Published in final edited form as:

Adv Funct Mater. 2018 February 28; 28(9): . doi:10.1002/adfm.201705291.

Integration of stiff graphene and tough silk for the design and fabrication of versatile electronic materials

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Abstract

The production of structural and functional materials with enhanced mechanical properties through the integration of soft and hard components is a common approach to Nature's materials design. However, directly mimicking these optimized design routes in the lab for practical applications remains challenging. For example, graphene and silk are two materials with complementary mechanical properties that feature ultrahigh stiffness and toughness, respectively. Yet no simple and controllable approach has been developed to homogeneously integrate these two components into functional composites, mainly due to the hydrophobicity and chemical inertness

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

of the graphene. In this study, well-dispersed and highly stable graphene/silk fibroin (SF) suspension systems were developed, which are suitable for processing to fabricate polymorphic materials, such as films, fibers, and coatings. The obtained graphene/SF nanocomposites maintain the electronic advantages of graphene, and they also allow tailorable mechanical performance to form including ultrahigh stretchable (with a strain to failure to $611 \pm 85\%$), or high strength (339 MPa) and high stiffness (7.4 GPa) material systems. More remarkably, the electrical resistances of these graphene/SF materials are sensitive to material deformation, body movement, as well as humidity and chemical environmental changes. These unique features promise their utility as wearable sensors, smart textiles, intelligent skins, and human-machine interfaces.

Graphical abstract

Keywords

Graphene; silk; processing; electronic materials

1. Introduction

Graphene has been utilized in a broad range of fields, *e.g.*, biomedicine, engineering, and aerospace industries, among others, due to its remarkable strength and electrical conductivity that arise from its two-dimensional sp^2 carbon honeycomb structure. Pristine graphene is the strongest known material with a tensile strength of 130 GPa, about 200 times stronger than steel.^[1] However, maintaining its high performance at the nano-scale to macro-scale in materials processing and composite material systems remains a major challenge. For example, centimeter scale graphene paper, produced from graphene nanosheets, only has a tensile strength of 293.3 MPa,^[1] around 443 times lower than that of single graphene nanosheet. The strain to failure of the same sample is only around 0.8%, far inferior to application requirements. Additional challenges with graphene include high price, poor biocompatibility, and degradability. Thus graphene is usually formed into composite materials with natural and synthetic polymers.^[2–4] Among them, silk is the toughest one with interest in many sectors of research and applications^[5–11] as a mechanical complement with graphene and the exceptional toughness of silk, reported as several times tougher than steel and Kevlar fibers.^[12] Additional other advantages, such as low cost, wide availability, excellent biocompatibility as well as tunable degradability, can also offset the limitations with graphene.^[13,14] However, despite these useful features, silk fibroin (SF) protein is immiscible with graphene, especially with high volume graphene fillings, due to the strong π - π interaction, hydrophobicity, and chemical inertness of the graphene nanosheets.^[2–4]

Hydrophilic graphene oxide, which has epoxy and hydroxyl groups on its graphene basal plane and carboxylic groups along the edges, usually serves as a graphene substitute to fabricate graphene oxide and silk nanocomposites. These graphene oxide/SF composites offered enhanced mechanical properties than silk and graphene materials alone, which are typically stiffer than pure silk materials and tougher than graphene oxide materials.^[5,7,8,11] However, mechanically, graphene oxide is much weaker than graphene, and electronically, it is an insulator.^[15] These disadvantages hinder functional applications in electronic, optoelectronic, and energy storage-related fields. With the aim of retaining the unique advantages of graphene, researchers have even attempted the feeding of graphene to silkworms and spiders to produce graphene-silk fibers directly.^[9,10] However, the content of graphene was insufficient to reach conductive percolation thresholds, thus limiting this approach for the production of conductive and mechanically reinforced silk fibers. One useful approach for production of the conductive protein/graphene-based hybrids is the integration of protein nanofibrils, such as silk nanofibrils^[5] and amyloid fibrils^[16,17], with reduced graphene oxide through hierarchical assembly. The resultant nanocomposites combined the physical properties of both constituents and can be developed into a variety of conductive functional materials, such as cell scaffolds, shape-memory films and enzyme sensors, although the mechanical properties of these materials still fall short for practical applications.

