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Highly Stretchable, Sensitive Strain Sensors with Wide Linear Sensing Region Based on Compressed Anisotropic Graphene Foam/Polymer Nanocomposites

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Abstract: Nanocomposite strain sensors composed of compressed honeycomb-like reduced-graphene-oxide (RGO) foams embedded in polydimethylsiloxane are facilely fabricated via unidirectional freeze-drying and simple mechanical compression. The microstructural characteristics of the nanocomposites endow the sensors with excellent flexibility, high stretchability and sensing sensitivity, as well as anisotropic mechanical and sensing performance when stretched along directions vertical and parallel to the aligned RGO cell walls (defined as transverse and longitudinal directions, respectively). In particular, the compression of the aligned RGO foams into thinner films results in more conductive pathways, greatly increasing the sensing sensitivity of the nanocomposite sensors. The sensors stretched along the transverse direction show an outstanding combination of high stretchability over 120 %, wide linear sensing region of 0 – 110 % and high strain sensing sensitivity with a gauge factor of around 7.2, while even higher strain sensitivity and lower sensing strain are exhibited along the longitudinal direction. Sensitive and reliable detection of human motions is also successfully demonstrated using these light-weight thin-film nanocomposite sensors.

Keywords: flexible sensors, stretchable, graphene, porous nanocomposites, human-motion monitoring

Introduction

Strain sensors capable of detecting mechanical deformation via measuring the change in electrical resistance have emerged as an attractive solution for a multitude of applications, such as robotics, artificial skin, human motion detection, and health monitoring.¹⁻⁶ For many of these applications, high sensitivity in a wide strain range is of vital importance. This desired feature cannot, however, be offered by conventional metallic or semiconducting strain sensors. The sensitivity of such a strain sensor can be characterized by its gauge factor (GF), which is defined as the ratio of relative electrical resistance change $((R-R_0)/R_0)$ to the applied strain, where R_0 and R are the resistance at 0 % strain and under stretch, respectively.^{3,7,8} For conventional metallic and semiconducting strain sensors, the GF is typically around 2, and the strain detection limit is usually only about 5 % or below.^{3,8} Thus, growing attention has been paid to the construction of novel flexible strain sensors through combining stretchable polymers, such as polydimethylsiloxane (PDMS), with various electrically conductive nanomaterials. The supporting polymers can provide high stretchability, human-friendliness, and good durability to the sensors, while the conductive nanomaterials offer the possibility of versatile structural design to obtain flexible strain sensing devices based on a diversity of working mechanisms.^{1,4,9}

Among various types of conductive nanomaterials, carbon nanomaterials have lower density and better affinity with polymers, as well as good electrical and mechanical properties,¹⁰⁻¹² which are favorable for light-weight flexible strain sensors.¹³⁻¹⁵ In particular, two-dimensional (2D) graphene layers with extraordinary electrical conductivity, superb mechanical property and extremely high specific surface area have been extensively explored as promising building blocks for the preparation of flexible strain sensors.^{1,7,14,16-23} Without structural manipulation, free-standing graphene films,^{24,25} as well as monolayer,²⁶

few-layer²⁷⁻³⁰ and multi-layer¹⁵ graphene films attached on polymer substrates, display relatively low stretchability. Under large mechanical deformation, sliding or even fracture is usually generated in graphene films due to the rigid nature of graphene in the basal plane.³¹ The performance of a graphene-based flexible strain sensor is, however, also highly dependent on its microstructure and the interaction between the graphene layers and supporting polymer. For example, Hong et al. prepared graphene films using chemical vapor deposition method and then transferred the films onto un-strained and pre-strained PDMS substrates, respectively: the former suffered from mechanical failure when the tensile strain was higher than 6 %, while the latter could be stretched to uniaxial strain as high as 30 %.³² Diversities of architectures composed of graphene layers, including percolative graphene films,^{28,30} graphene ripple,³¹ graphene woven fabrics,^{14, 20} rosette-like graphene,¹⁸ fish-scale-like graphene,³³ graphene yarn,³⁴ graphene fiber,¹⁹ graphene-based hybrids,^{8, 35} graphene aerogels and foams,^{16, 18, 36, 37} have been designed and fabricated to obtain highly stretchable strain sensors. For instance, graphene ripples were produced by a buckling approach on stretchable elastomeric substrates, which allowed the device to be stretched up to 30 % with a GF of about 2.³¹ Shi et al. attached fish-scale-like graphene slices on an elastic tape via a stretching/releasing process, and the sensors showed a tensile strain detection limit of up to 82 %, linear resistance/strain curve region of 0 – 60 % and a GF of around 16.2.³³ Notably, the linear relation between the relative resistance change and the applied strain is a very important parameter for quantitative strain detection.^{3, 7, 34} Strain sensors based on three-dimensional (3D) fragmentized graphene foams and graphene/nanocellulose composites with infiltrated PDMS have also been constructed, and both displayed very high strain detection limit (78 % and 100 %, respectively) and GF, whereas they both exhibited non-linear response between the relative resistance change and applied strain.^{8, 18} The graphene yarn-based strain sensors reported by Park, et al. showed very wide linear sensing region of up to 150 %, but the GF was relatively low (1.4).³⁴ The above examples show that

achieving simultaneous high stretchability, high sensitivity and wide linear sensing region for a flexible strain sensor still remains a great challenge.

In this work, highly stretchable, sensitive strain sensors based on anisotropic graphene foams supported on PDMS were constructed using a simple method. Firstly, by unidirectional freeze-drying²⁸⁻⁴¹ of graphene oxide (GO) aqueous suspensions followed by thermal annealing to convert GO to reduced GO (RGO), a RGO foam with elongated honeycomb-like structure was produced, as shown in Scheme 1, in which the micron-sized aligned pores were templated from the ice crystals grown in the unidirectional freezing process, while the vertically aligned cell walls were formed by stacked RGO layers. The RGO foam was then macroscopically compressed in a direction perpendicular to the aligned cell walls to obtain compressed RGO (CRGO) foam, which is in the form of a free-standing film, whereas still contains numerous smaller pores between the cell walls. These pores facilitate the diffusion of the PDMS prepolymer into the 3D porous architecture, enhancing the structural stability and reversible stretchability of the sensors. The aligned graphene cell walls give the CRGO/PDMS nanocomposites anisotropic sensing performance, i.e., the sensing performance along the growth direction of the cell walls (longitudinal direction marked in Scheme 1) and that in the direction perpendicular to the growth direction of the cell walls (transverse direction marked in Scheme 1) is different. More importantly, the compression of the RGO foam creates more contact area between the graphene-based cell walls, which efficiently improves the strain sensitivity upon stretching the CRGO foam/PDMS nanocomposites. These unique microstructural characteristics of the CRGO/PDMS nanocomposites allow the corresponding strain sensors to exhibit a measurable strain limit as high as 122 %, linear sensing region of 0 - 110 %, and high linear sensitivity (with GF of approximately 7.2) upon stretching in the transverse direction. When the nanocomposite strain sensors are stretched along the longitudinal direction, relatively narrow strain sensing range with much higher sensitivity can be achieved. Furthermore, our thin and flexible strain sensors can be well

attached to human body, and show excellent sensing performance in detecting various human motions, such as frequencies and angles of finger and knee bending.

Scheme 1. Schematics showing the as-prepared anisotropic RGO (left) and CRGO (right) foams with marked directions including the compressive direction, longitudinal direction that is parallel to the growth direction of the cell walls, and transverse direction that is perpendicular to the growth direction of the cell walls.

Experimental

Fabrication of aligned porous RGO and CRGO foam nanocomposites: GO was prepared by a modified Hummer's method.^{42, 43} The aligned porous GO foam was prepared by freezing the GO aqueous solution cast in a mould with Teflon container and stainless steel bottom immersed in liquid nitrogen, followed by freeze-drying the prepared hydrogels in the freeze-drying vessel ($-80\text{ }^{\circ}\text{C}$ and 10 Pa) for 24 h. Afterwards, the GO foams were heated at a speed of $10\text{ }^{\circ}\text{C}/\text{min}$ in a tube furnace and annealed at the temperature of $800\text{ }^{\circ}\text{C}$ for 2 h under argon atmosphere to obtain the aligned porous RGO foam. Density of the 3D RGO aligned porous architectures could be controlled by adjusting the water fraction of the GO aqueous solution. In a case of RGO porous architectures with density of $1.5\text{ mg}/\text{cm}^3$, GO aqueous solution containing 0.38 wt% GO was freeze-dried to obtain the GO foams with density of $6\text{ mg}/\text{cm}^3$, which were then thermal annealed to prepare the 3D RGO forms. The RGO foam was set between two clean glass side and compressed to obtain the free-standing and flexible

CRGO foam based film, which could still maintain the aligned graphene based cell walls and micron-sized pores microstructures.

