Binary Synergistic Sensitivity Strengthening of Bioinspired Hierarchical Architectures based on Fragmentized Reduced Graphene Oxide Sponge and Silver Nanoparticles for Strain Sensors and Beyond

Songfang Zhao,* Lingzhi Guo, Jinhui Li, Ning Li, Guoping Zhang,* Yongju Gao, Jia Li, Duxia Cao,* Wei Wang, Yufeng Jin, Rong Sun,* and Ching-Ping Wong

Recently, stretchable electronics have been highly desirable in the Internet of Things and electronic skins. Herein, an innovative and cost-efficient strategy is demonstrated to fabricate highly sensitive, stretchable, and conductive strain-sensing platforms inspired by the geometries of a spiders slit organ and a lobsters shell. The electrically conductive composites are fabricated via embedding the 3D percolation networks of fragmentized graphene sponges (FGS) in poly(styrene-block-butadiene-block-styrene) (SBS) matrix, followed by an iterative process of silver precursor absorption and reduction. The slit- and scale-like structures and hybrid conductive blocks of FGS and Ag nanoparticles (NPs) provide the obtained FGS–Ag-NP-embedded composites with superior electrical conductivity of 1521 S cm\(^{-1}\), high break elongation of 680%, a wide sensing range of up to 120% strain, high sensitivity of \(\approx 10^7\) at a strain of 120%, fast response time of \(\approx 20\) ms, as well as excellent reliability and stability of 2000 cycles. This huge stretchability and sensitivity is attributed to the combination of high stretchability of SBS and the binary synergistic effects of designed FGS architectures and Ag NPs. Moreover, the FGS/SBS/Ag composites can be employed as wearable sensors to detect the modes of finger motions successfully, and patterned conductive interconnects for flexible arrays of light-emitting diodes.
1. Introduction

Thanks to the increasing demands of body-attached electronic devices for health monitoring and biomedical applications, flexible, stretchable, and wearable sensors have been extensively explored.\(^{[1-5]}\) Recently, a myriad of sensitive wearable sensors have been developed based on various strain-sensing mechanisms, such as transistor, capacitive, piezoelectric, triboelectric, and piezoresistive sensing.\(^{[6-11]}\) No matter how these wearable sensors work, strain sensors with high sensitivity, large stretchability, broad sensing range, and ability to be driven at low voltage are highly desirable in diverse fields.\(^{[12,13]}\) Among these above-mentioned sensor types, piezoresistive strain sensors, which transduce strain/stress into electrical resistance signals, have gained tremendous attention due to their simplicity of design, low cost, easy signal collection, and potential high pixel density.\(^{[8,14]}\) As wearable devices, strain sensors should also be lightweight, and possess low modulus and a wide working range from a subtle strain region (breath motions, <1%) to a large strain region (joints motions, >55%). Unfortunately, traditional strain sensors using rigid materials (metal or semiconductors) usually exhibit a narrow sensing range (<5%) because they can withstand only very limited strain before fracture. Therefore, the development of strain sensors that are capable of detecting large strain (>55%) remains a challenge and is of compelling interest for emerging fields beyond the existing ones.\(^{[15-18]}\)

To address this hurdle, numerous efforts have been devoted. One approach (structures that stretch) is to design diverse geometries such as wave-like or net-shaped structures. However, the structure design involves time-consuming, complex, and high cost procedures that are not easily scalable. In addition, low sensitivities or gauge factors (GFs) hinder their extended applications as wearable sensors.\(^{[19,20]}\) Another promising one (materials that stretch) is to incorporate multidimensional conductive fillers, such as metal particles, carbon black, carbon nanotubes (CNTs), silver nanowires (Ag NWs), and graphene/graphene sponges, into the elastomeric matrix to achieve percolating network mechanism) and overlapping area of adjacent FGS (disconnected network mechanism) result in sensitivity strengthening, the corresponding piezoresistivity primarily results from the variation in tunneling resistance when the interfiller distance changes under external stress. Among them, graphene with outstanding mechanical and electrical features has been widely explored for strain sensors, which possess higher GFs and more controllable sensitivity. Ha and co-workers\(^{[25]}\) reported a highly stretchable and sensitive strain sensor based on fragmented graphene foam and polydimethylsiloxane (PDMS). The strain sensor possessed high stretchability over 70%, high durability over 10 000 stretching–releasing cycles, and tunable sensitivity with GF of 15 to 29. The employed graphene foam was assembled by chemical vapor deposition (CVD), which is pretty high-cost and time-consuming. Sun and co-workers\(^{[6]}\) demonstrated a flexible and stretchable strain sensor based on graphene foam/PDMS, which exhibited high sensitivity (a GF of 47.74 to 98.66), but low stretchability (30%). More recently, Shi and co-workers\(^{[26]}\) developed a high-performance strain sensor with a fish-scale-like graphene-sensing layer adhered on an elastic tape. The as-prepared strain sensor could detect both stretching and bending deformations with a broad working range (up to 82% strain), high sensitivity (a GF of 16.2 to 150), and excellent reliability (>5000 cycles), but low conductivity (13.5 S cm\(^{-1}\)). Despite the fact that proper structural design has been proved to be an effective strategy to achieve high sensitivity and stretchability, such as creating porous,\(^{[25]}\) net-shaped,\(^{[19]}\) or microwrinkled structures,\(^{[20]}\) the balance between stretchability and sensitivity of these materials is still unsatisfactory.

