Strain Sensors with Adjustable Sensitivity by Tailoring the Microstructure of Graphene Aerogel/PDMS Nanocomposites

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ABSTRACT: Strain sensors with high elastic limit and high sensitivity are required to meet the rising demand for wearable electronics. Here we present the fabrication of highly sensitive strain-sensors based on nanocomposites consisting of graphene aerogel (GA) and polydimethylsiloxane (PDMS), with the primary focus being to tune the sensitivity of the sensors by tailoring the cellular microstructure through controlling the manufacturing processes. The resultant nanocomposite sensors exhibit a high sensitivity with a gauge factor of up to approximately 61.3. Of significant importance is that the sensitivity of the strain sensors can be readily altered by changing the concentration of the precursor (i.e. an aqueous dispersion of graphene oxide) and the freezing temperature used to process the GA. The results reveal that these two parameters control the cell size and cell-wall thickness of the resultant GA, which may be correlated to the observed variations in the sensitivities of the strain

sensors. The higher the concentration of graphene oxide then the lower is the sensitivity of the resultant nanocomposite strain-sensor. Upon increasing the freezing temperature from -196 °C to -20 °C, the sensitivity increases and reaches a maximum value of 61.3 at -50 °C and then decreases with a further increase in freezing temperature to -20 °C. Furthermore, the strain sensors offer excellent durability and stability, with their piezoresistivities remaining virtually unchanged even after 10,000 cycles of high-strain loading-unloading. These novel findings pave the way to custom design strain sensors with a desirable piezoresistive behavior.

KEYWORDS: graphene aerogel, polydimethylsiloxane, microstructure, adjustable piezoresistivity, strain sensor

1. INTRODUCTION

With the increasing demand for wearable electronics, such as skin-surface mountable sensors and implanted sensors,¹ strain sensors (also termed ‘strain gauges’) capable of relatively high sensitivity and high elastic limit have attracted intense interest. Highly sensitive and stretchable sensors have great potential for broad applications such as flexible displays,² robotics,³ health-monitoring devices,⁴ and sports (e.g. performance monitoring and novice training).⁵ For instance, the movements of human joints can generate strains as high as 55% upon stretching and contracting.⁶ However, traditional metallic and semiconducting strain sensors can only detect very limited strains (of approximately 5%) and with a relatively low sensitivity (i.e. a gauge factor of approximately 2).⁷ (The gauge factor, k , for a given strain, ϵ , is defined by $\Delta R/\epsilon R_0$, where R_0 is the resistance of the unstrained strain sensor and ΔR is the change in resistance when subjected to an applied strain of ϵ). Nanoscale materials, such as metal nanoparticles,⁸ nanowires,⁹ carbon nanotubes,¹⁰ and two-dimensional graphene nanosheets¹¹ have been demonstrated to be promising building blocks for such flexible strain sensors. In particular, strain

1 sensors based on carbon nanomaterials are emerging as a leading solution for sensors possessing a
2 relatively high sensitivity and elastic limit due to their superior mechanical and electrical properties.
3 For instance, strain sensors developed by depositing thin films of vertically aligned single-wall carbon
4 nanotubes onto a silicone rubber (i.e. polydimethylsiloxane, denoted by PDMS) substrate exhibit an
5 elastic elongation to failure as high as 280%.³ However, these strain sensors have relatively low
6 sensitivities (gauge factor is approximately 1.6). More recently, strain sensors based on ultrathin
7 graphene films, with a ‘fish scale’ structure, have been developed, showing extremely high sensitivities
8 with a gauge factor of 1037 at 2% strain, but such sensors failed at a tensile strain of only about 4.4%.¹²
9 Therefore, despite numerous efforts to develop high-performance strain sensors, it is still a major
10 challenge to fabricate strain sensors that simultaneously demonstrate both high sensitivity and high
11 elastic limit before failure.

12
13 Three-dimensional (3D) structured graphene has attracted considerable attention due to its unique
14 properties, such as its relatively low density, large surface area and excellent electrical conductivity.
15 Diverse applications of 3D-structured graphene include energy-storage devices,¹³ chemical and
16 biological sensors¹⁴ and adsorbents in water treatment.¹⁵ Particularly, it has been demonstrated that the
17 electrical resistance of 3D-structured graphene decreases upon mechanical compression, making them
18 promising materials as pressure sensors.¹⁶⁻¹⁸ Nevertheless, so far, the 3D-structured graphene that has
19 been produced generally undergoes significant plastic deformation or shows low strength.¹⁹ Therefore,
20 it is of great importance to develop 3D-structured graphene possessing improved mechanical properties,
21 especially relatively high elasticity, which is required for the latest strain sensor applications.²⁰

22
23 Flexible polymer nanocomposites, based on 3D-structured graphene, have been fabricated by
24 infiltrating PDMS into the graphene network.²¹⁻²⁵ These unique polymer nanocomposites have

demonstrated almost a constant electrical resistance under tensile strains up to about 50% (with a gauge factor of approximately 0.6) due to the interconnected network of graphene.²² However, more recently, it has been reported that polymer nanocomposites based upon graphene foam are capable of sensing compressive and bending strains.²³⁻²⁵ For instance, Samad *et al.*^{23, 24} demonstrated that graphene foam/PDMS nanocomposites had maximum gauge factor of approximately 9, 14, and 28 under compressive strains of 10%, 20%, and 30%, respectively. Nevertheless, in spite of these findings, there is a lack of understanding of the piezoresistive behavior of such strain sensors under tensile deformation. Moreover, no studies have been reported on the effects of the microstructure of the 3D-structured graphene on the performance of strain sensors fabricated from such PDMS nanocomposites.