Fabrication of thin film CRGO/PDMS nanocomposite strain sensors: The CRGO foam based film (with a dimension of 22.00 mm × 10.00 mm × 0.06 mm) was put on the surface of the glass slide after pasted with two copper wires as electrodes using conductive silver adhesive (D05001, Beijing Emerging Technology Co. Ltd., China). Then the liquid PDMS prepolymer, after being degassed in a vacuum chamber and the ice water bath, was poured onto the glass slide with controllable thickness by adjusting the mass of PDMS. The good diffusion of the PDMS prepolymer into the existing micron-sized pores of CRGO foam led to a certain degree of expansion of these pores, and thickness of the sensors could reach between 0.38 – 0.50 mm together by controlling PDMS amount. After curing PDMS at 65 °C for 6 h, the CRGO foam/PDMS nanocomposite sensors were prepared successfully. In order to compare sensing performance, RGO foam/PDMS and thick CRGO foam (from a compressed 8 mm thick RGO foam)/PDMS nanocomposites, as well as the CRGO foam from a compressed RGO foams with higher density (3 mg cm⁻³) based PDMS nanocomposites were prepared. All nanocomposite sensors were prepared with similar distance between the two electrodes and width for better comparison.

Characterization: The microstructure of the porous architectures was investigated by scanning electron microscopy (SEM, JSM-7600F, Japan). The tensile performance of the nanocomposite sensors were evaluated by dynamic mechanical analysis (DMA, TA Q800). X-ray diffraction (XRD) measurements were carried out at room temperature with specular reflection mode (Cu K α radiation, X'Pert PRO, PANalytical, Holland). Raman spectra were obtained with a Renishaw in Via Raman Spectroscopy, using the 632.8 nm line of a He-Ne laser. Micromeritics TriStar II 3020 Surface Area and Porosity Analyzer was used to obtain nitrogen adsorption desorption isotherms and gave the Brunauer–Emmett–Teller (BET)

specific surface area. The electromechanical response of the strain sensors was evaluated by measuring the resistance using a Keithley 4200-SCS electrometer (Keithley, Cleveland, Ohio, USA) when each sample was subjected to uniaxial stretch by a home-built stretching stage. At least five specimens were tested for each type of nanocomposites. The measured electrical conductivities of the RGO foams, CRGO foams, and the CRGO foam/PDMS nanocomposites were similar in different directions due to the interconnected graphene-based cell walls. Mechanical and electromechanical tests of the sensors were performed when the tensile direction is along the transverse direction for all the samples unless mentioned otherwise.

Results and Discussion

The fabrication processes for the graphene-based foams with aligned micron-sized pores and the corresponding nanocomposite sensors are illustrated in **Fig. 1a-e**. The GO sheets are well and stably dispersed in water, and their lateral size is roughly in the range of 3 to 20 micrometers (Fig. 1a). In the freezing process, steep temperature gradient leads to the rapid formation of ice-crystal nuclei at the bottom and the unidirectional growth towards the upside of the suspension, causing GO being extruded and stacked between the ices (Fig. 1b). After the sublimation of ice via freeze-drying process, micron-sized pores templated from the ice crystals are formed, leading to a GO foam with aligned pores. In the subsequent thermal annealing, the majority of oxygen-containing groups on GO is removed, producing a RGO foam (Fig. 1c). The porosity and density of the foam can be controlled by adjusting the water fraction in the suspension. In this work, the densities of the GO and RGO foams are controlled to be approximately 4 and 1.5 mg cm⁻³, respectively. By compressing the RGO foam in a direction perpendicular to the cell wall growth direction, as shown in Scheme 1, with an adequate load, a flexible film of CRGO foam is obtained (Fig. 1d, f). The infiltration of PDMS prepolymer into the CRGO film and subsequent curing at 65 °C results in a robust

flexible nanocomposite film (Fig. 1e,g), which can be stretched easily to more than 100 % (Fig. 1h).

Fig. 1 Diagrams showing the preparation process for a CRGO/PDMS nanocomposite strain sensor: (a) SEM image of GO (scale bar is 10 μm) and optical image of the GO suspension (inset), (b) a schematic showing freezing process of the GO suspension, SEM images (scale bars are 100 μm) of the (c) RGO and (d) CRGO foams (red arrows in image b and c indicate the growth direction of the ice crystals and aligned cell walls, respectively), (e) schematics showing the process of making CRGO/PDMS nanocomposites, pictures of (f) a sheet of CRGO foam, (g) a CRGO/PDMS nanocomposite strain sensor, and (h) the sensor before (top) and after (bottom) being stretched over 100 %.

Pictures and SEM images in **Fig. 2** show macroscopic appearance and microstructures of GO, RGO and CRGO foams as well as the CRGO foam/PDMS nanocomposite sensors. The shapes of the GO and RGO foams (Fig. 2a, b) can be controlled by the dimensions of the mold. Both foams show good flexibility at the thickness of ~ 2 mm due to their low density, as well as the aligned pore and cell-wall structures (Fig. 2b, 2e, 2f, Fig. S1a). For the RGO foam, the interconnected cell walls give rise to a stable 3D architecture and 3D conductive pathway; each cell wall is estimated to have a thickness of more than ten nanometers, and thus each cell

wall is formed by stacking of tens of graphene layers. This estimation is supported by our BET measurement result, which indicates that the BET surface area of the RGO foam ($\sim 154 \text{ m}^2 \text{ g}^{-1}$) is much lower than the theoretical surface area of single-layer graphene ($2630 \text{ m}^2 \text{ g}^{-1}$).⁴⁴ The gaps between the nearest cell walls are in the range of 30 to 50 μm for the RGO foam at the low density of 1.5 mg cm^{-3} . After compression, the thickness is decreased from 2 mm for the RGO foam to $\sim 0.06 \text{ mm}$ for the CRGO foam (Fig. 2c, Fig. S1b-d), while the aligned cell walls are well retained albeit the size of the pores become smaller ($\sim 10 \mu\text{m}$) (Fig. 2g). The microstructure consisting of open pores and interconnected cell walls leads to the formation of graphene conductive networks, as well as similar conductivity in different directions for the aligned porous architectures. It is also worthwhile noting that the pores can ensure good infiltration of PDMS prepolymer into the 3D CRGO foam; meanwhile, closer contacts between the graphene cell walls create more conductive pathways, which is beneficial to inducing more conductive path change and hence larger resistance change of the nanocomposite strain sensor upon stretching. X-ray diffraction (XRD) patterns and Raman spectra (Fig. S2) confirm the effective reduction of the GO to RGO foam, and that the structure of the graphene layers in the CRGO foam is not altered by the compression force applied. The integration of the flexible CRGO foam with the supporting PDMS endows the nanocomposite with good stretchability, bendability, and twist-ability (Fig. 2d, Fig. 1g, 1h) owing to the good interface between the graphene foam and PDMS. Top and cross-sectional views of the nanocomposite manifest that the CRGO foam is well embedded in the PDMS matrix (Fig. 2h-k). In fact, the thickness of the nanocomposite is around 380-500 μm (Fig. 2i), which is much thicker than the CRGO foam ($\sim 60 \mu\text{m}$), implying that the infiltration of PDMS into the foam causes the expansion of the gaps between the cell walls to some extent. Even though, the alignment of the cell walls can be well retained in the CRGO foam/PDMS nanocomposite sensors, which is evident from the microstructures of the cross section (Fig. 2j, 2k, Fig. S3).

Fig. 2 Pictures of (a) GO and RGO foams showing their shape and dimensions, (b) a sheet of RGO foam showing its good flexibility, (c) a sheet of CRGO foam (inset: a cross-sectional optical image, scale bar is 60 μm), (d) a twisted CRGO/PDMS nanocomposite strain sensor. SEM images showing microstructures of (e) GO foam, (f) RGO foam, (scale bars are 100 μm for images e and f; scale bar is 1 μm for inset in image f), and (g) CRGO foam (scale bars are 100 and 10 μm for the left and the right two images, respectively). SEM images of the CROG/PDMS nanocomposite strain sensor: (h) top surface (scale bars are 100 μm for images h and i; inset: with higher magnitude and scale bar is 20 μm), (i) cross-sectional surface showing the thickness of the CRGO foam, (j) cross-sectional cryogenically-fractured surface parallel to the longitudinal direction showing distinguishable aligned graphene layers and (k) cross-sectional cryogenically-fractured surface parallel to the transverse direction showing the absence of aligned graphene layers (scale bars are 20 μm for images j and k; inset: with higher magnitude and scale bars are 1 μm).

