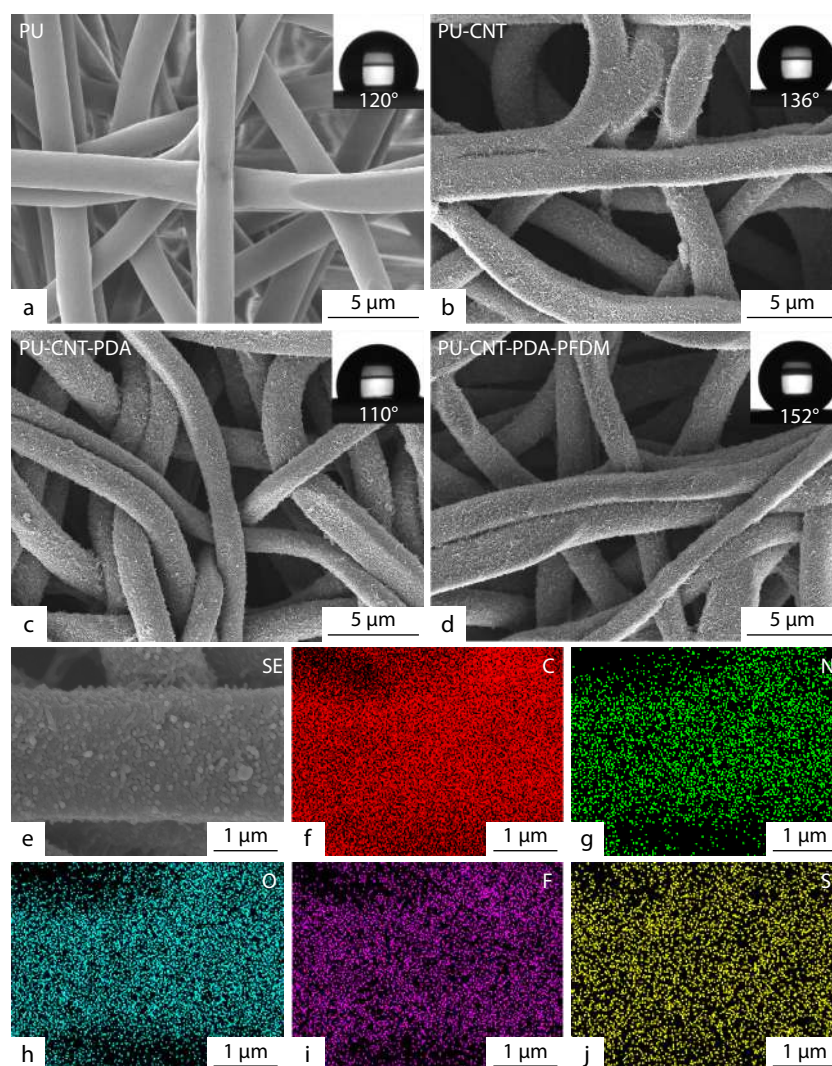


Fig. 2 (a) SEM image of PU fiber film and its WCA, (b) SEM image of PU-CNT fiber and its WCA, (c) SEM image of PU-CNT-PDA fiber and its WCA, (d) SEM image of PU-CNT-PDA-PFDM fiber and its WCA, (e–j) EDS of C, N, O, F, S corresponding elements in PU-CNT-PDA-PFDM.

cation. This may be attributed to the reducibility of PDA. It can reduce some oxygen-containing groups of CNT during the modification process (such as C—OH and C—O—C).^[38] A confocal Raman microscope (inVia Reflection, Renishaw, UK) with a 532 nm laser and Leica DM2700 objective lens (60×) was used to record Raman spectral imaging according to the characteristic signal of the D band of CNT. Meanwhile, the software Wire 3.2 is used to remove the cosmic rays and perform baseline correction on the obtained spectrum. It can be seen that CNT is distributed evenly on the surface of PU-CNT-PDA-PFDM, as shown in Fig. 3(b).

Fig. 3(d) shows the XRD spectra of PU films during different modification processes. As shown in Fig. 3(d), for neat PU films, a large diffraction peak appears at $2\theta=20.21^\circ$, which is generally believed to be related to the short-range regular order structure of PU hard and soft magnetic domains and the disordered structure of the amorphous phase of PU matrix.^[15] In addition, the characteristic diffraction peak of the PU can be clearly identified in different modification processes, which indicates that the crystal structure of PU film does not

change significantly after anchored CNT modification, but the diffraction peak becomes wider at the same time, which means that CNT affects the good short-range microstructure phase of soft and hard segments of the PU matrix, this may be due to the strong interfacial interaction between CNT and PU fibers, and the steric effect of CNT anchored on the fibers also affects the ordered aggregation of the soft and hard phases of PU matrix.^[45] At the same time, it can be seen from the XRD spectra combined with Raman spectra that the graphitization degree of conductive film increased after the addition of PDA and PFDM, so that the interaction of hard segments in PU is destroyed and more amorphous and disordered structures formed, as a result, the 2θ strength of PU-CNT-PDA and PU-PDA-PFDM films is a little lower than that of PU-CNT films.

The chemical composition of PU-CNT-PDA-PFDM and the chemical environment in which all elements are located can be characterized by XPS (Figs. 3e–3j). As shown in Fig. 3(e), the presence of C, N, O, N and F elements in the composite film can be seen in the full spectra. It is well known that CNT has a graphitized structure, and the surface carbon-contain-

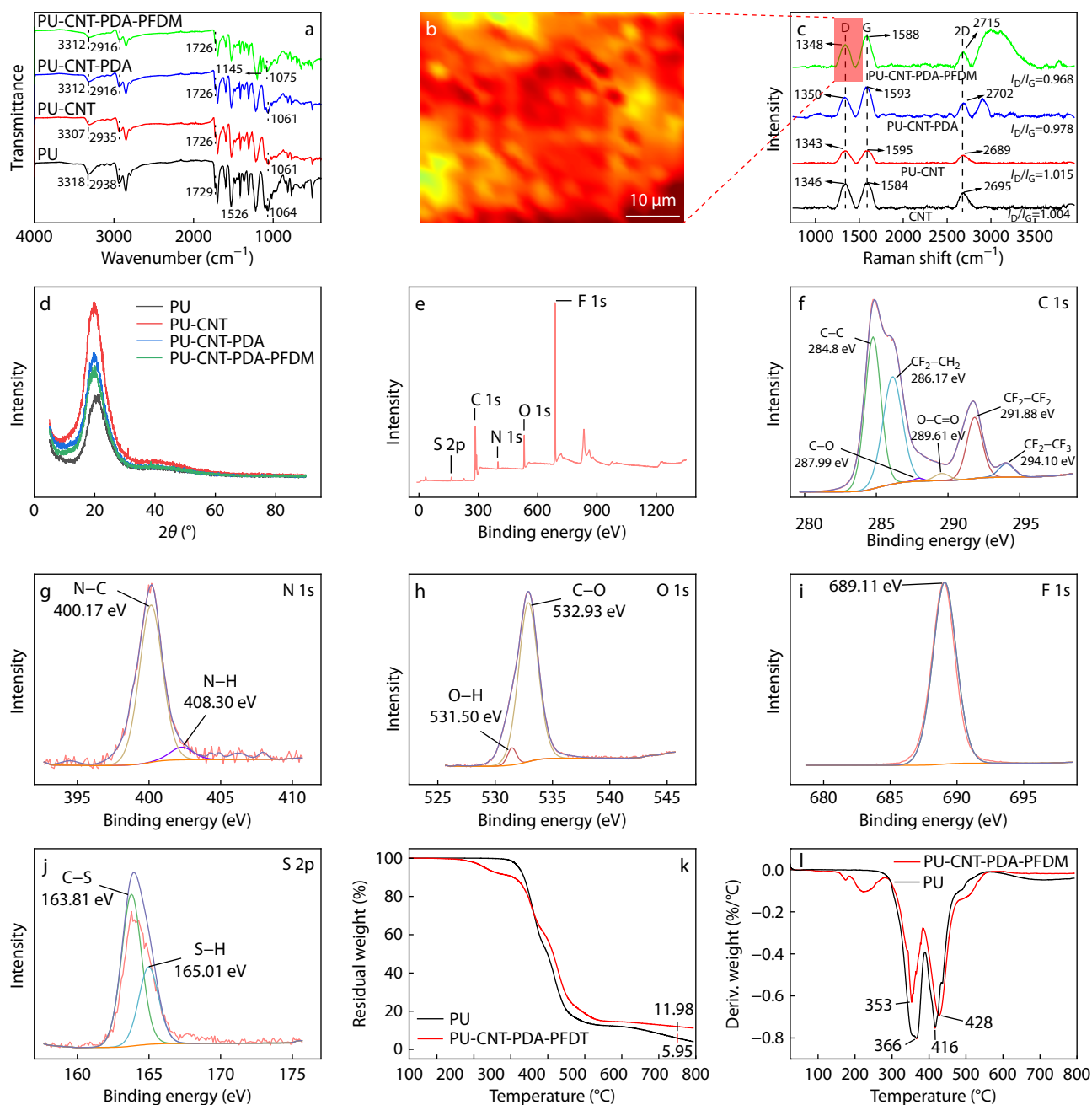


Fig. 3 (a) FTIR spectra, (b) Raman spectral imaging describes the distribution of CNT on the surface of PU-CNT-PDA-PFDM, (c) Raman spectra, (d) XRD patterns; (e–j) XPS spectra of PU-CNT-PDA-PFDM: (e) full spectrum, (f) C 1s peak fitting, (g) N 1s peak fitting, (h) O 1s peak fitting, (i) F 1s peak fitting, (j) S 2p peak fitting, (k) TG curves of PU and PU-CNT-PDA-PFDM; (l) DTG curves of PU and PU-CNT-PDA-PFDM.