The present work demonstrates effective approaches to control the microstructure of graphene aerogel (GA) for optimising the piezoresistivity of the GA/PDMS nanocomposite strain-sensors. The GA is produced via chemical reduction-induced self-assembly of graphene oxide sheets, followed by thermal annealing. An ‘environmentally-friendly’ reducing agent, L-ascorbic acid (i.e. vitamin C, denoted by VC) is used to induce gelation at 70 °C. Subsequent infiltration with PDMS and curing results in flexible polymer nanocomposites with high electrical conductivities and excellent mechanical properties. It should be noted that this production method for the 3D-structured graphene using VC does not require either (a) a high-cost chemical vapor deposition process or (b) time-consuming etching processes, which are commonly used for preparing graphene foam.^{23, 24} Therefore, it paves the way for the low-cost fabrication of high-performance graphene-based piezoresistive devices. We establish, for the first time, the relationship between the microstructures of the GAs and the strain-sensing performance of their PDMS nanocomposites, which enables the optimization of the properties of the strain sensor.

2. EXPERIMENTAL SECTION

Materials. Sylgard 184 silicone elastomer base and curing agent were supplied by Dow Corning Co. Ltd (Australia). Graphite flakes (100 mesh, ~ 150 μm flakes), potassium permanganate, concentrated sulfuric acid (98 wt%), concentrated phosphoric acid (85%), hydrochloric acid (36 wt%), hydrogen peroxide (30 wt%) and ethanol were purchased from Sigma-Aldrich. Vitamin C was obtained from the Chemist Warehouse (Melbourne, Australia). The high-purity silver-paste (Silver Paste PlusTM) was from SPI Supplies (US).

Preparation of GA. Graphene oxide (GO) was synthesized by an improved Hummers' method.²⁶ 10 mL of the resulting aqueous dispersion of GO (at 1mg/mL) was sonicated using a Sonics VCX-750 Vibra Cell Ultra Sonic Processor (40% amplitude, pulse duration: 5 second on, 5 second off) for 10 minutes and diluted for Atomic Force Microscopy (AFM) observation. The AFM image of the GO so produced is given in **Figure S1** in the **Supporting Information**, which shows the GO sheet having a thickness of 1.5 nm, and an average lateral length of hundreds of nanometers.

The GA was produced by a chemical reduction-induced self-assembly method using VC as the reducing agent, followed by thermal annealing.²⁷ VC was selected as the reducing agent due to (a) it being an environmentally-friendly material and (b) the reducing reaction producing no gaseous by-products.²⁷ In brief, 15 mL of the aqueous dispersion of GO, with concentrations of 1.83, 3.66, 7.00 and 14.0 mg/mL were prepared. (It should be noted that it is difficult to obtain bulk GA when GO dispersion of a lower concentration than 1.83 mg/mL was used, due to the relatively weak interactions between the reduced GO sheets.) Then VC, at a weight ratio of 1:4 (GO:VC), was added to the dispersion. The mixture was bath sonicated for 10 minutes and heated to 70 °C and then kept at 70 °C

for 18 h, without stirring. The resulting graphene hydrogel was subsequently immersed in water for 48 h to remove residual impurities. The hydrogel was then freeze-dried for 24 h to obtain a GA with an open cellular microstructure. To investigate the effects of the freezing temperature, hydrogels prepared from GO dispersion of 3.66 mg/mL were frozen at different temperatures (i.e. -196, -116, -80, -50, and -20 °C) before putting them in the freeze-dryer. (It should be noted that it is difficult to obtain strong and stable bulk GA at the higher freezing temperatures listed here when GO of 1.83 mg/mL was used.) Finally, the GA was thermally treated in a tube furnace at 750 °C for 2 h in an argon atmosphere to further reduce the GO to graphene.

Preparation of GA/PDMS nanocomposites. The GA/PDMS nanocomposites were prepared by using a vacuum-assisted infiltration method. The PDMS monomer was mixed with the curing agent to give a PDMS precursor at a weight ratio of 10:1. This precursor mixture was then magnetically stirred for 10 minutes and degassed for 30 minutes. The GA was immersed in the degassed PDMS precursor for 6 h and then taken out to an oven at 60 °C for 18 h for curing. As shown below, the resulting GA/PDMS nanocomposites maintained the original physical structure of the GA, without any observed changes to the microstructure of the GA. GA/PDMS nanocomposites containing GA possessing different microstructures were prepared. The percentages of GA in the nanocomposites (given in **Table S1** in the **Supporting Information**) were determined based on the weight of the nanocomposites and the density of the GA.