Prior to characterization of the electromechanical performance of the CRGO foam/PDMS strain sensors, the mechanical properties of the nanocomposite are measured, as shown in **Fig. 3a**. Under the cyclic tensile strain from 30 % to 100 % in the transverse direction (the direction perpendicular to the aligned graphene cell walls as shown in Scheme

1), the stress increases with increasing strain and can well return to the initial state, indicating no obvious damage of the structure under such a large deformation. The good reversibility can be maintained for more than 300 stretch/release cycles with 30 % strain (Fig. S4a, b), further demonstrating the excellent mechanical durability of the nanocomposite. Since the microstructure of the nanocomposite is anisotropic, it is also stretched in the longitudinal direction (the growth direction of the graphene cell walls). Compared with the high fracture strain of >120 % in the transverse direction, the fracture strain is only about 60 % in the longitudinal direction (Fig. S4c). It is well established that tensile strength and modulus of nanocomposites highly depend on the orientation of the nanofillers in the polymer matrices.^{45,46} Since the graphene-based cell walls are better connected and well aligned along the longitudinal direction, the tensile strength and modulus of the nanocomposite in this direction are significantly higher than the ones in the transverse direction (Fig. S4d, S4e). Less continuous cell walls in the transverse direction of the CRGO foam/PDMS nanocomposite lead to less fracture of the cell walls under large extension; less continuous cell walls also mean more elastic polymer between the cell walls, which is instrumental in energy absorption. In summary, a combination of better elastic performance and higher tensile fracture strain is obtained in the transverse direction whereas higher tensile strength and modulus are achieved in the longitudinal direction. Such anisotropic mechanical properties derived from the designed anisotropic porous graphene architectures are attractive for broadening the applications of the sensors.

Fig. 3 (a) Stress-strain curve and (b) the relative change in resistance of the CRGO/PDMS nanocomposite strain sensors under various strain loading; (c) the relative change in resistance versus time curves of the CRGO/PDMS strain sensors under repeated stretch-release process, (d) the relative resistance change ratio versus strain curves of various strain sensors, (e) the relative resistance change of the CRGO/PDMS strain sensor under 10 % strain at various strain frequencies, (f) life-time test of the CRGO/PDMS strain sensors under 30 % strain.

In the electromechanical tests of the CRGO foam/PDMS nanocomposite sensors, the electrical resistance increases immediately upon the application of a tensile strain in the transverse direction (Fig. S5a, S5b, S5e). A larger relative resistance change is observed in the first stretch-release cycle in comparison with those in the subsequent cycles, which can be attributed to the reconstruction of the conductive paths in the nanocomposite. The reconstruction of conductive paths is a common phenomenon reported for many composite sensors.^{18, 47, 48} After the initial several cycles, the relative resistance change stabilizes (Fig. S5c, S5d, S5f) and thus test results are recorded after the initial several cycles to obtain stable electromechanical responses. In the cyclic testing process, with gradually increasing the strain loading from 30 % to 100 %, the relative resistance change increases accordingly while the excellent reversibility is maintained (Fig. 3b). The increase of relative resistance change with the tensile strain can be attributed to increased disconnections between graphene sheets under

a larger deformation and hence a reduction in conductive paths in the nanocomposite. When the sensors are subjected to repeated stretch-release cycles, the relative resistance changes detected show excellent repeatability at each strain loading level in the strain range of 5 % to 100 %, indicating good reliability of the strain sensors (Fig. 3c). Furthermore, it is striking to see that good linear relationship between the relative resistance change and tensile strain is observed in a very wide strain range (0 % -110 %) for our nanocomposite sensors in the transverse direction (Fig. 3d, Table S1). The GF in the linear region is calculated to be around 7.2 ($R^2 = 0.968$), which is much higher than traditional metal- or semiconductor-based strain gauges. Compared with graphene foam-based composites reported in literatures, such as 3D fragmentized graphene foam/PDMS composites⁸ (strain detection limit of 78 %, non-linear response with GF ranging from 2.4 to 15.0), graphene/nanocellulose composite foams with infiltrated PDMS¹⁸ (strain detection limit of 100 %, non-linear response with GF ranging from 1.6 to 7.1), graphene aerogel/PDMS composites³⁶ (strain detection limit of 19 %, including a linear region with GF of 61.3 and a non-linear region), CVD graphene foam/PDMS composites³⁷ (strain detection limit of ~48%, including two linear regions with GF of 2.6 and 8.5, respectively, and a non-linear region), as well as some other typical graphene-based strain sensors listed in Table S2, our flexible CRGO foam/PDMS nanocomposite sensors exhibit high stretchability (up to 122 %), much wider linear sensing strain region (0 – 110 %) and fairly good sensitivity simultaneously. The combination of wide linear sensing strain range and good sensitivity is very useful for quantitatively monitoring mechanical deformation.

To full utilize the functions of the CRGO foam/PDMS strain sensors, the relative resistance change as a function of tensile strain is also measured in the longitudinal direction of the CRGO foam/PDMS nanocomposite. In the longitudinal stretching mode, two linear regions in the strain ranges of 0 – 30 % and 30 % -57 % are observed, and the corresponding GF (calculated based on the slope in the linear region) are 12.2 ($R^2 = 0.966$) and 27.0 ($R^2 = 0.988$), respectively. Compared with the transverse direction, more fracture of the graphene

cell walls are expected when the sensors are subjected to the strain in the longitudinal direction, as discussed earlier. This would result in more substantial disconnections of the graphene nanosheets and greater reduction of conductive paths, and hence higher relative resistance change and GF, while good reversibility and repeatability of the relative resistance change can still be observed when the sensors are subjected to 30 % strain in the longitudinal direction (Fig. S6). Such anisotropic sensing characteristics, which are derived from the anisotropic microstructure of the CRGO foam, may be useful for biaxial strain sensors, and provide enlightening information for design of novel strain sensors.

To understand the role played by the compression process, an uncompressed RGO foam /PDMS nanocomposite and a thicker CRGO foam/PDMS (prepared by the compression of a much thicker RGO foam (~ 8 mm) at the same compression ratio) nanocomposite were also tested by stretching in the transverse direction (Fig. 3d). The uncompressed RGO foam/PDMS nanocomposite sensor exhibits high stretchability but low GF (Fig. S7). Its strain sensitivity (GF is around 1.1 at 60 % strain) is much lower than that of the CRGO foam/PDMS (GF = 7.2 at the same strain) because the uncompressed 3D RGO foams have less connections or smaller contact area between the graphene cell walls in the transverse direction. This leads to fewer conductive networks in the uncompressed RGO foam/PDMS nanocomposites and thus less change in the conductive paths of the sensors upon large deformation. Interestingly, the GF of the thick CRGO foam/PDMS nanocomposites (< 1) is also much lower than that of the CRGO foam/PDMS nanocomposite sensors (Fig. S8), indicating that excess contacts between the graphene cell walls in a bulk sample are also not favored for improving strain sensing sensitivity of the sensors. Similarly, higher-density RGO foams (density = 3 mg cm^{-3}) are used to prepare the CRGO/PDMS nanocomposite sensors that show a GF between 4 and 5 under 50 % strain (Fig. S9), indicating that when the packing density of the graphene cell walls is too high, the strain-induced resistance change would also reduce. The above results show that the contacting area between the graphene cell walls and

the number of conductive paths are the key factors controlling the sensitivity of the strain sensors.

The sensing performance of the CRGO foam/PDMS nanocomposites was also characterized at various strain rates, i.e., 10 % strain was applied with the strain loading frequency varying from 0.016 to 1 Hz (Fig. 3e). Same relative resistance change is observed at different frequencies due to strong adhesion between the graphene layers and PDMS in the nanocomposite sensors,²⁷ demonstrating the potential of the sensors for quantitatively monitoring various kinds of mechanical deformation, no matter fast or slow. Moreover, the sensors display good repeatability and reversibility for more than 1000 stretch-release cycles under the tensile strain of 30 % in the transverse direction (Fig. 3f), showing the excellent durability and reliability of the CRGO foam/PDMS nanocomposite sensors.

