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Self-reinforcing graphene coatings on 3D printed elastomers for flexible radio frequency antennas and strain sensors

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Keywords: reduced graphene oxide, conductive ink, radio frequency antenna, strain sensor, flexible electronic

Abstract

The emergence of the Internet of Things (IoT) necessitates the development of electronic components with various form factors and mechanical properties. 3D printing is an effective tool to realize objects with arbitrary form factors. Various 3D printable materials have recently been commercialized; among them, stretchable materials are particularly useful in the IoT because they enable adaptability in the dimensional change of the electronics. Most of these stretchable materials are, however, not electrically conductive; conductive coating can enable the functionality. Here, we propose a self-reinforcing conductive coating strategy, which reduced graphene oxide (RGO) self-assembles to wrap graphene nanoflakes (GNF) as a conductive binder that can also achieve mechanical integrity. The conductivity of the GNF-RGO coating reaches $4.47 \times 10^4$ Sm$^{-1}$. To demonstrate the potential applications of the GNF-RGO coating, applying the coating on 3D printed porous elastomers enabled flexible radio frequency (RF) antennas and strain sensors. The RF antenna shows high radiation efficiency and maintains excellent performance under bending conditions. The coating also produces a strain sensor with a gauge factor of $\sim 13$ up to 40% of strain. We foresee that the electrically conductive GNF-RGO composite coating can provide versatile functionalization strategy in flexible electronics and in wearable biomedical devices.

1. Introduction

The emergence of the Internet of Things (IoT), which targets all living and nonliving objects to be accessible to a network to share the data, necessitates the development of an antenna with various form factors enabled by novel materials [1]. While the antenna component of the IoT must be included without causing a significant increase in the price of the object, a printed radio frequency (RF) antenna provides the antenna functionality at an affordable price [2]. Whereas the objects for the IoT typically have irregular topography, conventional antennas fabricated on rigid materials do not offer the required form factors and topological conformity to the object. In wearable healthcare application, which is one of promising fields for the IoT, the objects include human skin, garment, and accessories, to name a few. They often are topographically corrugated and dimensionally stretchable/compressive. It is critical for the IoT, including the antenna component, to offer seamless integration to the objects to collect reliable physiological and kinematic data from human subjects [3, 4]. Therefore, it is critical to develop an affordable processing route for the stretchable antenna component with various form factors; 3D printing of stretchable material could be a promising option.

3D printing is a versatile technique that can realize various form factors tailored to meet specific needs for applications [5]. Among various 3D printing techniques, fused deposition modeling (FDM), through which an object with an arbitrary form factor is created within a layer-by-layer deposition by extruding thermoplastic materials, is the most popular option because the required 3D printer is highly affordable. A limitation of the FDM is that it can print only
thermoplastic polymers that can be extruded upon moderate heating. There are a few flexible or stretchable materials that have been commercialized specifically for FDM [6]. A recently commercialized FDM printable material, GEL-LAY™ Filament, provides a porous internal structure, which allows mechanical flexibility and a significantly enhanced surface area. With a designed post-treatment chemistry, the foamy material can allow 3D printed structures with various functionalities by coating the interior and exterior surfaces.

A wide range of materials have been employed as conductive inks for printed electronics [7]. Most of these materials require rather harsh post-printing treatment. Such a process has caused compatibility problems with many substrates used for flexible electronics, such as paper, plastic sheet, or elastomer, which may denature upon heat and acid treatments. For example, conductive inks based on metal nanoparticles can achieve high conductivity, but require a sintering process at high temperature or other severe chemical or energetic post treatments to remove stabilizing agents or oxide layers. Noble metals allow rather mild post-treatment conditions, but they are generally expensive [8]. Conductive polymer is another popular choice, but chemical stability has been a critical issue that prevents its widespread use [9]. Carbon-based conductive inks, especially graphene-based inks, have been suggested as a balanced combination between high conductivity, mild processing, and chemical stability [10].

