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# Ultra-sensitive flexible strain sensor based on graphene nanocrystallite carbon film with wrinkle structure



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#### ABSTRACT

Flexible strain sensor is under high demand for detecting the various movements of human, but it is still a challenge to integrate high sensitivity and high stretchability simultaneously in a single flexible strain sensor. Here, based on a multi-scale structure design idea, an ultra-sensitive and highly stretchable strain sensor is fabricated using graphene nanocrystallite carbon film with wrinkle structure. In nano-scale, the intrinsic piezoresistive property of graphene nanocrystallite and the tunneling effect between graphene nanocrystallites bring an ultrahigh gauge factor of 1071. In micro-scale, the strain induced ordered parallel wrinkles and perpendicular microcracks to the strain direction can guarantee the flexible strain sensor stable under a maximum strain of 15%. Application tests of detecting the movement of muscles around eye, throat and wrist are conducted. These application tests prove that this strain sensor has high sensitivity, wide measurement range and rapid responsibility, suggesting a great potential in monitoring human activities.

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#### 1. Introduction

Nowadays, flexible strain sensor draws a lot of attentions in both scientific researches and industrial applications because of the versatile applications such as biomedical applications [1], body motion monitoring [2-4], and human-machine interface [5,6]. Unlike the conventional materials like metals, the newly developed stretchable strain sensors are mainly fabricated with lowdimensional carbon materials (graphene, carbon blacks and carbon nanotubes) [7], nanowires [8], nanoparticles [9], and their hybrid structures [10]. Stretchability and gauge factor (GF), which means the relative change of the resistance versus applied strain, are considered to be the major factors evaluating the performance of the flexible strain sensor. High stretchability could guarantee a large working range and increase the endurance of a strain sensor, while high sensitivity could make a strain sensor capture subtle change in movement. Equipping both high sensitivity and high stretchability in a single flexible strain sensor could effectively broaden the application scope of flexible strain sensor. But there is

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usually a trade-off between high stretchability and high sensitivity [6].

In order to achieve the desired performances, novel materials and smart structure designs are key factors. Three main categories of carbon materials-based strain sensors could be identified based on their mechanisms for obtaining different GFs, including disconnection [7], crack propagation [8,9], and tunneling effectbased strain sensors [10-13]. Strain sensors based on disconnection are usually polymer/carbon materials hybrid structure. With different strain applied, the connection and disconnection of carbon materials in polymer would lead the change of resistance and thus brings a moderate GF value less than 80. This type of strain sensor has an outstanding stretchability usually higher than 70%, which is attributed to the good stretchability of the polymer. This kind of strain sensor has a good potential in detecting the large scale movement of human [14]. Strain sensors based on cracks exhibit a wide range of performances. As the split of cracks would cut off local electrons conduction, the length and density of cracks in micro-scale are key factors influence the GF. It is reported that in a unique aligned-carbon nanotube strain sensor, the cracks could form a multi-parallelogram structure, which could effectively help the sensor sustain strain up to 280%. But the GF value was only 0.82 based on the local split of carbon nanotube [15]. Some novel bio-





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inspired crack-based strain sensors exhibit ultrahigh sensitivity with GF higher than 2000 or even up to 6000 but relative small strain around 2% [16,17]. Thus, there are still some contradictions for integrating both of the high sensitivity and stretchability in a single crack-based strain sensor. Strain sensors based on tunneling effect mechanism could bring a high GF owing to the exponential increase in resistance when the distance between adjacent conductors increases. A kind of nanographene strain sensor based on tunneling effect could obtain a high GF value of 300 with a strain of 0.3% [18]. And by further tuning the grain size and density, a much higher GF value of 600 with a strain of 1.6% could be obtained [19]. This kind of strain sensor provides a different method to obtain ultrahigh sensitivity, but could not sustain a high strain. Based on the above mentioned works, different kinds of strain sensors have their own merits and limitations. Recently, Ren and Yang et al. developed two kinds of crack-based strain sensor equipped with ultrahigh sensitivity and good stretchability by taking use of unique high density crack structure. An electronic skin is developed by multilayer graphene with an ultrahigh GF of 673 and large strain range of 10% [20]. And a kind of graphene ink fabricated strain sensor exhibits an ultrahigh GF of 1054 and could sustain a high strain of 26% [21]. Besides the crack-based strain sensor, other strain sensors which can integrate different mechanisms by using proper nano-structure materials and micro-structure designs may have a good potential to equip both ultrahigh sensitivity and high stretchability.