In nature, spiders could detect surrounding vibrations via their crack-shaped slit system near their leg joints between metatarsus and tarsus bones.\(^{[27]}\) Inspired by the slit geometry, ultrahigh sensitive sensors could be designed based on microcrack junctions, but with low stretchability. Lobsters could prohibit their bodies with arbitrary deformation from damage via their overlapped shells. Inspired by the overlapped geometry, high stretchability could be achieved via structure design.\(^{[28]}\) Moreover, 3D fragmented sponge-like conductive fillers have numerous effective contact areas under tensile strain, which could be employed as shell materials to obtain high stretchability. Considering sensitivity, stretchability, and scalability, designing a novel material based on synergistic effects of crack and a disconnection mechanism would be attractive for future stretchable electronics. Herein, we demonstrate an innovative and cost-efficient strategy to fabricate highly sensitive, stretchable, and conductive strain-sensing platforms based on fragmented graphene sponges (FGS), Ag nanoparticles (NPs), and poly(styrene-block-butadiene-block-styrene) (SBS). GS, which is assembled and reduced by hydroiodic acid/acetic acid (HI/HAc), is fragmentized into microsized fragments in toluene via sonication. Rearranged FGS featuring 3D percolation networks are embedded in SBS matrix to achieve highly stretchable composites, which could absorb silver precursors easily. Then a huge amount of Ag ions are reduced to Ag NPs directly inside and outermost surface of the stretchable composites. The slit- and shell-like structures provide the obtained FGS–Ag-NP-embedded SBS composite (FGS/SBS/Ag) with large stretchability (680%), superior electrical conductivity (1521 S cm\(^{-1}\)), a wide sensing range (up to 120% strain), high sensitivity (\(>10^7\) at 120% strain), fast response time (<30 ms), as well as excellent reproducibility over 2000 cycles. The key novelty to achieve the stretchability and sensitivity simultaneously lies in binary synergistic effects of Ag NPs and FGS: one is that variations of microcrack junctions in Ag NP layer (crack mechanism) and overlapping area of adjacent FGS (disconnection mechanism) result in sensitivity strengthening, the other is that FGS tend to bridge the disconnected networks of Ag NPs under tensile strain. As a proof of concept, FGS/SBS/Ag composites could be employed as wearable sensors to detect the modes of finger motions successfully, and patterned conductive interconnects for flexible arrays of light-emitting diodes (LEDs). We believe that our hierarchical structure design would open up new opportunities for the widespread fabrication and application of stretchable devices.
2. Results and Discussion

