

Making a Bilateral Compression/Tension Sensor by Pre-Stretching Open-Crack Networks in Carbon Nanotube Papers

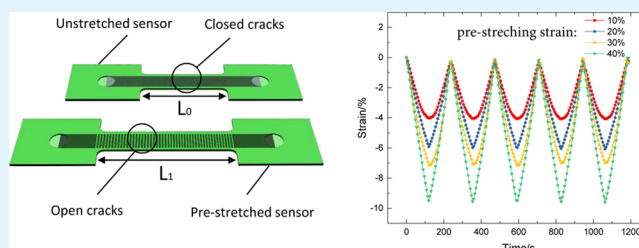
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Supporting Information

ABSTRACT: Highly stretchable strain sensors are key elements of new applications in wearable electronics and soft robotics. Most of the available technologies only measure positive strain (stretching), and cannot measure negative strains (compression). We propose here a stretchable technology that enables the measurement of both negative and positive strains with high sensitivity. A carbon nanotube paper is pre-cracked to introduce a well-controlled network of open cracks as the sensing element; then, the pre-cracked paper is sandwiched by a thermoplastic elastomer. The resulting sensor is also pre-stretched and subjected to thermal annealing, which removes any residual stress so that the pre-stretched configuration remains stable. This process results in a stretchable structure with a network of open cracks that is sensitive to both negative and positive strains. We demonstrate that such sensors can measure negative strains up to -13% with high sensitivity and robust stretchability.

KEYWORDS: compression, stretchable, strain sensor, cracks, SWCNT



1. INTRODUCTION

New demands in human-body motion detection,^{1–5} soft robotics,^{6–8} and structure health monitoring,^{9–12} have increased the need for stretchable strain sensors in the recent years. On the basis of carbon black,¹³ carbon nanotubes (CNTs),^{7,14} silver nanowire,¹⁵ graphene,^{6,16} conductive nanoparticles,^{17,18} or conductive polymers,^{19,20} these sensors meet engineering needs in terms of sensitivity, stretchability, linearity, stability, and response time. However, most existing works focus on improving the performance of sensors subjected to positive strains (stretching). There is no technological solution today for monitoring negative strains (compression) using flexible and stretchable sensors with high sensitivity. Yet, this is key to developing fully functional e-skins for monitoring complex strain states.^{21,22} Moreover, monitoring negative strains is often critical for thin structures as it can drive buckling and global instabilities that could be detrimental. Conventional metal strain gauges sense both negative and positive strain regimes with excellent linearity, but are limited to monitoring low strains ($-5\% < \text{strain} < 5\%$). Previously reported flexible and stretchable strain sensors are even less capable of measuring negative strains ($< 4\%$).²³ This limits the further development and applications of such sensors. Despite the technological need for reliable and highly sensitive systems capable of monitoring compressive strains, the existing solutions still feature limited performance due to the small change in resistance during compression inherited from their intrinsic design principles.

Some of the best sensors for monitoring both compression and stretching are based on either conductive aerogels or

conductive films. Owing to their high porosity (some aerogels have porosity of 99%), aerogels have an excellent compressibility of up to 90%.^{24–26} With the addition of a conductive nanomaterial, aerogels also show good piezoresistance, with a high relative change in resistance under compressive strains. Conductive Ag hybrid aerogels supported by alginate/nitrogen-doped CNTs can be compressed up to 60% with a relative change in resistance ($\Delta R/R_0$) of about -1 .²⁷ This good sensing performance of conductive aerogels is ascribed to the increasing area of the cross-section area when their cells close under compressive strain.^{27,28} Such aerogels are mainly used as pressure sensors.^{29,30} However, despite their good compressibility, they show poor stretchability due to the weak strength of their connecting cell walls.³¹ Some highly stretchable strain sensors use conductive films of CNTs, graphene particles, nanoparticles, liquid metal, or poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) to measure some negative strains.^{21–23,32,33} The sensing mechanism in these sensors can be separated into two types: change in the cross-sectional area^{23,33} and change in the density of the conductive network.^{21,22,32} Good stretchability and compressibility were demonstrated in a strain sensor made of liquid conductors embedded in microchannels, whose cross-sectional area changed when loaded.³³ However, due to the toxic nature of liquid metal, it is hazardous to fabricate and use such sensors. Recently, a strain sensor based on a graphene film deposited on

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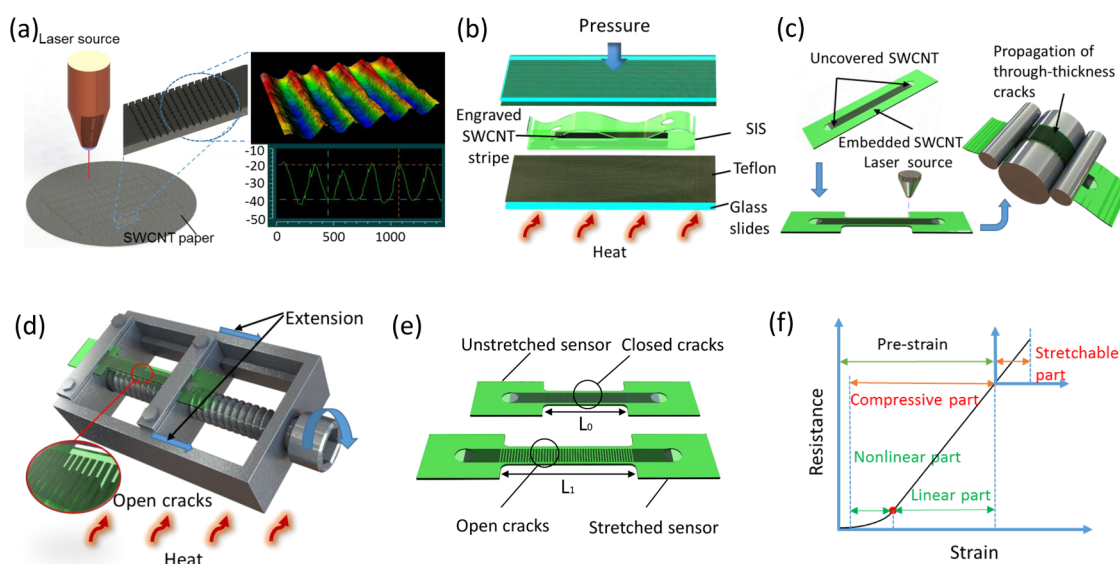


Figure 1. Manufacturing strategy for strain sensors based on SWCNT paper with pre-opened cracks. (a) The laser engraving process and three-dimensional (3D) profile image of the laser-engraved SWCNT paper. (b) Embedding laser-engraved SWCNT strip into the polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) elastomer film. (c) Cutting of the final sample shape and roll-to-roll pressing to propagate cracks through the thickness of the strip. (d) Pre-stretching the sample to generate a well-controlled network of pre-opened cracks in the SWCNT strip. (e) Sensors with closed cracks (before stretching) and with opened cracks (after stretching). (f) The proposed strategy moves the reference no-strain configuration from point A to point B, which makes the sensor capable of measuring both positive and negative strains, i.e., both stretching and compression.