2. Results and Discussion

In the present study, we first designed new dissolution routes to generate well-dispersed graphene/SF suspensions, with a composition ratio that could be tunable. The critical step is to select appropriate solvent systems to: (i) dissolve SF and (ii) disperse graphene nanosheets. LiBr/H₂O dissolution and water-dialysis is the most common route to extract SF from degummed *Bombyx mori* (*B. mori*) silkworm cocoon silk fibers.^[18] However, the resulting SF aqueous solution is incompatible with graphene, due to the extreme hydrophobicity of graphene. Hexafluoroisopropanol (HFIP)^[19–22] and CaCl₂/formic acid (FA)^[23,24] are two additional solvents to dissolve silk fibers, and our initial attempts confirmed these two solvent systems with potential to disperse graphene nanosheets. Accordingly, the primary challenge is to improve the dispersion capability of graphene in these solutions.

Recently, Jakus *et al.* developed a liquid graphene ink consisting of a majority of graphene and a minority of polylactide-co-glycolide.^[25] This 3D printable graphene ink was successfully processed into biocompatible scaffolds under ambient conditions, although the obtained structures were fragile (The detailed description of such graphene ink can be found in experimental section). In our experiments, we found that this graphene ink could disperse in both HFIP and FA/CaCl₂ solvents, even without ultrasonic treatment. Thus, two optimized routes to produce homogeneous graphene/SF dispersions were prepared based on these two solvents (Figure 1A). For the optimized HFIP dissolution protocol, *B. mori* silkworm cocoon silk fibers were degummed and dissolved in aqueous 9.3 mol L⁻¹ LiBr solution with heating at 60 °C for 1 hour. Then, the solution was dialyzed with deionized water to obtain aqueous SF solution, followed by freeze-drying into a SF foam, which could directly dissolve in HFIP with a concentration of SF up to 25 wt%. Next, the liquid graphene

ink with desired weight ratios was directly added into SF/HFIP solution with strong vortexing. The resultant graphene/SF/HFIP suspension is uniform and stable at room temperature. A 10 wt% graphene/SF/HFIP suspension with (weight ratio of Graphene and SF is 50:50) is stable over several months (Figure 1C). The second route established from the graphene/SF/FA/Ca²⁺ system (Figure 1B), *B. mori* silkworm cocoons were degummed and dried to loose silk fibers, which were then directly dissolved in FA/CaCl₂ solution with a CaCl₂ concentration of 5% w/v. Further, the liquid graphene ink was mixed with the FA/Ca²⁺ solution to obtain well-dispersed graphene/SF/FA/Ca²⁺ suspensions. As with the graphene/SF/HFIP suspensions, the graphene/SF/FA/Ca²⁺ dispersions are stable at room temperature for several months (Figure 1D).

After obtaining these well-dispersed graphene/SF suspensions, we focus on fabricating functional graphene/SF materials (Figure 2, Figure S1, Supporting Information). For simplicity, the hybrid materials in this paper are labeled according to the graphene/SF weight ratios. For example, 50:50 means that the weight ratio of graphene and SF was 50:50 (wt/wt). In all experiments, the total concentration of solutes (graphene and SF) was fixed to 10 wt%, because these suspensions maintained an adequate balance between dispersion uniformity and fluidic rheological properties. Additionally, the materials produced by graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions are termed graphene/SF and graphene/SF/Ca²⁺, respectively. First, the graphene/SF or graphene/SF/Ca²⁺ films are obtained by solution casting at room temperature (Figure 2A-D, Figure S1, Supporting Information). The rapid evaporation of HFIP or FA resulted in film formation in a chemical hood at room temperature in 2-4 hours, and the residual solvent can entirely remove by heating the as-cast films at 60 °C for 2 hours (Figure S2, Supporting Information). These resulting films maintained the conductivity of graphene and also greatly enhanced the flexibility of graphene (Figure 2B,C). For example, the 75:25 graphene/SF films can be cut, bent and folded to arbitrary constructions (Figure 2C), in sharp contrast to the brittle characteristics of pristine graphene materials. Additionally, these films even endure high-energy processing, such as laser cutting, which is usually used for metal and hard polymer machining. A graphene/SF film with a thickness of 50 μm was directly cut into a reentrant honeycomb structure with spline resolution of 500 μm (Figure 2D). This particular structure is known as an auxetic (meta-)construction with a negative Poisson's ratio and has been widely applied in tissue engineering and biosensors. The mesostructure of the films was disclosed by scanning electronic microscopy (SEM). A free-standing film with a thickness of ~100 μm reveals a uniform and porous structure (Figure 3A). High-resolution SEM images (Figure 3B, Figure S3, Supporting Information) indicate that the SF has assembled into uniformly distributed silk nanofibrils with diameters around 100 nm on the graphene surface, consisting of the dominant β-sheet structures (primary secondary structure in silk nanofibrils) detected from FTIR spectra (Figure S4, Supporting Information).^[26,27] The similar self-assembly behavior is also observed in reduced graphene oxide/SF aqueous solutions, indicating the strong interface between graphene and SF molecules.