ing groups generally include C—C (284.80 eV), C—O (287.99 eV) and O—C=O (289.61 eV) (Figs. 3f and 3h).^[46] Meanwhile, as shown in Fig. 3(f), CF₂—CH₂ (286.17 eV), CF₂—CF₂ (291.88 eV), and CF₂—CF₃ (294.10 eV) appear in the XPS spectra of C 1s, representing the successful reaction of PFDM on the surface of the film, this is also confirmed by a peak of 689.11 eV in the XPS spectrum of F 1s (Fig. 3i). The peaks at 400.17 eV and 402.30 eV in the N 1s spectra belong to N—C and N—H, respectively (Fig. 3g), the presence of N 1s also indicates that PDA has been successfully deposited on the fibers of PU-CNT (Fig. 3g).^[47] S 2p spectrum is generally used to assess the

chemical bonds between alkanethiols and substrates. According to previous studies, catechol or amino groups of PDA can provide active sites for aldehyde or thiol groups in Schiff base or Michael addition reactions.^[41] As shown in Fig. 3(j), C—S and S—H are formed on PU-CNT-PDA-PFDM, representing the successful introduction of thiols.

TG is carried out to research the thermal properties of the materials. The TG and derivative thermogravimetric (DTG) curves of PU and PU-CNT-PDA-PFDM are shown in Figs. 3(k) and 3(l). A two-step degradation process can be observed in the DTG curve. The first step is related to the decomposition

of the urethane in the hard segments, and the second step is attributed to the decomposition of PU soft segment.^[48] As shown in Fig. 3(k), the char residues of PU and PU-CNT-PDA-PFDM at 750 °C are 5.95% and 11.98%, respectively, indicating that the thermal properties of modified PU fiber may be improved. It can be seen in Fig. 3(l) that the temperatures corresponding to the maximum loss rates of PU and PU-CNT-PDA-PFDM are 366 and 428 °C, respectively. This further suggests that the continuous modification of CNT and PDA can positively affect the improvement of thermal stability. The improved thermal stability of PU-CNT-PDA-PFDM further proves the good dispersion of CNT on PU fiber surface and the strong interaction between CNT and PU fiber.

Superhydrophobicity and Corrosion Resistance of the Superhydrophobic Flexible Strain Sensor

The WCA of a material is generally determined by two factors. The lower the surface energy and the rougher the surfaces of materials are, the larger the WCA will be.^[49,50] In this work, the electrospinning method provides a rough surface, and the PFDM could lower the surface energy. To evaluate the effect of dopamine polymerization time on PFDM graft reactions on polymer surfaces and the effect of fluoride time on the WCA of the film, two experiments are conducted: (1) The polymerization time of dopamine on PU-CNT film is altered, and the fluoride time is fixed at 12 h. (2) The polymerization time of dopamine on PU-CNT film is fixed at 6 h, and the fluoride time is altered. Fig. 4(a) shows the influence of dopamine polymerization time on the WCA. When the dopamine polymerization time is 6 h, the WCA reaches its maximum value (152°). Because the polymerization time of dopamine is short, and the surface of fibers cannot be completely covered by PDA, the grafting of PFDM onto PDA is prevented. On the contrary, when the polymerization time of dopamine is more than 6 h, the reason for the decrease in WCA may be attributed to the fact that the PDA forms a thin layer on the fiber and decreases the surface roughness of the film. Fig. 4(b) shows the influence of fluoride time on the WCA, it can be found that the WCA increases with the increase in fluoride time. When the fluoride time reaches 12 h, WCA reaches its maximum (150°), and there is no obvious change in WCA after 12 h. Therefore, when the polymerization time of dopamine is 6 h and the fluoride time is 12 h, the WCA of PU-CNT-PDA-PFDM reaches its maximum (152°).

To test the corrosion resistance of PU-CNT-PDA-PFDM at different pH conditions and whether PU-CNT-PDA-PFDM can maintain hydrophobicity under different strains. The influence of different conditions on the wettability of PU-CNT-PDA-PFDM is investigated. Figs. 4(c) and 4(d) describe the influence of different pH and strain conditions on the WCA of the PU-CNT-PDA-PFDM, and it can be seen that the WCA of PU-CNT-PDA-PFDM can still maintain about 140° even in strong acid solution (pH=1) and base solution (pH=13). As shown in Fig. 4(d), due to the surface roughness of the PU-CNT-PDA-PFDM being damaged during the stretch, the WCA decreases, but the droplet remains spherical in the tensile process, and the WCA can reach 146° at 100% strain. Figs. 4(e) and 4(g) show the digital photos of the films before and after modification, respectively. After modification, the film remains soft and can be folded. Notably, we add artificial sweat salt, HCl (pH=2) and NaOH (pH=12) drops onto the PU-CNT-

PDA-PFDM which at 0% strain and 100% strain respectively. As shown in Figs. 4(f) and 4(h), different droplets are still full and round on the surface of the PU-CNT-PDA-PFDM, and the WCA is above 140°, which also provides the foundation for the application of the PU-CNT-PDA-PFDM under extreme conditions.

Sensing Performance and Sensing Mechanism of the Superhydrophobic Flexible Strain Sensor

In order to verify the stability of the sensor under high frequency and fast signal response, it is necessary to test the dynamic resistance of the sensor. Fig. 5(a) shows the dynamic resistance of the PU-CNT-PDA-PFDM sensor in $\epsilon=2\%$, 20%, 50%, and 100% cyclic tensile tests, and these sensing signals are the 10 cycles in the tests. During the test, the sensing signals in the previous several cycles are discarded because they are unstable, the value of $\Delta R/R_0$ increases rapidly under the first cycle of stretching, and $\Delta R/R_0$ cannot be recovered to its initial value in time after the release of the tension. One of the reasons is that the irreversible macromolecule segment motion in the polymer materials causes permanent damage to the conductive network in the sensor. After the first few cycles, the sensing signals begin to be stable, because polymer materials tend to return to their original configuration to maintain their thermodynamic equilibrium state after the stress is released. It can be seen from Fig. 5(a) that in the different tests, the response modes of sensors are the same. At the same time, as shown in Fig. 5(b), the response patterns of sensing signals at different frequencies of tensile strains are similar, this property is essential for obtaining reliable responses to different external stimuli. Those indicate that the prepared sensor has good stability for cyclic stretching and continuous response. As a strain sensor, response speed is a very important performance parameter, which represents the speed at which the sensor converts the external strain into an electrical response. Response speed is usually evaluated by response time and recovery time. The shorter the response time and recovery time, the better the sensor can reflect the corresponding situation in real time, which is very important in human movement and health monitoring. The tensile speed is set at 300 mm/min to minimize errors caused by loading time and unloading time, so that the sensor is loaded with a 2% quasi-transient step strain. As shown in Fig. 5(c), it is measured that the response time and recovery time of the sensor causing 90% of the current change under this strain and tensile rate are 150 and 140 ms, respectively. The results confirmed that the prepared sensor could respond quickly to external strain.