Graphene nanocrystallite carbon (GNC) film is a kind of carbon film with graphene nanocrystallites embedded in the amorphous matrix [22]. Graphene nanocrystallites could capture excess electrons and act as good aisles for electron conduction [23,24]. The compact distribution of graphene nanocrystallites also indicates a tunneling effect between adjacent graphene nanocrystallites in GNC film. Based on the special nano-scale structure of GNC film, the GNC film has a good potential in obtaining high GF. On the other hand, by taking use of the micro-scale structure design of wrinkles [25] or cracks [15], the stretchability of strain sensor could be effectively improved. Therefore, GNC film, as a kind of different carbon materials has not been used in developing flexible strain sensor, has a good potential to fabricate highly sensitive and highly stretchable flexible strain sensor.

In this study, GNC films were deposited on Si substrate with a 300 nm SiO<sub>2</sub> layer and then transferred onto polydimethylsiloxane (PDMS) substrate to fabricate the carbon film-based flexible strain sensors. The behavior of resistance versus strain was studied. The photos obtained by optical microscope were carried out to reveal the micro-structure change when the flexible sensors were stretched. Combined with transmission electron microscope (TEM), Raman and optical microscope results, the ultrahigh GF value of GNC film was discussed. And application tests on wrist, throat and eye were performed to verify the flexible strain sensor could both detecting the large scale and subtle movements of human.

#### 2. Experimental details

#### 2.1. Deposition process of GNC film

As shown in Fig. 1(a), the GNC films were deposited on Si substrate with 300 nm SiO<sub>2</sub> layer in a mirror confinement electron cyclotron resonance (ECR) sputtering system with low energy electron irradiation. The Si substrate was cleaned in acetone and ethanol bath successively by ultrasonic waves. Before film deposition, the vacuum chamber was pumped down to  $8 \times 10^{-5}$  Pa and the argon was inflated to keep the working pressure with  $1 \times 10^{-1}$  Pa. Then the argon gas was charged with 2.45 GHz microwave at the ECR point where magnetic field was 875 G. To

attract the sputtering ions, a bias voltage of -500 V was applied to the carbon target. The substrate was applied with positive bias to form the electron irradiation. The size of graphene nanocrystallites was controlled by tuning the substrate bias from 40 V to 80 V [22]. An amorphous carbon film (a-C) was also fabricated with a substrate bias of -5 V in a divergent electron cyclotron resonance system. The thicknesses of all films were controlled to be 40 nm. The detailed information of ECR apparatus and depositing process could be found in our former work [20,26].

#### 2.2. Fabrication process of the strain sensor

The base and curing agent of PDMS (Dow Corning Sylgard 184) were mixed in 10:1 mass ratio. After stirring well, the liquid PDMS was extracted with a syringe and dripped into a container and the thickness of the PDMS was controlled to 2 mm. Then the circle container was placed in a fridge with a temperature of 5 °C for 12 h. After this, the circle container was placed in a constant temperature and low vacuum oven and dried at 70 °C for 1 h to form the solid PDMS. Then the PDMS was cut to a size of 1 cm  $\times$  5 cm to obtain a solid PDMS substrate.