a poly(dimethylsiloxane) substrate was reported to be capable of measuring negative strains, but its compressibility was limited to just -0.22% .²¹ Nanoparticles embedded in a stretchable substrate, such as CNTs embedded in Ecoflex, have also been reported.²² Such sensors can monitor negative strains, but over a very small range compared to positive strains. One issue is that the conductivity of a percolated film is almost constant when subjected to negative strains. Most of these technological solutions rely on a conductive network that is already well percolated in the uncompressed configuration. Compressions only increase the density of contact between particles that does not result in a large change in resistance. This explains the poor performance of these technologies in sensing compression. The method we show here overcomes this weakness, while maintaining an excellent performance when subjected to positive strains. The fundamental idea is to make the network poorly conductive in the uncompressed (0-strain) configuration but introducing discontinuities that can be closed in compression and quickly restore their conductivity.

To expand the high performance of strain sensors to the measurement of negative strains, we introduce a new strategy based on pre-opened cracks in single-wall carbon nanotube (SWCNT) paper. High-density network of pre-cracks are inserted into an SWCNT paper through laser engraving technology. Such a CNT paper with pre-cracks are then placed into a thermoplastic elastomer. The pre-cracks are first forced to propagate through the thickness using a roll-to-roll pressing technique.³⁴ Then, we open the cracks using a dedicated stretching device. The stresses in the substrate caused by stretching are removed through an annealing process. Well-opened cracks (those with crack-opening distance, COD, as large as $75\ \mu\text{m}$) allow us to achieve a maximum compressibility of -13% . Furthermore, the high density of cracks is useful to obtain a highly linear response for the sensor. A wide

measuring range in compressive strain coupled with excellent linearity will be attractive in stretchable electronics.

2. EXPERIMENTAL SECTION

2.1. Materials. The SWCNT papers were mainly made of single-walled carbon nanotubes (SWCNTs) provided by CheapTubes, Inc. The geometrical specifications provided by the supplier have been double checked: length from 5 to $30\ \mu\text{m}$ and outer diameter from 1 to 2 nm.

Polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) with 22 wt % styrene and methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) were purchased from Sigma-Aldrich. Dichloromethane (DCM) with over 99.5 wt % purity was purchased from Alfa Aesar.

2.2. Preparation of the SWCNT Paper. We refer the reader to a previous study in which the preparation method has been fully detailed.^{7,34} The procedure is briefly described in Figure S1. Briefly, the process is based on the dispersion of SWCNTs in methanesulfonic acid, followed by membrane filtration. Special care was taken to remove residual stresses in the SWCNT paper.

2.3. Laser-Engraving on the SWCNT Paper. We create the pre-cracks by laser ablation on the surface on the SWCNT paper. We used a PLS6MW—Multi-Wavelength Laser Platform. The processing parameters have been optimized in a previous study,³⁴ and examples of resulting grooves are shown in Figure S2. The spacing between the pre-cracks, D , were $0.25\ \text{mm}$. We then cut the paper into strips in a dimension of $27 \times 3\ \text{mm}^2$ for preparing the strain sensors.

2.4. Preparation of SIS Film. The procedure is described in Figure S3. Dichloromethane (DCM) was used to dissolve polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) grains and a homogeneous SIS film was obtained by a solution-casting process. SIS solution was prepared by sealing 20 g of SIS grains with 180 g of dichloromethane (DCM) in a glass bottle, and stirred for 1 h at 800 rpm/min speed. Then 150 g of the solution was placed into a steel container ($59 \times 7 \times 20\ \text{cm}^3$) with a cap for evaporating for 12 h. The semitransparent SIS film was then peeled off from the bottom of the steel container. The thickness of the SIS film measured by a micrometer was about $0.33 \pm 0.02\ \text{mm}$. The SIS film was then cut into strips in a dimension of $15 \times 50\ \text{mm}^2$. Two holes with 2 mm