2.1. Concept of Bioinspired Architecture

In nature, spiders have crack-shaped slit organs near their leg joints between the metatarsus and tarsus tones, while lobsters have overlapped shells on their bodies, as depicted in Figure 1a and Figure S1 (Supporting Information). Thus, the slit geometry enables the spiders to detect small external force vibrations in their surroundings. Inspired by the ability, we mimic the geometry of the slit systems to design sensors by selecting the rigid and spherical Ag NPs as conductive blocks to form percolation networks in elastomer. When being stretched, mechanical microcracks are generated and propagated in the Ag NP layer. Then, microcracks get close and form a crack junction after being released. This repeated reversible disconnection–reconnection of the crack junctions results in the breakage-recovery of the conductive paths accompanied by electrical resistance variations. Notably, the electrical conductance experiences a sudden drop from a finite value when the edges of the cracks are in contact, to zero when being disconnected. These cracks mimicking slit geometry of spiders endow the sensors with high sensitivity to detect external deformation clearly. However, the conductive paths would be lost under high strain, thus resulting in the failure of response to larger strain. Inspired by the shell geometry of lobsters, conductive layers based on 1D, 2D, or 3D conductive blocks, could be introduced to bridge the disconnected networks. Upon stretching, high-dimensional blocks slide and rearrange with sufficient contacting nodes, resulting in smaller resistance changes compared with that based on 0D conductive blocks (Figure S2, Supporting Information). To the best of our knowledge, FGS-based conductive blocks have interconnected porous structure. When the conductive networks are stretched, the slippage of the skeletons of 3D conductive blocks and the slippage of the whole 3D conductive blocks occur in the direction of elongation simultaneously, decreasing the overlapped areas between adjacent sponge-like blocks. Due to more effective contact areas and sponge structure of FGS-based conductive blocks, conductive layers based on FGS enable strain sensors to possess high stretchability and sensitivity simultaneously. Therefore, inspired from the unique geometries of spider and lobster, hybrids of conductive Ag NPs and FGS are selected as conductive fillers to form percolation networks in elastomer, assembling strain sensors with both super sensitivity and stretchability.

2.2. Fabrication and Characterization of FGS/SBS/Ag Composites

The scalable fabrication process of FGS and highly stretchable FGS/SBS/Ag composites is schematically illustrated in Figure 1b. The procedure involves four main steps: 1) synthesis of 3D FGS, 2) construction of conductive networks based on 3D FGS, 3) infiltration of SBS matrix into the conductive networks, 4) absorption and reduction of Ag precursor, generating Ag NPs. First, reduced graphene oxide (rGO) hydrogel is assembled via HI/HAc at mild conditions, which could eliminate the oxygen-containing group of GO sheets, realizing a wettability transformation from hydrophilicity to hydrophobicity. Following the freeze-drying of the freezed hydrogel, the GS with interconnected porous structure are immersed in toluene, and fragmentized into 50–100-µm-sized fragments via sonication. A certain amount of FGS/toluene solution is drop-cast into an aluminum-foil mold. Note that the uniformity of the FGS conductive networks is an important parameter for stable and predictable response of the strain sensor. After drop-casting of FGS solution, the aluminum foil mold is exposed to infrared lamp light, which could provide uniform and gradual heating throughout
the FGS conductive networks, achieving uniform and homogeneous networks. Subsequently, SBS, which is selected due to its high elasticity, is infiltrated into the FGS networks to fabricate stretchable FGS/SBS composites. Intrinsically, the SBS molecular chain shrinks and curls under nature conditions. When the FGS/SBS composite is immersed in ethanol, the SBS will swell, and the molecular chains extend greatly and become loose, which facilitates the absorption of ethanol along with silver trifluoroacetate (STA). To absorb the Ag precursor efficiently by FGS/SBS composite, it should be immersed in a 15% STA/ethanol solution for at least 30 min. During the swelling process, STA and ethanol are both rapidly absorbed into the FGS/SBS composite due to the coordination interaction between Ag$^+$ and unsaturated or aromatic bonds, and the ion–dipole interaction between the trifluoroacetate anions (CF$_3$COO$^-$) and the hydroxyl group of ethanol.$^{[3,32]}$ As shown in Figure 1c, the FGS/SBS composite is freestanding and highly stretchable, which is verified by the fact that no destruction appears after multicycles of stretching–releasing. This superior stretchability results from the 3D macroporous structure and loosely stacked structure, which facilitates the infiltration of SBS matrix and sliding of FGS during the stretching. Fortunately, Ag NPs are introduced into the FGS/SBS composite via an iterative process of Ag precursor absorption and reduction, endowing the composite with both high conductivity ($1521 \text{ S cm}^{-1}$) and stretchability. It should be noted that the morphology of GS plays a vital role in fabricating stretchable composites. GS is also fabricated via the sol-cryo method, namely GS$_{sc}$. FGS$_{sc}$ conductive networks tend to crack and delaminate from the SBS substrate during the stretching status of FGS$_{sc}$/SBS composite (Figure 1b; Figure S3, Supporting Information). Compared with GS assembled by HI/HAc, the honeycomb cell of GS$_{sc}$ has a lager wall, which enables the FGS$_{sc}$ networks to possess more compact porous structure, inhibiting the efficient infiltration of SBS into the FGS$_{sc}$ networks. The weak interfacial bonding and large stiffness mismatch between FGS and SBS results in the occurrence of crack and delamination upon stretching. Moreover, the more serious phenomenon of crack and delamination occurs after the releasing of graphene nanosheets/SBS composites (Figure S4, Supporting Information), indicating that loosely porous structure is one important parameter for SBS infiltration. Figure 1d,e demonstrates the structure differences of planar rGO paper, FGS network, FGS/SBS composite, and FGS/SBS/Ag NPs composite via comparing CA. The CA of deionized water on the planar rGO paper is 94.4°, suggesting the hydrophobicity after reduction. The FGS network possesses larger CA (108.1°), which is attributed to that its porous structure and micrometer-scaled roughness enables the water on such a surface to be in Wenzel state.$^{[33]}$ These hydrophobicity and unique porous structures could allow SBS/toluene solution penetration. SBS is penetrated into the macropores to form smooth surface, resulting in the decrease of CA. The CA further decreases after generation of Ag NPs in the FGS/SBS composite. While the CA of the ethanol on these substrates is 24.2°, 21.8°, 39.2°, and 16.5°, respectively, also indicating the structure differences after a series of processing. These huge differences in CA confirm the oleophilic characteristic of surface of rGO. Especially, the porous rough structure enables the FGS to be more oleophilic (21.8°), which facilitates the infiltration of SBS solution. Moreover, the difference of CA of water and ethanol on the FGS/SBS composite indicates that Ag precursor and L-ascorbic acid (LAA) should be dissolved in low polar solvent, which could be diffused into the matrix of SBS, resulting in the generation of Ag NPs inside of SBS.$^{[35]}$