The schematic illustration of the strain sensor fabrication process is shown in Fig. 1(b). The as-deposited GNC film was cut into square with the size of 5 mm  $\times$  5 mm, as shown in inset (i). The GNC film possesses a unique nano-structure that the amorphous matrix is embedded with graphene nanocrystallites. Then the sample was coated with a thin polymethyl methacrylate (PMMA) layer on the spin coater with a rotation rate of 2000 round per minute and then heated for 3 min with 120 °C. as shown in inset (ii). After which, the sample was immersed in 10% Hydrofluoric Acid (HF) solute for 3–4 h to dissolve the SiO<sub>2</sub> layer and totally separated from the original substrate, as shown in inset (iii). After that, the sample was transferred to flexible PMDS substrate in pure water and immersed in acetone for 5 min to dissolve the PMMA layer to obtain the carbon film/PDMS sample, as shown in inset (iv). During this step, random wrinkles formed on the transferred film because of the water drainage. When the sample was dry, platinum (Pt) wires were fixed on the transferred carbon film by conductive silver adhesive (EPOXY H20E 10Z), which need to be heated for 1 h with 70 °C in low vacuum (around  $10^{-1}$  Pa). Finally, another droplet of PDMS was dropped onto the strain sensor and heat at 70 °C for 1 h to encapsulate the strain sensor. As a result, a flexible GNC-filmbased strain sensor was fabricated, which possess unique microscale wrinkle structure and nano-scale nanocrystalline structure, as shown in inset (v).

## 2.3. Structure characterization and sensing properties measurement

The sample was pasted on a computer controlled tensile test machine which was able to apply uniaxial tensile strain to a thin film material and the Pt wires were connected to a terminal. A high precision source meter (Keithley 2611B) was used to measure the relative change in the resistance as the strain sensor was stretched. The Keithley 2611B was connected to the computer, so that the results can be observed on the computer through the software of Kickstart measurement software.

The nanostructure of the carbon film were observed with a TEM (JEM-3200FS, JEOL) operated at 300 kV. The bonding structures of the films were studied by Raman spectra. In order to study the bonding structure of the wrinkle area, a mapping test ( $5 \times 8$  points at a 42 µm  $\times$  7 µm area) was conducted at a wrinkle area of a transferred GNC film on SiO<sub>2</sub> substrate, which was obtained with a laser confocal Raman spectroscopy (LabRAM HR Evolution, Horiba). The 532 nm laser spot size was 2 µm using a 100  $\times$  objective, and



**Fig. 1.** Fabrication processes of the GNC film-based flexible strain sensor with wrinkle structure. (a) Deposition process of GNC film with ECR sputtering and electron irradiation. (b) Fabrication process of the flexible strain sensor. (i) As-deposit GNC film with graphene nanocrystalline structure. (ii) GNC film on Si substrate coated with PMMA. (iii) Float GNC film with PMMA. (iv) GNC film on PDMS. Random wrinkles form at this step owing to the drainage of water. (v) GNC film-based strain sensor. (A colour version of this figure can be viewed online.)

the spectrum region was between 1100 and 2000 cm<sup>-1</sup>. In-situ strain tests were conducted under an optical microscopy (Nikon H550S) to evaluate the relationship between electrical resistance change and film structures evolution under strain.

#### 2.4. Application tests

The application tests were conducted by fixed the strain sensors at wrist, throat and around eye to detect the bending and waving of wrist, speaking and swallowing of throat and blink of eye. The resistance changes of the strain sensor were recorded by the same system as mentioned in 2.3.

#### 3. Results and discussions

#### 3.1. Characterization of the strain sensor

Fig. 2(a) presented a typical optical photo of a carbon film-based flexible strain sensor. The GNC film with a size of 5 mm  $\times$  5 mm was transferred onto the PDMS substrate and two Pt wires were connected to the strain sensor by conductive silver adhesive electrodes. Fig. 2(b) showed the microstructure of the transferred carbon film on PDMS. There were many random wrinkles on the samples. The formation of these wrinkles should be attributed to the water drainage during the transfer process, which was same as the graphene transfer process [27,28].