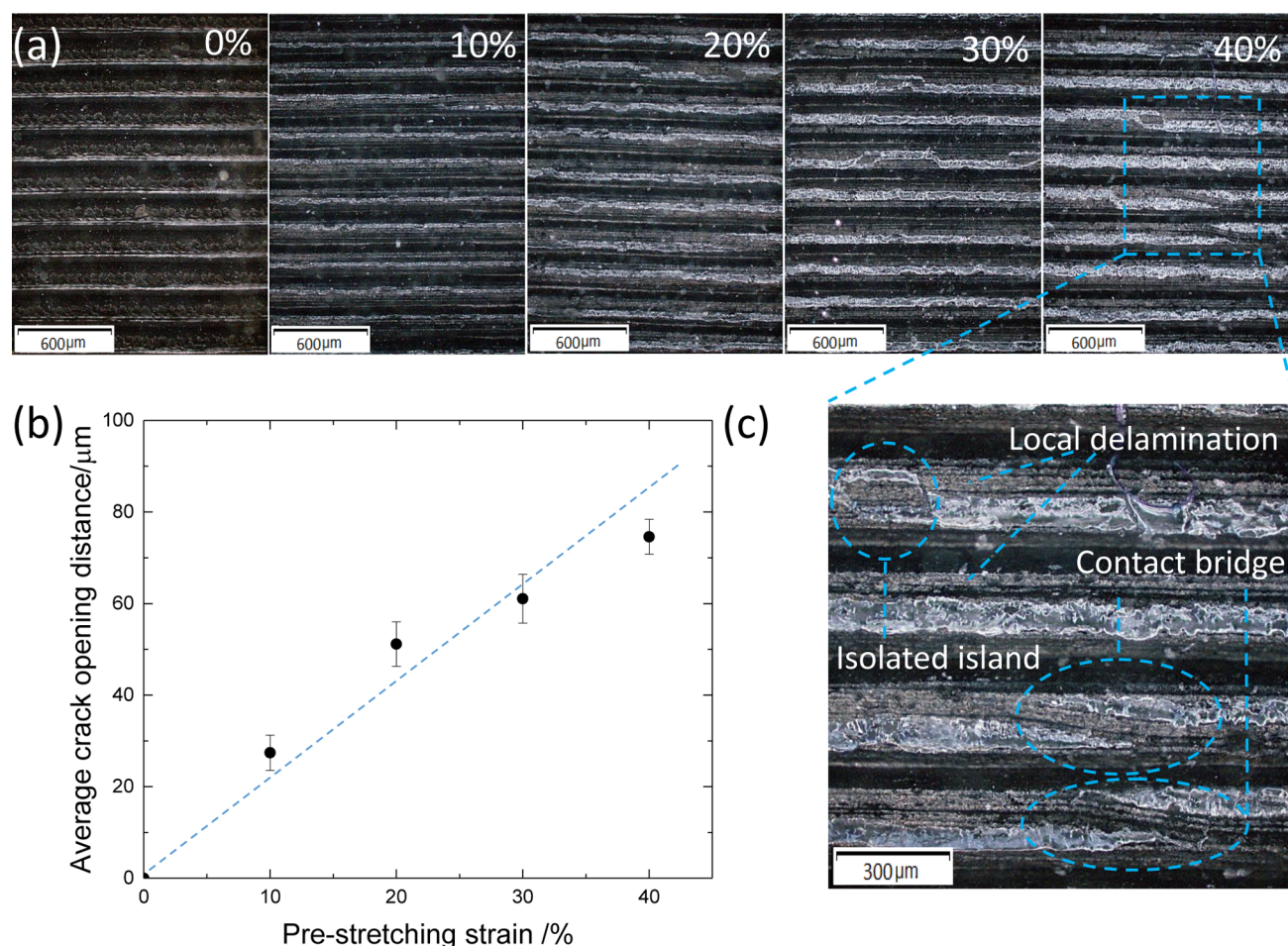


Figure 2. Open cracks with the different pre-stretching strains of 0–40%. (a) Crack images for strain sensors with 0, 10, 20, 30, and 40% pre-stretching strains. The crack-opening distance increases with the pre-stretch. (b) Average crack-opening distance with the applied pre-stretching strain. (c) Isolated island and contact bridge from the 40% pre-stretched sample.

diameter were drilled in the central line of the SIS strip for connecting copper wires, as shown in Figure 1e.

2.5. Preparation of SWCNT Paper-Based Strain Sensors. The SWCNT paper strips were deposited on the SIS substrate. Next, we covered the assembly by a second SIS layer. The sample was sandwiched in the middle of two glass slides covered with Teflon paper. Two steel blocks weighting around 2 kg were placed onto a glass slide to give the samples a uniform pressure, and at the same time the sample was heated at 120 °C for 2 h. Dog-bone shape (Figure 1c) samples were made by a laser cutting machine (Universal Laser Systems). We forced the pre-cracks to propagate through the thickness by a roll-to-roll pressing method. We have demonstrated this method meticulously in our previous study.^{7,14,34} Then the samples were given different pre-stretching 10, 20, 30, 40%, by a tensile device as shown in Figure S4a. To release the internal stresses, all the samples were annealed at 90 °C for 1 h. Finally, copper wires were used as electrodes by connecting them to the SWCNT strip through the holes.

2.6. Characterization. We investigated the microstructure of the paper using scanning electron microscopy (Quanta 3D, FEI Company) and profilometry (NewView 7100). A 5944 Instron machine was used for the compression tests. For avoiding sample buckling by direct compression, we glued the sample on an SIS strip in a direction parallel to the width of the SIS strip (as shown in Figure S4c). When we stretch the SIS strip, the Poisson effect induced the compression of the sample in the transverse direction. To maintain a symmetric configuration and avoid bending of the SIS strip, we glued a thin SIS block which is the same size as our sensor on the opposite side of the SIS strip at the same position of the strain sensor. The SIS

strip was clamped by the Instron machine (as shown in Figure S4d). We used a digital camera (SensiCam, PCO AG company) to take pictures of the sensor surface under different negative strains. These pictures were post processed with the digital image correlation (DIC) software VIC 2D (Correlated Solutions company) to calculate the strain. The electrical resistance of the specimen was measured with a KEYSIGHT 34461A digital multimeter. First, we investigated the dynamic response of the strain sensors through five loading/unloading cycles in which the distance between the grip is 75 mm and the maximum strain is 50% at a speed of 20 mm/min. After this, we investigated the measuring range of our sensor in compression. We subjected every sensor to monotonous negative strains by extending the SIS strip with the rate of 20 mm/min until the resistance does not change. The distance between the grip was 40 mm. The gauge factor (GF) was defined by $GF = (\Delta R/R_0)/\epsilon$. R_0 is the initial resistance. $\Delta R/R_0$ is the relative change in resistance and ϵ is the measured strain. To demonstrate the long-term performance of the sensor, we performed 1000 cycles for each sample, for which the maximum applied strain is near the maximum measurable strain. The loading/unloading rate of the SIS strip is 80 mm/min. We investigated the response of our best sensor under different compression rates (50, 100, 200, 400, 600, and 800 mm/min). In this part the distance between the grip is 100 mm, and the extension is 50 mm. Finally, we investigated the hysteresis under different compressive strains. The loading process contains three parts: loading up to different extension levels (20, 30, 40, 50 mm); held for 60 s; and relaxing. In this process the distance between the grip is 100 mm.