To comprehend the sensing mechanism more deeply, the microstructures of the CRGO/PDMS nanocomposite sensors were observed in a cyclic stretch-release process, as shown in **Fig. 4**. The SEM images of the sensors at the initial state (without stretching) (Fig. 4a) show well aligned graphene cell walls and good interface between graphene layers and PDMS matrix. Micron-sized pores in the CRGO foam can facilitate the infiltration of the PDMS into the 3D foam so that the aligned graphene-based conductive paths are well reserved in the nanocomposite. Upon stretching along the transverse direction, cracks appear between the graphene sheets in the cell walls (Fig. 4b), and it is expected that the cracks would grow with increasing tensile strain. The interconnected graphene-based cell walls in the 3D CRGO foam can maintain the stability of the CRGO foam/PDMS nanocomposite sensors when subjected to high stretched strains. Therefore, the generation and growth of the cracks not only lead to a reduction of conductive paths and hence an increase of the overall resistance of the sensors, but also effectively absorb the mechanical energy originated from the large mechanical deformation, preventing the fracture of the graphene layers to avoid the mechanical failure of the sensors under large deformation. Consequently, high stretchability,

wide linear sensing region and high strain sensitivity can be achieved simultaneously with our CRGO foam/PDMS nanocomposite sensors as discussed above. When the strain applied is released (back to the strain-free state), reconnections between the graphene cell walls at crack locations are observed (Fig. 4c), which contributes to the restoration of the low resistance. It is worth noting that some irreversible micro-cracks still exist after the initial stretch/release cycles, i.e., they cannot thoroughly disappear even the strain is back to zero, resulting in the irreversible resistance change of the sensors in the initial cycles, as discussed earlier (Fig. S5). Nevertheless, the reversibility and repeatability are excellent after the initial few cycles due to the interconnected graphene-based conductive paths derived from the interconnected cell walls of the 3D CRGO foams. The observations on microstructures are consistent with the strain sensing test results, further verifying the critical role of the microstructures played in strain sensing.

Fig. 4 Microstructures of the CRGO/PDMS nanocomposite strain sensors: (a) in unloaded states, (b) at stretched state (with 50 % strain), and (c) after the stress is released (single arrows indicate the direction of the aligned cell walls, while the double-headed arrow shows the stretching direction of the sensors).

Since our CRGO foam/PDMS nanocomposite sensors are thin, highly flexible and stretchable, they can be easily attached to human body as wearable devices for detection of human motions. **Fig. 5a** shows the detected signal of relative resistance change of the sensor attached on a finger, which bends with gradually increased amplitude. When the finger bends to a small angle and then keeps steady, the resistance of the sensor initially increases due to the stretching caused by the bend, and then keeps stable after the pulse that is caused by the intrinsic viscoelastic characteristic of PDMS.^{18, 49} Bending of the finger to a larger angle is equivalent to the application of a larger strain, and the corresponding relative resistance change detected by the attached sensor is indeed larger. More interestingly, when the finger bends and moves back in various frequencies, the sensors can also detect the timing and frequencies of this series of motions very well (Fig. 5b-f). Based on the measured electrical signals from the sensor, we can easily deduce that in the testing period, the finger repeatedly bends and moves back quickly with similar amplitude, and number of bends in each short interval of only a few seconds increases gradually from one, two, three, five, seven to nine times (Fig. 5c-f). Notably, even the speed of the movement is fast, the sensor can still detect and distinguish it well, which is consistent with the ability of the sensors for sensing strains at various frequencies shown in Fig. 3. The motion of a knee with various bending amplitudes or frequencies can also be well detected (Fig. 5g-h). Knee bending cannot be as fast as finger bending, whereas the strain caused by the knee bending is much larger than finger bending. Indeed, significantly larger relative resistance change is observed for knee bending than finger bending, showing the usefulness of our sensors in detection of various human motions, from small strain to relatively large strain activities.

Fig. 5 Detections of human motions: finger bending activities with (a) increasing amplitude and (b-f) increasing frequencies (c-f are horizontally magnified views of b), (g-i) knee bending activities with various amplitudes and frequencies (h and i are horizontally magnified views of g).

Conclusions

In this study, highly stretchable strain sensors based on CRGO foam/PDMS nanocomposites are constructed through combining the unidirectional freeze-drying method with a simple physical compression. The CRGO foam, featuring anisotropic micron-sized pores and aligned holey graphene cell walls, enables full infiltration of the PDMS prepolymer. The resultant nanocomposites exhibit good interfaces between the graphene cell walls and PDMS matrix, together with anisotropic conductive networks resulted from the aligned graphene cell walls. The microstructural characteristics of the CRGO foam/PDMS nanocomposites offer the sensors excellent flexibility, high stretchability and good sensing

sensitivity, as well as anisotropic mechanical and sensing performance when stretched along the longitudinal and transverse directions. The transverse directional sensing strain can reach as high as 122 % together with a very wide linear sensing region of 0 – 110 % and a high GF of around 7.2, while longitudinal directional GF can reach from 12.2 to 27.0 with sensing strain up to 57 %. Mechanism studies show that compressing RGO foam results in more conductive pathways in the resultant CRGO foam, and hence a much increased GF of the CRGO foam/PDMS nanocomposite sensors. Good flexibility, high stretchability and light weight of these nanocomposite thin film sensors, along with their good reversibility and durability, allow their successful use for sensitive and reliable monitoring of human motions, such as finger and knee bending activities. Compared with most graphene-based strain sensors reported in literatures, the effective design of the microscopic- and macroscopic-scale structures of the CRGO foam/PDMS nanocomposite strain sensors leads to their superior sensing performance in terms of a combination of high stretchability, wide linear sensing region and excellent sensitivity. Moreover, the anisotropic strain sensing capability arisen from the specifically designed anisotropic microstructures is also instructive for design of novel strain sensors with various microstructures in future.

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Highly Stretchable, Sensitive Strain Sensors with Wide Linear Sensing Region Based on Compressed Anisotropic Graphene Foam/Polymer Nanocomposites

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Abstract: Nanocomposite strain sensors composed of compressed honeycomb-like reduced-graphene-oxide (RGO) foams embedded in polydimethylsiloxane are facilely fabricated via unidirectional freeze-drying and simple mechanical compression. The microstructural characteristics of the nanocomposites endow the sensors with excellent flexibility, high stretchability and sensing sensitivity, as well as anisotropic mechanical and sensing performance when stretched along directions vertical and parallel to the aligned RGO cell walls (defined as transverse and longitudinal directions, respectively). In particular, the compression of the aligned RGO foams into thinner films results in more conductive pathways, greatly increasing the sensing sensitivity of the nanocomposite sensors. The sensors stretched along the transverse direction show an outstanding combination of high stretchability over 120 %, wide linear sensing region of 0 – 110 % and high strain sensing sensitivity with a gauge factor of around 7.2, while even higher strain sensitivity and lower sensing strain are exhibited along the longitudinal direction. Sensitive and reliable detection of human motions is also successfully demonstrated using these light-weight thin-film nanocomposite sensors.

Keywords: flexible sensors, stretchable, graphene, porous nanocomposites, human-motion monitoring

Introduction

Strain sensors capable of detecting mechanical deformation via measuring the change in electrical resistance have emerged as an attractive solution for a multitude of applications, such as robotics, artificial skin, human motion detection, and health monitoring.¹⁻⁶ For many of these applications, high sensitivity in a wide strain range is of vital importance. This desired feature cannot, however, be offered by conventional metallic or semiconducting strain sensors. The sensitivity of such a strain sensor can be characterized by its gauge factor (GF), which is defined as the ratio of relative electrical resistance change $((R-R_0)/R_0)$ to the applied strain, where R_0 and R are the resistance at 0 % strain and under stretch, respectively.^{3,7,8} For conventional metallic and semiconducting strain sensors, the GF is typically around 2, and the strain detection limit is usually only about 5 % or below.^{3,8} Thus, growing attention has been paid to the construction of novel flexible strain sensors through combining stretchable polymers, such as polydimethylsiloxane (PDMS), with various electrically conductive nanomaterials. The supporting polymers can provide high stretchability, human-friendliness, and good durability to the sensors, while the conductive nanomaterials offer the possibility of versatile structural design to obtain flexible strain sensing devices based on a diversity of working mechanisms.^{1,4,9}