In addition to film, fiber is a useful material format for functional applications.^[22] Although SF solutions have been widely used for fabricating regenerated silk fibers,^[28] reports that combine graphene and SF to spin artificial fibers are limited. Only a few papers attempted to spin mechanically enhanced regenerated graphene oxide/SF fibers.^[8] Considering the high

viscosity and stability of graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions, we further used them to fabricate graphene/SF fibers (Figure 2E-G). Wet-spinning techniques, ejection of the spinning dope into a coagulation bath (70% v/v ethanol aqueous solution in this study) are adapted to generate graphene/SF and graphene/SF/Ca²⁺ fibers (Figure 2E, Figure S1, Supporting Information).^[28] the 10 wt% graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions with 50:50 graphene/SF ratio can be spun continually by extrusion with a hand held device (Figure 2F and Movie 1). Because of the rapid diffusion rate of HFIP and FA, once the suspensions are spun into 70% v/v ethanol solution, they rapidly harden into fibers, which can be directly taken out of ethanol solution without any post-processing, such as post-drawing, dehydration or crystallization. The continuously spun fibers can reach up to meter scale without any cracks in the limited testing that was conducted on these samples. These as-spun fibers exhibit useful mechanical performance; a single 56 mg fiber hold a 213 g weight without breaking (insert image in Figure 2F). In contrast, regenerated silk fibers^[28,29] or graphene fibers^[30] produced by same methods are brittle and too weak to be measured via standard mechanical testing. Figure 3C and D present typical cross-section morphologies of the as-spun graphene/SF fibers. The graphene and SF fuse together with honeycomb-like porous structures without gaps or cracks (Figure 3D).

We also used these two graphene/silk suspensions to directly write or print desired patterns on polypropylene substrates (Figure 2H-K). As a low-cost, rapid, and user-friendly technique, direct writing is of interest as a promising electronic prototyping strategy.^[31] Figure 2I shows the Chinese character of “silk” written on a polypropylene plate using a Chinese brush with 50:50 graphene/SF/FA/Ca²⁺ suspension. A stable handwritten conductive graphene/silk pattern is formed after short curing at room temperature (about 2 min). The conductive pattern bonded firmly to the substrate and can withstand hundreds of rounds of tear tests using a commercial adhesive tape (left top image in Figure 2J). The bonding between the two materials is also confirmed by cross-sectional SEM images, which display a sharp well-bonded boundary without any significant gaps between the two layers (Figure 3E and F).

The versatile processability of the graphene/silk materials allows the generation of various functional materials, such as filtration membranes,^[32] mechanically enhanced fibers,^[8] smart conductive coatings,^[22] and wearable devices, as well as chemical and diagnostic sensors.^[33] In this investigation, we focus on wearable electronics and solvent sensors, due to the biocompatibility, conductivity, and mechanical flexibility and tunability of the materials. Wearable electronics, such as electronic skins and sensors, must offer semiconductive properties and be mechanically compatible with biological tissues, with characteristics of low modulus, flexibility, and stretchability.^[34] The graphene/SF/Ca²⁺ film system matches these requirements. Graphene/SF/Ca²⁺ films with 20 wt% graphene, for example, is stretched more than three times their initial length without breaking (insert image in Figure 4A), displaying much larger strain to failure (more than 300%) than most reported polymer/graphene materials. The typical stress-strain curves of graphene/SF/Ca²⁺ films, when the graphene concentration is increased from 10 wt% to 40 wt%, are presented in Figure 4A and Table 1. Remarkably, these films exhibit ultrahigh stretchability, with strain to failure up to 611±85% for 10 wt% graphene samples. The strain to failure still maintains