Characterization. The morphology of the GA and the GA/PDMS nanocomposites were examined using a scanning electron microscope (a FEI Nova NanoSEM). The nanocomposite specimens were cryogenically fractured in liquid nitrogen and then coated with a thin layer of gold prior to observation. Raman spectra (using a Perkin-Elmer Raman Station 400), X-ray diffraction (XRD) patterns (using a

1 Bruker D8 Advance diffractometer with Cu-K α radiation, $\lambda = 1.54 \text{ \AA}$), X-ray photoelectron spectra
2 (using a Thermo K-alpha instrument) were collected to characterize the degree of reduction of the GA.
3 Porosity analysis was performed using a Micromeritics ASAP 2400 surface analyzer via nitrogen
4 adsorption at $-196 \text{ }^{\circ}\text{C}$, with the samples being degassed at $150 \text{ }^{\circ}\text{C}$ overnight prior to the adsorption
5 measurements.

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7 Mechanical tests were carried out using a tensile testing machine (Instron Model 4466). The
8 GA/PDMS nanocomposites were tested first under quasi-static tension and subsequently under cyclic
9 tensile loading-unloading cycles. Specimens of 35 mm (length) $\times$ 5 mm (width) $\times$ 3 mm (thickness)
10 were prepared for testing. The displacement-controlled quasi-static loading was carried out at a strain
11 rate of $6\%/ \text{min}$, while the cyclic loading-unloading tests were carried out by applying a sinusoidal
12 cyclic load at a frequency of 0.08 Hz . The nanocomposite was cyclically loaded to various strain levels,
13 as described later, before being completely unloaded in each cycle. To test the piezoresistivity of the
14 GA/PDMS nanocomposites, copper wires were attached to the two ends of the strain sensor using
15 conductive silver-paste adhesive. The current, I , versus voltage, V , curves were obtained via recording
16 the current whilst a linearly-increasing voltage (of up to 3 V) was applied to the sensors. The in-situ
17 changes in the electrical resistance were measured during the mechanical tests by a HBM unit capable
18 of providing the value of electrical resistance directly. The sensitivity of the sensor is expressed
19 quantitatively as the gauge factor, k , which was defined above.

20 21 **3. RESULTS AND DISCUSSION**

22 **3.1 Tailoring the microstructures of the GA**

23 Self-assembly of GO occurs when the GO network in the solution is reinforced by enhanced bonding
24 forces developing, such as hydrogen bonds or π - π interactions.²⁸ When VC is added into an aqueous

dispersion of GO, the GO sheets are gradually reduced. This reduction restores the π - π interaction between the sheets, resulting in a cross-linked network of reduced GO. The chemical and structural attributes of the GO and GA were analyzed using XRD, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) (see **Figure S2** in the **Supporting Information**) and the results clearly confirmed the reduction of the GO sheets. **Figure S3** shows a photograph of GA prepared using GO of 1.83 mg/mL and at a freezing temperature of -196 °C. The GA possesses a 3D open, porous network with an average cell size of about 40 μ m as shown in **Figure 1a**. A close-up view of this macroporous cellular structure (**Figure 1e**) reveals that the graphene sheets stack in a facial-linking pattern and the cell walls consist of thin layers of stacked graphene nanosheets.

In the present work, GAs of different microstructures were produced, via changing (a) the concentration of GO in the aqueous dispersion and (b) the subsequent drying conditions. Firstly, aqueous dispersions of GO of four different concentrations (i.e. 1.83, 3.66, 7.0, and 14.0 mg/mL) were employed to produce the GAs, and the four different graphene hydrogels so prepared were then frozen at -196 °C for freeze drying. Honeycomb-like 3D macroporous architectures are observed for all the GAs, as shown in **Figure 1**. Two important features of the cellular structures are found to be governed by the GO concentration. Firstly, the cell size of the GA produced using GO of 1.83 mg/mL is observed to be about 40 μ m, which decreases gradually upon increasing the GO concentration and falls to about 10 μ m for the GA produced from a GO of 14 mg/mL (**Table 1**). Secondly, the cell walls for the GA produced from the relatively high concentrations of GO appear to be thicker (**Figures 1e-f**), which is confirmed by the calculations based on **Equation S3** discussed in the **Supporting Information**. The formation of the relatively thicker walls may be attributed to the fact that the GO sheets tend to stack together at higher concentrations of GO. During the course of the reduction of the GO, the reduced GO sheets stack and cross-link, forming an interconnected network.²⁹ The higher the

concentration of the GO, then the greater are the chances for the GO to stack and cross-link with neighboring GO sheets, leading to thicker, but relatively smaller cells.