Among various types of conductive nanomaterials, carbon nanomaterials have lower density and better affinity with polymers, as well as good electrical and mechanical properties,¹⁰⁻¹² which are favorable for light-weight flexible strain sensors.¹³⁻¹⁵ In particular, two-dimensional (2D) graphene layers with extraordinary electrical conductivity, superb mechanical property and extremely high specific surface area have been extensively explored as promising building blocks for the preparation of flexible strain sensors.^{1,7,14,16-23} Without structural manipulation, free-standing graphene films,^{24,25} as well as monolayer,²⁶

few-layer²⁷⁻³⁰ and multi-layer¹⁵ graphene films attached on polymer substrates, display relatively low stretchability. Under large mechanical deformation, sliding or even fracture is usually generated in graphene films due to the rigid nature of graphene in the basal plane.³¹ The performance of a graphene-based flexible strain sensor is, however, also highly dependent on its microstructure and the interaction between the graphene layers and supporting polymer. For example, Hong et al. prepared graphene films using chemical vapor deposition method and then transferred the films onto un-strained and pre-strained PDMS substrates, respectively: the former suffered from mechanical failure when the tensile strain was higher than 6 %, while the latter could be stretched to uniaxial strain as high as 30 %.³² Diversities of architectures composed of graphene layers, including percolative graphene films,^{28,30} graphene ripple,³¹ graphene woven fabrics,^{14, 20} rosette-like graphene,¹⁸ fish-scale-like graphene,³³ graphene yarn,³⁴ graphene fiber,¹⁹ graphene-based hybrids,^{8, 35} graphene aerogels and foams,^{16, 18, 36, 37} have been designed and fabricated to obtain highly stretchable strain sensors. For instance, graphene ripples were produced by a buckling approach on stretchable elastomeric substrates, which allowed the device to be stretched up to 30 % with a GF of about 2.³¹ Shi et al. attached fish-scale-like graphene slices on an elastic tape via a stretching/releasing process, and the sensors showed a tensile strain detection limit of up to 82 %, linear resistance/strain curve region of 0 – 60 % and a GF of around 16.2.³³ Notably, the linear relation between the relative resistance change and the applied strain is a very important parameter for quantitative strain detection.^{3, 7, 34} Strain sensors based on three-dimensional (3D) fragmentized graphene foams and graphene/nanocellulose composites with infiltrated PDMS have also been constructed, and both displayed very high strain detection limit (78 % and 100 %, respectively) and GF, whereas they both exhibited non-linear response between the relative resistance change and applied strain.^{8, 18} The graphene yarn-based strain sensors reported by Park, et al. showed very wide linear sensing region of up to 150 %, but the GF was relatively low (1.4).³⁴ The above examples show that

achieving simultaneous high stretchability, high sensitivity and wide linear sensing region for a flexible strain sensor still remains a great challenge.

In this work, highly stretchable, sensitive strain sensors based on anisotropic graphene foams supported on PDMS were constructed using a simple method. Firstly, by unidirectional freeze-drying²⁸⁻⁴¹ of graphene oxide (GO) aqueous suspensions followed by thermal annealing to convert GO to reduced GO (RGO), a RGO foam with elongated honeycomb-like structure was produced, as shown in Scheme 1, in which the micron-sized aligned pores were templated from the ice crystals grown in the unidirectional freezing process, while the vertically aligned cell walls were formed by stacked RGO layers. The RGO foam was then macroscopically compressed in a direction perpendicular to the aligned cell walls to obtain compressed RGO (CRGO) foam, which is in the form of a free-standing film, whereas still contains numerous smaller pores between the cell walls. These pores facilitate the diffusion of the PDMS prepolymer into the 3D porous architecture, enhancing the structural stability and reversible stretchability of the sensors. The aligned graphene cell walls give the CRGO/PDMS nanocomposites anisotropic sensing performance, i.e., the sensing performance along the growth direction of the cell walls (longitudinal direction marked in Scheme 1) and that in the direction perpendicular to the growth direction of the cell walls (transverse direction marked in Scheme 1) is different. More importantly, the compression of the RGO foam creates more contact area between the graphene-based cell walls, which efficiently improves the strain sensitivity upon stretching the CRGO foam/PDMS nanocomposites. These unique microstructural characteristics of the CRGO/PDMS nanocomposites allow the corresponding strain sensors to exhibit a measurable strain limit as high as 122 %, linear sensing region of 0 - 110 %, and high linear sensitivity (with GF of approximately 7.2) upon stretching in the transverse direction. When the nanocomposite strain sensors are stretched along the longitudinal direction, relatively narrow strain sensing range with much higher sensitivity can be achieved. Furthermore, our thin and flexible strain sensors can be well

attached to human body, and show excellent sensing performance in detecting various human motions, such as frequencies and angles of finger and knee bending.

Scheme 1. Schematics showing the as-prepared anisotropic RGO (left) and CRGO (right) foams with marked directions including the compressive direction, longitudinal direction that is parallel to the growth direction of the cell walls, and transverse direction that is perpendicular to the growth direction of the cell walls.

Experimental

Fabrication of aligned porous RGO and CRGO foam nanocomposites: GO was prepared by a modified Hummer's method.^{42, 43} The aligned porous GO foam was prepared by freezing the GO aqueous solution cast in a mould with Teflon container and stainless steel bottom immersed in liquid nitrogen, followed by freeze-drying the prepared hydrogels in the freeze-drying vessel ($-80\text{ }^{\circ}\text{C}$ and 10 Pa) for 24 h. Afterwards, the GO foams were heated at a speed of $10\text{ }^{\circ}\text{C}/\text{min}$ in a tube furnace and annealed at the temperature of $800\text{ }^{\circ}\text{C}$ for 2 h under argon atmosphere to obtain the aligned porous RGO foam. Density of the 3D RGO aligned porous architectures could be controlled by adjusting the water fraction of the GO aqueous solution. In a case of RGO porous architectures with density of $1.5\text{ mg}/\text{cm}^3$, GO aqueous solution containing 0.38 wt% GO was freeze-dried to obtain the GO foams with density of $6\text{ mg}/\text{cm}^3$, which were then thermal annealed to prepare the 3D RGO forms. The RGO foam was set between two clean glass side and compressed to obtain the free-standing and flexible

CRGO foam based film, which could still maintain the aligned graphene based cell walls and micron-sized pores microstructures.

Fabrication of thin film CRGO/PDMS nanocomposite strain sensors: The CRGO foam based film (with a dimension of 22.00 mm × 10.00 mm × 0.06 mm) was put on the surface of the glass slide after pasted with two copper wires as electrodes using conductive silver adhesive (D05001, Beijing Emerging Technology Co. Ltd., China). Then the liquid PDMS prepolymer, after being degassed in a vacuum chamber and the ice water bath, was poured onto the glass slide with controllable thickness by adjusting the mass of PDMS. The good diffusion of the PDMS prepolymer into the existing micron-sized pores of CRGO foam led to a certain degree of expansion of these pores, and thickness of the sensors could reach between 0.38 – 0.50 mm together by controlling PDMS amount. After curing PDMS at 65 °C for 6 h, the CRGO foam/PDMS nanocomposite sensors were prepared successfully. In order to compare sensing performance, RGO foam/PDMS and thick CRGO foam (from a compressed 8 mm thick RGO foam)/PDMS nanocomposites, as well as the CRGO foam from a compressed RGO foams with higher density (3 mg cm^{-3}) based PDMS nanocomposites were prepared. All nanocomposite sensors were prepared with similar distance between the two electrodes and width for better comparison.

Characterization: The microstructure of the porous architectures was investigated by scanning electron microscopy (SEM, JSM-7600F, Japan). The tensile performance of the nanocomposite sensors were evaluated by dynamic mechanical analysis (DMA, TA Q800). X-ray diffraction (XRD) measurements were carried out at room temperature with specular reflection mode (Cu K α radiation, X'Pert PRO, PANalytical, Holland). Raman spectra were obtained with a Renishaw in Via Raman Spectroscopy, using the 632.8 nm line of a He-Ne laser. Micromeritics TriStar II 3020 Surface Area and Porosity Analyzer was used to obtain nitrogen adsorption desorption isotherms and gave the Brunauer–Emmett–Teller (BET)

specific surface area. The electromechanical response of the strain sensors was evaluated by measuring the resistance using a Keithley 4200-SCS electrometer (Keithley, Cleveland, Ohio, USA) when each sample was subjected to uniaxial stretch by a home-built stretching stage. At least five specimens were tested for each type of nanocomposites. The measured electrical conductivities of the RGO foams, CRGO foams, and the CRGO foam/PDMS nanocomposites were similar in different directions due to the interconnected graphene-based cell walls. Mechanical and electromechanical tests of the sensors were performed when the tensile direction is along the transverse direction for all the samples unless mentioned otherwise.