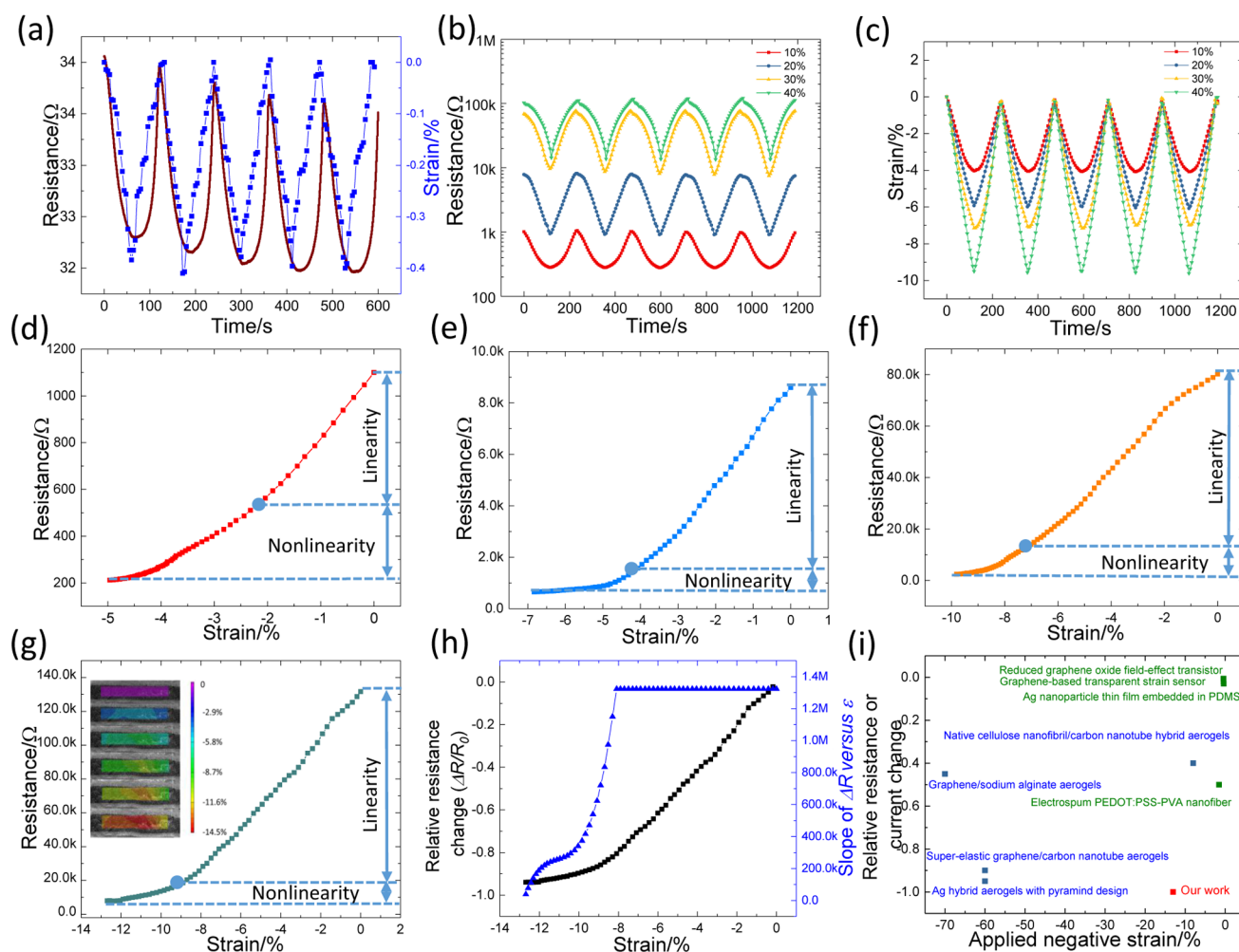


Figure 3. Strain sensing performance with different pre-stretching strains. (a) The performance of 0% pre-stretching strain sensor (closed cracks) under compression, showing poor negative strain measurability. (b) Dynamic response of strain sensors with 10, 20, 30, and 40% pre-stretching ratio (open cracks), respectively, to five compressing and relaxing cycles. (c) The strain of the sensors as shown in figure (b) measured by digital image correlation (DIC). (d–g) Resistance change to the negative strain of the sensors with 10, 20, 30, and 40% pre-stretching strain showing the measuring range of the negative strain increasing with the pre-stretching ratio. (h) The relative resistance change to strain of strain sensor with 40% pre-stretching ratio, showing good linearity and sensitivity. (i) Relative resistance or current change as a function of applied negative strain of recently reported film style and sponge style strain sensors.

3. RESULTS AND DISCUSSION

3.1. Controlled Pre-Opened Cracks in SWCNT Papers.

The design strategy that makes this sensor capable of monitoring both negative and positive strains is illustrated in Figure 1. The crucial step is introducing a network of pre-opened transverse cracks into the SWCNT paper. The cracks (and the conductive interface between the SWCNT paper and the substrate) are the key sensing elements.³⁴ These cracks are operational during stretching to detect positive strains, but the permanent pre-opening makes them also operational for measuring negative strain. The main challenges are introducing a well-controlled crack network and controlling the opening of these cracks. First, we obtained the SWCNT paper through the vacuum filtration method and optical fiber laser engraving, as shown in Figure 1a. An optical profilometer is used for three-dimensional mapping of the morphology of a typical laser-engraved SWCNT strip, which shows a crack density of 4 mm^{-1} (Figure 1a). We used the laser engraving method to achieve a high pre-crack density on the surface of the SWCNT paper, as we proved in our previous study that increasing the crack density improves the stretchability and linearity of the

strain sensor.³⁴ Figure 1b shows the process of embedding the laser-engraved SWCNT strip between the two polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) elastomer film substrates. SIS is a thermoplastic elastomer that can be reshaped by heating and stretching, which is necessary for opening the cracks. In principle, this method could be extended to any other thermoplastic elastomer. The through-thickness pre-cracks are generated on an SWCNT strip by a roll-to-roll press process (Figure 1c).³⁴ The result is a dog-bone shaped sensor with a quasi-periodical network of well-developed through-thickness cracks in the SWCNT strip. To obtain different levels of crack openings, we stretch the sensor to elongations of 0, 10, 20, 30, and 40%, using the small mechanical frame shown in Figure 1d. To keep the cracks open after removing the stretching device, we release the stress in the elastomer by heating the sensor at 90°C for 1 h while stretched. The results prove that the stretching and stress-releasing processes efficiently control the average crack opening. In Figure 1e, we compare a sensor with closed cracks to a sensor with open cracks. The relative elongation of the sensor is defined by $\varepsilon = (L_1 - L_0)/L_0$, where L_0 is the

length of the sensor with closed cracks, and L_1 is the length of the sensor with open cracks. The open-crack structure benefits the performance of the sensor when monitoring negative strain in two ways. First, the open-crack structure has a very low mechanical compressive stiffness; thus, the sensor remains globally very soft even when subjected to negative strains. This keeps the measurement from being polluted when operating on delicate substrates. Second, the open-crack structure increases the magnitude of the relative change in resistance, which benefits the sensitivity of the sensor by raising the initial resistance (Figure 1f). Also, as shown in Figure 1f, the reference configuration of the sensor shifts from point A, where the cracks are closed, to point B, where the cracks are already open in the stress-free state. This redistributes the measurement range to include both negative and positive strain regimes, and the balance between these is controlled by pre-opening the cracks.

Figure 2a shows the morphology of the pre-opened cracks under different pre-stretching strains. The average COD of the through-thickness cracks is correlated to the prescribed pre-stretching extension. These open cracks act as “slide rheostat” through their ability of adjusting the initial conductivity of the sensor. Moreover, the open cracks in SWCNT paper create a sufficient gap for operating in a negative strain regime. The evolution of COD with the pre-stretching strain is almost linear (Figure 2b). Similar to our previous study, local delamination was observed at the interface between the SWCNT paper and the thermoplastic substrate, and is expected to play a crucial role in the sensing mechanism (Figure 2c).³⁴ Some small isolated fragments are visible inside the contact bridges, due to the high pre-stretching strain applied to the film. These fragments could be avoided by increasing the depth of the initial laser engraving pattern, but this would also reduce the cross-section of the cracks available for current transfer, which could be even more detrimental to the overall performance of the sensors.

3.2. Strain Sensing. The change in resistance and the corresponding strain over time during five cycles of compressing and releasing loading are shown in Figure 3a for a strain sensor with 0% pre-stretching strain. The maximum negative strain that this sensor can detect is close to 0.4%, and the relative change in resistance at maximum negative strain is only $\Delta R/R_0 = -0.06$. This poor performance indicates that, without the pre-opened cracks, cracked SWCNT papers cannot be used for the reliable monitoring of negative strains, because the compression of an already percolated CNT film does not dramatically modify the number of CNT-to-CNT contacts or the CNT-to-CNT distance at these contact points.