Figure 1. Effects of the concentration of GO in the aqueous dispersion on the microstructures of the GAs produced: (a) 1.83, (b) 3.66, (c) 7.0, and (d) 14.0 mg/mL, respectively. Magnified SEM images of the GAs produced from GO with a concentration of 1.83 and 14 mg/mL are presented in (e) and (f), respectively. (Note: the freezing temperature used to produce the GAs was -196 °C.)

The microstructure of the GAs can also be changed by using different temperatures for the freeze-drying step. In this part of study, the concentration of the GO was fixed at 3.66 mg/mL and the GAs

1 were prepared using different freezing temperatures of -116, -80, -50, and -20 °C. No noticeable
2 changes in the volume of the resultant GAs were observed, indicating that the density of the GAs
3 remained almost unchanged. As shown in **Figure 2**, the interconnected 3D porous structures for the
4 GAs produced at the higher freezing temperatures are similar to those prepared at -196 °C. However,
5 the cell size increases from about 28 μm for a freezing temperature of -196 °C to about 350 μm at -20
6 °C (**Table 1**). Moreover, it may be seen that the cell-wall thickness also increases upon increasing the
7 freezing temperature, consistent with the estimate based on **Equation S3**. The cell walls consist of
8 multiple layers of graphene nanosheets, which is particularly apparent for the GA produced at a
9 freezing temperature of -20 °C, as indicated in **Figure 2e**. The cells are shaped by the ice crystals
10 during freeze-drying.^{13, 30} A higher freezing temperature leads to a relatively slower crystallization rate,
11 resulting in crystals with larger sizes. After the sublimation of the ice, cells of different sizes are left
12 behind. In addition, the volume of water expands when frozen into ice, which tends to make the
13 graphene nanosheets stack together. During the growth of larger crystals, a relatively larger number of
14 graphene nanosheets will be pushed together, resulting in thicker cell walls. The nitrogen adsorption-
15 desorption studies (**Figure S5**) show that the GAs possess a hierarchical microstructure composed of
16 both meso-cells and macro-cells and the BET surface areas of different GAs are given in **Table 1**.

Figure 2. Effect of freezing temperatures: (a) -116 °C; (b) -80 °C; (c) -50 °C, and (d) -20 °C on the cellular microstructure of the GAs produced using GO dispersion of 3.66 mg/mL. The image (e) was taken from the rectangular area in (d).

1 **Table 1.** Microstructure details of the GAs produced via the different production conditions.

GO concentration (mg/mL)	Freezing temperature (°C)	Cell size (μm)	Cell-wall thickness (μm)	Density (mg/cm ³)	BET surface area (m ² /g)
1.83	-196	40 ± 5	0.037 ± 0.006	4.65	115
3.66	-196	28 ± 6	0.044 ± 0.011	8.15	69
7.00	-196	18 ± 5	0.046 ± 0.013	13.05	44
14.0	-196	10 ± 5	0.048 ± 0.010	24.34	50
3.66	-116	85 ± 28	0.135 ± 0.021	8.09	61
3.66	-80	160 ± 50	0.250 ± 0.015	7.95	60
3.66	-50	215 ± 90	0.338 ± 0.036	7.99	43
3.66	-20	350 ± 100	0.550 ± 0.018	8.05	49

2

3 **3.2 Mechanical properties and electrical conductivities of the GA/PDMS nanocomposites**

4 The GA/PDMS nanocomposites were prepared through back-filling the cells of the GAs with PDMS,
5 as described above. **Figure 3a** shows the typical microstructures of the GA/PDMS nanocomposites,
6 revealing that the interconnected network of the cellular structure of the GA in the nanocomposite is
7 similar to that of the pure GA. The magnified SEM image shown in **Figure 3b** demonstrates that the
8 cells are filled with the PDMS matrix and that the cell walls appear to be well bonded to the PDMS
9 matrix.

Figure 3. (a) Microstructure of GA/PDMS nanocomposite and (b) a high magnification image. The red dotted lines indicate the outlines of the cells of the GA. (Note: the GA was prepared using a GO dispersion of 1.83 mg/mL and a freezing temperature of -196 °C.)

Typical stress versus strain curves of the GA/PDMS nanocomposites containing GAs possessing different microstructures are presented in **Figures S6a-b**. The nanocomposites show a comparable strength, a significantly higher modulus but a lower elongation at break, compared with the pure PDMS (**Table S1**). The modulus of the GA/PDMS nanocomposite increases upon increasing the GO concentration from 1.83 to 3.66 mg/mL, and decreases thereafter. A similar trend is observed for the tensile strength. These observations are consistent with recently published work^{28, 31} on the mechanical properties of epoxy/3D-graphene nanocomposites. The graphene-matrix interfaces and the physically assembled graphene sheets are the relatively weak sites and may therefore act as defects²⁸. At a relatively low GO concentration, the GO sheets are well-dispersed in water as single or few-layered sheets. The resultant GA has relatively thin cell walls, which is favorable to achieving strong adhesion with the PDMS. Upon increasing the GO concentration, the GO sheets tend to stack with each other and thus result in GA with relatively thick cell walls. It is, therefore, easier for cracks to propagate at the graphene-PDMS interface and between loosely assembled graphene sheets. This may well account for the decrease of the modulus and strength at high GO concentrations. The elongations at break for