Impressively, when the sensor is stretched to a large strain, the shoulder peak appears in the curve during the tension release process, as shown in Fig. 5(d). In general, the shoulder peak is caused by competition between the destruction and recovery of the conductive network during the test. The sensor curves of relatively small strains (2% and 20%) (Fig. 5a) show no obvious shoulder peak, while the sensor curves of large strains (300%) (Fig. 5d) show an obvious shoulder peak, which can also be observed in other polymer-based sensors.^[12] This phenomenon may be caused by the disorientation of the conductive network induced by fibers during the tension release process. In this process, the resistance changes because the separated fibers tend to be in random

orientation and contact with each other, especially for the random orientation of fibers perpendicular to the tensile direction. In addition, because the contact points between the fibers parallel to the tensile direction are reduced during the tension release process, which can offset the reduction in resistance to some extent. The generation of shoulder peaks may be caused by the competition between the two factors mentioned above. It is generally believed that a small strain will cause slight damage to the conductive path and make it

easier to recover after tension release. However, a larger strain will cause serious damage to the conductive network and lead to fierce competition between the destruction and reconstruction of the conductive path during the recovery process. As shown in Fig. 5(f), the $\Delta R/R_0$ - t curve of the sensor is tested for 8500 cycles over a long work life to demonstrate extreme stability at 20% strain. No obvious signal fluctuation can be observed in Figs. 5(f) and 5(e), indicating that the sensor has good stability and durability. The stripping test of

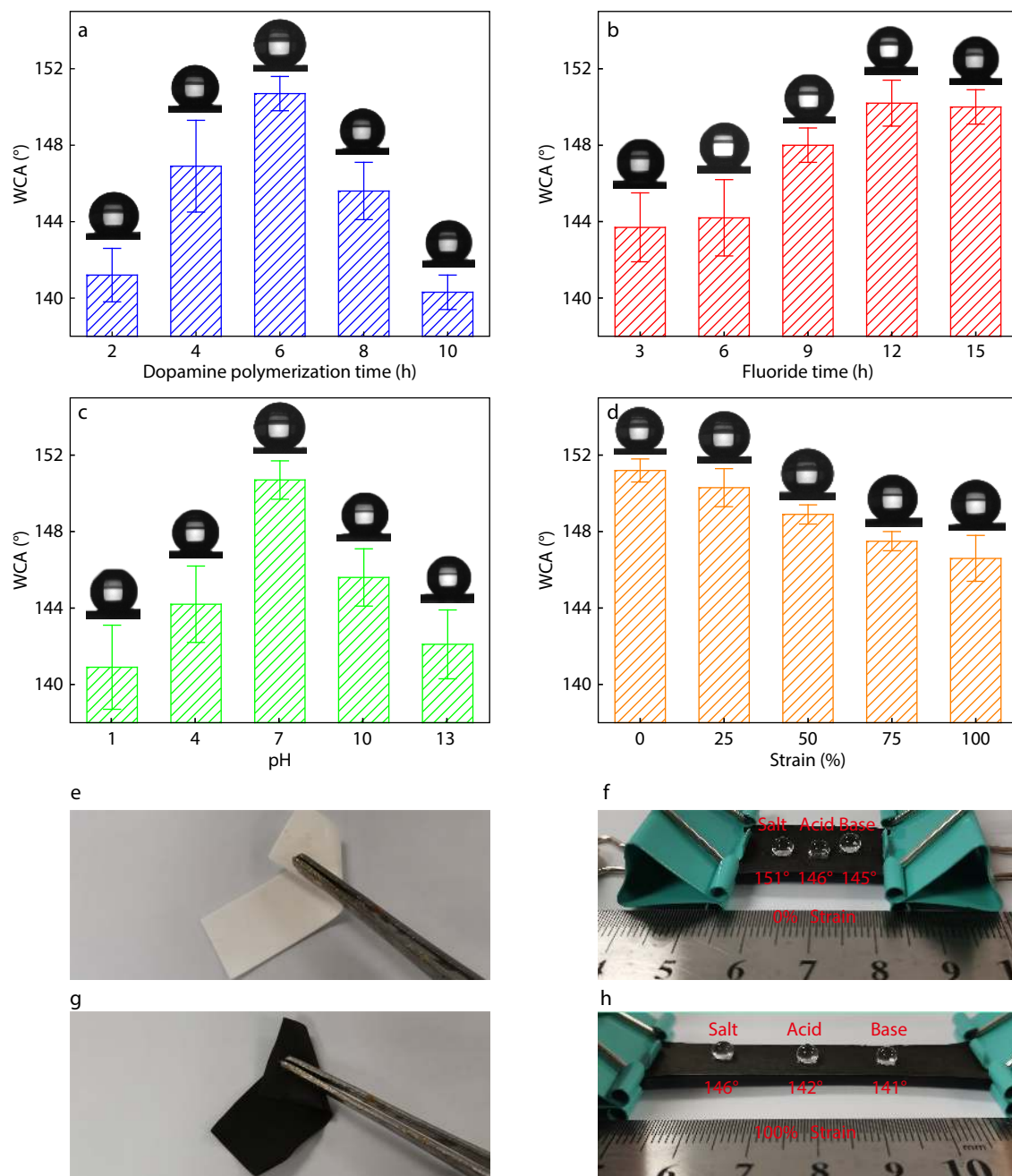


Fig. 4 (a) The influence of deposition time of PDA on the superhydrophobicity of the film; (b) The influence of fluoride time on the superhydrophobicity of the film; (c) The WCA of the PU-CNT-PDA-PFDM under different pH value; (d) The WCA of the PU-CNT-PDA-PFDM at different strains; (e) Digital photos of PU film surface morphology; (f) Digital photos of salt, acid and base contact angle on the PU-CNT-PDA-PFDM surface at 0% strain; (g) Digital photos of PU-CNT-PDA-PFDM surface morphology; (h) Digital photos of salt, acid and base contact angle on the PU-CNT-PDA-PFDM surface at 100% strain.

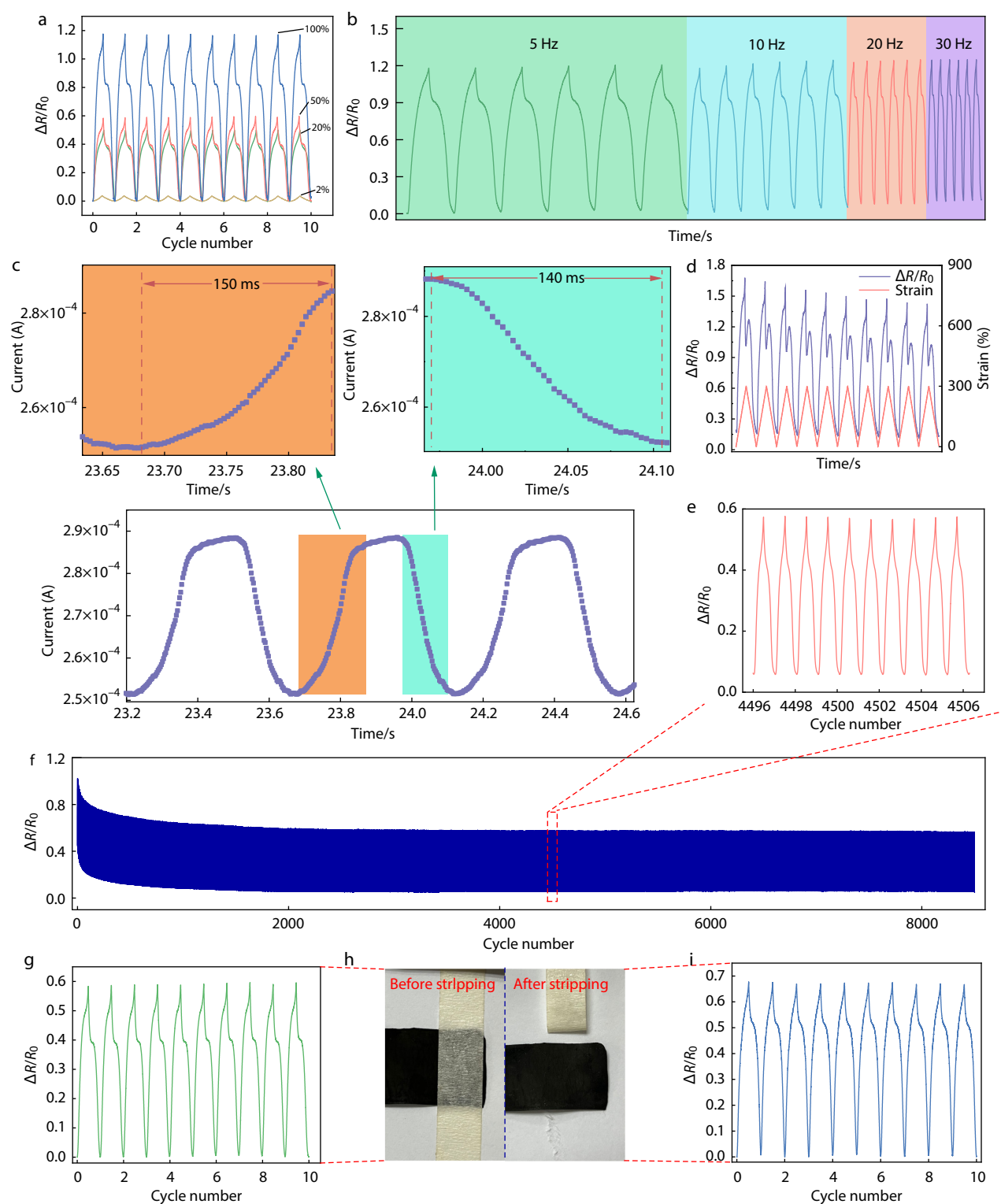


Fig. 5 (a) $\Delta R/R_0$ - t curve of the sensor at 2%, 20%, 50% and 100% strains for 10-cycles; (b) $\Delta R/R_0$ - t curve of the sensor at different frequencies; (c) Response time and recovery time test; (d) $\Delta R/R_0$ - t and stress-strain curves of the sensor at 300% strains for 10-cycles; (e) Partial amplification of 8500-cycle test; (f) $\Delta R/R_0$ - t curve of the sensor for 8500-cycle test; (g) Sensor signal before the tape is stripped; (h) Digital photos of adhesive tape on the sensor before and after stripping; (i) Sensing signal of the sensor after the tape is stripped.