We plot the dynamic responses of the sensors with 10, 20, 30, and 40% pre-stretching strains during five compressing–releasing cycles in Figure 3b,c, respectively. Figure 3b,c show that the resistance change follows closely with the applied strain with high reversibility and stability (note that the different shapes and maximum amplitudes of the applied strains are related to the fact that all the films have different maximum compression-bearing strains, and that the loading is obtained by transversally mounting the sample on a substrate under loading). In Figure 3b, we see that the resistance of the four sensors under 0% strain increases with the pre-stretching strain, i.e., the resistance increases with the COD of the pre-opened cracks, as shown in Figure 1f.

We also investigate the change in resistance against the applied negative strain during monotonous loading with 10, 20,

30, and 40% pre-stretching strains (shown in Figure 3d–g). The negative strain is measured by digital image correlation (DIC) (Figures 3g and S5). From the above four figures (Figure 3d–g), we notice similar features in the responses of all the sensors. First, the change in resistance is always linear with respect to the compressive strain. The resistance stabilizes when the maximum measurable negative strain is reached. This is totally compatible with the sensing mechanisms of crack-based stretchable sensors.^{7,14,34} The current flow is dominated by two conductive channels, the conductive networks between cracks and the conductive interface between the SWCNT paper and the SIS elastomer. These two conductive channels play significantly different roles during loading. The conductive networks between the cracks only operate when the separation between the cracked fragments is very small (similar to or less than the length of the CNTs). This mechanism explains the nonlinear change in resistance when the cracks are close to closing because the change in the density of the conductive percolated network is nonlinear at that stage. The second channel mentioned above is the conduction through the delaminated area between the CNT paper fragments and the substrate. This delaminated area is coated with a residual thin film of conductive particles, which become adhered to the substrate during delamination and provide a residual conductivity. This interface remains conductive even when very stretched (e.g., more than 150% elongation) and the change in resistance is linear with the strain.³⁴ So, the linear part shown in Figure 3d–g, is dominated by the conductive interface between the SWCNT paper and the elastomer, and the conductive networks between the cracks dominate the nonlinear part. By increasing the pre-stretching ratio from 10 to 40%, the balance between these two parts can be adjusted. Also, the measuring range for negative strain is increased from 5 to 13%, and linear part is increased from 2 to 9%. This trend, shown in Figure 3f, suggests that increasing the pre-stretching strain dramatically increases the negative strain measuring range and the relative importance of the linear part as shown in Figure 3f. Contrary to the linear part, the working length of the nonlinear part remains constant (around 3%), no matter what the pre-stretching elongation is, as it is fully determined by the length of the individual SWCNTs bridging the fragments. Pre-stretching is a way to distribute the operational measuring range of the sensor between compressive and negative strain regimes. The operational range in tension is then reduced compared to configurations without pre-stretching, but the sensors still exhibit excellent performance in tension. We tested the four sensors under 50% tensile strain (shown in Figure S8). The tensile properties are not much changed compared to our previous study.³⁴

We then plot the resistance changing rate with strain and the relative change in resistance ($\Delta R/R_0$) with strain for the sample with 40% pre-stretching strain as shown in Figure 3h. We used the slope (rate of change in the resistance with strain: $\Delta R/\epsilon$) to represent the sensitivity in Figure 3h. The high constant value at the beginning of the compression indicates a highly sensitive and linear behavior during the first stage. Then, the sensitivity decreases quickly when the strain increases above 8% and the response becomes nonlinear with respect to the crack closure. The relative change in resistance ($\Delta R/R_0$) can be seen as a good measure of merit. The minimum value of $\Delta R/R_0$ is -1 when the maximum change in resistance is possible (the resistance evolves between R_0 and 0 over the whole measurement range). The value for our sensor (shown