The sample of GNC film fabricated with substrate bias of +80 V was used to study the structure and performance of the strain sensor. The graphene nanocrystalline structure of the films was confirmed by high-resolution TEM observation. The plan view

image in Fig. 2(c) clearly revealed the nanocrystalline structure of the GNC film. Nanocrystallites, as marked with the white circles, were distributed uniformly in the GNC film as shown in Fig. 2(c). And the layer number of the nanocrystallites was less than 5 layers as presented, which indicates a graphene nanocrystalline structure rather than graphite structure. The inset image in Fig. 2(c) was the FFT filtering result performed at the yellow dot line square area. Two white light spots were obviously found, which implied the existence of ordered graphene nanocrystallites layer structure. The distance between the adjacent graphene nanocrystallites was less than 3 nm according to the TEM observation. The existence of graphene nanocrystallites was further confirmed by a Raman spectrum of a thick GNC film and the fitting of its 2D peak, which demonstrated a similar electronic structure to bilayer graphene according to our former work [29,30] (See Fig. S1 in Supplementary data).

As for the transferred carbon film, many small wrinkles were on it. The bonding structure at wrinkles was important for analyzing the property of the transferred film. However, the Raman spectrum of PDMS possessed many peaks ranging from 1100 to 2000 cm<sup>-1</sup>, which made it difficult to analyze the Raman spectrum of carbon film on PDMS. Therefore, the GNC film was transferred onto another SiO<sub>2</sub> substrate to compare the difference of bonding state at wrinkle and flat zone. Fig. 2(d) presented the Raman spectra of the transferred GNC film ranging from 1100 to 2000 cm<sup>-1</sup> at flat zone and wrinkle (point A and B in Fig. 2(e)), respectively. Each of the spectra showed a D peak near 1340 cm<sup>-1</sup> and a G peak near 1600 cm<sup>-1</sup>, which indicated an ordered nanocrystalline structure. The D peak arises due to the presence of  $sp^2$  carbon atoms in rings with defects, while the G peak arises due to the presence of  $sp^2$ 



**Fig. 2.** Characterizations of the flexible strain sensor. (a) Optical photo of carbon film strain sensor. (b) Microstructure of the strain sensor with wrinkle structure. (c) High resolution TEM images of GNC film. The inset figure shows the FFT result. Two white spots verified the nanocrystalline structure. (d) Raman comparison of GNC film at certain points of flat zone and wrinkle. (e) Raman mapping results for a typical wrinkle. (left) local optic photo, (middle)  $I_D/I_G$  and (right) D peak position at the same area.

carbon atoms in both rings and chains [31]. Comparing with the Raman spectrum at the flat zone, the height ratio of D peak to G peak  $(I_D/I_G)$  increased prominently and both of the D and G peaks shifted to lower frequency at the wrinkle, which was also called red shift. The red shift of the D and G peak can be understood on the basis of the elongation of the carbon-carbon bonds, which weakens the bonds and therefore lowers their vibrational frequency [32]. This phenomenon was similar to single layer graphene under strain that the G peak of graphene would shift to lower frequency and split into two peaks [33,34]. And the strain would also open the optical band gap of graphene and influence its electrical properties [35]. For graphene layer, wrinkles would lead to the resistance increase [25]. As for GNC film, the resistance of transferred GNC film on PDMS was around 2 times larger than that of the as-deposit film, which should be ascribed to the transfer process induced wrinkles and defects.

A Raman mapping was also conducted at a wrinkle to verify the change of bonding structure. Fig. 2(e) presents the optic photo,  $I_D/I_G$ and D peak position at the same area, respectively. In the optic photo, the flat zone was green because of the SiO<sub>2</sub> substrate, while the wrinkle was gray. As for the  $I_{\text{D}}/I_{\text{G}}$  and D peak position images, clear differences could be found between the flat zone and wrinkle. In the  $I_D/I_C$  image, the position of wrinkle was red, which proved a high  $I_D/I_G$  value comparing with the flat zone. And in the D peak position image, the position of wrinkle was blue, which indicated a red shift of D peak comparing with the flat area. The mapping results verified the change of the Raman spectra and indicated a change of bond length at wrinkles. The Raman spectra of different samples and the Raman spectra of a-C film at flat zone and wrinkle were presented in Fig. S2. (See Supplementary data) The Raman spectra of a-C film at flat zone and wrinkle showed a similar tendency as GNC film, that the I<sub>D</sub>/I<sub>G</sub> increased and the D peak shifted to lower frequency.