202±67% even when the graphene weight content is as high as 40 wt%. This ultrahigh stretchability stems from the random coil conformation of the SF molecules, as well as the strong water absorbing capacity of Ca^{2+} ions in the films. FTIR spectra of the graphene/SF/ Ca^{2+} films reveal that the SF mainly present as random coil structures (Figure S5, Supporting Information),^[35] thus the SF chains more easily adjust their structure than SF with β -sheet structure to adapt to the tensile deformation. Meanwhile, the calcium ions in the films can capture water molecules from the atmosphere through coordination; a Ca^{2+} ion can coordinate 6-8 water molecules via the oxygen atoms.^[36,37] As plasticizers, water molecules can soften the films and increase the toughness. Figure 4C summarizes the strength and toughness relationships of graphene/SF/ Ca^{2+} films in comparison with other polymer/graphene oxide and polymer/MMT materials, two of the most studied mechanically enhanced polymer/nanocomposite systems.^[4,38] The mechanical performance of these new graphene/SF/ Ca^{2+} films fills an empty mechanical space of polymer nanocomposites (blue color area in Figure 4D). This region, which combines high stretchability and low modulus, a good match for wearable device applications. After summarizing the strength and Young's modulus of all samples in an Ashby plot (Figure 4D),^[39] the values of these graphene/SF/ Ca^{2+} composites are in the top region of natural elastomers and higher than synthetic elastomers.

Figure 4B shows the typical stress-strain curves of graphene/SF films with graphene concentrations from 25 wt% to 75 wt%. Like other polymer nanocomposites, such as graphene oxide/polydopamine^[40] and graphene oxide/chitosan^[41], the addition of SF improved the strength and toughness of nanocomposites. The nanocomposite with 25 wt% graphene shows the best mechanical properties with strength, stiffness, and strain to failure of 242 ± 66 MPa, 4 ± 1 GPa, and $8\pm3\%$, respectively. The strength and Young's modulus of the graphene/SF systems locate in the empty (gap) region among natural silk fibers, natural ceramics and ceramic composites (Figure 4D), suggesting the synergistic effect of SF and graphene. These properties are in line with other mechanical advantageous nanocomposites with an elegant balance between strength and toughness.

A spline with a dimension of $2\text{ cm}\times 2\text{ mm}\times 200\text{ }\mu\text{m}$ was used to assess the electronic properties of these graphene/SF/ Ca^{2+} materials. The splines with graphene weight percent of 10 wt%, 20 wt%, and 40 wt% give resistances of 1600 ± 300 , 682 ± 132 , and 261 ± 76 k Ω , respectively (Table 1). Meanwhile, when applying a tensile force on the splines, the resistance of the splines increases synchronously with sample deformation (Figure 5A, Movie 2). These conductive and mechanical behaviors of graphene/SF/ Ca^{2+} systems make them good candidates for wearable electronics, such as strain sensors.^[42–45] Figure 5B shows the relationship between the electrical resistance and the applied strain for a specimen with a gauge length of 30 mm. The electrical resistance changes smoothly as the strain increased without discontinuity, even when the strain reaches 300%. In fact, achieving highly stable conductive changes remains a major challenge in conductive particulate nanocomposites, especially, under large deformations, because the conductive fillers disconnect under deformation due to the limited filler content in these composites. Once the conductive filler contents are below the percolation threshold, the filler percentage that forms a conductive network, the conductivity of the composites is lost. Another important strain gauge parameter, gauge factor (GF), is defined as the relative resistance change divided by

the applied strain, $GF = (R/R_0)/\epsilon$,^[42] are presented in Figure 5C. The GFs increase linearly from 0.13 to 0.47 during deformation from 0 to 300%, revealing similar GF changes with strain gauges prepared from pure MWCNT networks in bucky-paper (with GF of 0.34).^[43] To estimate practical applications, we adhered a spline on the surface of a balloon and controlled the deformation by using a commercial pump (Figure 5D). The resistance responds in real time upon deformation of the balloon, with increased value with the expansion of the balloon, and declines immediately once the balloon is shrunk. These strain sensors are also suitable to monitor body motion. For example, the resistance change of the strain sensor follows the movement of a finger when it is fixed on a glove (Figure 5E). The resistance increases further and then reduce progressively with finger position changed in a straight-clench-straight cycle. It is worth noting that the resistance of the graphene/SF/Ca²⁺ nanocomposites could not be entirely recovered in terms of their original length immediately after large deformations, due to the relaxation of the SF chains. This problem can be (or partially) resolved by cross-linking the SF chains through chemical or enzymatic reactions.^[46] The present graphene/SF/Ca²⁺ systems more tend to be applied as disposable strain sensors for monitoring large deformations.