To depict the structure transformation during the whole fabrication of the FGS/SBS/Ag stretchable composites, scanning electron microscopy (SEM) characterizations are shown in Figure 2. GS possesses an interconnected macroporous structure with pores sizes ranging from tens to hundreds of micrometers, and the cell walls are made up of numerous graphene sheets with wrinkles or crumples during the self-assembly process (Figure 2a–d). The wrinkling structure could generate more porous structure, and enhance the interaction between the FGS networks and SBS. When the GS is being fragmentized by sonication, GS is subjected to applied stress, which is focused on the joints instead of being uniformly distributed in each position of GS. Moreover, the honeycomb walls thicken at the intersections of the branches, enabling the joints of the GS to be more rigid and brittle than the branches. This concentrated stress and unique brittle/soft behavior enable the graphene layer to be torn from the vertices, instead of being pulverized into small particles, thus the FGS still maintain the similar 3D structure with that of original GS. When the FGS/toluene is drop-cast onto the Al foil, the FGS would be rearranged to form a 3D conductive percolation network via the surface contact among the adjacent individual FGS. Top-view SEM images clearly reveal that the rough and porous structure exists, resulting from 3D interconnected porous FGS and loosely stacked layer via force-free design. These structures are different from those of other work fabricated by CVD$^{[34]}$ vacuum filtration,$^{[35]}$ or evaporation techniques$^{[36]}$ based on other morphological blocks, which exhibit compact top surfaces prohibiting elastomer or other materials infiltration and embedding. A representative high-magnification view is shown in Figure 2f. The 3D interconnected porous structure and heavily buckling structures play a critical function in constructing loosely stacked network with sufficient void spaces for liquid penetration, internal structure transformation, and stress release. Cross-sectional SEM images of the rearranged FGS percolation network are also shown in Figure 2k,l. It could be seen that the porous structure exists throughout the entire thickness, and the thickness could be tuned via controlling the volume of FGS/toluene solution. Numerous nano/macroscale pores collectively suck SBS by capillarity to produce the FGS/SBS composite, and the percolation network is fully embedded in the SBS matrix, which is confirmed by SEM images of the samples after SBS infiltration (Figure 2g,h,m,n). When the swollen composites are dipped in the LAA solution, the absorbed Ag ions are reduced, generating numerous Ag NPs at both layers, which merge with one another to form a continuous shell (Figure 2i,j,o,p). As shown in Figure 1b, the color of the FGS/SBS/Ag composite changes to grey from the black of FGS/SBS composite due to the formation of continuous Ag shells. However, due to the different structure
at the top and bottom of FGS/SBS composite (top part has more SBS, while bottom part has more FGS), different amounts of Ag precursor and different swelling volumes during absorption, result in the different morphologies of Ag layers after reduction (Figure S5, Supporting Information). It should be noted that the top or bottom surface of FGS/SBS/Ag composite is identified by the state of FGS formed in Al foil. Figure 2o,p and Figure S6 (Supporting Information) show that the Ag NPs exist on the surface and inside of the composites simultaneously, and the generated Ag NPs are connected to each other, constructing a percolation network. Interestingly, the sizes of Ag NPs inside the film are smaller than that at the surface, due to the restriction of the matrix to the growth of Ag NPs, and the same phenomena exist in our previous and Lee et al. work.[3,37]