the GA/PDMS nanocomposites, however, are relatively low when compared to pure PDMS and the values show a decreasing trend upon increasing the GO concentration, which may be due to the relatively brittle nature of GA.³² The freezing temperature used to produce the GA also affects the properties of the resultant nanocomposites. For example, the strength (542 kPa) and modulus (9312 kPa) drop to 451 and 4294 kPa, respectively, upon increasing the freezing temperature from -196 to -20 °C (**Table S1**). Compared with pure PDMS, the elongation at break is lower but no significant differences are observed for the nanocomposites containing GA produced at the different freezing temperatures.

The GA/PDMS nanocomposites were also tested under cyclic tensile loading-unloading to a maximum strain of 10%. The stress-strain responses are shown in **Figure S6c**. There is a slight hysteresis which is commonly observed for elastomers.^{20, 25} The GA/PDMS nanocomposites exhibit no significant plastic deformation, which indicates their structural robustness. The curves for the first cycle and the 500th cycle are given as the inset of **Figure S6c**. Although there is a slight decrease in the modulus after 500 cycles of loading-unloading, the maximum stress retains over 90% of its original value and tends to stabilize, indicating that the cyclic deformation does not induce substantial internal structural change. The excellent structural integrity after cyclic loading makes the GA/PDMS nanocomposites very promising candidates for strain-sensing applications.

The electrical conductivities of the GA/PDMS nanocomposites are given in **Figure S7**. It is seen that the electrical conductivity increases upon increasing the GO concentration, and that a maximum value of approximately 21.3 S/m is achieved when GO dispersion of 14 mg/mL was employed. Moreover, it is interesting to note that the electrical conductivity decreases gradually to 9.1 S/m as the freezing temperature is increased to -20 °C, even though the composites contain a very similar concentration of GA (**Figure S7b**). This decrease in the electrical conductivity may be correlated to the changes in the

microstructure of the GA. The correlation of the electrical properties to the microstructure of the present GA/PDMS nanocomposites is analogous to that of graphene/polymer nanocomposites prepared via the conventional method (i.e. via direct dispersion in the polymer matrix). It is well-known³³ that the more uniform the degree of dispersion then higher is the electrical conductivity of the polymer nanocomposite. As discussed in the above section, the cell size and cell wall thickness of the GA increase upon increasing the freezing temperature, which is essentially equivalent to an aggregation of the graphene. Thus, for a given volume of such GA/PDMS nanocomposites, there are fewer electrical pathways available, leading to a lower electrical conductivity. This further demonstrates that the microstructure of the GA plays a significant role in controlling the properties of the resulting GA/PDMS nanocomposites.

3.3 Piezoresistivity of the GA/PDMS nanocomposites

3.3.1 Quasi-static tensile loading

The piezoresistive behavior of the GA/PDMS nanocomposites under quasi-static tensile loading was investigated in order to explore initially their potential use as strain sensors. Firstly, the current-voltage curves of the GA/PDMS nanocomposites subjected to strains of 0% (i.e. un-strained sensor), 1%, 5%, and 10% were measured. The results shown in **Figure S8** demonstrate linear current-voltage characteristics. Moreover, the relative change in resistance ($\Delta R/R_0$) increases with the applied strain (ε) up to the failure strain of the nanocomposites (**Figures 4a-b**). The value of $\Delta R/R_0$ shows an initial linear dependency upon the applied strain and increases exponentially thereafter. The gauge factor, k , is determined by linear regression analysis of the data in the initial linear region:

$$\frac{\Delta R}{R_0} = k\varepsilon \quad (1)$$

The values so determined are shown in **Figures 4c-d**. It is noteworthy that the value of k is dependent upon how the GA in the nanocomposite was produced. For example, the value of k decreases from 39.3

1 to 6.2 with an increasing GO concentration from 1.83 to 14.0 mg/mL, respectively. In addition, the
2 sensitivity of the strain sensor can also be altered by changing the freezing temperature. For example,
3 the value of k is 17.7 for strain sensors consisting of GA prepared from GO dispersion of 3.66 mg/mL
4 and using a freezing temperature of -196°C ; and this value increases to 61.3 as the freezing
5 temperature is increased to -50°C . However, a further increase in the freezing temperature to -20°C
6 then causes a reduction in k to 23.1. **Figure 5a** illustrates the microstructural changes observed in the
7 GAs from altering the GO concentration and/or the freezing temperature. From **Figure 5b**, it may be
8 seen that larger cells result in a higher sensitivity, whereas thicker cell walls lead to a lower sensitivity.