Besides, the utility of these graphene/SF/Ca²⁺ nanocomposites can be expanded to detect humidity, touching and breathing. Our recent study confirmed that Ca²⁺ ions in silk/carbon nanotube system have strong capability to capture water from the environment through coordination complexes.^[22] The resistance of these SF/Ca²⁺/conductive filler systems is sensitive to humidity changes, which can sense and monitor finger-touching (Figure 5F) and breathing (Figure 5G). The resistances are modulated in real-time upon finger touching and breathing and are still sensitive to these external stimuli after more than ten cycles.

In contrast, in some conductive sensor systems such as diagnostic and biochemical sensors, the materials are required to exhibit high strength and chemical stability,^[33] and high-strength graphene/SF materials are better for these applications than the graphene/SF/Ca²⁺ system. For example, The highest strength, modulus, and toughness of the graphene/SF nanocomposites (Figure 4C and D) are 339 MPa, 7.4 GPa and 15.3 MJ m⁻³, respectively, comparable with the highest values recently reported in other polymer nanocomposites, such as reduced graphene oxide/MMT/PVA (strength of 356.0 MPa and toughness of 7.50 MJ m⁻³)^[47] and graphene oxide/chitosan (526.7 MPa, 19.0±1.4 GPa, and 17.69 MJ m⁻³)^[41]. These mechanical advantages of the graphene/silk system support potential applications in mechanically stable electronic sensors. Thus, we designed a graphene/SF conductive sensor to monitor ethanol concentrations in aqueous ethanol solutions, with potential applications in solvent detection. A graphene/SF sensor was connected with a multimeter and mounted on the bottom of a petri dish. Then a 10 μ L water/ethanol solution was dropped on top of the sensor. The resistance of the sensor changes according to solvent evaporation. Because of the hydrophobicity and ethanol-affinity of the graphene, the resistance changes directly related to the ratio of water and ethanol in the solution dropped on the surface (Figure 5H). The graphene/SF sensor has the most significant response to the pure ethanol addition, with a sharp increase with the decrease in resistance. However, only a slight increase in resistance is observed for pure water additions, with the resistance at the beginning growing from 4.2 to 16.0 k Ω , which then remains at a long plateau region without further changes in resistance. The 50:50 water/ethanol solution addition, however, responds with a change in

resistance between that of pure water and ethanol. Although water/ethanol solutions can induce the formation of β -sheets in SF (known as the conformational transition), the conformational transition rates are much longer than the resistance change rates observed in the present graphene/SF system. Additionally, with increased water and ethanol ratios, the rate of changing of the conformational transition and resistance did not correlate with each other. For instance, according to previous findings, pure ethanol cannot induce the conformation transition of SF films,^[48] however, in the graphene/SF sensor, pure ethanol induced the largest change in resistance. The 50:50 ethanol/water solution needed ~15 minutes to trigger the conformational transition of the SF film,^[48] while the change in resistance of the graphene/SF sensors had finished in ~8 min. These results demonstrate that the changes in resistance of the graphene/SF systems stem from the evaporation of ethanol instead of the conformation transition of SF molecules.

3. Conclusion

In summary, we developed graphene/silk nanocomposites that combined the mechanical, electronic, and biomedical advantages of each component. The incompatibility of these two elements was overcome through the design of an optimized dissolution strategy. Here, HFIP or FA/Ca²⁺ based methods allowed silk and graphene to be blended homogeneously with the desired weight ratio, in sharp contrast to the traditional route where only limited graphene oxide or carbon nanotubes can be loaded. Remarkably, these graphene/SF solutions can be easily processed into different material formats where the mechanical, electronic and processing advantages offer the possibility for future functional applications. The mechanical and electronic properties of resultant graphene/SF materials can be tailored through controlling graphene/SF ratios or by selecting the dissolution strategy or making different material formats. For demonstration, we utilized these versatile and smart graphene/SF materials to monitor object deformation, body movement, finger touching and breathing as well as solvent content. These attractive functions encourage further exploration of their applications in wearable sensors, smart textiles, intelligent skins and human-machine interfaces.

Experimental Section

Preparation of degummed silk fibers—*B. mori* silkworm cocoons were degummed by boiling in two 30 min changes of 0.5% (w/w) NaHCO₃ solution. The degummed silk fibers were washed with distilled water and allowed to air dry at room temperature.