Moreover, introduction of FGS and generation of Ag NPs is also identified by X-ray diffraction (XRD) pattern of FGS/SBS and FGS/SBS/Ag (Figure 3a). As expected, two diffraction peaks at $2\theta = 20.1^\circ$ and $23.8^\circ$ are corresponding to the amorphous region of SBS and FGS, indicating that the chemical reduction occurred successfully during the assembly process of GO. Another five diffraction peaks appearing at $2\theta = 38.1^\circ$, $44.1^\circ$, $64.4^\circ$, $77.3^\circ$, and $81.3^\circ$ are attributed to the (111), (200), (220), (311), and (222) crystal planes of the face-centered cubic (fcc) of Ag NPs.[33] Figure 3b provides the results of thermogravimetric analysis (TGA), which show that the FGS has excellent thermal stability after reduction, the weight fractions of FGS and Ag NPs in the FGS/SBS/Ag conductive composites are $\approx 4.4\%$ and $50.9\%$, respectively. The excellent stretchability is of great importance for high-strain sensors applied in human–machine interactive electronics. To verify the superiority of stretchable composite fabricated by our innovative strategy, flexible composite is also fabricated by filtration-embedding technique, which can only be stretched to extreme limited strain (5%) and will be fractured upon further stretching, leading to disconnection of conductive paths (Figure 3c). Conversely, the stretchable composite can be stretched as high as 300% without mechanical failure. Note that the stretchability is determined by the mechanical fracture of the embedded elastic matrix. To quantificationally investigate the influence of FGS and Ag NPs on the stretchable behavior of the composites, the stress–strain curves are demonstrated in Figure 3d. It could be seen that the elongation at break of the FGS/SBS is 1020%, which is virtually unaffected with the introduction of FGS, due to the unique embedding technique. In contrast, the elongation at break and tensile strength is changed to 680% and 3.50 MPa when the Ag NPs are generated after three cycles of Ag precursor absorption and reduction, leading to the enhancement of the stiffness of the composites.

Importantly, compared with other strategies to construct percolation networks, such as CVD, template-assisted
approach, and filling microchannel with liquid metals, our approach is based on solution-processable graphene at room and mild conditions, and it can be readily scaled up. Although GS has been prepared by CVD or template-assisted approaches,[8,38] CVD is high-cost and time-consuming, while template-assisted approach requires complex etching processes to eliminate templates. The sol–gel approach in our work is significantly advantageous than the previous methods in terms of fabrication complexity, production costs, and scalability. Second, compared with conductive networks based on other building blocks (0D, 1D, 2D nanofillers), FGS possesses an interconnected porous structure to ensure the sufficient void space for elastomer penetration, and has larger contact area, enlarging the GF of the sensor. In addition, the structure and thickness of the rearranged FGS network can be well-controlled via tuning the freezing temperature and volume of FGS/toluene solution. Third, compared with photolithography technique and other molds, the patterning of percolation networks with aluminum foil is relatively cost-effective and enables designing the electrodes in various shapes and sizes in a facile process. Fourth, compared with generation of Ag NPs via electroless deposition, it could enable Ag NPs to be generated on both the surface and inside the FGS/SBS composite, resulting in the maintenance of conductive paths under tensile strain. While the electroless-deposited Ag NPs exist only on the surface, the Ag layers would be fractured upon stretching, leading to the loss of conductive paths. Finally, compared with direct blending of nanofillers and substrate, it could introduce a higher and controlled FGS and Ag NPs into the stretchable matrix without considering phase separation and poor mixed compatibility, resulting in the degradation of mechanical properties. For example, graphene-nanosheet-based stretchable composites fabricated by blending or infusing approaches possess low electrical conductivity or GF. Moreover, excess graphene (>0.25 wt%) tends to aggregate, hindering the charge transfer between conductive fillers under strain.[18,23] Although the approach possesses a myriad of above-mentioned superiorities, the iterative procedure of the approach proceeds slowly due to multiple steps for absorption and reduction of Ag precursor. To improve the efficiency of fabricating the FGS/SBS/Ag composites, the FGS/SBS composite should be thin enough to shorten the absorption time of Ag precursor by tuning the amounts of FGS and SBS. As a consequence, the combination of high stretchability of SBS and the binary synergistic effects of designed FGS architecture and Ag NPs would endow the FGS/SBS/Ag composites with excellent stretchability, conductivity, and sensitivity simultaneously, and hold great potential in stretchable electronics. Here, as a proof of concept, the FGS/SBS/Ag composites are employed as strain sensors to detect the human motion and conductive interconnects for flexible arrays of LEDs.