The dispersion strategies of graphene inks are generally classified into two categories: (1) direct dispersion of graphene in a good solvent such as N-Methyl-2-pyrrolidone (NMP) or dimethylformamide (DMF) without additives [11, 12] and (2) employment of binder materials, such as ethyl cellulose, as additives [13, 14]. Using the former method, Hu et al inkjet-printed a binder-free graphene/NMP suspension on the paper, followed by rolling compression to achieve the conductivity value of $4.3 \times 10^4$ S m$^{-1}$ [15]. A drawback of the method is that NMP, a popular solvent that disperses graphene nanoflakes, typically causes swelling or dissolving of polymer substrates for the printing, leading to distortion or fracture of the printed graphene traces. In addition, the absence of active chemical binding between the graphene nanoflakes causes poor mechanical integrity that may induce the fracture of the printed graphene traces. The latter method that employs binder material can provide enhanced mechanical integrity by covalent bonding. However, the binder compromises the conductivity, thus a thermal post-treatment to decompose the material is needed, which is not ideal for flexible substrates. If the binder material itself is electrically conductive, on the other hand, both electrical conductivity and mechanical integrity can be achieved at the same time.

In this paper, we present a new processing method to fabricate conductive structures with an arbitrary shape factor via 3D printing followed by a carbonaceous conductive layer coating. FDM 3D printing of a commercial rubber/poly(vinyl alcohol) (rubber/PVA) blend filament provides a facile pathway to generate an arbitrary flexible and porous substrate. Then, we utilized reduced graphene oxide (RGO) as a binder material to wrap the graphene nanoflakes (GNFs); we named the composite material GNF-RGO. Using the processing method, we fabricated flexible antennas and strain sensors.

2. Methods

2.1. Flexible substrate fabrication

A PORO-LAY GEL-LAY filament (MatterHackers Inc., USA) was purchased and used as-is to print porous 3D structures as a substrate. The filament is composed of polymer blends of PVA and an unspecified elastomeric component. After printing, selective dissolution of the PVA component in water leaves the elastomeric component with a microscopic porous structure. Ultrasonication for 3 d is required for the complete dissolution of the PVA. An overnight drying in vacuum oven at 80 °C allows for the thorough removal of water. The resulting structure is bendable, foldable, and slightly stretchable with a good shape resilience.

2.2. GNF-RGO coating fabrication

Graphene nanoflakes (N008-N, Angstrom Materials Inc., USA) were used as received. Various amounts of GNFs were added into a GO solution (4 mg GO ml$^{-1}$ in the water, Graphenea Inc., Spain) to form the GNF-GO suspension. The mixture was cast on a flexible 3D printed substrate at 80 °C for quick evaporation of the solvent. The substrates with the GNF-GO coating were collected followed by a two-step reduction process. The first reduction step was done with a mild reducing agent, L-ascorbic acid (vitamin-C, 8 mg ml$^{-1}$ in the water, Sigma-Aldrich, USA). The reaction was done with a distillation apparatus in an oil bath at 95 °C overnight [16]. The substrates with the GNF-RGO coating were dialyzed in the deionized water. For the selected samples, the second reduction step was done with a stronger reducing agent, 50 mM NaBH$_4$ in the water (Sigma-Aldrich, USA) for 4 h to improve the electrical conductivity [17], followed by dialysis in the deionized water. Then, the samples were dried for an hour in a convection oven at 120 °C.

Hereafter, we denote the samples using the code $\text{ratio-#}$ after the names of GNF-GO or GNF-RGO, where the $\text{ratio}$ is the mass ratio of GNF-GO in the suspension and # is the number of iterations of the chemical reduction procedure. For example, GNF-GO-5 represents the GNF-GO mixture with a 5:1 mass ratio that did not undergo any reduction procedure as a
control sample. GNF-RGO-5-1 indicates that the composite underwent a reduction process using L-ascorbic acid. GNF-RGO-5-2 indicates that the reduced composite underwent an additional reduction step using NaBH₄ solution.