Figure 4. Relative resistance change, $\Delta R/R_0$, as a function of the applied strain upon quasi-static loading for the GA/PDMS nanocomposites containing GA produced (a) using different concentrations of GO (at a freezing temperature of -196 °C) and (b) at different freezing temperatures (with a GO concentration of 3.66 mg/mL); (c) and (d) summarize the effects of the GO concentration and the freezing temperature on the gauge factor, k .

Figure 5. (a) Schematic illustration of the GAs achieved from varying the concentration of the GO and/or the freezing temperature; and (b) the gauge factor, k , versus the architecture of the GAs, i.e., cell size and cell-wall thickness, of the GAs in the GA/PDMS nanocomposite sensors.

3.3.2 Cyclic loading

The GA/PDMS nanocomposite containing GA produced from GO of 1.83 mg/mL and a freezing temperature of -196 °C was employed to investigate the piezoresistive behavior under cyclic loading. The nanocomposite was subjected to a cyclic tensile loading-unloading spectrum with increasing steps in the maximum strains attained of 1%, 5%, 10%, followed by decreasing steps in the maximum strains attained of 5% and 1%. At each step, the samples were subjected to 100 cycles. The spectrum is defined by the steps ‘I’ to ‘V’ in **Figures 6a** and **6b**.

1 The relative changes in resistance, $\Delta R/R_0$ are given in **Figure 6a**. The results pertinent to the first two
 2 cycles are shown in **Figure 6b**. The value of $\Delta R/R_0$ is 40% at 1% strain, rising to 193% and 397% at 5%
 3 and 10% strain, respectively. It was observed that the maximum value of $\Delta R/R_0$ drops slightly during
 4 the initial few cycles and then tends to stabilize. Moreover, irreversible resistance changes are observed
 5 after the initial stretching, which are presumably due to the partial rupture of the 3D graphene network.
 6 Further, this irreversible change becomes more noticeable upon increasing the maximum applied strain,
 7 which indicates an enhanced irreversible deformation of the graphene network.
 8
 9 **Figure 6c** gives the corresponding $\Delta R/R_0$ versus ϵ curves for the first two cycles of ‘stretch-release’,
 10 while **Figure 6d** shows the gauge factor, k , for the strain sensors. During the initial quasi-static loading
 11 (i.e. the first half-cycle for each step), the strain sensors behave approximately linearly up to a
 12 maximum strain of 10% and the value of k was determined to be 39.3 by linear regression analysis.
 13 This value is in excellent agreement with that determined from the quasi-static loading, as reported
 14 above. During unloading, the sensors exhibit a nonlinear response as shown in **Figure 6c**, with the
 15 values of the gauge factor now depending strongly on the applied strain, ϵ , as well as the maximum
 16 strain imposed. In addition, the cyclic piezoresistivity curves taken to 5% maximum strain have
 17 approximately the same slope upon unloading as that of the unloading line for the strain sensor taken to
 18 a maximum strain of 10%, suggesting a self-similar behavior. It is of interest to note that the
 19 GA/PDMS strain sensors exhibit a strong memory effect. That is, once the strain sensor has been
 20 subjected to a certain maximum strain, the subsequent piezoresistivity curves differ significantly from
 21 the strain sensors that have not experienced that level of maximum strain. For example, in **Figure 6c**,
 22 the piezoresistivity curve for ‘loading IV’ differ significantly from that pertinent to ‘loading II’. In
 23 other words, the GA/PDMS strain sensors can remember the level of the maximum strain they have
 24 experienced in their loading-unloading history.

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It is proposed that the experimental data for the loading and unloading cycles can be approximated by the following relationship, as demonstrated in **Figure 6e**:

$$\frac{\Delta R}{R_0} = k \varepsilon_{\max} f\left(\frac{\varepsilon - \varepsilon_{\min}}{\varepsilon_{\max} - \varepsilon_{\min}}\right) \quad (2)$$

where k is the gauge factor for the initial monotonic loading, and $\varepsilon_{\max}$ and $\varepsilon_{\min}$ denote the maximum and minimum applied strains of a cycle, respectively. The function f can be approximated by a Taylor expansion or third-order polynomial:

$$f(x) = Ax + Bx^2 + Cx^3 \quad (3)$$

where the parameters A , B , and C can be obtained by a nonlinear regression analysis of the piezoresistivity data, giving the values of 2.66, -3.0, and 1.29, respectively. The reasonably good correlation between the experimental data and **Equation (2)** reveals that the observed memory effect can indeed be adequately captured by a simple model.

In a different set of cyclic loading-unloading tests to investigate the long-term durability, the strain sensors were subjected to 10,000 cycles up to a maximum strain of 10% (**Figure 6f**). The GA/PDMS nanocomposite strain sensors exhibited excellent durability and stability. The electrical response of the strain sensor remained virtually unchanged after 10,000 cycles in the low strain region ($\leq 2.0\%$). In the relatively higher strain region, the value of $\Delta R/R_0$ remains almost the same with little variation after 1,000 cycles, with only a small shift to a higher value of $\Delta R/R_0$ being observed after 3,000 cycles.