Results and Discussion

The fabrication processes for the graphene-based foams with aligned micron-sized pores and the corresponding nanocomposite sensors are illustrated in **Fig. 1a-e**. The GO sheets are well and stably dispersed in water, and their lateral size is roughly in the range of 3 to 20 micrometers (Fig. 1a). In the freezing process, steep temperature gradient leads to the rapid formation of ice-crystal nuclei at the bottom and the unidirectional growth towards the upside of the suspension, causing GO being extruded and stacked between the ices (Fig. 1b). After the sublimation of ice via freeze-drying process, micron-sized pores templated from the ice crystals are formed, leading to a GO foam with aligned pores. In the subsequent thermal annealing, the majority of oxygen-containing groups on GO is removed, producing a RGO foam (Fig. 1c). The porosity and density of the foam can be controlled by adjusting the water fraction in the suspension. In this work, the densities of the GO and RGO foams are controlled to be approximately 4 and 1.5 mg cm⁻³, respectively. By compressing the RGO foam in a direction perpendicular to the cell wall growth direction, as shown in Scheme 1, with an adequate load, a flexible film of CRGO foam is obtained (Fig. 1d, f). The infiltration of PDMS prepolymer into the CRGO film and subsequent curing at 65 °C results in a robust

flexible nanocomposite film (Fig. 1e,g), which can be stretched easily to more than 100 % (Fig. 1h).

Fig. 1 Diagrams showing the preparation process for a CRGO/PDMS nanocomposite strain sensor: (a) SEM image of GO (scale bar is 10 μm) and optical image of the GO suspension (inset), (b) a schematic showing freezing process of the GO suspension, SEM images (scale bars are 100 μm) of the (c) RGO and (d) CRGO foams (red arrows in image b and c indicate the growth direction of the ice crystals and aligned cell walls, respectively), (e) schematics showing the process of making CRGO/PDMS nanocomposites, pictures of (f) a sheet of CRGO foam, (g) a CRGO/PDMS nanocomposite strain sensor, and (h) the sensor before (top) and after (bottom) being stretched over 100 %.

Pictures and SEM images in **Fig. 2** show macroscopic appearance and microstructures of GO, RGO and CRGO foams as well as the CRGO foam/PDMS nanocomposite sensors. The shapes of the GO and RGO foams (Fig. 2a, b) can be controlled by the dimensions of the mold. Both foams show good flexibility at the thickness of ~ 2 mm due to their low density, as well as the aligned pore and cell-wall structures (Fig. 2b, 2e, 2f, Fig. S1a). For the RGO foam, the interconnected cell walls give rise to a stable 3D architecture and 3D conductive pathway; each cell wall is estimated to have a thickness of more than ten nanometers, and thus each cell

wall is formed by stacking of tens of graphene layers. This estimation is supported by our BET measurement result, which indicates that the BET surface area of the RGO foam ($\sim 154 \text{ m}^2 \text{ g}^{-1}$) is much lower than the theoretical surface area of single-layer graphene ($2630 \text{ m}^2 \text{ g}^{-1}$).⁴⁴ The gaps between the nearest cell walls are in the range of 30 to 50 μm for the RGO foam at the low density of 1.5 mg cm^{-3} . After compression, the thickness is decreased from 2 mm for the RGO foam to $\sim 0.06 \text{ mm}$ for the CRGO foam (Fig. 2c, Fig. S1b-d), while the aligned cell walls are well retained albeit the size of the pores become smaller ($\sim 10 \mu\text{m}$) (Fig. 2g). The microstructure consisting of open pores and interconnected cell walls leads to the formation of graphene conductive networks, as well as similar conductivity in different directions for the aligned porous architectures. It is also worthwhile noting that the pores can ensure good infiltration of PDMS prepolymer into the 3D CRGO foam; meanwhile, closer contacts between the graphene cell walls create more conductive pathways, which is beneficial to inducing more conductive path change and hence larger resistance change of the nanocomposite strain sensor upon stretching. X-ray diffraction (XRD) patterns and Raman spectra (Fig. S2) confirm the effective reduction of the GO to RGO foam, and that the structure of the graphene layers in the CRGO foam is not altered by the compression force applied. The integration of the flexible CRGO foam with the supporting PDMS endows the nanocomposite with good stretchability, bendability, and twist-ability (Fig. 2d, Fig. 1g, 1h) owing to the good interface between the graphene foam and PDMS. Top and cross-sectional views of the nanocomposite manifest that the CRGO foam is well embedded in the PDMS matrix (Fig. 2h-k). In fact, the thickness of the nanocomposite is around 380-500 μm (Fig. 2i), which is much thicker than the CRGO foam ($\sim 60 \mu\text{m}$), implying that the infiltration of PDMS into the foam causes the expansion of the gaps between the cell walls to some extent. Even though, the alignment of the cell walls can be well retained in the CRGO foam/PDMS nanocomposite sensors, which is evident from the microstructures of the cross section (Fig. 2j, 2k, Fig. S3).

Fig. 2 Pictures of (a) GO and RGO foams showing their shape and dimensions, (b) a sheet of RGO foam showing its good flexibility, (c) a sheet of CRGO foam (inset: a cross-sectional optical image, scale bar is 60 μm), (d) a twisted CRGO/PDMS nanocomposite strain sensor. SEM images showing microstructures of (e) GO foam, (f) RGO foam, (scale bars are 100 μm for images e and f; scale bar is 1 μm for inset in image f), and (g) CRGO foam (scale bars are 100 and 10 μm for the left and the right two images, respectively). SEM images of the CRGO/PDMS nanocomposite strain sensor: (h) top surface (scale bars are 100 μm for images h and i; inset: with higher magnification and scale bar is 20 μm), (i) cross-sectional surface showing the thickness of the CRGO foam, (j) cross-sectional cryogenically-fractured surface parallel to the longitudinal direction showing distinguishable aligned graphene layers and (k) cross-sectional cryogenically-fractured surface parallel to the transverse direction showing the absence of aligned graphene layers (scale bars are 20 μm for images j and k; inset: with higher magnification and scale bars are 1 μm).

Prior to characterization of the electromechanical performance of the CRGO foam/PDMS strain sensors, the mechanical properties of the nanocomposite are measured, as shown in **Fig. 3a**. Under the cyclic tensile strain from 30 % to 100 % in the transverse direction (the direction perpendicular to the aligned graphene cell walls as shown in Scheme

1), the stress increases with increasing strain and can well return to the initial state, indicating no obvious damage of the structure under such a large deformation. The good reversibility can be maintained for more than 300 stretch/release cycles with 30 % strain (Fig. S4a, b), further demonstrating the excellent mechanical durability of the nanocomposite. Since the microstructure of the nanocomposite is anisotropic, it is also stretched in the longitudinal direction (the growth direction of the graphene cell walls). Compared with the high fracture strain of >120 % in the transverse direction, the fracture strain is only about 60 % in the longitudinal direction (Fig. S4c). It is well established that tensile strength and modulus of nanocomposites highly depend on the orientation of the nanofillers in the polymer matrices.^{45,46} Since the graphene-based cell walls are better connected and well aligned along the longitudinal direction, the tensile strength and modulus of the nanocomposite in this direction are significantly higher than the ones in the transverse direction (Fig. S4d, S4e). Less continuous cell walls in the transverse direction of the CRGO foam/PDMS nanocomposite lead to less fracture of the cell walls under large extension; less continuous cell walls also mean more elastic polymer between the cell walls, which is instrumental in energy absorption. In summary, a combination of better elastic performance and higher tensile fracture strain is obtained in the transverse direction whereas higher tensile strength and modulus are achieved in the longitudinal direction. Such anisotropic mechanical properties derived from the designed anisotropic porous graphene architectures are attractive for broadening the applications of the sensors.

Fig. 3 (a) Stress-strain curve and (b) the relative change in resistance of the CRGO/PDMS nanocomposite strain sensors under various strain loading; (c) the relative change in resistance versus time curves of the CRGO/PDMS strain sensors under repeated stretch-release process, (d) the relative resistance change ratio versus strain curves of various strain sensors, (e) the relative resistance change of the CRGO/PDMS strain sensor under 10 % strain at various strain frequencies, (f) life-time test of the CRGO/PDMS strain sensors under 30 % strain.