2.3. Conductivity measurement
The electrical conductivity was evaluated with a four-point probe station (Pro4-4400, Lucas Signatone, USA) connected to a Keithley 2400 source measure unit. The thickness of the GNF-RGO coating on the substrate was obtained by cross-sectional SEM image. The cross-section of the sample was prepared by immersing the fabricated antenna in the liquid nitrogen for several seconds and manually broken into two pieces. For each synthesis condition, we obtained statistical results from five samples of different batches. The durability test of the sample was tested by repeated bending (radius of curvature of 1 cm) and releasing (no bending) cycles at 1 Hz frequency on a customized mechanical tester (UniVert, CellScale, Canada) equipped with a Keithley 2400 source measure unit.

2.4. Antenna fabrication
Once the GNF-RGO coating was synthesized on a 3D printed flexible substrate, the samples were compressed at 10 MPa to get compact coating on the substrate (figure 1(a)). A SubMiniature version A (SMA) connector was attached to the GNF-RGO coating by silver paste, and cured in a convection oven at 120 °C for 4 h. Then, the GNF-RGO antenna was dipped into a commercial room-temperature vulcanizing silicone (Shin-Etsu, Japan) for packaging. The silicone was cured for an hour to conclude the fabrication of the flexible GNF-RGO antenna. A photograph of an as-prepared GNF-RGO antenna is shown in figure 1(c), which can be bent (figure 1(d)) and twisted (figure 1(e)).

2.5. Antenna performance characterization
A simple vertical half-wave dipole antenna provides an omnidirectional donut-shaped radiation pattern which is adequate for applications that need a high coverage of radiation and data transfer [18, 19]. This type of antenna radiates the power almost uniformly in all directions in a given plane. It consists of two identical conductors each with the size of a quarter of the resonating wavelength. Each conductor is connected to one side of the feed line to power up the antenna.

We measured the E-plane and the H-plane of the dipole antenna by the RFxpert measurement tool from EMSCAN [20, 21], which is capable of measuring the radiating-near-field region and then projects the results to the far-field region. The efficiency of the antenna was quantified by reflection coefficient, which showed how much power fed to the antenna reflects as a function of frequency. For measuring the reflection coefficient, a vector network analyzer (VNA, E8362B) was used.

2.6. Strain sensor fabrication
The strain sensor was fabricated by coating GNF-RGO-5-2 on a 3D printed serpentine-shaped substrate. Two copper sheets were attached to both ends of the serpentine-shaped substrate as the electrodes by the silver paste, followed by curing in the
convection oven at 120 °C for 4 h. Then, the strain sensor was encapsulated by the silicone, according to the protocol described in the antenna fabrication section.

2.7. Strain sensor performance characterization

Tensile tests were conducted equipped with a Keithley 2400 source measure unit. The samples underwent three loading-unloading cycles with 5 mm min$^{-1}$ strain speed.

3. Results and discussion

3.1. GNF-RGO: morphology before and after compression

Figure 2(a) illustrates the morphological evolution during the processing. After the addition of GNF into the GO solution, a suspension of the GNF-GO is formed. The GO in the suspension served as a dispersant to stabilize the GNF owing to its planar 2D structure and hydrophilicity [22]. During the evaporation of the water in the suspension, the GO sheets were self-assembled into GO papers [23], and the GNFs were intercalated between the GO sheets. After the reduction, the average distance between the GO sheets was reduced because the chemical reduction caused the removal of labile oxygen-containing functional groups in the GO [24]. In the final GNF-RGO coating, the RGO plays a role as a binder to keep mechanical integrity while maintaining high electrical conductivity. As a result, we obtain a composite that is flexible without powder disintegration owing to the self-reinforcing nature of the RGO that wraps the GNF. This trait is suitable for application in flexible electronics.