2.3. Strain-Sensing Performance

The unique design of FGS/SBS/Ag composite endows it with certain conductivity upon stretching. The electromechanical characteristics of the FGS/SBS and FGS/SBS/Ag composite are depicted in Figure 4. The FGS/SBS composite exhibits excellent linear current–voltage ($I$–$V$) characteristics under different strains, thus indicating the Ohmic behavior of the composite. In addition, the slopes of $I$–$V$ curves decreases with the applied strain indicating the increase of resistance, which is attributed to the decrease of the overlapping area among the adjacent FGS pieces upon stretching, and the simultaneous increase of the distance between the FGS (Figure 4a; Figures S7–S9, Supporting Information). The introduction of Ag NPs could enhance the conductivity of the FGS/SBS/Ag composite significantly without changing its original Ohmic behavior (Figure 4b). These high conductivity (1521 S cm$^{-1}$) and linear $I$–$V$ behaviors of the FGS/SBS/Ag composites enable them as strain sensors to work at low working voltage, which is another advantage of our innovative design. Moreover, relative resistance variations versus strains are also investigated in Figure 4c, where $R_0$ is the initial electrical resistance at 0% strain. Note that electrical-resistance–strain hysteresis during stretching/relaxing process is one important issue of conductive electrodes. To eliminate the hysteresis effect, the stretching/relaxing rate should be relatively slow, and thus the conductive building blocks (FGS and Ag NPs) have enough time to recover their conductive
paths, resulting in stable resistance. It could be seen that the electrical resistance increases with the increase of strain, and a relative resistance change of $1.5 \times 10^9\%$ is observed at 120% strain for stretchable FGS/SBS/Ag composite. To demonstrate the superiority of Ag NPs on the piezoresistive effect, stretchable FGS electrode with fully embedded structures is also fabricated and compared, as shown in Figure 4c. A relative resistance change of $6.7 \times 10^7\%$ is observed at 120% strain for stretchable FGS/SBS composite. Moreover, SBS/Ag NPs composites possess high sensitivity, but low stretchability at the absence of FGS or CNTs (Figure S10, Supporting Information).[3] This piezoresistivity is mainly attributed to the formation of microcracks in the Ag NPs network and the change of the contact conditions for electron conduction, such as break of contacts, contact area, and spacing variation upon stretching. The GF is the simplest performance parameter to represent the sensitivity of the strain sensor, which describes the relative resistance changes depending on external strain ($\epsilon$), $GF = (\Delta R/R_0)/\epsilon$. GF as a function of applied strain is shown in Figure 4d. The GF of FGS/SBS/Ag composite increases from 20.5 at 10% strain to $1.25 \times 10^7$ at 120% strain, while the GF of FGS/SBS composite ranges from 36.7 to $5.6 \times 10^5$. These significant improved piezoresistive responses at high strains mainly arise from the severe separation among conductive blocks (FGS and Ag NPs) at higher strains, such as break of contacts, contact area, and spacing variation upon stretching. That is to say, on the one hand, upon stretching, Ag NPs separate apart from each other, leading to fewer contact areas, larger interspacing, or even break at high strains, which contribute to the high GF at high strains. On the other hand, the FGS and Ag NPs could be employed as conductive bridges to construct effective percolation network, endowing the FGS/SBS/Ag composites with certain electrical conductivity under high strains. Remarkably, multicycle tests (Figure 4e; Figure S11, Supporting Information) indicate the excellent cycling stability and repeatability of the FGS/SBS/Ag composites at 50% and 90% strains. Actually, $R_0$ increases irreversible during the initial few cycles, and their resistance–strain relation tends to be stable after several cycles of stretching/releasing. This irreversibility can be attributed to the partial detachment or slippage of conductive blocks, and these reconstruction and irreversible deformations of the composites reduce the number of conductive paths. In general, the degree of the irreversible deformation depends on the magnitude of the maximum external strain. Thus, prior to strain sensor assembly, several cycles of stretching/releasing are implemented to achieve reproducible results.