#### 3.2. Performance tests of the strain sensor

Fig. 3(a) presents the relative resistance change ( $\Delta R/R_0$ ) versus strain of GNC strain sensor. The sensitivity of a strain sensor is described by GF as following:  $GF=(R-R_0)/(R_0 \times \varepsilon) = \Delta R/(R_0 \times \varepsilon)$ . Where R<sub>0</sub> is the resistance under zero strain; R is the resistance under certain strain; and  $\varepsilon$  reflects the deformation of the sensor. Three main stages could be distinguished. The strain range from 0 to 4% was defined as stage 1. In stage 1, the change of strain could bring a moderate GF value around 87. This GF value was comparative to many polymer-based flexible strain sensors and large enough for identifying different strains. The strain range from 4% to 15% was defined as stage 2. In stage 2, a good linearity between  $\Delta R/$ R<sub>0</sub> and strain could be found and an excellent GF of 1071 could be obtained under the strain of 15%. The strain range larger than 15% was defined as stage 3. In this stage, the  $\Delta R/R_0$  changed sharply when the strain increased, and a much higher GF value of 1570 could be obtained. But the high strain would induce irreversible change of the resistance due to the structure change of the strain sensor. The dash lines were the linear fits of each stage, and the slopes of each line were also given as K. Since there were three stages existing, the K values could represent the relative change of resistance in each stage. In stage 1 and 2, the K values were close to the maximum GF values of the two stages. In stage 3, a high K value of 9090 could be obtained, which indicates an unstable state with the high strain. Fig. 3(b) presents the repeatability and stability of the strain sensor under different strains. The  $\Delta R/R_0$  value kept stable and the  $\Delta R/R_0$  value change was smooth at the stretch and release stages for all the strain ranges. Fig. 3(c) presents the cycling test performed under the strain of 10%, which is at the middle of the



**Fig. 3.** Performances of the flexible strain sensors. (a) The relative resistance change ( $\Delta R/R_0$ ) versus strain of strain sensor. (b) The repeatability and stability of the strain sensor under the strain of 2%, 6%, 10% and 14%. (c) The 150 times cycling tests under the strain of 10%. The inset figure presents a zoom-in image of the cycling test. (d) The GF values of GNC films fabricated with different substrate bias and a-C film in different stages. The sample of a-C film only has two stages because its resistance exceeds the measurement range. (A colour version of this figure can be viewed online.)

stage 2. The strain sensor was stretched to the strain of 10% and then kept for 2 s dwell time before released. An excellent stability during 150 stretching and releasing was obtained and at the dwell time the  $\Delta R/R_0$  values kept stable. Fig. 3(d) presents the max GF value of the GNC films fabricated with different substrate bias and the a-C film in different stages. The sample of a-C film only had two stages because its resistance exceeded the measurement range with a large strain. All the GNC samples showed a similar tendency that the GF values increased at each stage. But with the decrease of the substrate bias, the GF value decreased at each stage. This should be explained that when the substrate bias decreased, the decrease of graphene nanocrystallite size would increase the resistance of the as-deposited samples, which could notably reduce the GF values as a result. And it should be noticed that in stage 2 the GF value of GNC film-based strain sensor (1071) was much higher than that of the a-C film-based strain sensor (45.5), which means the nano-structure of GNC film is a key factor to obtain ultra-high GF value. The resistances of the same sample shown in Fig. 3(a) under different strains were presented in Fig. S3. It should be noticed that the resistance of the unstrained GNC film was only 4.02 k $\Omega$ , while that of the unstrained a-C film was  $1.7 \text{ M}\Omega$ . When used as flexible strain sensor, the low resistance of GNC could effectively reduce energy consumption in industry application [16]. The resistance and relative resistance change  $(\Delta R/R_0)$  versus strain of a-C filmbased strain sensor were presented in Fig. S4(a). (See Supplementary data) The resistance of a-C film would also increase with the increase of strain, but the relative resistance change of a-C film was far smaller than that of GNC film when strain increased.