the adhesive tape is also conducted to evaluate the adhesion of CNT on the film, and the results show that CNT is difficult to strip from the film, further indicating that there is a strong in-

terface interaction between CNT and PU, as shown in Fig. 5(h). By comparing the sensing signal of the sensor before and after stripping (Figs. 5g and 5i), it is found that the sens-

ing signal has little change, the reason may be that the sensor before stripping has residual strain after tensile, and the initial resistance value has slightly changed. Through the above sensing signal test, it can be seen that the PU-CNT-PDA-PFDM sensor simultaneously shows excellent sensitivity to different tensile frequencies and strains, rapid response ability, excellent stability, and durability.

To prove that the PU-CNT-PDA-PFDM sensor can maintain its reliable sensitivity and stability in a humid environment, we evaluate the sensing properties of the PU-CNT-PDA sensors in an environment with 100% humidity (in the process of testing, using a spray humidifier to spray artificial sweat, which simulates the motion perspire humidity environment), the results of the sensing signal are shown in Fig. 6(a). At the end of the 5th test cycle, the PU-CNT-PDA sensor appears to have an abnormal sensing signal. The signal fluctuation is large, and the sensor loses its stability. However, the signal of the PU-CNT-PDA-PFDM sensor remain stable without significant fluctuation, as shown in Fig. 6(b). In addition, the PU-CNT-PDA-PFDM sensor is immersed in water for 2 days, and it is found that the PU-CNT-PDA-PFDM sensor still remain stable after 1000 cycles (Fig. 6d). Fig. 6(c) shows a local magnification of the sensing signal in Fig. 6(d). Through the above sensing signal test, it can be observed that the PU-CNT-PDA-PFDM sensor shows a stable signal under extreme humidity and a sweating environment. The above performance further supports the sensor playing a role in the practical application.

In order to further understand the sensing mechanism and electrical response of the PU-CNT-PDA-PFDM sensor. We first test the mechanical properties of PU film in different modification processes. The mechanical properties of them are shown in Fig. 7(a). It can be seen from the stress-strain curves of the materials that the mechanical properties of the modified film are improved. Compared to the PU, the tensile

strength of the PU-CNT-PDA-PFDM increases from 4.20 MPa to 7.69 MPa, Young's modulus increases from 1.11 MPa to 2.19 MPa and the elongation at break increase from 402% to 432%. The reasons for the improvement of mechanical properties may include three parts: (1) Under the action of ultrasonic, CNT is anchored on the surface of PU fiber, and they pull the fiber closer by connecting, thus reducing the slip of the fiber in the tensile process.^[35] (2) Due to the uniform distribution of CNT on the PU fiber surface and the good interfacial interaction between CNT and PU fiber, effective stress transfer is promoted. (3) After the conductive fiber is wrapped in a PDA layer, the PDA layer can effectively transfer the stress during the tensile. In a word, the excellent mechanical properties can meet the wearable requirements of the flexible strain sensor.

Sensitivity is an important parameter of the sensor. Fig. 7(b) shows the curve of resistance change rate ($\Delta R/R_0$) and strain ε during a single tensile test. The sensitivity of the sensor is usually quantified by the gauge factor ($GF=d(\Delta R/R_0)/d\varepsilon$, ε is the strain). As shown in Fig. 7(b), when the strain of the sensor is 0%–25%, 25%–50% and 50%–100%, the GF value of the sensor is 3.43, 1.51, and 0.56, respectively (GF values correspond to the slopes at three different stages of the curve, as shown by the red line in Fig. 7b). As we know, this is not a relatively high value. However, through the comparison of some superhydrophobic strain sensors that have used CNT as a conductive filler in recent years, as shown in Fig. 7(c), it is found that the sensor shown in this work still has the leading performance.^[10,16–21,29,51,52] The above performance further supports the sensor playing a role in the practical application.

In order to fundamentally understand the tensile sensitivity of the PU-CNT-PDA-PFDM sensor, SEM is used to observe the micromorphology of the sensor in different tensile states. Figs. 7(d)–7(f) show the SEM images of the sensor at $\varepsilon=20\%$,

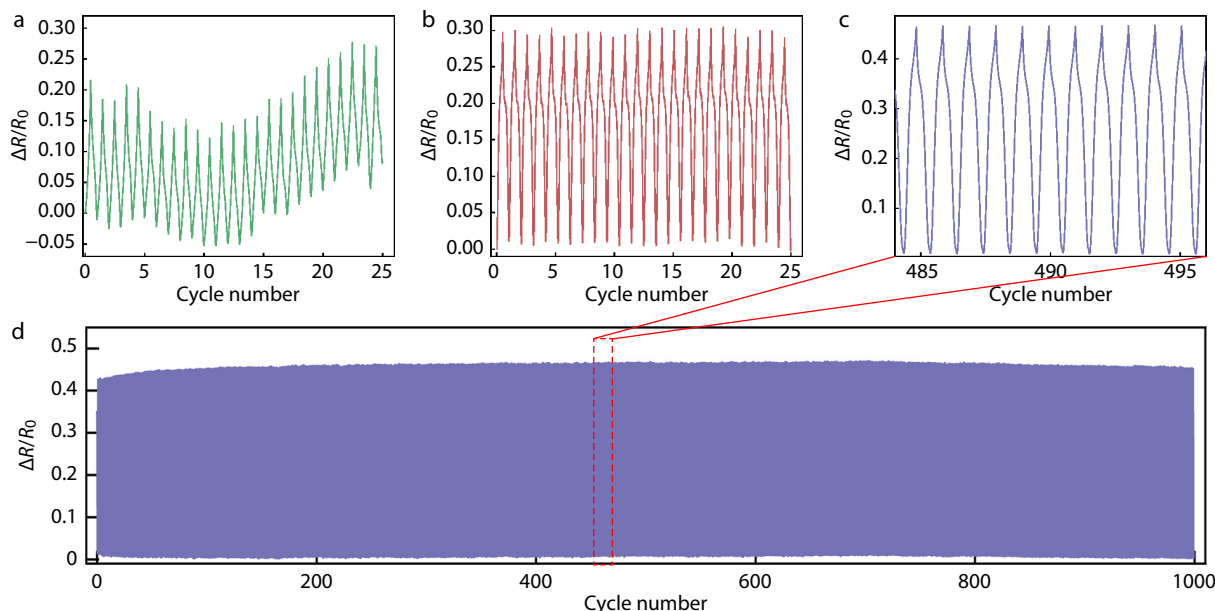


Fig. 6 (a) $\Delta R/R_0$ - t curve of PU-CNT-PDA sensor for 25-cycle at 100% humidity; (b) $\Delta R/R_0$ - t curve of PU-CNT-PDA-PFDM sensor for 25-cycle at 100% humidity; (c) Partial amplification of 1000-cycle test; (d) $\Delta R/R_0$ - t curve of PU-CNT-PDA-PFDM sensor for 1000-cycle after soaking in water for 48 h.