Figure 6. (a) The strain versus time curve (top) and the corresponding resistance change, $\Delta R/R_0$, (bottom) under progressively increasing steps in the maximum strain from 1% ('I'), 5% ('II'), to 10% ('III') followed by decreasing steps in the maximum strain to 5% ('IV') and then 1% ('V'), with 100 cycles for each step; (b) zoom-in figure showing the first two cycles in each step in (a); (c) the corresponding $\Delta R/R_0$ versus ϵ curves during the first 2 cycles for each step; (d) the gauge factor, k ,

versus strain curves during loading (i.e. stretching) in the first 2 cycles for each step and for quasi-static loading; (e) the normalized experimental data and fitting results (**Equation 2**) from the cyclic loading-unloading results; (f) $\Delta R/R_0$ versus ϵ curves for multiple-cycle tests up to 10,000 cycles. (The number of cycles after which the measurement was conducted is indicated.)

The effects of (a) the GO concentration in the aqueous dispersion and (b) the freezing temperature used to produce the GA on the piezoresistivity of the resulting GA/PDMS sensors have also been investigated by repeatedly stretching and unloading the composites to 5% maximum strain level. The relative resistance changes during the first 10 cycles are given in **Figure 8**. When cyclically loaded up to the same maximum strain level, the relative resistance change $\Delta R/R_0$ varies. As mentioned previously, cyclically loading and unloading to a 5% maximum tensile strain causes a 193% change in the electrical resistance for the nanocomposites containing GA produced from a GO concentration of 1.83 mg/mL and at a freezing temperature of -196 °C. However, the change in electrical resistance decreases to 95%, 73%, and 53% as the GO concentration is increased to 3.66, 7.0, and 14.0 mg/mL, respectively. Moreover, the resistance change also depends on the freezing temperature employed. Upon the application of a 5% maximum strain, the GA/PDMS nanocomposite containing GA produced at -50 °C exhibits the largest change in resistance of about 310%. Characteristic $\Delta R/R_0$ versus strain curves, and the corresponding gauge factors, are shown in **Figures S8a-d**. The values of $\Delta R/R_0$ of all the sensors exhibit similar dependencies on the applied strain. The gauge factor increases upon decreasing the GO concentration, whilst the nanocomposite containing GA produced using a freeze-drying temperature of -50 °C shows the highest gauge factor. The experimental data in **Figures S8a and S8b** are correlated using **Equation (2)** and results are shown in **Figure S8e**, further verifying that the experimental data fits very well to the predictions of **Equation (2)**.

Figure 8. The resistance change under 10 cycles of loading-unloading of the GA/PDMS nanocomposites containing GA being produced (a) using different GO concentrations at a freezing temperature of -196 °C and (b) at different freezing temperatures using GO dispersion of 3.66 mg/mL. (Maximum applied strain is 5%)

3.4 Piezoresistivity mechanisms in the GA/PDMS nanocomposite strain-sensors

The mechanisms associated with the piezoresistivity behavior of heterogeneous carbon nanofillers/polymer nanocomposites have been studied experimentally and numerically.³⁴⁻³⁷ In general, the piezoresistive behavior is governed by three main mechanisms: (a) external loads causing partial or complete breakage of the conductive paths formed by the conductive nanofillers, (b) a change of tunneling resistance due to a change in the distance between adjacent conductive nanofiller particles, and (c) the intrinsic piezoresistivity of the conductive nanofillers. Considering the last of these three mechanisms, the intrinsic piezoresistivity of monolayer and few-layer graphene has been investigated previously.³⁸⁻⁴¹ The gauge factor for graphene is estimated to be only about 2.4 due to its rigid and stable crystal structure. The load transfer from PDMS to graphene in the present sensors may cause deformation of the graphene sheets, leading to changes in the electrical resistance. However, the gauge factor measured in the present work is much higher than 2.4. Therefore, it is believed that the intrinsic

piezoresistivity of graphene is not the dominant mechanism, but the mechanisms (a) and (b) are the key factors which dictate the piezoresistive response of the GA/PDMS strain sensors.

To understand the mechanisms underlying the changes in resistance of these strain sensors, the fracture surfaces of the nanocomposites were examined. The samples were cyclically loaded-unloaded up to a 10% strain for 200 cycles before being cryogenically-fractured for subsequent SEM investigation. **Figure 9a** shows a representative SEM image of the GA/PDMS nanocomposite, demonstrating an interconnected graphene network. Some of the interconnections at the cell corners (i.e. cross-linking sites, as indicated by the ‘blue circles’) remain intact while some interconnections (as indicated by the ‘red circles’) are broken. **Figure 9b** shows an example where the contact between graphene sheets at the cell corner is lost. **Figures 9c-d** show that the cell walls consist of compactly stacked graphene nanosheets. This structure is similar to that of graphene thin-film strain sensors,^{12, 42} where the resistance change is mainly caused by the change of the overlap area and contact resistance. **Figure 9e** schematically illustrates the proposed structural changes of the graphene network in the GA/PDMS nanocomposites under an applied strain. When subjected to a relatively low tensile strain, slippage of the neighboring graphene nanosheets leads to a relatively smaller overlap area. Indeed, recent work by Li *et al.*¹² has demonstrated that a smaller overlap area implies a weaker overlap of electron clouds, and therefore a higher electrical resistance. Upon increasing the applied strain, the overlap area is further reduced and the contact between neighboring nanosheets is eventually broken (**Figure 9e**), resulting in a further increase in the electrical resistance. Moreover, some of the interconnections at the cell corners may also be broken leading to a reduced number of conductive pathways, and hence an increase in the electrical resistance is observed. Upon releasing the applied strain, the graphene sheets return to their original positions and reconnect, and so the original resistance is recovered.