In the electromechanical tests of the CRGO foam/PDMS nanocomposite sensors, the electrical resistance increases immediately upon the application of a tensile strain in the transverse direction (Fig. S5a, S5b, S5e). A larger relative resistance change is observed in the first stretch-release cycle in comparison with those in the subsequent cycles, which can be attributed to the reconstruction of the conductive paths in the nanocomposite. The reconstruction of conductive paths is a common phenomenon reported for many composite sensors.^{18, 47, 48} After the initial several cycles, the relative resistance change stabilizes (Fig. S5c, S5d, S5f) and thus test results are recorded after the initial several cycles to obtain stable electromechanical responses. In the cyclic testing process, with gradually increasing the strain loading from 30 % to 100 %, the relative resistance change increases accordingly while the excellent reversibility is maintained (Fig. 3b). The increase of relative resistance change with the tensile strain can be attributed to increased disconnections between graphene sheets under

a larger deformation and hence a reduction in conductive paths in the nanocomposite. When the sensors are subjected to repeated stretch-release cycles, the relative resistance changes detected show excellent repeatability at each strain loading level in the strain range of 5 % to 100 %, indicating good reliability of the strain sensors (Fig. 3c). Furthermore, it is striking to see that good linear relationship between the relative resistance change and tensile strain is observed in a very wide strain range (0 % -110 %) for our nanocomposite sensors in the transverse direction (Fig. 3d, Table S1). The GF in the linear region is calculated to be around 7.2 ($R^2 = 0.968$), which is much higher than traditional metal- or semiconductor-based strain gauges. Compared with graphene foam-based composites reported in literatures, such as 3D fragmentized graphene foam/PDMS composites⁸ (strain detection limit of 78 %, non-linear response with GF ranging from 2.4 to 15.0), graphene/nanocellulose composite foams with infiltrated PDMS¹⁸ (strain detection limit of 100 %, non-linear response with GF ranging from 1.6 to 7.1), graphene aerogel/PDMS composites³⁶ (strain detection limit of 19 %, including a linear region with GF of 61.3 and a non-linear region), CVD graphene foam/PDMS composites³⁷ (strain detection limit of ~48%, including two linear regions with GF of 2.6 and 8.5, respectively, and a non-linear region), as well as some other typical graphene-based strain sensors listed in Table S2, our flexible CRGO foam/PDMS nanocomposite sensors exhibit high stretchability (up to 122 %), much wider linear sensing strain region (0 – 110 %) and fairly good sensitivity simultaneously. The combination of wide linear sensing strain range and good sensitivity is very useful for quantitatively monitoring mechanical deformation.

To full utilize the functions of the CRGO foam/PDMS strain sensors, the relative resistance change as a function of tensile strain is also measured in the longitudinal direction of the CRGO foam/PDMS nanocomposite. In the longitudinal stretching mode, two linear regions in the strain ranges of 0 – 30 % and 30 % -57 % are observed, and the corresponding GF (calculated based on the slope in the linear region) are 12.2 ($R^2 = 0.966$) and 27.0 ($R^2 = 0.988$), respectively. Compared with the transverse direction, more fracture of the graphene

cell walls are expected when the sensors are subjected to the strain in the longitudinal direction, as discussed earlier. This would result in more substantial disconnections of the graphene nanosheets and greater reduction of conductive paths, and hence higher relative resistance change and GF, while good reversibility and repeatability of the relative resistance change can still be observed when the sensors are subjected to 30 % strain in the longitudinal direction (Fig. S6). Such anisotropic sensing characteristics, which are derived from the anisotropic microstructure of the CRGO foam, may be useful for biaxial strain sensors, and provide enlightening information for design of novel strain sensors.

To understand the role played by the compression process, an uncompressed RGO foam /PDMS nanocomposite and a thicker CRGO foam/PDMS (prepared by the compression of a much thicker RGO foam (~ 8 mm) at the same compression ratio) nanocomposite were also tested by stretching in the transverse direction (Fig. 3d). The uncompressed RGO foam/PDMS nanocomposite sensor exhibits high stretchability but low GF (Fig. S7). Its strain sensitivity (GF is around 1.1 at 60 % strain) is much lower than that of the CRGO foam/PDMS (GF = 7.2 at the same strain) because the uncompressed 3D RGO foams have less connections or smaller contact area between the graphene cell walls in the transverse direction. This leads to fewer conductive networks in the uncompressed RGO foam/PDMS nanocomposites and thus less change in the conductive paths of the sensors upon large deformation. Interestingly, the GF of the thick CRGO foam/PDMS nanocomposites (< 1) is also much lower than that of the CRGO foam/PDMS nanocomposite sensors (Fig. S8), indicating that excess contacts between the graphene cell walls in a bulk sample are also not favored for improving strain sensing sensitivity of the sensors. Similarly, higher-density RGO foams (density = 3 mg cm⁻³) are used to prepare the CRGO/PDMS nanocomposite sensors that show a GF between 4 and 5 under 50 % strain (Fig. S9), indicating that when the packing density of the graphene cell walls is too high, the strain-induced resistance change would also reduce. The above results show that the contacting area between the graphene cell walls and

the number of conductive paths are the key factors controlling the sensitivity of the strain sensors.

The sensing performance of the CRGO foam/PDMS nanocomposites was also characterized at various strain rates, i.e., 10 % strain was applied with the strain loading frequency varying from 0.016 to 1 Hz (Fig. 3e). Same relative resistance change is observed at different frequencies due to strong adhesion between the graphene layers and PDMS in the nanocomposite sensors,²⁷ demonstrating the potential of the sensors for quantitatively monitoring various kinds of mechanical deformation, no matter fast or slow. Moreover, the sensors display good repeatability and reversibility for more than 1000 stretch-release cycles under the tensile strain of 30 % in the transverse direction (Fig. 3f), showing the excellent durability and reliability of the CRGO foam/PDMS nanocomposite sensors.

To comprehend the sensing mechanism more deeply, the microstructures of the CRGO/PDMS nanocomposite sensors were observed in a cyclic stretch-release process, as shown in **Fig. 4**. The SEM images of the sensors at the initial state (without stretching) (Fig. 4a) show well aligned graphene cell walls and good interface between graphene layers and PDMS matrix. Micron-sized pores in the CRGO foam can facilitate the infiltration of the PDMS into the 3D foam so that the aligned graphene-based conductive paths are well reserved in the nanocomposite. Upon stretching along the transverse direction, cracks appear between the graphene sheets in the cell walls (Fig. 4b), and it is expected that the cracks would grow with increasing tensile strain. The interconnected graphene-based cell walls in the 3D CRGO foam can maintain the stability of the CRGO foam/PDMS nanocomposite sensors when subjected to high stretched strains. Therefore, the generation and growth of the cracks not only lead to a reduction of conductive paths and hence an increase of the overall resistance of the sensors, but also effectively absorb the mechanical energy originated from the large mechanical deformation, preventing the fracture of the graphene layers to avoid the mechanical failure of the sensors under large deformation. Consequently, high stretchability,

wide linear sensing region and high strain sensitivity can be achieved simultaneously with our CRGO foam/PDMS nanocomposite sensors as discussed above. When the strain applied is released (back to the strain-free state), reconnections between the graphene cell walls at crack locations are observed (Fig. 4c), which contributes to the restoration of the low resistance. It is worth noting that some irreversible micro-cracks still exist after the initial stretch/release cycles, i.e., they cannot thoroughly disappear even the strain is back to zero, resulting in the irreversible resistance change of the sensors in the initial cycles, as discussed earlier (Fig. S5). Nevertheless, the reversibility and repeatability are excellent after the initial few cycles due to the interconnected graphene-based conductive paths derived from the interconnected cell walls of the 3D CRGO foams. The observations on microstructures are consistent with the strain sensing test results, further verifying the critical role of the microstructures played in strain sensing.

Fig. 4 Microstructures of the CRGO/PDMS nanocomposite strain sensors: (a) in unloaded states, (b) at stretched state (with 50 % strain), and (c) after the stress is released (single arrows indicate the direction of the aligned cell walls, while the double-headed arrow shows the stretching direction of the sensors).

Since our CRGO foam/PDMS nanocomposite sensors are thin, highly flexible and stretchable, they can be easily attached to human body as wearable devices for detection of human motions. **Fig. 5a** shows the detected signal of relative resistance change of the sensor attached on a finger, which bends with gradually increased amplitude. When the finger bends to a small angle and then keeps steady, the resistance of the sensor initially increases due to the stretching caused by the bend, and then keeps stable after the pulse that is caused by the intrinsic viscoelastic characteristic of PDMS.^{18, 49} Bending of the finger to a larger angle is equivalent to the application of a larger strain, and the corresponding relative resistance change detected by the attached sensor is indeed larger. More interestingly, when the finger bends and moves back in various frequencies, the sensors can also detect the timing and frequencies of this series of motions very well (Fig. 5b-f). Based on the measured electrical signals from the sensor, we can easily deduce that in the testing period, the finger repeatedly bends and moves back quickly with similar amplitude, and number of bends in each short interval of only a few seconds increases gradually from one, two, three, five, seven to nine times (Fig. 5c-f). Notably, even the speed of the movement is fast, the sensor can still detect and distinguish it well, which is consistent with the ability of the sensors for sensing strains at various frequencies shown in Fig. 3. The motion of a knee with various bending amplitudes or frequencies can also be well detected (Fig. 5g-h). Knee bending cannot be as fast as finger bending, whereas the strain caused by the knee bending is much larger than finger bending. Indeed, significantly larger relative resistance change is observed for knee bending than finger bending, showing the usefulness of our sensors in detection of various human motions, from small strain to relatively large strain activities.