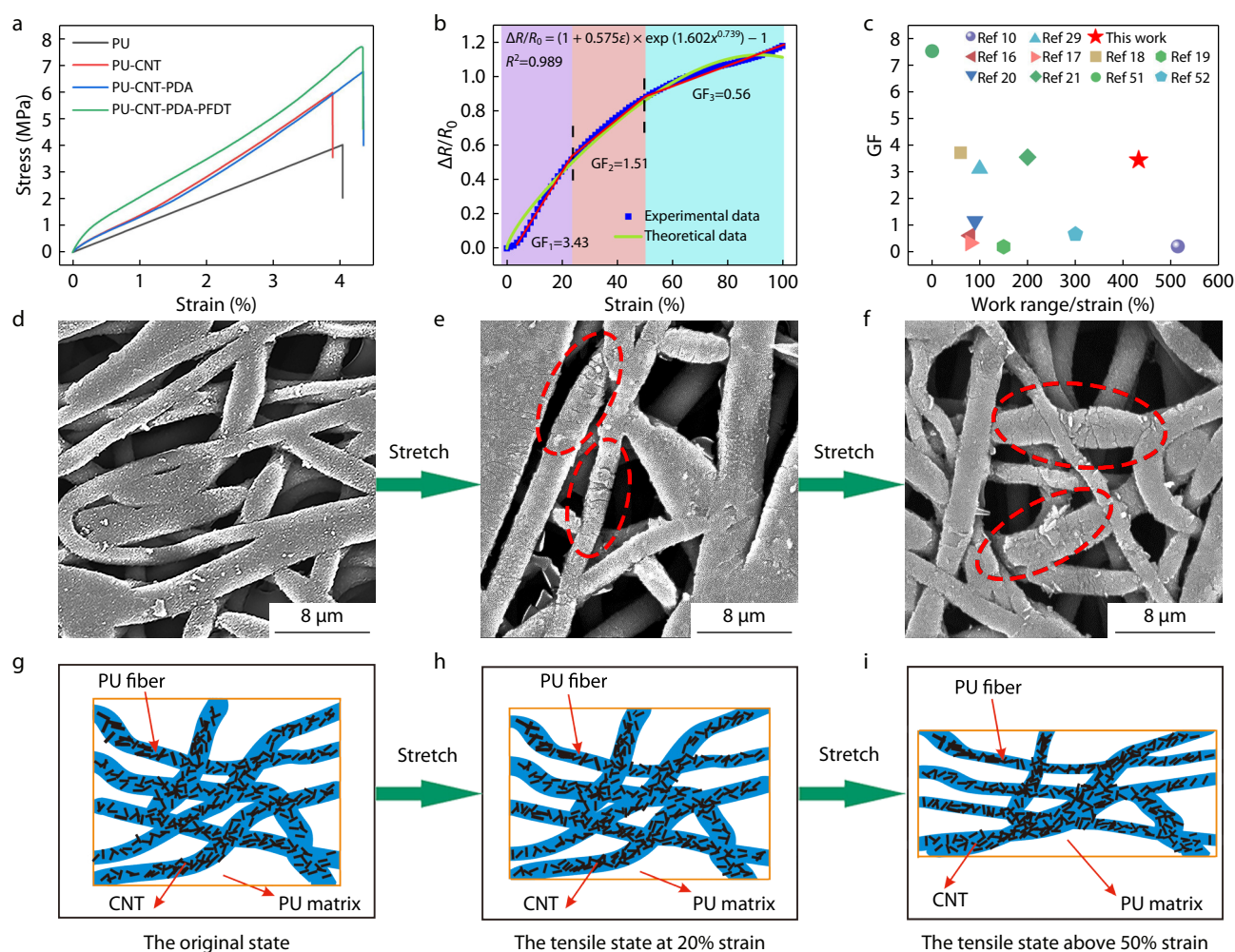


Fig. 7 (a) Stress-strain curves of PU and PU-CNT-PDA-PFDM; (b) The relative resistance change ($\Delta R/R_0$) of the sensor as a function of strain; (c) Comparison of superhydrophobic sensors using CNT as conductive filler in recent years; (d–f) SEM images of strain at 20%, 50% and 100% of PU-CNT-PDA-PFDM sensor; Schematic diagram of the evolution of a conducting network during stretching: (g) the original state, (h) the tensile state at 20% strain, and (i) the tensile state above 50% strain.

50% and 100%, It can be seen that in the case of $\epsilon=20\%$, no obvious damage occurs in the shell coated on the fiber surface. When the $\epsilon=50\%$, the shell on the fiber surface has some obvious cracks, the conduction pathway has been damaged to some extent. When the strain increase to 100%, the conduction pathway is seriously damaged, which further verifies the phenomenon of acromion in the above PU-CNT-PDA-PFDM sensor under large strain.

In this work, the change in resistance can be explained based on the tunnel model proposed by Simmons. Based on the tunnel model, the electrical conductivity of the strain sensor is related to both the physical contact between the sensing elements and the gap between the sensing elements (generally defined as a tunnel). When the adjacent conductive fillers are very close to each other (about 1–2 nm), there is still electron transport. In addition, some studies have shown that the impact of electron tunneling on the resistance is greater than the contact resistance. That is to say, although the overlapping conductive filler separation distance is not far, beyond the minimum distance of electron tunneling, the resistance will change significantly, which further proves that

the sensor has a greater GF value and higher sensitivity at 0%–25%.^[53] Figs. 7(g)–7(i) show the schematic diagram of the tunneling theory. During the working process, due to the good elasticity of the polymer substrate, the strain sensor can still return to its initial form after deformation. The total resistance of the PU-CNT-PDA-PFDM is a function of both the resistance through each conductive particle and the PU matrix.^[54] Assuming that the resistance of the PU-CNT-PDA-PFDM is constant everywhere, the resistance of the path perpendicular to the current can be ignored. When tension is applied to both ends of the PU-CNT-PDA-PFDM, some conductive fibers are separated from each other, and the contact points between conductive fillers are reduced, at the same time, the gap (tunnel) distance of the conductive filler increases, leading to an increase in resistance. Moreover, the higher the tensile strain, the fewer the contact points, the farther the distance of conductive fillers, and the actual number of conductive paths is further reduced. So, the number of conductive particles and conductive paths play important roles in resistance. The total resistance can be described by Eq. (1):^[54]

$$R = \frac{L(R_m + R_c)}{N} \quad (1)$$

where R , R_m , and R_c are the resistances of the composite material, the resistance between two adjacent particles, and the resistance of one particle, respectively. L is the number of particles forming a conductive path, and N is the number of conductive paths. According to Simmons' model, when the degree of separation between particles is very large, no current flows through the separation between particles, but if the separation is small, tunnel currents may flow through it, and the tunneling current I generated under a certain applied voltage is given by Eq. (2):^[55]

$$I = \frac{3\sqrt{2m\phi}}{2s} \left(\frac{e}{h}\right)^2 V \exp\left(-\frac{4\pi s}{h} \sqrt{2m\phi}\right) \quad (2)$$

where m and e are the mass and charge of the electron, respectively, h is Planck's constant, V is the voltage, s is the average distance between conductive particles, and ϕ is the barrier height between adjacent particles, which can be obtained by the subtraction of the polymer's work function from the conductor's. Because the electron tunneling probability depends on the thickness of the insulating barrier, almost all the tunneling occurs within a small area. Let a^2 be the effective cross-sectional area for electron tunneling, then the resistance R_m between two adjacent particles can be given by the following Eq. (3):^[55]

$$R_m = \frac{V}{a^2 I} = \frac{8\pi h s}{3a^2 e^2} \exp(\gamma s), \gamma = \frac{4\pi}{h} \sqrt{2m\phi} \quad (3)$$

Since the resistance between two adjacent particles is much greater than the resistance of one particle (R_m is much larger than R_c), the resistance of the particle can be ignored ($R_m + R_c \approx R_m$). Substituting Eq. (3) into Eq. (1) obtains Eq. (4):^[56,57]

$$R = \frac{L}{N} \left(\frac{8\pi h s}{3a^2 e^2} \right) \exp(\gamma s) \quad (4)$$

when the tension is applied to the sensor, according to the tunnel model, the tunneling distance between adjacent particles changes from s_0 to s (the change of the distance between particles from s_0 to s satisfies a linear function under axial stress), and the number of conductive paths changes from N_0 to N . The change of s_0 and N_0 can be expressed as following Eqs. (5) and (6):^[57]

$$s = s_0 (1 + K\varepsilon) \quad (5)$$

$$N = N_0 \exp\left[-(A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4)\right] \quad (6)$$

where s_0 and N_0 are the tunneling distance between adjacent particles in the initial state and the number of conductive paths in the initial state, respectively. The ε is the uniaxial strain generated by the sensor. A , B , C and D are constants. K is a constant that depends on the type of conductive particles and the measurement conditions. Thus, $\Delta R/R_0$ can be obtained by substituting Eqs. (5) and (6) into Eq. (4):

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} = \frac{R}{R_0} - 1 = \left(\frac{N_0 s}{N s_0}\right) \exp[\gamma(s - s_0)] - 1 \quad (7)$$

$$= (1 + K\varepsilon) \exp[\gamma(s - s_0) + (A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4)] - 1$$

make $[-(A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4)] = f(\varepsilon)$, so the $[\gamma(s - s_0) - f(\varepsilon)]$ can be expressed as the tunnel barrier height (ϕ) and the relationship between the change of the conductive path (M), so

we could obtain Eq. (8):

$$w\varepsilon^n = [\gamma(s - s_0) - f(\varepsilon)] \quad (8)$$

the function of $\Delta R/R_0$ and strain ε can be obtained by substituting Eq. (8) into Eq. (7), which can be described by Eq. (9):

$$\frac{\Delta R}{R_0} = (1 + K\varepsilon) \exp(w\varepsilon^n) - 1 \quad (9)$$

in Eq. (9), the constant K represents the change rate of the distance between adjacent particles, and the constants w and n represent the change in the number of conductive paths, $K=0.575$, $w=1.602$, and $n=0.739$ can be obtained through the fitting. Those parameters play crucial roles in the conductivity and sensitivity of the sensor.^[57] It can be seen in Fig. 7(b) that the tunneling theory concurs well with the experimental results. So the tunneling theory can well explain a series of resistance changes caused by stretching of the PU-CNT-PDA-PFDM sensor.