Compared to the GFs of the previously reported strain sensors based on diverse building blocks, the value ($1.25 \times 10^7$) is pretty high. To compare these values, we plot a map of the maximum values of both GF and the corresponding tensile strain for a series of strain sensors (Figure 4f; Table S1, Supporting Information).[39–50] It could be seen that these previous strain sensors usually have narrow sensing ranges and/or low sensitivity, and we have achieved comparable GF and stretchability simultaneously via our novel hybrid structure design. We suggest that stretchable FGS/SBS/Ag composites with both high sensitivity and high stretchability are superior candidates for strain-sensing applications, considering the significantly improved piezoresistive responses than their counterparts, such as 0D/1D hybrids (OH-SBS/CNT/Ag NPs,[3] Ag NWs/Ag NPs/SBS)[37] and 0D/2D hybrids (graphene/Ag NPs/polyurethane).[18]

In order to understand the operating principle of the FGS/SBS/Ag composite more precisely, some assumptions are proposed: 1) the bonding strength between Ag NPs is uniform, and maximum allowable strains between Ag NPs before bond breaking are randomly distributed; 2) Ag NPs are attached to the substrate until the adhesion force
between NPs and substrate is smaller than a critical value, and separated if the applied force exceeds the critical value. The sensing mechanism and microstructures of the percolation network under different strains are demonstrated in Figure 5. As shown in Figure 5a, dual conductive networks embedded in SBS matrix undergo a series of mechanical deformations while being subjected to stretching/releasing. In detail, on one hand, when an applied tensile strain exceeds the allowable strain, initial microcracks are generated and propagated through the Ag NP network during the elongation process. Here, the electrical current path becomes narrower and longer due to the hindrance effects of the enlarged microcracks, resulting in the resistance increase of the composites upon stretching (Figure 5c,d). Upon larger strain, the Ag NPs network is divided into a continuous sea–island structure (Figure S12, Supporting Information). Interestingly, no exfoliation of the Ag layer from the rubber substrate occurs during stretching. Numerous Ag NPs are embedded in SBS substrate, and this mosaic structure enables the adhesion force to bear the applied force. Moreover, the bonding strength between surficial Ag NPs is also strong enough, which is tested by common tape.[3] Then, during the release process (Figure 5e–g), the strains between Ag NPs network decrease and become smaller than the maximum allowable strain, which enables most Ag NPs to reconnect with adjacent Ag NPs. Thus, most opened microcracks are closed again and the electrical resistance recovers close to the initial value ($R_0$). Note that a small fraction of Ag NPs are not completely closed, resulting in an irreversible increase of resistance. On the other hand, before stretching, FGS overlaps to adjacent FGS to form a percolation network, and electrons can get through the overlapped FGS within the percolation network. Due to the low friction between FGS and large stiffness mismatch between FGS and SBS, the overlapping areas and electrical connection of adjacent FGS slices changes upon stretching, resulting in change in their contact resistance (disconnection mechanism). At higher strains, some FGS are separated, generating some cracks, leading to a remarkable increase in resistance, which is attributed to the decrease of conductive pathways (Figures S9 and S12, Supporting Information). When the composite is released back to 0% strain, the distance between the FGS decreases and the overlapping areas increases. However, the irreversible increase of $R_0$ appears due to the reconstruction of FGS and the hysteresis of SBS. Moreover, Ag NPs and FGS could also be considered as bridges to construct the conductive paths between the disconnected networks. These synergistic effects of FGS and Ag NPs enable the FGS/SBS/Ag composites to possess high sensitivity and stretchability simultaneously.