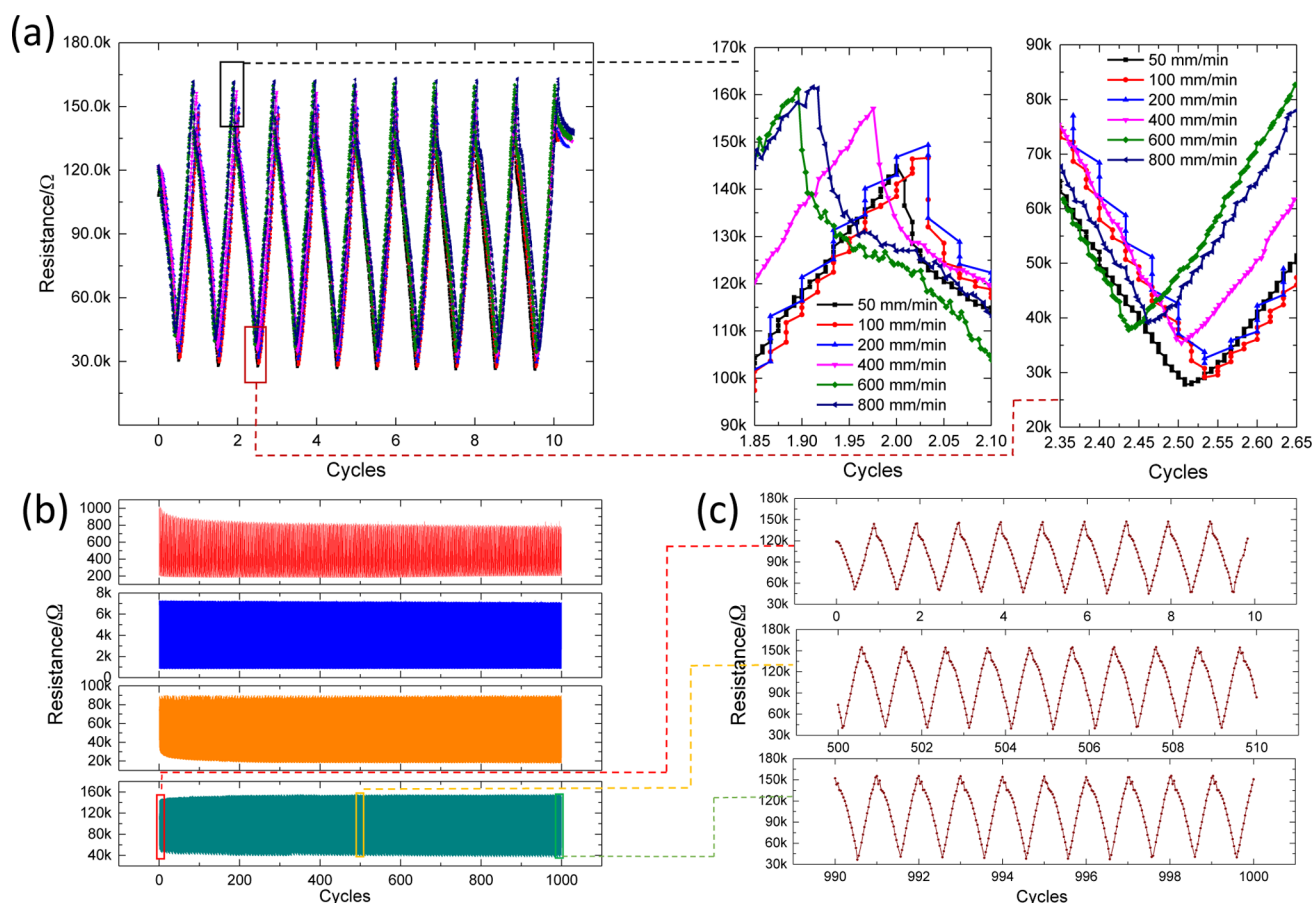


Figure 4. Loading rate sensitivity, hysteresis, and stability of pre-stretched SWCNT/SIS sensors under prescribed negative strains. (a) The dynamic response of strain sensor with 40% pre-stretching strain under different loading rates demonstrates the influence of loading speed. (b) Dynamic responses of strain sensors with 10, 20, 30, and 40% pre-stretching strain during 1000 compressing and relaxing cycles. (c) Repeatability of strain sensor with 40% pre-stretching strain at cycles 1–10, 500–510, and 990–1000, as indicated in (b).

in Figure 3h) at the maximum negative strain is -0.94 . For comparison, we plot $\Delta R/R_0$ for recently reported strain sensors under negative strain in Figure 3i. The studies are divided into two groups: conductive aerogel-based sensors and conductive film-based sensors. Our sensor has the most significant $\Delta R/R_0$ in both two groups and the highest negative strain measurement capability of the film-based strain sensors. Even though the conductive aerogel-based technology performs very well in both negative strain monitoring and relative change in resistance, its poor stretchability limits its applications in both negative and positive strain sensing.

Figure 4a shows the dynamic response of the sensor with a 40% pre-stretching ratio under different loading rates. The resistance curve shifts slightly upward with increasing loading rates. This slight dependency on the loading rate in the response is related to the rate-dependent behavior of the thermoplastic elastomer that bridges the fragments. However, the rate dependency is very limited due to the incorporation of the stiff and elastic SWCNT film. We test the sensing stability of our four sensors with 10, 20, 30, and 40% pre-stretching strains during 1000 cycles of compressing and relaxing near their measuring range limit (Figure 4c,d). The results show that the resistance of the sensors remains nearly unchanged, but increases slightly in the beginning. We also test the hysteresis of our best sensor (40% pre-stretching strain) under step-increasing loading (more details in the Experimental

Section), and the sensor performs correctly with limited hysteresis, as shown in Figure S6.

3.3. Strain Sensing Application. We manufacture an artificial skin (Figure S7) that incorporates our sensor for monitoring complicated strain states under different loading modes, as shown in Figure 5. We embed 48 sensors, which are divided into 16 groups. Each group contains a “strain rosette” in the SIS film, forming a robust artificial skin (Figure 5a). The strain rosette is composed of three sensors arranged in a Y shape for monitoring strains in different directions. Four stretchable electrodes made of CNT mixed and SIS are used to connect the sensors to the external multimeters to avoid damage during loading (Figure 5b). The artificial skin is fixed to a loading plate made of carbon-fiber reinforced epoxy for pre-stretching the artificial skin to open cracks in the embedded sensors (Figure 5c). To release the stress caused by pre-stretching, the artificial skin is heated while fixed on the loading device in an oven at 90°C for 2 h. For testing the capability of this artificial skin to monitor complex in-plane strain states, we designed two loading modes: mode I corresponds to stretching in eight directions (Figure 5d), and mode II corresponds to four fixed points that stretch vertically while releasing horizontally (Figure 5e). For mode I, we calculate the expected local strain distribution (equivalent von Mises strain) at the location of each strain sensor by finite element method (FEM), as shown in Figure 5f. The results show that all the strains are positive. Then, we measure the