Practical Application: Full Range of Human Motion and Physiological Detection

As a sensor, the PU-CNT-PDA-PFDM sensor can also convert human motion signals into electrical sensing signals. Fig. 8(a) shows the motion diagram of the finger bending or straightening, and the monitoring curve of finger bending and straightening sensing signals. The labeled peak signal is the sensor signal when the finger bends, and the bottom signal represents the straightening of the finger. Similar to finger motion, wrist motion also has similar sensing signals, as shown in Fig. 8(b). Only because the strain of wrist motion is small, the amplitude variation of sensing signals is also small. Fig. 8(c) shows the motion diagram of the elbow motion and the sensing signal of the elbow motion. The peak signal represents elbow bending, and the signal at the bottom represents elbow straight. Fig. 8(d) shows the motion diagram of the knee motion and its sensing signal. Similar to finger motion and elbow motion, the sensing signals of knee motion have a similar peak signal and bottom signal corresponding to the bending and straightening of the knee. By monitoring the motion of the fingers, elbows and knees, it can see when the joint motion range is small, the sensor strain is small, and the change in $\Delta R/R_0$ is also small. Similarly, a large motion range will cause a large change in $\Delta R/R_0$. Therefore, the PU-CNT-PDA-PFDM sensor can monitor the motion of human joints. In addition, we also test physiological signals such as drinking and vocalization. When the subjects drink water continuously, continuous and stable sensing signals can also be monitored (Fig. 8e). We install sensors on subjects' throats to monitor the vocal cord motion during vocalization. Fig. 8(f) shows the monitoring curve of the throat sensing signal. The subjects said two words during the test: "Sensor" and "Hello." The peak characteristics of detection signals are different for different detection words. In addition, we test the sensor's ability to transform motion signals in different environments. Video S1 (in the electronic supplementary information, ESI) is used as a control to show the response of finger joint motion and corresponding electrical signals. Video S2 (in ESI) shows the finger joint motion and corresponding electrical signal response after artificial sweat drops are dropped on the sensor surface during the sensor work. These results show that the sensor has a sensitive electrical response to the small strain caused by joint motion, and it can be applied to an environment of high humidity and sweat. Based on the above tests, it can be proved that our

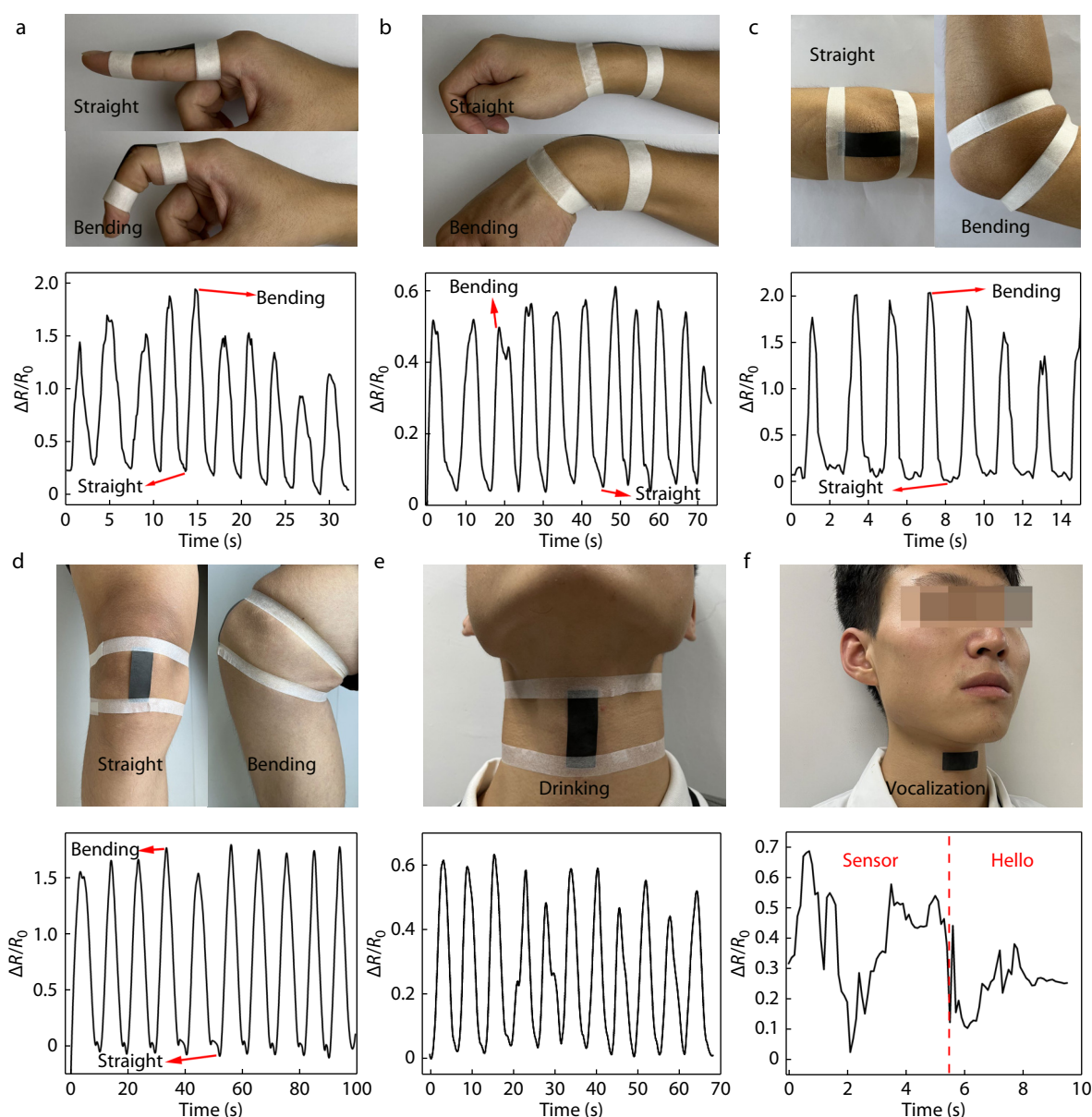


Fig. 8 Wearable strain sensors based on PU-CNT-PDA-PFDM are used to monitor various human motions. (a) A finger motion diagram and monitoring curve generated by finger motion; (b) Wrist motion map and monitoring curve generated by wrist motion; (c) Elbow motion diagram and monitoring curve generated by elbow motion; (d) Knee motion diagram and monitoring curve generated by knee motion; (e) Throat motion diagram and monitoring curve generated by throat motion (drinking); (f) Throat motion diagram and monitoring curve generated by throat motion (vocalization).

sensor can be used to monitor different joint motions and physiological signals of the human body. Thus, we believe our sensor can be used in the future.

CONCLUSIONS

In this work, PU film is obtained by the electrospinning method, and CNT is anchored on the fiber with the help of ultrasonic, so that the PU-CNT has conductivity. Finally, PDA and PFDM are used to modify the conductive film. Because the PFDM grafted on the PDA has low surface energy, the WCA of the obtained sensor reaches 152°. Compared with neat PU, the Young's modulus, elongation at break and tensile strength of PU-CNT-

PDA-PFDM are significantly improved. Furthermore, this sensor under different strains can keep an excellent sensing response pattern. Even in the simulated 100% humidity environment or after 8500 tensile tests, the sensing signal is stable and changes little. In different pH solutions and strain conditions, the water droplets on the surface of the sensor can remain spherical, and the WCA is above 140°. At the same time, the response mechanism and sensing mechanism of the sensor in this research are explained by tunneling theory. The sensor is also suitable for the monitoring of human joint motion and physiological signals (such as finger motion, elbow motion, knee motion, wrist motion and throat motion), which supports the application prospect of this multilayer flexible strain sensor

in wearable electronic products.

Conflict of Interests

The authors declare no interest conflict.