Preparation of SF foam—A 10 % (w/v) solution of degummed SF in aqueous 9.3 mol L⁻¹ LiBr solution was prepared by heating to 60°C for 1 hour. This solution was dialyzed with deionized water at room temperature to generate SF aqueous solution with a protein concentration ~5 wt %. Next, the SF aqueous solution was frozen at -20 °C overnight and followed by freeze-drying processing for 3 days to obtain the SF foam.

Preparation of graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions—3D printing graphene ink was purchased from Sigma-Aldrich, USA. The length/width and thickness of the graphene was 1-20 μ m and 1-15 nm, respectively. The density of the ink

was 1.5-1.8 g/mL at 25 °C with a viscosity of 25-45 Pa·s (20 °C). The ink could be stored at 2-8 °C for more than 6 months. The method to produce this 3D printable graphene ink was based on the synthesis reported by Jakus et al.^[25] Typically, the inks were synthesized by thorough mixing of polylactide-co-glycolide (85:15) copolymer, graphene powder (3-8 atomic layers thick, 5-20 μm long and wide), and a 10:2:1 by mass mixture of dichloromethane, ethylene glycol butyl ether, and dibutyl phthalate, where 0.6 g of dibutyl phthalate was added for every 2.2 g (1 cm³) graphene.^[25]

For graphene/SF/HFIP suspensions, SF foam with desired weight was dissolved in HFIP solution. SF foam could be dissolved thoroughly in around 1 hour at 60 °C. After the SF/HFIP solution was obtained, 3D printing graphene ink with a calculated weight was added, and the homogeneous graphene/SF/HFIP suspensions were generated by vortexing at room temperature for ~5 minutes.

For graphene/SF/FA/Ca²⁺ suspensions, the dry degummed silk fibers were dissolved in FA/CaCl₂ solution (weight ratio of 1:20), after sufficient and intensive vortexing at room temperature for around 5 min to obtain the SF/FA/CaCl₂ solution. Next, 3D printing graphene ink was added with the help of intensive vortexing at room temperature for ~5 minutes to yield graphene/SF/FA/CaCl₂ suspensions with different ratios.

After the process, graphene ink dispersed homogeneously in HFIP or FA/CaCl₂ solvent with no flocculants or aggregates of SF and graphene observed. These graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions are stable at room temperature for several months. Because the HFIP and FA are toxic solvents, all of these steps should be conducted in a chemical hood with the necessary precautions. Also, the container used for dissolution must be tightly sealed to avoid evaporation of HFIP and FA.

Graphene/SF and graphene/SF/Ca²⁺ processing—The graphene/SF and graphene/SF/Ca²⁺ films were obtained by graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspension casting, respectively. Typically, a 15g graphene/SF or graphene/SF/Ca²⁺ suspension was poured into a polystyrene weigh dish and then was placed in a chemical hood to evaporate the solvent. Because of the rapid evaporation of the HFIP or FA, the solid graphene/SF or graphene/SF/Ca²⁺ films formed in around 2-4 hours. In order to remove the residual solvent in the films, they were transferred to a glass substrate and heated at 60 °C for 2 hours. FTIR spectroscopy confirmed the removal of residual HFIP or FA under these conditions. Wet-spinning was used to produce graphene/SF and graphene/SF/Ca²⁺ fibers. Specifically, 10 wt% graphene/SF/HFIP or graphene/SF/FA/Ca²⁺ suspensions were transferred to 10 mL syringes with inner needle diameters of 1.25 mm. Then, the suspensions were directly extruded into 70% v/v ethanol aqueous solution from the syringe needle at room temperature by hand. The as-spun fibers were directly transferred into water, followed by washing several times to remove HFIP or FA residuals. A Chinese writing brush was used to write the graphene/SF or graphene/SF/Ca²⁺ suspensions on the polypropylene plates, a stable handwritten conductive graphene/SF or graphene/SF/Ca²⁺ pattern was formed after two minutes of curing at room temperature. The same methods were used to produce films, and the HFIP and FA were removed thoroughly after heating at 60 °C for 2

hours. All steps should be conducted in a chemical fume hood with the necessary precautions.