#### 3.3. Microstructure observation of the strain sensor

Fig. 4(a)-(f) present the change of a local area of the GNC strain sensor (the same sample of Fig. 3(a)) under the strain ranging from 0% to 15%. Fig. 4(a) presents the unstrained sample, which was spread with many small random shrinking wrinkles and a few huge

wrinkles. Fig. 4(b) presents the sample under 4% strain, some small wrinkles turned to the stretch direction and the resistance increased moderately. Fig. 4(c) presents the sample under 10% strain, cracks split under this strain and all the initial random wrinkles became parallel to the stretch direction. Fig. 4(d) presents the sample under 15% strain, which is the critical strain between stage 2 and stage 3 in Fig. 3(a), the oriented wrinkles parallel to the strain direction covered most area of the sample and the width of cracks increased. It should be noticed that only a few cracks existed and the cracks would be blocked at the initial huge wrinkles that the length of the crack was 50 µm-250 µm under 15% strain. And all the cracks were nearly perpendicular to the stretch direction. The crack generation and elongation mode of carbon film-based strain sensor was similar to that of graphene based-strain sensor, and the cracks generated at the stress concentrated areas to release the accommodated stress in the first a few stretch/release cycles [36]. After a few stretch/release cycles, cracks of the strain sensor became stable and would not generate and elongate under the same maximum strain. The pre-exist wrinkles and cracks could release local high tension and guarantee the carbon film-based strain sensors obtain stable resistance value under high strain. But under a much higher strain, dense cracks would break the intact structure of the flexible strain sensor and degenerate the performance of the strain sensor. The micro-structure change of a-C film under different strains were presented in Figs. S4(b-e). (See Supplementary data) The micro-structure evolution of a-C film under different strain was similar with that of the GNC film, which could verify the notable difference in GF values between the two kinds of film should not be attribute to the micro-structure.

As crack is one of the major features of the flexible strain sensor, the effect of crack should be further clarified. For the carbon filmbased strain sensor, once a crack formed, it would block the conduction of electrons and could not recover. The length of the cracks would be an important factor influencing the resistance. Fig. 4(e) and (f) present the shape change of cracks under different strains of



**Fig. 4.** Micro-scale in-situ observation of a strain sensor under different strain. Optical microscope photos of a strain sensor under (a) 0% (b) 4% (c) 10% and (d) 15%. Zoom-in photos of the strain sensor under (e) 10% and (f) 15%. With the increase of strain, the length of the circled crack decreased, while the width of the circled crack increased notably. (A colour version of this figure can be viewed online.)

10% and 15%. Under 10% strain, for the crack marked with the yellow circle, the length was 58.2  $\mu$ m and the width was 1.0  $\mu$ m. When the strain increased to 15%, for the same crack, the length decreased to 57.2  $\mu$ m while the width increased notably to 2.0  $\mu$ m. On one side, the length of cracks would not change notably under different strains. Once the cracks formed and became stable, the influence of the cracks on resistance would be small, which means the mechanisms for obtaining ultrahigh GF in the GNC film-based strain sensor should be ascribed to the nanostructure rather than the micro-scale cracks. Therefore, the mechanisms of obtaining ultrahigh sensitivity for the GNC film-based strain sensor should be different from those crack-based ultra-sensitive strain sensors [20,21]. On the other side, considering the width of the cracks could increase notably with strain increase, the existence of the cracks could effectively increase the stretchability of the strain sensors.