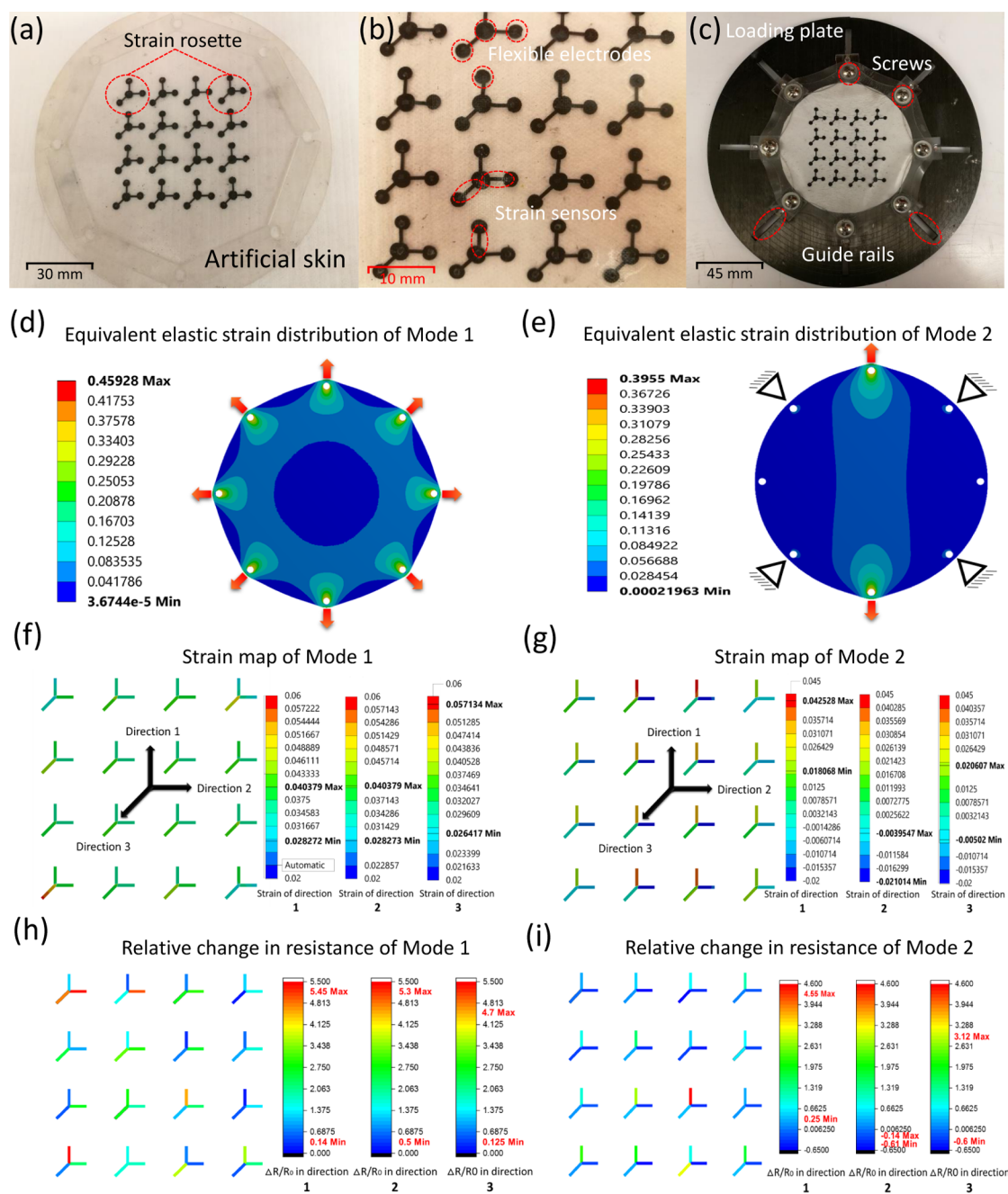


Figure 5. Strain monitoring on the surface of an artificial skin. (a) The artificial skin contains a strain rosette matrix that monitors strain at different points and in different directions. (b) The strain rosettes embedded in the artificial skin. Each strain rosette has four flexible electrodes and three strain sensors. (c) The setup for pre-stretching the artificial skin and loading the artificial skin with different modes. The artificial skin is fixed to the loading device with screws, and the screws move along guide rails for different pre-stretching and loading modes. The global strain distribution of the artificial skin under loading mode I (d) and mode II (e), calculated by FEM. The local strain distributions at different points on the strain rosettes under mode I (f) and mode II (g), calculated by FEM. The relative change in resistance of the strain rosettes under mode I (h) and mode II (i).

relative resistance of each sensor under mode I. The results are all positive, which means that all the sensors experience positive extension (Figure 5h), indicating that the artificial skin successfully detects the tensile strain state. Figure 5g shows an FEM simulation of the local strain distribution for each strain sensor in mode II. Most of the sensors along direction 1 and direction 3 experience a positive expansion, but the sensors along direction 2 are all under compressive strain. To prove the performance of this artificial skin under mode II, we measure the relative resistance of all the sensors embedded in the

artificial skin, as shown in Figure 5i. Although it is better to calibrate each strain sensor with DIC, we just measure the relative resistance of the sensors for simplicity. The results for relative resistance are consistent with the FEM results, as shown in Figure 5g. On the basis of the results for mode I and mode II, we confirm that it is possible to use our sensor as a soft mechanosensor for measuring complex strain states, i.e., not only for measuring just positive (stretching) strains, but also for negative (compressive) strains.

4. CONCLUSIONS

In summary, pre-cracked and pre-stretched strain sensors, in which the cracks are activated through uniaxial extension and stress relaxation processes, can measure both negative and positive strains over a wide range of loading with good linearity and high sensitivity. The sensor that was pre-stretched to a 40% strain achieved the measurement of a 13% negative strain. The pre-stretching and stress relaxation processes introduced here have the potential to be applied to other nanocomposites for extending the proposed concept.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b08166.

Sample preparation and characterization, additional results on strain sensing (PDF)