Characterization—The morphologies of graphene/SF or graphene/SF/Ca²⁺ materials (films, fibers, and coatings) were characterized by SEM (Ultra 55 field emission scanning electron microscopy, Carl Zeiss AG, Harvard University Center for Nanoscale Systems) at an acceleration voltage of 5 kV. To prevent electrical charging, all specimens were coated with a 5-nm-thick Pd/Pt layer before observation. The mechanical properties of fibers were tested by an Instron 3366 machine (Instron, Norwood, US) in tensile mode at 25°C and 70% relative humidity with a tensile speed of 0.5 mm min⁻¹. FTIR measurements were carried out by Jasco FTIR-6200 spectrometer (Jasco FTIR-6200, Jasco Instruments, Easton, MD). For each measurement, 64 interferograms were co-added, and Fourier-transformation employed a Genzel-Happ apodization function to yield spectra with a nominal resolution of 4 cm⁻¹. The resistance of graphene/SF or graphene/SF/Ca²⁺ materials were measured using a Fluke 87V Digital Multimeter. Before the tests, the splines with a dimension of 2 mm × 2 cm × 200 μm were firmly fixed to multimeter test leads. To record the resistance changes of the graphene/SF/ Ca²⁺ splines during tensile deformation, the digital multimeter was connected to the top and bottom clamp, and a digital video camera was used to record the tensile process until the sample failed. The resistance values were extracted from each frame with a time resolution of ~0.3 s. Similarly, to assess the resistance changes of graphene/SF materials during finger touching and breathing, the splines with dimensions 2 mm × 2 cm × 200 μm were adhered on a cotton textile or a mask surface, then the touching and breathing processes were recorded by a digital video camera. The related time and resistance values were directly extracted from each frame of recorded video.

Supplementary Material

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Acknowledgments

We acknowledge Harvard University Center for Nanoscale Systems (CNS) for providing AFM and SEM measurements. The CNS is a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. 1541959. This work was supported by NIH (U01 EB014976), with additional support provided by ONR (N00014-16-1-2333 and N000141612333), AFOSR (FA9550-11-1-0199, FA9550-17-1-0333 and FA9550-14-1-0015), the NIH (R01DE016525) and the NSF IGERT program. S. Ling acknowledges the starting grant of ShanghaiTech University.

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Figure 1. The pathways to fabricate the well-dispersed graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions

A, the route to produce graphene/SF/HFIP suspension. **B**, the process to produce graphene/SF/FA/Ca²⁺ suspension. **C** and **D**, photographs of the graphene/SF/HFIP (**C**) and graphene/SF/FA/Ca²⁺ suspension (**D**) after incubation at room temperature for 7 days.

Figure 2. The versatile processability of graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ suspensions

A-D, graphene/SF films produced from 10 wt% 75:25 graphene/SF/HFIP suspension. **A**, schematic diagram of solution casting method to make graphene/SF films. **B-D**, photographs of graphene/SF films. The graphene/SF films are flexible and conductive and can be folded or cut into arbitrary geometries. **E-G**, graphene/SF fibers spun from 10 wt% 50:50 graphene/SF/HFIP suspension. **E**, schematic of the wet-spinning method to generate graphene/SF fibers. **F** and **G**, photographs of the wet-spinning process (**F**) and the resultant fibers (**G** and insert image in **F**) obtained from graphene/SF/HFIP suspensions. The

graphene/SF suspension solidified immediately once extruded into 70% v/v aqueous ethanol solution and the graphene/SF fibers were stable and strong. **H-K**, graphene/SF coating produced from 10 wt% 50:50 graphene/SF/FA/Ca²⁺ suspension. **H**, schematic of direct writing to make graphene/SF/Ca²⁺ coatings. **I-K**, photographs of graphene/SF coating generated by direct writing using a Chinese writing brush. The solidified coating layer bonded intensively with the polypropylene substrate and can withstand hundreds of rounds of tear tests using a commercial adhesive tape (**J**). The tear test did not destroy the conductive graphene/SF coating (**K**). Moreover, no resistance change was observed.

Figure 3. SEM images of graphene/SF/HFIP and graphene/SF/FA/Ca²⁺ materials

A, the cross-sectional SEM image of the graphene/SF film. **B**, surface SEM image of the graphene/SF film. The image reveals that SF was assembled into silk nanofibrils on the surface of the graphene. **C**, cross-sectional SEM image of the graphene/SF fiber. **D**, high-resolution SEM image of the cross-section of the graphene/SF fibers, indicating the porous structure of the fiber. **E**, cross-sectional SEM image of graphene/SF/Ca²⁺ coating. The top layer is the graphene/SF/ Ca²⁺ coating; the bottom layer is the polypropylene plate. **F**, high-resolution SEM image of the interface between of graphene/SF/Ca²⁺ coating and polypropylene plate.