The morphological evolution of the GNF-RGO coating was examined by SEM. The SEM images in figures 2(b) and (c) show the morphology of the GNF-GO-5, which did not undergo reduction or compression steps. Here, it can be confirmed that the GO forms a blanket-like network structure that wraps GNF particles everywhere. Each GNF particle, a stack of aggregated graphene platelets wrapped in the GO envelope, had an average thickness of ∼50 nm (characterized by a separate SEM imaging; not shown) with a lateral dimension of ∼1 μm. After repeating the reduction and compression steps twice, figures 2(d) and (e) show the top-view SEM images of the GNF-RGO-5-2. Here, the structure of the GNF-RGO became more compact.

3.2. GNF-RGO: conductivity optimization

A four-point probe measurement was used to evaluate the electrical conductivities of GNF-RGO coatings. As shown in figure 3, GNF-GO coatings were not conductive before reduction because GO is an insulator. After the first reduction by L-ascorbic acid, the GNF-RGO composites were electrically conductive. The conductivity values increased with the increasing GNF concentration in the precursor suspension. At the low ratio of GNF:RGO (i.e., low GNF content), the electrical conductivity was limited because of the abundance of the oxygen-containing functional groups in the RGO sheets that were left unreduced after the L-ascorbic acid treatment. The higher content of the GNF in the composite film increased the conductivity, as shown by the contrast between GNF-RGO-2-1 and GNF-RGO-5-1, which exhibited conductivity values of 0.72 ± 0.22 × 10$^{4}$ and 2.49 ± 0.28 × 10$^{4}$ S m$^{-1}$, respectively. The electrical conductivity of GNF-RGO-10-1, 2.61 ± 0.30 × 10$^{4}$ S m$^{-1}$, was however not higher than that of the GNF-RGO-5-1.

A subsequent treatment by a stronger reducing agent, NaBH$_4$, was shown to be efficient to remove the oxygen-containing functional groups in the RGO sheet [17]. Here, the electrical conductivity values were drastically improved, as presented in figure 3.
The conductivity of GNF-RGO-5-2 reached the highest conductivity value of \(4.47 \pm 0.61 \times 10^4\) Sm\(^{-1}\). Interestingly, the conductivity of GNF-RGO-10-2, \(4.16 \pm 1.07 \times 10^4\) Sm\(^{-1}\), was not higher than that of GNF-RGO-5-2. Moreover, the GNF-RGO-10-2 coating was more brittle than GNF-RGO-5-2 due to the reduced amount of RGO binder.

A drawback of using NaBH\(_4\) was an intensive bubbling observed during the reduction. This occasionally caused the delamination of the composite coating, which was the reason that we did not perform NaBH\(_4\) treatment as the first reduction step. The conductivity results of GNF-RGO-10-2 had a certain degree of inconsistency as indicated by a large standard deviation.

Therefore, we came to the conclusion that there is an optimum ratio of GNF:RGO to provide the best combination of electrical conductivity and mechanical integrity. A certain fraction of RGO in the composite coating is critical to maintain the sufficient mechanical integrity whereas the increasing fraction of GNF increases the conductivity. Our results suggest that the mass ratio of GNF:GO = 5 in the suspension is the balanced point between the electrical conductivity and mechanical integrity. In addition, the two-step reduction protocol using a weaker reducing agent, followed by a stronger reducing agent turned out to be an effective combination. The first reduction step using L-ascorbic acid provides mechanical integrity and moderate electrical conductivity to the composite coating. The second reduction step using NaBH\(_4\) provides a further enhancement of electrical conductivity. Further chemical characterizations of the GNF-RGO coating can be found in the supplementary information available online at stacks.iop.org/FPE/2/035001/mmedia.