Fig. 5 Detections of human motions: finger bending activities with (a) increasing amplitude and (b-f) increasing frequencies (c-f are horizontally magnified views of b), (g-i) knee bending activities with various amplitudes and frequencies (h and i are horizontally magnified views of g).

Conclusions

In this study, highly stretchable strain sensors based on CRGO foam/PDMS nanocomposites are constructed through combining the unidirectional freeze-drying method with a simple physical compression. The CRGO foam, featuring anisotropic micron-sized pores and aligned holey graphene cell walls, enables full infiltration of the PDMS prepolymer. The resultant nanocomposites exhibit good interfaces between the graphene cell walls and PDMS matrix, together with anisotropic conductive networks resulted from the aligned graphene cell walls. The microstructural characteristics of the CRGO foam/PDMS nanocomposites offer the sensors excellent flexibility, high stretchability and good sensing

sensitivity, as well as anisotropic mechanical and sensing performance when stretched along the longitudinal and transverse directions. The transverse directional sensing strain can reach as high as 122 % together with a very wide linear sensing region of 0 – 110 % and a high GF of around 7.2, while longitudinal directional GF can reach from 12.2 to 27.0 with sensing strain up to 57 %. Mechanism studies show that compressing RGO foam results in more conductive pathways in the resultant CRGO foam, and hence a much increased GF of the CRGO foam/PDMS nanocomposite sensors. Good flexibility, high stretchability and light weight of these nanocomposite thin film sensors, along with their good reversibility and durability, allow their successful use for sensitive and reliable monitoring of human motions, such as finger and knee bending activities. Compared with most graphene-based strain sensors reported in literatures, the effective design of the microscopic- and macroscopic-scale structures of the CRGO foam/PDMS nanocomposite strain sensors leads to their superior sensing performance in terms of a combination of high stretchability, wide linear sensing region and excellent sensitivity. Moreover, the anisotropic strain sensing capability arisen from the specifically designed anisotropic microstructures is also instructive for design of novel strain sensors with various microstructures in future.

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Supporting Information

Highly Stretchable, Sensitive Strain Sensors with Wide Linear Sensing Region Based on Compressed Anisotropic Graphene Foam/Polymer Nanocomposites

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Fig. S1 Pictures showing (a) a flexible GO foam, (b) the corresponding RGO foam and (c-d) CRGO foam.

Fig. S2 (a) XRD patterns of the GO, RGO and CRGO foams, showing a strong characteristic peak at around 10.7° and no obvious graphite peak for the GO foam, and a broad peak at around 26° caused by the disorder in the graphene layers for the RGO and CRGO foams. The XRD patterns indicate the effective reduction of the GO to RGO foam. (b) Raman spectra of the GO, RGO and CRGO foams. The ratio of the I_D to I_G increases significantly from 0.86 to 1.28 when the GO is reduced to RGO, which can be attributed to the decreased average size of the sp^2 domain after thermal annealing treatment of GO. The I_D to I_G ratio remains similar when RGO is compressed to form CRGO, demonstrating insignificant structural change of the graphene layers after the compressive process.^{18, 42}

Fig. S3 Cryogenically-fractured surfaces of the CRGO/PDMS strain sensors: (a) the fractured surface parallel to the longitudinal direction with distinguishable aligned graphene layers and (b) the fractured surface parallel to the transverse direction, showing the absence of the aligned graphene layers in this plane. (Scale bars are 100, 10, 10 and 1 μm from left to right columns, respectively.)

Fig. S4 (a-b) Dynamic mechanical performance of the CRGO/PDMS nanocomposite strain sensors under 30 % cyclic strain (minor hysteresis can be observed due to the mechanical properties of PDMS), (c) stress versus strain curves of the strain sensors stretched along transverse and longitudinal directions, and schematics showing the strain sensors stretched along (d) transverse and (e) longitudinal direction.

Fig. S5 (a, c) Resistance change and (b, d) relative resistance change of the CRGO/PDMS nanocomposite strain sensors at stretched strain of 30 %: (a, b) stretched from the initial state and (c, d) stretched after pre-stretching. (e, f) Relative resistance change of CRGO/PDMS nanocomposite strain sensors at stretched strain of 100 %: stretched (e) from the initial state and (f) after pre-stretching.

Fig. S6 Relative resistance change of the CRGO/PDMS nanocomposite strain sensors under a cyclic strain along the longitudinal direction.

Fig. S7 Relative resistance change versus time curves of uncompressed RGO foam/PDMS nanocomposites under cyclic strains of (a) 37.5 % and (b) 60.0 %.

Fig. S8 Relative resistance change versus time curves of the thicker CRGO foam/PDMS nanocomposites under cyclic strain of 60 %. The foam was prepared by compressing a RGO foam with thickness of 8mm.

Fig. S9 Relative resistance change versus time curves of the higher-density CRGO foam/PDMS nanocomposites under cyclic strains of (a) 30 % and (b) 50 %. The foams were prepared by compressing the RGO foams with a density of 3 mg/cm^3 .

Table S1. Calculated GF of a CRGO foam/PDMS nanocomposite sensor in the transverse direction at various strains.

Strain	10.0 %	27.2 %	40.8 %	54.4 %	68 %	81.6 %	95.3 %	108.9 %	122.5 %
GF	8.2	9.2	8.2	7.4	7.2	6.9	7.0	6.9	8.3

Table S2. Strain sensing performance of the graphene-based sensors

Device	Gauge factor	Cyclic strain	Linear region	Measurable strain limit	Response type	Notes
Compressed aligned porous graphene foam/PDMS	7.2	100%	0 - 110%	~122%	Linear	Transverse direction
(This work)	12.2 27.0	30%	0 - 30%, 30% - 57%	~57%	2 Linear region	Longitudinal direction
Graphene-nanocellulose /PDMS ¹	1.6 - 7.1	/		100%	Exponential	
Graphene yarn/PDMS ²	1.4	100%	0 - 150%	150%	Linear	
Graphene fiber/PDMS ³	3.7	50%	0 - 15%	200%	Linear & exponential	
CVD graphene foam coated with PDMS ⁴	1- 2	55%		95%	Exponential	
Fish-scale-like graphene on elastic tape ⁵	16.2	30%	0 - 60%	82%	Linear & exponential	
Fragmentized graphene foam/PDMS ⁶	2.4-15	50%		78%	Exponential	
CVD graphene foam/PDMS ⁷	2.6, 8.5	25%	0 - 18%, 22% - 40%	~48%	2 Linear & exponential	
Graphene-CNT/PDMS ⁸	100	40%	10% - 40%	40%	Linear	
Graphene woven fabrics/PDMS ⁹	35 -10 ⁶	10%	/	30%	Exponential	
Graphene ripple/PDMS ¹⁰	2	/	0 - 30%	30%	Linear	Resistance decrease
Graphene aerogel/PDMS ¹¹	61.3	~10%	0 - 12%	~19%	Linear & exponential	
Graphene platelets/PDMS ¹²	27.7 -164.5	10%		12.1%	Exponential	
Monolayer graphene on PDMS ¹³	~151	/	3% - 4.5%	5%	/	

Suspended graphene ribbon ¹⁴	1.9	3%		3%	Linear	
Rosette graphene/PDMS ¹⁵	2.4	2%	0 - 2%	7.1%	Linear & exponential	Perfect reversible only under 2%
Ultrathin graphene film on PDMS ¹⁶	228	2%	0 - 2%	~4.4%	Linear & exponential	Few-layer graphene
Percolative graphene film on PET substrate ¹⁷	15	1.7%	0 - 1.7%	/	Linear	
Few-layer graphene on PDMS ¹⁸	6.1	1%	0 - 1%	/	Linear	
Graphene nanoplatelet on PET ¹⁹	8.59	0.16 %	0.1%	0.16%	Linear	
SWCNT/Graphene nanoplatelet on PET ¹⁹	5.01	0.16 %	0.1%	0.16%	Linear	
Freestanding Graphene film ²⁰	/	/	/	0.85%	/	
Graphene/PVDF ²¹	12.1	0.13	0 - 0.13%	/	Linear	

/: not shown, the numbers in the square brackets denote the numbers of references which are at the end of the supporting information.

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Highly Stretchable, Sensitive Strain Sensors with Wide Linear Sensing Region Based on Compressed Anisotropic Graphene Foam/Polymer Nanocomposites

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