#### 3.4. High stretchability and ultra-high sensitivity mechanisms

In order to comprehend the ultrahigh sensitivity and high stretchability of the GNC film-based strain sensor more clearly, the schematic illustration of the stretch process is presented in Fig. 5 to explain the mechanisms. Fig. 5(a) presents the schematic illustration of the flexible strain sensor and the test circuit. Fig. 5(b) and (c) illustrate a local area with and without strain in micro-scale and are used to explain the high stretchability mechanisms. The

combination of the wrinkles and cracks contribute to the high stretchability (15%) of the carbon film-based flexible strain sensors. When strain is not applied on the flexible strain sensor, the wrinkles are shrinking and the direction of the wrinkles is random, as illustrated in Fig. 5(b). When strain is applied to the strain sensor, the initial wrinkles and newly formed wrinkles would all be stretched and became parallel to the stretch direction, as illustrated in Fig. 5(c). As for the cracks, when the applied strain is not larger than the maximum strain, only the width could be changed by the strain while the length would not increase. The change in the cracks for the same maximum strain is also fully recoverable, which indicates the cracks would mainly contribute to the high stretchability but influence less to the sensitivity.

Fig. 5(d) and (e) illustrate the structure change of the GNC film with and without strain in nano-scale and are used to explain the ultrahigh sensitivity mechanisms. When the GNC film is not under strain, the distance between adjacent graphene nanocrystallites is smaller than 3 nm in the amorphous matrix. The graphene nanocrystallites act as good electron transportation media in the film. And owing to the compact distribution of the graphene nanocrystallites, the tunneling effect could help the electrons transportation effectively. When strain is applied on the GNC film, two major changes will happen. The first change is the distance between adjacent graphene nanocrystallites will increase along the stretch direction. The second change is the graphene nanocrystallites will be stretched along the stretch direction as a result.

On one hand, when the distance between adjacent graphene nanocrystallites increases, the tunneling current between adjacent graphene nanocrystallites would decrease. The tunneling cut-off distance between two graphene sheets insulated with polymers is determined to be around 2-3 nm [37,38]. Because the energy barrier of the amorphous matrix in GNC is hard to obtain, we could roughly estimate the tunneling cut-off distance in the GNC film should be larger than that distance in polymer, which has a lower conductivity comparing with amorphous carbon film. Because the distance of adjacent graphene nanocrystallites is less than 3 nm as shown in Fig. 2(c), the stretch could lead the tunneling current decrease between some of the graphene nanocrystallites as a result. The decrease of tunneling current could increase the resistance of the strain sensor effectively.

On the other hand, the stretch of the graphene nanocrystallites under uniaxial strain would degenerate the electron transportation capability of graphene nanocrystallites. It is reported that the quantum confinement effect could change the electrical property of small-size graphene from semi-metal to semiconductor [39]. The width of graphene smaller than 15 nm is reported small enough to induce the change [40]. The semiconductor properties of graphene quantum dot and nano-ribbon made it possible to influence their electrical properties by applying strain [41]. The nano-size of graphene nanocrystallites within the GNC film makes it electrical properties more like graphene quantum dot or nano-ribbon. When the graphene nanocrystallites are under stretch, the conductivity will be influenced and the number of free electron within the graphene nanocrystallites will decrease as a result. Some theoretical calculations show 10% strain could induce the conductivity of armchair graphene nanoribbon decrease 7 times [42], which indicates a GF value around 70. The combination of the two factors is believed to be the major factors that contribute to the ultrahigh GF of the GNC film. And as mentioned above, the co-work of tunneling effect and deformation of graphene nanocrystallites contribute the ultrahigh GF value of 1071.

#### 3.5. Application tests of the strain sensor

Fig. 6 presents the practical applications of the flexible strain





**Fig. 5.** Mechanisms of the high stretchability and ultra-high sensitivity. (a) The schematic illustration of the flexible strain sensor. The micro-scale schematic illustration of (b) unstrained state of the strain sensor in micro-scale (c) strained state of the strain sensor in micro-scale, which are used for explaining the high stretchability. The nano-scale schematic illustration of (d) unstrained state nanostructure of GNC film and (e) strained state nanostructure of GNC film, which are used for explaining the ultrahigh sensitivity. (A colour version of this figure can be viewed online.)