The durability of the sample with the GNF-RGO-5-2 coating without PDMS encapsulation was tested by repeated bending (radius of curvature of 1 cm) and releasing (no bending) cycles at 1 Hz frequency. We performed a comparative study between GNF-RGO-5-2 (test sample) and pressed GNF (control) on the 3D printed elastomer substrate. For the GNF coating, a certain amount of GNF powder was spread on the substrate, and then compressed at 10 MPa to get compact coating. The thickness of the GNF coating was controlled to be the same as that of GNF-RGO-5-2 (\(\sim 20\) \(\mu\)m). The result of the cycle test is shown in figure 4(a). No obvious resistance change was observed for the GNF-RGO-5-2 coating up to 1000 cycles. In contrast, the normalized resistance (resistance normalized by the initial value) of the GNF coating was rapidly increased. The resistance of the GNF coating increased to ten times its original resistance after \(\sim 400\) cycles. The dramatic enhancement of durability in the mechanical and electrical properties of the GNF-RGO-5-2 coatings is due to the covalent bonding between the RGO ‘envelopes’ that wrap the GNF, whereas the covalent bonding was introduced from the chemical reduction process. The optical microscopy image in figure 4(b) (pristine) and 4(c) (after 1000 cycles) shows the durability of the coating. Here, only indistinctive buckling can be observed after 1000 cycles. However, the GNF control sample shows a severe loss of materials after undergoing bending stress cycles, as evidenced by comparing figure 4(d) (pristine) and 4(e) (after 1000 cycles). Therefore, the RGO-wrapping process can be described as ‘self-reinforcing’ which can be useful for the practical application of GNF particles.
3.3. Antenna performance

Before designing the antenna, we needed to characterize the substrate (which the antenna is printed on) to extract its dielectric constant and loss tangent. Using a Keycom dielectric measurement open mode probe [25], the dielectric constant and loss tangent of the substrate are obtained to be 3.6 and 0.06, respectively. Using a HFSS software, a prototype of the antenna was designed to align the center frequency at 2.45 GHz. The antenna was connected to a SMA connector by silver paste. Figure 5 shows the reflection coefficient and radiation pattern of the fabricated antenna.

Figure 5(a) depicts the simulated and measured reflection coefficient of the fabricated dipole antenna. Here, the simulation and measurement showed an acceptable agreement near the resonant frequency of 2.45 GHz. The discrepancy between the simulation and measurement results at the frequencies larger than 3 GHz is probably due to a non-ideal connection between the SMA connector and two branches of the dipole antenna. The dielectric constant and loss tangent values of the substrate characterized and used in the simulation have a certain tolerance that may cause the discrepancy. We also used constant values for the parameters of the graphene in the whole frequency band in the simulations; however, they may vary as a function of frequency in the given range. To show that the antenna is flexible, the performance of the antenna was monitored under a range of bending radii (BR). Figure 5(b) shows the effect of BR of the dipole antenna on the reflection coefficient. Here, a bandwidth (BW; the normalized range of frequencies with the reflection coefficient below −10 dB) of 35% was achieved at the frequencies between 2.1 and 3 GHz for BR values up to 2.5 cm.

The measured 3D radiation pattern depicted in figure 5(c) shows a perfect donut-shaped pattern as expected. Figures 5(e) and 5(d) display the measured E-plane and H-plane of the antenna, respectively, for different bend radius. For different BRs, the H-plane
remained omnidirectional and the E-plane kept the donut-shaped pattern. The measured peak gain at the center frequency is 0.3 dBi which indicates that the antenna has an acceptable performance.

### 3.4. Strain sensor

The GNF-RGO-5-2 composite was tested as a potential material for a strain sensor. Figure 6(a) shows a systematic increase in the resistance of a serpentine-shaped GNF-RGO-5-2 coating up to 40% strain. When the sample was stretched more than the 40%, the silicone encapsulation layer was delaminated from the coating due to the buckling effect. The 3D printed serpentine shape allowed the device to measure strain values that exceed the 5% limit of conventional metal strain gauges [26], as well as ~10% for some graphene-based strain sensors [27, 34]. The increased resistance upon stretching can be explained by the model of overlapped graphene sheets, where the degree of overlapping between the graphene sheets dictates the overall resistance [29]. With increasing strain, the GNFs and RGO sheets tend to lose connectivity, resulting in an increase of the contact resistance between the GNFs and RGO sheets.