Figure 4. Mechanical properties of graphene/SF and graphene/SF/Ca²⁺ films

A, typical stress-strain curves of graphene/SF/Ca²⁺ films produced from 10 wt% graphene/SF/FA/Ca²⁺ suspensions with different weight percentages of graphene. The insert images are the photographs of the graphene/SF/Ca²⁺ spline with 20 wt% graphene before and after stretching. The spline was still stable with the strain around 300%. **B**, typical stress-strain curves of graphene/SF films produced from 10 wt% graphene/SF/HFIP suspensions with different weight percentages of graphene. **C**, comparison of the strength and toughness of graphene/SF and graphene/SF/Ca²⁺ materials with other mechanical advantageous polymer nanocomposites. The related data was extracted from refs [4] and [38]. **D**, comparison of the strength and stiffness (Young's modulus) of graphene/SF and graphene/SF/Ca²⁺ materials with other natural and synthetic materials. Ashby plot of natural and synthetic materials are adapted from ref [39].

Figure 5. Graphene/SF and graphene/SF/Ca²⁺ electronics

A and **B**, photographs of graphene/SF/Ca²⁺ spline with dimensions of 2 mm × 2 cm × 200 μm before (**A**) and after (**B**) tensile stretching, indicating resistance changes before and after spline stretching. **C**, strain-dependence of relative resistance changes for graphene/SF/Ca²⁺ nanocomposites. The insert plot is the dependence of the gauge factor of graphene/SF/Ca²⁺ nanocomposites on the strain. Open circles denote experimental data. The solid line represents the values calculated from the equation of $GF = (\Delta R/R_0)/\epsilon$. **D**, the relative resistance changes for graphene/SF/Ca²⁺ nanocomposites during balloon deformation. The graphene/SF/Ca²⁺ spline adhered to the balloon surface. The insert photographs show the three states during balloon deformation, which correspond to the three points in time-relative resistance change plot. **E**, the relative resistance changes for graphene/SF/Ca²⁺ nanocomposites during finger movement. The relative resistance change follows finger movement. **F** and **G**, resistance responses of graphene/SF/Ca²⁺ nanocomposites for finger-touching (**F**) and breathing (**G**). **H**, resistance response of graphene/SF nanocomposites for aqueous ethanol solution with different ethanol and water volume ratios. The insert scheme shows the experimental setup used for measurement.

Table 1 Resistance and mechanical properties of graphene/SF and graphene/SF/Ca²⁺ films.

Sample	Graphene weight percentage	Resistance (k Ω) ^{a)}	Conductivity (S/m)	Stress (MPa)	Strain (%)	Modulus (GPa)	Toughness (MJ m ⁻³)
Graphene/SF ^{b)}	25%	1700 $\pm$ 300	0.032 $\pm$ 0.008	242 $\pm$ 66	8.1 $\pm$ 2.7	4.0 $\pm$ 1.1	11.6 $\pm$ 3.6
	50%	10 $\pm$ 2	5 $\pm$ 1	177 $\pm$ 14	4.4 $\pm$ 0.6	6.0 $\pm$ 1.1	4.1 $\pm$ 0.8
	75%	0.765 $\pm$ 0.137	67 $\pm$ 12	49 $\pm$ 6	2.2 $\pm$ 0.5	5.0 $\pm$ 1.3	0.7 $\pm$ 0.2
Graphene/SF/Ca ²⁺ ^{c)}	10%	1600 $\pm$ 300	0.032 $\pm$ 0.006	0.5 $\pm$ 0.1	611 $\pm$ 85	0.004 $\pm$ 0.001	3.3 $\pm$ 0.6
	20%	682 $\pm$ 132	0.08 $\pm$ 0.01	4.2 $\pm$ 1.3	382 $\pm$ 59	0.135 $\pm$ 0.005	13.9 $\pm$ 4.7
	40%	261 $\pm$ 76	0.21 $\pm$ 0.06	5.9 $\pm$ 1.5	202 $\pm$ 67	0.079 $\pm$ 0.069	10.3 $\pm$ 3.2

^{a)} The resistances of graphene/SF or graphene/SF/Ca²⁺ materials were measured using the samples with a dimension of 2 mm $\times$ 2 cm $\times$ 200 μ m.^{b)} Graphene/SF films are made from 10 wt% graphene/SF/HFIP suspension with different graphene weight percentage.^{c)} Graphene/SF/Ca²⁺ films are made from 10 wt% graphene/SF/FA/Ca²⁺ suspension with different graphene weight percentage.