Electronic Supplementary Information

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REFERENCES

- Meng, K. Y.; Xiao, X.; Wei, W. X.; Chen, G. R.; Nashalian, A.; Shen, S.; Xiao, X.; Chen, J. Wearable pressure sensors for pulse wave monitoring. *Adv. Mater.* **2022**, *34*, e2109357.
- Khalid, M. A. U.; Chang, S. H. Flexible strain sensors for wearable applications fabricated using novel functional nanocomposites: a review. *Compos. Struct.* **2022**, *284*, 115214.
- Liu, Y. H.; Pharr, M.; Salvatore, G. A. Lab-on-skin: a review of flexible and stretchable electronics for wearable health monitoring. *ACS Nano* **2017**, *11*, 9614–9635.
- Gao, W. C.; Wu, W.; Chen, C. Z.; Zhao, H.; Liu, Y.; Li, Q.; Huang, C. X.; Hu, G. H.; Wang, S. F.; Shi, D.; Zhang, Q. C. Design of a superhydrophobic strain sensor with a multilayer structure for human motion monitoring. *ACS Appl. Mater. Interfaces* **2022**, *14*, 1874–1884.
- Chen, J. W.; Yu, Q. L.; Cui, X. H.; Dong, M. Y.; Zhang, J. X.; Wang, C.; Fan, J. C.; Zhu, Y. T.; Guo, Z. H. An overview of stretchable strain sensors from conductive polymer nanocomposites. *J. Mater. Chem. C* **2019**, *7*, 11710–11730.
- Li, Z. Y.; Zhai, W.; Yu, Y. F.; Li, G. J.; Zhan, P. F.; Xu, J. W.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Shen, C. Y. An ultrasensitive, durable and stretchable strain sensor with crack-wrinkle structure for human motion monitoring. *Chinese J. Polym. Sci.* **2021**, *39*, 316–326.
- Jia, S. S.; Deng, S. L.; Qing, Y.; He, G. J.; Deng, X. H.; Luo, S.; Wu, Y. Q.; Guo, J.; Carmalt, C. J.; Lu, Y.; Parkin, I. P. A coating-free superhydrophobic sensing material for full-range human motion and microliter droplet impact detection. *Chem. Eng. J.* **2021**, *410*, 128418.
- Cai, Y. C.; Shen, J.; Ge, G.; Zhang, Y. Z.; Jin, W. Q.; Huang, W.; Shao, J. J.; Yang, J.; Dong, X. C. Stretchable $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/carbon nanotube composite based strain sensor with ultrahigh sensitivity and tunable sensing range. *ACS Nano* **2018**, *12*, 56–62.
- Pan, Q.; Tong, N. J.; He, N. F.; Liu, Y. X.; Shim, E.; Pourdeyhimi, B. P.; Gao, W. Electrospun Mat of poly(vinyl alcohol)/graphene oxide for superior electrolyte performance. *ACS Appl. Mater. Interfaces* **2018**, *10*, 7927–7934.
- Wang, L.; Chen, Y.; Lin, L. W.; Wang, H.; Huang, X. W.; Xue, H. G.; Gao, J. F. Highly stretchable, anti-corrosive and wearable strain sensors based on the PDMS/CNTs decorated elastomer nanofiber composite. *Chem. Eng. J.* **2019**, *362*, 89–98.
- Liu, Y.; Wang, H.; Zhao, W.; Zhang, M.; Qin, H. B.; Xie, Y. Q. Flexible, stretchable sensors for wearable health monitoring: sensing mechanisms, materials, fabrication strategies and features. *Sensors* **2018**, *18*, 645.
- Liu, H.; Li, Q. M.; Zhang, S. D.; Yin, R.; Liu, X. H.; He, Y. X.; Dai, K.; Shan, C. X.; Guo, J.; Liu, C. T.; Shen, C. Y.; Wang, X. J.; Wang, N.; Wang, Z. C.; Wei, R. B.; Guo, Z. H. Electrically conductive polymer composites for smart flexible strain sensors: a critical review. *J. Mater. Chem. C* **2018**, *6*, 12121–12141.
- 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.
- Trung, T. Q.; Duy, L. T.; Ramasundaram, S.; Lee, N. E. Transparent, stretchable, and rapid-response humidity sensor for body-attachable wearable electronics. *Nano Res.* **2017**, *10*, 2021–2033.
- Li, Y. H.; Zhou, B.; Zheng, G. Q.; Liu, X. H.; Li, T. X.; Yan, C.; Cheng, C. B.; Dai, K.; Liu, C. T.; Shen, C. Y.; Guo, Z. H. Continuously prepared highly conductive and stretchable SWNT/MWNT synergistically composited electrospun thermoplastic polyurethane yarns for wearable sensing. *J. Mater. Chem. C* **2018**, *6*, 2258–2269.
- Sahoo, B. N.; Woo, J. H.; Algadi, H.; Lee, J. H.; Lee, T. Superhydrophobic, transparent, and stretchable 3D hierarchical wrinkled film-based sensors for wearable applications. *Adv. Mater. Technol.* **2019**, *4*, 1900230.
- Fan, T.; Xue, S. S.; Zhu, W. B.; Zhang, Y. Y.; Li, Y. Q.; Chen, Z. K.; Huang, P.; Fu, S. Y. Multifunctional polyurethane composite foam with outstanding anti-impact capacity for soft body armors. *ACS Appl. Mater. Interfaces* **2022**, *14*, 13778–13789.
- Ma, W. J.; Jiang, Z. C.; Lu, T.; Xiong, R. H.; Huang, C. B. Lightweight, elastic and superhydrophobic multifunctional nanofibrous aerogel for self-cleaning, oil/water separation and pressure sensing. *Chem. Eng. J.* **2022**, 430.
- Park, C.; Kim, T.; Samuel, E. P.; Kim, Y.-I.; An, S.; Yoon, S. S. Superhydrophobic antibacterial wearable metallized fabric as supercapacitor, multifunctional sensors, and heater. *J. Power Sources* **2021**, *506*, 230142.
- Wang, L.; Huang, X. W.; Wang, D.; Zhang, W. M.; Gao, S. J.; Luo, J. C.; Guo, Z.; Xue, H. G.; Gao, J. F. Lotus leaf inspired superhydrophobic rubber composites for temperature stable piezoresistive sensors with ultrahigh compressibility and linear working range. *Chem. Eng. J.* **2021**, *405*, 127025.
- Li, Z. X.; Ye, L. J.; Shen, J. Q.; Xie, K. Y.; Li, Y. J. Strain-gauge sensing composite films with self-restoring water-repellent properties for monitoring human movements. *Compos. Commun.* **2018**, *7*, 23–29.
- Zhang, K. M.; Wang, Z.; Liu, Y. T.; Zhao, H. Y.; Gao, C. H.; Wu, Y. M. Cephalopods-inspired repairable MWCNTs/PDMS conductive elastomers for sensitive strain sensor. *Chinese J. Polym. Sci.* **2022**, *40*, 384–393.
- Wang, J. J.; Zhang, Q.; Ji, X. X.; Liu, L. B. Highly stretchable, compressible, adhesive, conductive self-healing composite hydrogels with sensor capacity. *Chinese J. Polym. Sci.* **2020**, *38*, 1221–1229.
- Guo, Y.; Zhong, M. J.; Fang, Z. W.; Wan, P. B.; Yu, G. H. A wearable transient pressure sensor made with MXene nanosheets for sensitive broad-range human-machine interfacing. *Nano Lett.* **2019**, *19*, 1143–1150.
- Wei, Y.; Chen, S.; Yuan, X.; Wang, P. P.; Liu, L. Multiscale wrinkled microstructures for piezoresistive fibers. *Adv. Funct. Mater.* **2016**, *26*, 5078–5085.
- Liao, X. Q.; Liao, Q. L.; Zhang, Z.; Yan, X. Q.; Liang, Q. J.; Wang, Q. Y.; Li, M. H.; Zhang, Y. A highly stretchable ZnO@fiber-based multifunctional nanosensor for strain/temperature/UV detection.