The resistance increased irreversibly after the first loading-unloading cycle. And then the output curve of the sensor became consistent between the second and third loading-unloading cycles. An earlier study pointed out the fact that some irreversible cracks are

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**Figure 5.** (a) The simulated and measured reflection coefficient of the dipole antenna, (b) the measurement results for different values of BRs, (c) the measured 3D radiation pattern, (d) the measured E-plane at 2.45 GHz for different BRs, (e) the measured H-plane at 2.45 GHz for the different BR.

**Figure 6.** (a) The relative changes in resistance for the loading-unloading cycles versus strain. Inset: the optical image of the strain sensor. (b) The calculated gauge factor versus strain for the loading and releasing steps in the second and third cycles.
generated during the first loading cycle, which account for the increased resistance. But, at the same time, they allowed structural relief for repeated loading-unloading cycles [28]. Such structural relief resembles the stretchability of a rigid object as a result of kirigami [26]. Here, we considered the first loading-unloading cycle as the initialization process for the strain sensor; in other words, we showed that the sample preparation of the strain sensor was concluded after the first loading-unloading cycle. Therefore, the performance of the strain sensor was evaluated based on the second and the third cycles.

The slope reflects the gauge factor (GF), which is the sensitivity of the sensor to strain, given by equation (1) [30],

\[
GF = \left( \frac{\Delta R}{R_0} \right) / \varepsilon,
\]

where \(\Delta R/R_0\) is the relative change in resistance and \(\varepsilon = \Delta L/L_0\) is the mechanical strain. The gauge factor obtained from the loading and releasing steps in the second and third cycles were shown in figure 6(b). Here, we obtained the GF values of ~13 up to 40% strain. The gauge factor values were higher than the conventional metal strain sensor (GF ≈ 2), and close to carbon nanotube-polymer composite strain sensor (GF between 5 and 22) [31], and sensor utilizing graphene-polymer composites (GF ≈ 12) [32]. The operating range (strain ~40%) of the fabricated strain sensor is also wider than the previously reported graphene-based sensors (up to 20%) [27, 33–36].

4. Conclusion

In summary, we have introduced a self-reinforcing nanocomposite of graphene nanoflakes that are enclosed by self-assembled GO particles. A two-step acid treatment protocol reduced GO into RGO, enhancing the electrical conductivity of the composite coating. The substrate material was a 3D printed porous elastomer prepared by a commercial filament material. The whole process was conducted at a temperature lower than 120 °C without using any organic solvent. The GNFRGO composite coatings were applied on 3D printed objects to transform the non-functional elastomers into flexible RF antennas and strain sensors. We foresee that the electrical conductive GNF-RGO composite coating can be utilized in various applications in flexible electronics and in wearable biomedical devices.

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Author contributions

X L conceived of the idea presented in this paper with guidance from H-J C; X L and Y F designed and performed the material preparation and characterization; M M H and H S designed the antenna structure and characterized its performance with guidance from P M; A K designed and fabricated the 3D printed substrate with guidance from H-J C; X L, Y F, and A K designed and performed the strain sensor experiments with guidance from H-J C; X L, M M H, A K and Y F wrote the paper with feedback provided by P M and H-J C.

Conflicts of interest

The authors declare no conflict of interest.

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Supporting Information

Self-Reinforcing Graphene Coatings on 3D Printed Elastomers for Flexible Radio Frequency Antennas and Strain Sensors

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1. GNF-RGO Chemical Characterization

Chemical characterization: A field emission scanning electron microscope (FE-SEM; Sigma, Zeiss) was utilized for the morphological study. X-ray diffraction (XRD) patterns were recorded on a Rigaku RU-200B X-ray diffractometer with a rotating anode X-ray generator using Cu Kα radiation (40 kV, 110 mA). X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis spectrometer with monochromatized Al Kα. The C1s peak at 284.6 eV was used to calibrate all XPS spectra. A Renishaw In Via microscope system was used to collect Raman spectra from samples. A 785 nm diode laser was used as an excitation source.