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G.L. and J.Z. conceptualized and supervised the study. Y.X., J.Z., and R.T. performed the experiments. Y.X., J.Z., X.X., and G.L. worked on the data analysis. G.L., Y.X., and J.Z. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.; Futaba, D. N.; Hata, K. A Stretchable Carbon Nanotube Strain Sensor for Human-motion Detection. *Nat. Nanotechnol.* **2011**, *6*, 296–301.
- (2) Zhou, J.; Mulle, M.; Zhang, Y. B.; Xu, X. Z.; Li, E. Q.; Han, F.; Thoroddsen, S. T.; Lubineau, G. High-ampacity Conductive Polymer Microfibers as Fast Response Wearable Heaters and Electro-mechanical Actuators. *J. Mater. Chem. C* **2016**, *4*, 1238–1249.
- (3) Miura, H.; Fukuyama, Y.; Sunda, T.; Lin, B.; Zhou, J.; Takizawa, J.; Ohmori, A.; Kimura, M. Foldable Textile Electronic Devices Using All-organic Conductive Fibers. *Adv. Eng. Mater.* **2014**, *16*, 550–555.
- (4) Yang, T.; Wang, W.; Zhang, H.; Li, X.; Shi, J.; He, Y.; Zheng, Q.-s.; Li, Z.; Zhu, H. Tactile Sensing System Based on Arrays of Graphene Woven Microfabrics: Electromechanical Behavior and Electronic Skin Application. *ACS Nano* **2015**, *9*, 10867–10875.
- (5) Yan, C.; Wang, J.; Kang, W.; Cui, M.; Wang, X.; Foo, C. Y.; Chee, K. J.; Lee, P. S. Highly Stretchable Piezoresistive Graphene-nanocellulose Nanopaper for Strain Sensors. *Adv. Mater.* **2014**, *26*, 2026–2027.
- (6) Cheng, Y.; Wang, R.; Sun, J.; Gao, L. A Stretchable and Highly Sensitive Graphene-Based Fiber for Sensing Tensile Strain, Bending, and Torsion. *Adv. Mater.* **2015**, *27*, 7365–7371.
- (7) Zhou, J.; Hu, Y.; Xu, X.; Han, F.; Lubineau, G. Fragmented Carbon Nanotube Papers for Ultrasensitive, Stretchable Strain Sensors. *ACS Appl. Mater. Interfaces* **2017**, 4835–4842.
- (8) Zhou, J.; Xu, X.; Xin, Y.; Lubineau, G. Coaxial Thermoplastic Elastomer-Wrapped Carbon Nanotube Fibers for Deformable and Wearable Strain Sensors. *Adv. Funct. Mater.* **2018**, No. 1705591.
- (9) Wang, X.; Gu, Y.; Xiong, Z.; Cui, Z.; Zhang, T. Silk-molded Flexible, Ultrasensitive, and Highly Stable Electronic Skin for Monitoring Human Physiological Signals. *Adv. Mater.* **2014**, *26*, 1336–1342.
- (10) Liu, Z.; Qi, D.; Hu, G.; Wang, H.; Jiang, Y.; Chen, G.; Luo, Y.; Loh, X. J.; Liedberg, B.; Chen, X. Surface Strain Redistribution on Structured Microfibers to Enhance Sensitivity of Fiber-Shaped Stretchable Strain Sensors. *Adv. Mater.* **2018**, *30*, No. 1704229.
- (11) Park, J.; You, I.; Shin, S.; Jeong, U. Material Approaches to Stretchable Strain Sensors. *ChemPhysChem* **2015**, *16*, 1155–1163.
- (12) Kang, I.; Schulz, M. J.; Kim, J. H.; Shanov, V.; Shi, D. A Carbon Nanotube Strain Sensor for Structural Health Monitoring. *Smart Mater. Struct.* **2006**, *15*, 737–748.
- (13) Wu, X.; Lu, C.; Han, Y.; Zhou, Z.; Yuan, G.; Zhang, X. Cellulose Nanowhisker Modulated 3D Hierarchical Conductive Structure of Carbon Black/natural Rubber Nanocomposites for Liquid and Strain Sensing Application. *Compos. Sci. Technol.* **2016**, *124*, 44–51.
- (14) Zhou, J.; Xu, X.; Hu, Y.; Lubineau, G. Deformable and Wearable Carbon Nanotube Microwire-based Sensors for Ultra-sensitive Monitoring of Strain, Pressure and Torsion. *Nanoscale* **2017**, *9*, 604–612.
- (15) Amjadi, M.; Pichitpajongkit, A.; Lee, S.; Ryu, S.; Park, I. Highly Stretchable and Sensitive Strain Sensor Based on Silver Nanowire-elastomer Nanocomposite. *ACS Nano* **2014**, *8*, 5154–5163.
- (16) Zhou, J.; Lubineau, G. Improving the Electrical Conductivity in Polycarbonate Nanocomposites Using Highly Conductive PEDOT/PSS Coated MWCNTs. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6189–6200.
- (17) Chen, S.; Wei, Y.; Yuan, X.; Lin, Y.; Liu, L. A Highly Stretchable Strain Sensor Based on a Graphene/silver Nanoparticle Synergic Conductive Network and a Sandwich Structure. *J. Mater. Chem. C* **2016**, *4*, 4304–4311.
- (18) Rahimi, R.; Ochoa, M.; Yu, W.; Ziaie, B. Highly Stretchable and Sensitive Unidirectional Strain Sensor via Laser Carbonization. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4463–4470.
- (19) Roh, E.; Hwang, B.-U.; Kim, D.; Kim, B.-Y.; Lee, N.-E. Stretchable, Transparent, Ultrasensitive, and Patchable Strain Sensor for Human-machine Interfaces Comprising a Nanohybrid of Carbon Nanotubes and Conductive Elastomers. *ACS Nano* **2015**, *9*, 6252–6261.
- (20) Sun, B.; Long, Y.-Z.; Liu, S.-L.; Huang, Y.-Y.; Ma, J.; Zhang, H.-D.; Shen, G.; Xu, S. Fabrication of Curled Conducting Polymer Microfibrous Arrays via a Novel Electrospinning Method for Stretchable Strain Sensors. *Nanoscale* **2013**, *5*, 7041–7045.
- (21) Bae, S.-H.; Lee, Y.; Sharma, B. K.; Lee, H.-J.; Kim, J.-H.; Ahn, J.-H. Graphene-based Transparent Strain Sensor. *Carbon* **2013**, *51*, 236–242.
- (22) Amjadi, M.; Yoon, Y. J.; Park, I. Ultra-stretchable and Skin-mountable Strain Sensors Using Carbon Nanotubes-Ecoflex Nanocomposites. *Nanotechnology* **2015**, *26*, No. 375501.
- (23) Liu, N.; Fang, G.; Wan, J.; Zhou, H.; Long, H.; Zhao, X. Electrospun PEDOT: PSS-PVA Nanofiber Based Ultrahigh-strain Sensors with Controllable Electrical Conductivity. *J. Mater. Chem.* **2011**, *21*, 18962–18966.
- (24) Lv, P.; Yu, K.; Tan, X.; Zheng, R.; Ni, Y.; Wang, Z.; Liu, C.; Wei, W. Super-elastic Graphene/carbon Nanotube Aerogels and Their Application as a Strain-gauge Sensor. *RSC Adv.* **2016**, *6*, 11256–11261.
- (25) Wang, M.; et al. Electrical Behaviour of Native Cellulose Nanofibril/carbon Nanotube Hybrid Aerogels under Cyclic Compression. *RSC Adv.* **2016**, *6*, 89051–89056.
- (26) Huang, H.-D.; Liu, C.-Y.; Zhou, D.; Jiang, X.; Zhong, G.-J.; Yan, D.-X.; Li, Z.-M. Cellulose Composite Aerogel for Highly Efficient Electromagnetic Interference Shielding. *J. Mater. Chem. A* **2015**, *3*, 4983–4991.

- (27) Zhao, S.; Zhang, G.; Gao, Y.; Deng, L.; Li, J.; Sun, R.; Wong, C.-P. Strain-driven and Ultrasensitive Resistive Sensor/switch Based on Conductive Alginate/nitrogen-doped Carbon-nanotube-supported Ag Hybrid Aerogels with Pyramid Design. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22823–22829.
- (28) Yuan, X.; Wei, Y.; Chen, S.; Wang, P.; Liu, L. Bio-based Graphene/sodium Alginate Aerogels for Strain Sensors. *RSC Adv.* **2016**, *6*, 64056–64064.
- (29) Wang, M.; Anoshkin, I. V.; Nasibulin, A. G.; Korhonen, J. T.; Seitsonen, J.; Pere, J.; Kauppinen, E. I.; Ras, R. H.; Ikkala, O. Modifying Native Nanocellulose Aerogels with Carbon Nanotubes for Mechanoresponsive Conductivity and Pressure Sensing. *Adv. Mater.* **2013**, *25*, 2428–2432.
- (30) Samad, Y. A.; Li, Y.; Schiffer, A.; Alhassan, S. M.; Liao, K. Graphene Foam Developed with a Novel Two-Step Technique for Low and High Strains and Pressure-Sensing Applications. *Small* **2015**, *11*, 2380–2385.
- (31) Tang, Y.; Gong, S.; Chen, Y.; Yap, L. W.; Cheng, W. Manufacturable Conducting Rubber Ambers and Stretchable Conductors from Copper Nanowire Aerogel Monoliths. *ACS Nano* **2014**, *8*, 5707–5714.
- (32) Lee, J.; Kim, S.; Lee, J.; Yang, D.; Park, B. C.; Ryu, S.; Park, I. A Stretchable Strain Sensor Based on a Metal Nanoparticle Thin Film for Human Motion Detection. *Nanoscale* **2014**, *6*, 11932–11939.
- (33) Park, Y.-L.; Chen, B.-R.; Wood, R. J. Design and Fabrication of Soft Artificial Skin Using Embedded Microchannels and Liquid Conductors. *IEEE Sens. J.* **2012**, *12*, 2711–2718.
- (34) Xin, Y.; Zhou, J.; Xu, X.; Lubineau, G. Laser-engraved Carbon Nanotube Paper for Instilling High Sensitivity, High Stretchability, and High Linearity in Strain Sensors. *Nanoscale* **2017**, *9*, 10897–10905.