- Adv. Funct. Mater.* **2016**, *26*, 3074–3081.
- 27 Li, G. J.; Dai, K.; Ren, M. N.; Wang, Y.; Zheng, G. Q.; Liu, C. T.; Shen, C. Y. Aligned flexible conductive fibrous networks for highly sensitive, ultrastretchable and wearable strain sensors. *J. Mater. Chem. C* **2018**, *6*, 6575–6583.
 - 28 Zhou, X.; Zhu, L.; Fan, L.; Deng, H.; Fu, Q. Fabrication of highly stretchable, washable, wearable, water-repellent strain sensors with multi-stimuli sensing ability. *ACS Appl. Mater. Interfaces* **2018**, *10*, 31655–31663.
 - 29 Liu, K.; Yang, C.; Song, L. H.; Wang, Y.; Wei, Q.; Alamusi; Deng, Q.; Hu, N. Highly stretchable, superhydrophobic and wearable strain sensors based on the laser-irradiated PDMS/CNT composite. *Compos. Sci. Technol.* **2022**, *218*, 18954.
 - 30 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 nano-sponge/silicone composite for human motion detection. *Nanoscale* **2017**, *9*, 6680–6685.
 - 31 Tadakaluru, S.; Thongsuwan, W.; Singjai, P. Stretchable and flexible high-strain sensors made using carbon nanotubes and graphite films on natural rubber. *Sensors* **2014**, *14*, 868–876.
 - 32 Wang, Y. L.; Jia, Y. Y.; Zhou, Y. J.; Wang, Y.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Shen, C. Y. Ultra-stretchable, sensitive and durable strain sensors based on polydopamine encapsulated carbon nanotubes/elastic bands. *J. Mater. Chem. C* **2018**, *6*, 8160–8170.
 - 33 Zhang, M. C.; Wang, C. Y.; Wang, H. M.; Jian, M. Q.; Hao, X. Y.; Zhang, Y. Y. Carbonized cotton fabric for high-performance wearable strain sensors. *Adv. Funct. Mater.* **2018**, *27*, 1604795.
 - 34 Wang, N.; Xu, Z. Y.; Zhan, P. F.; Dai, K.; Zheng, G. Q.; Liu, C. T.; Shen, C. Y. A tunable strain sensor based on a carbon nanotubes/electrospun polyamide 6 conductive nanofibrous network embedded into poly(vinyl alcohol) with self-diagnosis capabilities. *J. Mater. Chem. C* **2017**, *5*, 4408–4418.
 - 35 Guan, X. Y.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Yan, X. R.; Shen, C. Y.; Guo, Z. H. Carbon nanotubes-adsorbed electrospun PA66 nanofiber bundles with improved conductivity and robust flexibility. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14150–14159.
 - 36 Zhan, P. F.; Zhai, W.; Wei, W. Y.; Ding, P.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Shen, C. Y. Stretchable strain sensor with high sensitivity, large workable range and excellent breathability for wearable electronic skins. *Compos. Sci. Technol.* **2022**, 10.1016/j.compscitech.2022.109720.
 - 37 Seyedin, S.; Uzun, S.; Levitt, A.; Anasori, B.; Dion, G.; Gogotsi, Y.; Razal, J. M. MXene composite and coaxial fibers with high stretchability and conductivity for wearable strain sensing textiles. *Adv. Funct. Mater.* **2020**, *30*, 1910504.
 - 38 Li, B.; Luo, J. C.; Huang, X. W.; Lin, L. W.; Wang, L.; Hu, M. J.; Tang, L. C.; Xue, H. G.; Gao, J. F.; Mai, Y.-W. A highly stretchable, superhydrophobic strain sensor based on polydopamine and graphene reinforced nanofiber composite for human motion monitoring. *Compos. Part B: Eng.* **2020**, *181*, 107580.
 - 39 Gao, J. F.; Wang, H.; Huang, X. W.; Hu, M. J.; Xue, H. J.; Li, R.K.Y. Electrically conductive polymer nanofiber composite with an ultralow percolation threshold for chemical vapour sensing. *Compos. Sci. Technol.* **2018**, *161*, 135–142.
 - 40 Huang, X. W.; Li, B.; Wang, L.; Lai, X. J.; Xue, H. G.; Gao, J. F. Superhydrophilic, underwater superoleophobic, and highly stretchable humidity and chemical vapor sensors for human breath detection. *ACS Appl. Mater. Interfaces* **2019**, *11*, 24533–24543.
 - 41 Cao, N.; Yang, B.; Barras, A.; Szunerits, S.; Boukherroub, R. Polyurethane sponge functionalized with superhydrophobic nanodiamond particles for efficient oil/water separation. *Chem. Eng. J.* **2017**, *307*, 319–325.
 - 42 Cheng, B. X.; Lu, C. C.; Li, Q.; Zhao, S. Q.; Bi, C. S.; Wu, W.; Huang, C. X.; Zhao, H. Preparation and properties of self-healing triboelectric nanogenerator based on waterborne polyurethane containing diels-alder bonds. *J. Polym. Environ.* **2022**, DOI: 10.1007/s10924-022-02586-z.
 - 43 Moya, A.; Kemnade, N.; Osorio, M.R.; Cherevan, A.; Granados, D.; Eder, D.; Vilatela, J. J. Large area photoelectrodes based on hybrids of CNT fibres and ALD-grown TiO₂. *J. Mater. Chem. A* **2017**, *5*, 24695–24706.
 - 44 Gao, J. F.; Wang, L.; Guo, Z.; Li, B.; Wang, H.; Luo, J. C.; Huang, X. W.; Xue, H. G. Flexible, superhydrophobic, and electrically conductive polymer nanofiber composite for multifunctional sensing applications. *Chem. Eng. J.* **2020**, *381*, 122778.
 - 45 Barick, A. K.; Tripathy, D. K. Preparation, characterization and properties of acid functionalized multi-walled carbon nanotube reinforced thermoplastic polyurethane nanocomposites. *Mater. Sci. Eng. B* **2011**, *176*, 1435–1447.
 - 46 Li, L. X.; Zhang, J. P. Superamphiphobic, magnetic, and elastic silicone sponges with excellent temperature stability. *Adv. Mater. Interfaces* **2016**, *3*, 1600517.
 - 47 Liu, M. Y.; Zhou, J. F.; Yang, Y.; Zheng, M.; Yang, J. J.; Tan, J. G. Surface modification of zirconia with polydopamine to enhance fibroblast response and decrease bacterial activity *in vitro*: a potential technique for soft tissue engineering applications. *Colloids Surf B Biointerfaces* **2015**, *136*, 74–83.
 - 48 Zhao, H.; Li, K. C.; Wu, W.; Li, Q.; Jiang, Y.; Cheng, B. X.; Huang, C. X.; Li, H. N. Microstructure and viscoelastic behavior of waterborne polyurethane/cellulose nanofiber nanocomposite. *J. Ind. Eng. Chem.* **2022**, *110*, 150–157.
 - 49 Yan, Y. Y.; Gao, N.; Barthlott, W. Mimicking natural superhydrophobic surfaces and grasping the wetting process: a review on recent progress in preparing superhydrophobic surfaces. *Adv. Colloid Interface Sci.* **2011**, *169*, 80–105.
 - 50 Zhao, H.; Gao, W. C.; Li, Q.; Khan, M. R.; Hu, G. H.; Liu, Y.; Wu, W.; Huang, C. X.; Li, R.K.Y. Recent advances in superhydrophobic polyurethane: preparations and applications. *Adv. Colloid Interface Sci.* **2022**, *303*, 102644.
 - 51 Li, Q. M.; Liu, H.; Zhang, S. D.; Zhang, D. B. H.; Liu, X. H.; He, Y. X.; Mi, L. W.; Zhang, J. X.; Liu, C. T.; Shen, C. Y.; Guo, Z. H. Superhydrophobic electrically conductive paper for ultrasensitive strain sensor with excellent anticorrosion and self-cleaning property. *ACS Appl. Mater. Interfaces* **2019**, *11*, 21904–21914.
 - 52 Wang, Z. F.; Huang, Y.; Sun J. F.; Huang, Y.; Hu, H.; Jiang, R. J.; Gai, W. M.; Li, G. M.; Zhi, C. Y. Polyurethane/cotton/carbon nanotubes core-spun yarn as high reliability stretchable strain sensor for human motion detection. *ACS Appl. Mater. Interfaces* **2016**, *8*, 24837–24843.
 - 53 Du, Y. Z.; Yu, G. X.; Dai, X. Y.; Wang, X. D.; Yao, B.; Kong, J. Highly stretchable, self-healable, ultrasensitive strain and proximity sensors based on skin-inspired conductive film for human motion Monitoring. *ACS Appl. Mater. Interfaces* **2020**, *12*, 51987–51998.
 - 54 Wang, X.; Liu, X. H.; Schubert, D. W. Highly sensitive ultrathin flexible thermoplastic polyurethane/carbon black fibrous film strain sensor with adjustable scaffold networks. *Nanomicro Lett.* **2021**, *13*, 159–177.
 - 55 Zhang, X. W.; Pan, Y.; Zheng, Q.; Yi, X. S. Time dependence of piezoresistance for the conductor-filled polymer composites. *Polymer physics* **2000**, *38*, 2739–2749.
 - 56 Huang, J. Y.; Li, D.W.; Zhao, M.; Mensah, A.; Lv, P. F.; Tian, X. J.; Huang, F. L.; Ke, H. Z.; Wei, Q. F. Highly sensitive and stretchable CNT-bridged AgNP strain sensor based on TPU electrospun membrane for human motion detection. *Adv. Electron. Mater.* **2019**, *5*, 1900241.
 - 57 Zhao, S. G.; Lou, D. D.; Li, G. J.; Zheng, Y. J.; Zheng, G. Q.; Dai, K.; Liu, C. T.; Jiang, Y. L.; Shen, C. Y. Bridging the segregated structure in conductive polypropylene composites: an effective strategy to balance the sensitivity and stability of strain sensing performances. *Compos. Sci. Technol.* **2018**, *163*, 18–25.