Raman spectroscopy was used to probe the bonding structure of the carbonaceous materials. There are three distinguishable bands presented in Figure S1a. First, the D-mode (disordered band) was located between 1330 and 1360 cm⁻¹. Second, the G-mode (tangential mode), which corresponds to the stretching mode in the graphite plane, was located at 1580 cm⁻¹. Third, the second-order modes, conventionally denoted as 2D, was located at 2680–2690 cm⁻¹ [1, 2]. The relative intensity of D-mode and G-mode (I_D/I_G) depends strongly on the density of defects in the graphitic material. A larger I_D/I_G value suggests a higher density of sp³ carbon due to structural defects [2]. The values of I_D/I_G increase from 0.43 in GNF to 1.18 in GNF-GO-5, indicating that the structure of carbon in GNF-GO-5 is less ordered compared to that of pure GNFs because of the GO content. After the L-ascorbic acid reduction, The I_D/I_G value increases to 1.87, which indicates a further increase of sp³ carbon (i.e., decrease of the sp² carbons; an ideal graphene has 100% sp² bonding) upon GO reduction in the GNF-GO composite film [3].

The chemical compositions at the surfaces of samples were investigated by X-Ray photoelectron spectroscopy (XPS). As presented in Figure S1b, the carbon to oxygen atomic ratios (C:O) of the starting materials were 51.6 for the GNF and 1.7 for GO. After mixing the GNF and GO, the measured C:O values in GNF-GO-5 is 3.8. This value is significantly lower than the value calculated from the weight percent of each component, which is 11.7. The discrepancy can be explained by surface segregation of GO upon drying of the solvent. It is well known that XPS measures the chemical composition of the very top of the surface (~5 nm at the condition of operation) [4]. The SEM image of GNF-GO-5 (Figure 2b) also did not show indicative features of flaky GNFs exposed at the surface; a layer of GO seemed to be on the top of the GNFs. Both features strongly indicates that the majority of the signals collected by XPS was generated from the GO. After the L-ascorbic acid reduction, the C:O value of GNF-RGO-5-1 was increased to 7.8. The C:O value was further increased to 10.7 in the GNF-RGO-5-2, implying further reduction of the RGO.

XRD patterns of GNF, GNF-GO-5, GNF-RGO-5-1 and GNF-RGO-5-2 are shown in Figure S1c. All four samples showed two peaks at 2θ = 26.5° and 54.9°, which can be attributed to the (002) and (004) planes of graphitic carbon [5]. The inset shows a magnified view at the 2θ values ranging from 10° to 15°, GNF-GO-5 exhibited a reflection with the peak at 2θ = 11.6°, attributed to GO (001) [6], which is the evidence of GO existence in the GNF-GO composite coating. This peak was not observed in GNF-RGO-5-1 and GNF-RGO-5-2, indicating that reduction by L-ascorbic acid destroyed periodic stacking between GO layers which existed in the as-prepared control sample (i.e., GNF-GO).
Figure S1. (a) Raman spectra of GNF, GNF-GO-5, GNF-RGO-5-1, and GNF-RGO-5-2. (b) Atomic ratio of carbon and oxygen obtained from XPS profiles. (c) XRD spectra of GNF, GNF-GO-5, GNF-RGO-5-1, and GNF-RGO-5-2. The inset is a magnified view at low 2θ region (between 10 and 15 degrees). X-ray photoelectron spectroscopy (XPS) profiles near (d) O1s and (e) C1s peaks.
2. Evaluating the Resistance Change of GNF-RGO Coating under Bending.

The resistance change of GNF-RGO-5-2 coating (without the PDMS encapsulation) versus bending radius of curvature was measured by using Keithley 2400 source measure unit (Figure S2). No obvious resistance change of the samples was observed upon bending with the radius of curvature ranged from infinite to 0.5 cm. The result indicates the GNF-RGO coating is suitable for the flexible electronic application.

![Graph showing resistance change vs. curvature](image)

**Figure S2.** The resistance changes of GNF-RGO-5-2, and GNF coating versus the radius of curvature.

**References for Supporting Information**