1 It is expected the change in the electrical resistance of GA/PDMS nanocomposites largely depends on
2 the microstructure of the GA. The number of cross-linking sites, indicated by the cell size, directly
3 determines the number of conductive paths. The smaller the cells, the larger the number of the cross-
4 linking sites at a given volume and hence more conductive paths are present. In this case, the resistance
5 change is less sensitive to the breakage of such conductive paths. Furthermore, the change in resistance
6 with strain is affected by the thickness of the cell-walls. As the cell-wall thickness increases, the
7 resistance is less sensitive to strain due to the fact that the overlap area remains almost unchanged. The
8 decreased cell size and thicker cell walls of the GA by increasing the GO concentration lead to a lower
9 piezoelectric sensitivity. As the freezing temperature increases, the cells enlarge, which should bring
10 about a relatively higher sensitivity. On the other hand, the cell-wall thickness increases, thereby
11 leading to a lower sensitivity. Therefore, it is to be expected that the GA/PDMS nanocomposite
12 containing GA produced at an intermediate freezing temperature (i.e. -50 °C) would exhibit a higher
13 piezoelectric sensitivity than those prepared at -196 or -20 °C, consistent with the experimental results
14 **(Figure 4b).**

Figure 9. (a) Fracture surface of the GA/PDMS nanocomposite; (b) a magnified SEM image taken from the a red-circled region in (a) indicating the broken contact at the cell corners of the GA; (c) and (d) SEM images showing the compactly stacked graphene sheets in the cell walls of the GA; (e) schematic illustrations of the proposed structural change of the graphene network of GA under an applied tensile strain. (The magenta dashed lines in (a) and (c) indicate the graphene network.)

Finally, it is noteworthy that the strain sensors developed in the present work demonstrate a high sensitivity (i.e. with a gauge factor, k , of up to 61.3) coupled with a relatively high stretchability (i.e. up to a strain of 19%). Thus, when the present GA/PDMS nanocomposite strain-sensors are compared to those recently developed in the literature (**Table S2**), the contradiction between piezoelectric sensitivity and stretchability is now resolved for strain sensors required to operate in the intermediate range of strain levels. Equally important is the fact that the piezoelectric sensitivity of the strain sensor can be optimized by controlling the cell size and cell-wall thickness of the GA via changing the two key parameters in the production process for the GA.

4. CONCLUSIONS

In the present work, highly-sensitive strain sensors have been fabricated based on GA/PDMS nanocomposites. GAs with different cell architectures have been produced by varying two key process parameters used in their production: (a) concentration of the GO used and/or (b) freezing temperature employed for freeze-drying. It has been found that the cell size of the GA decreases, while the cell-wall thickness increases, upon increasing the GO concentration. By increasing the freezing temperature from -196 to -20 °C, both the cell size and cell-wall thickness increased. The cell architecture in the GA has been shown to affect both the mechanical and electrical properties of the resulting nanocomposites.

The piezoresistivities of the GA/PDMS strain-sensors have been investigated and relatively high gauge factors of up to 61.3 were achieved. The GA/PDMS strain sensors exhibit excellent durability and stability, as evidenced by a virtually unchanged electrical response after 10,000 loading-unloading cycles. Moreover, the piezoelectric sensitivity of the strain sensor can be optimized by controlling the cell size and cell-wall thickness of the GA, via changing the two key process parameters in the production of the GA. Essentially, it is found that larger cell sizes of the GA result in a higher

sensitivity, whereas thicker cell walls of the GA lead to a lower sensitivity. This new understanding of the role, and hence control, of the microstructure of the GA used in GA/PDMS nanocomposites strain sensors make it now possible to custom design, and so optimize, strain sensors with a specific piezoresistive behavior.

ASSOCIATED CONTENT

Supporting Information.

Additional table and figures including: 1) AFM of GO; 2) Raman, XRD, and XPS of GA; 3) A photograph of the as-produced GA; 4) Estimation of cell-wall thickness of GA; 5) Porosity data; 6) Mechanical and electrical properties of the GA/PDMS nanocomposites; 7) Piezoresistivity of the GA/PDMS nanocomposites containing GA with different microstructures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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