The simultaneous incorporation of excellent mechanical robustness and giant GF is a key merit in practical applications, which could significantly extend its lifetime and application fields. The reproducibility of the FGS/SBS/Ag composites is evaluated, as given in Figure 6a. It could be seen that the strain sensor remains pretty stable after repeated stretching/releasing cycles. To observe these trends more clearly, a random curve is extracted and enlarged, which also indicates excellent reproducibility (Figure 6b), resulting from the desirable tension–resilience behavior of SBS, high mobility of Ag NPs, and the large contact area of FGS. To further enhance the reproducibility, selection of

Figure 5. a) Schematic illustration of sensing mechanism of FGS/SBS/Ag composite under stretching/releasing processes; microcracks are initiated and propagated under external strains. SEM images of the microcrack junctions on the FGS/SBS/Ag composite at $\varepsilon = 0\%$ (b), $\varepsilon = 5\%$ (c), $\varepsilon = 50\%$ (d), $\varepsilon = 30\%$ (e), $\varepsilon = 10\%$ (f), and $\varepsilon = 5\%$ (g), respectively. A number of microcracks opened at higher strain by a tensile load as compared to the relaxed status.
polymer with high elastic behavior, package of the FGS/SBS/Ag NPs composite in high elastic polymer or preconditioning step with cycles of stretching–releasing may be effective. For example, the resistance change tends to be more stable after cycles of stretching–releasing cycles (∼30 s of duration) (Figure S13, Supporting Information). Moreover, the FGS/SBS/Ag composite possesses a fast response time of ∼20 ms (Figure S14, Supporting Information), which is fairly comparable or superior to others. The fast response time could ensure a stable response of tensile strain and realize the synchronous monitoring of human motions. As proof-of-concept applications of FGS/SBS/Ag-composite-based sensor, a highly stretchable strain–gauge sensor capable of detecting human motion such as finger bending is demonstrated in Figure 6c. When the finger slowly bends toward the palm, and then releases repeatedly, the finger motion is faithfully recorded by the continuous variation of current, demonstrating a favorable reproducibility. Depending on the motion modes of finger, e.g., bending speed, degree, and retaining time, different waveforms appear in the sensing curves. For example, the signals with continuous, static, and pulse state are generated via controlling the motion modes of finger, indicating an important branch of wearable electronics.

2.4. Patterned Flexible Interconnector

Due to the overlapping of FGS and existence of multiple conductive paths, FGS/SBS/Ag conductive composites could maintain high conductivity under nontensile states, so we demonstrate the fabrication of flexible LED arrays using FGS/SBS/Ag composites as interconnects. FGS/SBS/Ag composites are cut into desirable ribbons and attached to half-cured SBS. Subsequently, commercially available GaN white LEDs are glued onto the conductive ribbons with conductive silver epoxy (Figure 6d; Figure S15, Supporting Information). As expected, the light intensity of the LED with the applied turn-on voltage of 3 V is almost retained without decrease under bending, twisting, or folding deformations (Figure 6e–h; Figure S15, Supporting Information). These deformations do not enable the electrical resistance to increase, thus partial voltage dispensed to the LED lamp do not decrease, leading to the unchanged brightness intensity.[3] These simple demonstrations confirm the feasibility of FGS/SBS/Ag composites as flexible interconnects while maintaining original conductivity under diverse nontensile deformations.

3. Conclusions

In conclusion, we demonstrate an innovative and cost-efficient strategy to develop a high-performance strain-sensing platform based on FGS, Ag NPs, and SBS. The unique configurations provide the FGS/SBS/Ag composites with superior electrical conductivity of 1521 S cm⁻¹, high break elongation of 680%, a wide sensing range of up to 120% strain, high sensitivity of ∼10⁷ at 120% strain, fast response time of ∼20 ms, as well as excellent reliability and stability over 2000 cycles. The key novelty to achieve the stretchability and sensitivity simultaneously lies in the combination of the microcrack-junction sensing mechanism, the disconnection mechanism, and the double bridge functions of Ag NPs and FGS. As a proof of concept, FGS/SBS/Ag composites could be employed as wearable sensors to detect the modes of finger motions successfully, and patterned conductive interconnects for flexible arrays of LEDs. We believe that this facile but efficient
strategy for manufacturing strain-sensitive materials will make a step toward stretchable circuits for emerging human-machine devices.

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

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Conflict of Interest
The authors declare no conflict of interest.