Fig. 6. Application tests of the flexible strain sensors. a) Wrist bends with different angles test. b) Wrist random fast waves test, and 5 times of waving could be detected in 1 s. c) Different throat vibrant test by saying different word. d) Swallow test. e) Eye opens and closes test. f) Eye blinks test.

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sensor. Fig. 6(a) and (b) present the tests on the wrist, which are used to prove the strain sensor is capable for detecting large scale movement of human. As shown in Fig. 6(a), the wrist bent and held with different angles ranging from 0° to a maximum bend angle of 60°. With the wrist bend angle increasing, the relative resistance change also increased. And it could be noticed that when the wrist kept bending on a certain angle, the relative resistance change would keep stable. As shown in Fig. 6(b), the strain sensor could record the fast movement of human wrist. The inset image in Fig. 6(b) showed that 5 times waving of wrist in 1s could be recorded, which indicated a rapid response time of 200 ms of the strain sensor. Fig. 6(c) and (d) present the tests on the throat, which are used to prove the strain sensor is capable for detecting complex and medium scale movements of human. As shown in Fig. 6(c), the strain sensor was pasted at the upper and lower positions of throat. By saying different words like "I", "love" and "nano", the different movements induced resistance change of the muscles and bones could be distinguished. Fig. 6(d) presents the test of swallow, the strain sensor pasted at the upper throat could clearly record each time of the swallow movements. Fig. 6(e) and (f) present the tests at the eye side, which are used to prove the strain sensor is capable for detecting the subtle movements of human. As shown in Fig. 6(e), the very subtle movement of muscles around eves could be detected. The open of eye could bring tension around the eye muscles, while the close of eye would release the tension, and thus brought the change of the resistance. This test exhibited that the strain sensor could distinguish a relative resistance change as low as 1%. Fig. 6(f) presents the detection of eve blink, the pulsing signals of each time blink could be clearly identified. As those application tests have proven, by taking the advantage of the ultrahigh sensitivity and high stretchability, the GNC film-based strain sensors have good potentials in both monitoring the body motion and detecting subtle facial expressions, which may bring a possibility to use it in medical and virtual reality industrial.

The carbon film-based strain sensor still has a great potential for further developing flexible strain sensor with higher sensitivity and higher stretchability. On one hand, high sensitivity could be obtained by designing nano-scale structure to tailor the size and density of graphene nanocrystallites, which could be realized by changing the irradiation energy, density or using other technology like doping. On the other hand, high stretchability could be realized by designing micro-scale structure to release the local high tension, which could be realized by controllable pattern, texture or wrinkles by using lithography or pre-stretch technology. The idea of multiscale design could broaden the path for developing novel flexible strain sensor in the future.

#### 4. Conclusions

In summary, ultra-sensitive and highly stretchable GNC filmbased flexible strain sensors were fabricated based on an idea of multi-scale structure design. The GNC film-based flexible strain sensor possessed an ultrahigh GF of 1071 and was recoverable under a high strain of 15%. The ultrahigh sensitivity of GNC filmbased flexible strain sensor came from the unique nano-scale graphene nanocrystallite structure, which was attributed to the decrease of tunneling current between graphene nanocrystallites and deformation of graphene nanocrystallites under strain. The high stretchability was ascribed to the micro-scale structure change that the stretch of pre-existed wrinkles and width increase of cracks under strain. The study on cracks declared that under the same maximum strain, the cracks would contribute more to the high stretchability of the strain sensor rather than bring high sensitivity. The application tests proved some typical applications including detecting the movements of muscles around eye, throat and wrist, suggesting a great potential in monitoring of human activities.

#### **Author contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. <sup>1</sup>These authors contributed equally.

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#### Appendix A. Supplementary data

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