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Highly sensitive and stretchable piezoresistive strain sensor based on conductive poly(styrene-butadiene-styrene)/few layer graphene composite fiber

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ABSTRACT

High stretchability and sensitivity are the major desired requirements of strain sensors for wearable electronics applications, especially in health and medical monitoring. Herein, a highly sensitive and stretchable strain sensor based on conductive poly(styrene-butadienestyrene)/few layer graphene (SBS/FLG) composite fiber is fabricated through an easy and scalable wet-spinning process. Owing to the super flexibility of SBS matrix and the excellent electrical and mechanical properties of FLG, the SBS/FLG fiber based strain sensor revealed superior performance, including wide workable strain range (>110%), superior sensitivity (gauge factor of 160 at a strain of 50% and of 2546 at a strain of 100%), and durability. Furthermore, the mechanism behind the excellent performances of SBS/FLG fiber based sensors is discussed in detail.

1. Introduction

The next generation electronics are predicted to be fiber-based with flexible, stretchable, and wearable features. Strain sensors, as an important subpart of wearable electronics, present widespread potential applications including human-motion detection, personalized health monitoring, and human-machine interaction [1,2]. Flexible strain sensor devices are designed to be attached to the clothing or even directly mounted on the human skin to measure the strain induced by human movements. Strain sensors can transduce the mechanical deformations into electrical signals upon stretching and releasing owing to the piezoresistive effect. Effective wearable strain sensors for human motion monitoring must possess high stretchability ($\varepsilon > 50\%$ where ε is the strain), sensitivity, flexibility, stability, and lightweight. Apparently, conventional strain sensors based on semiconducting and metallic materials cannot fulfill the requirements of wearable strain sensors due to their friability and poor stretchability (usually $\varepsilon < 5\%$). To date, various approaches have been proposed to fabricate strain sensors with high stretchability by combining electrical conductive nanomaterials with flexible and stretchable polymers. However, most of the reported strain sensors failed to simultaneously attain high sensitivity (indicated by gauge factor, GF) and high stretchability (indicated by tolerable strain), which limits their applications in monitoring large motions (e.g. joints movements) of the human body. For example, Wang et al. developed a graphene-based strain sensor, which possessed an extremely high GF (1000 under 2–6% strains), but the strain sensor was only able to withstand strains of up to 7% [3]. On the contrary, Yamada et al. reported a highly stretchable carbon nanotubes-polydimethylsiloxane (PDMS) film based strain sensor with wide workable strain range (up to 280%), but the strain sensor only had a GF of 0.06 within a strain range of 200% strain [1]. Lipomi et al. reported a strain sensor based on transparent elastic films of carbon nanotubes that could stretch out to 150% strain. Unfortunately, it exhibited a GF less than 2.6 at 150% strain [4]. Yan et al. reported a highly stretchable graphene-nanocellulose nanopaper that could stretch out to 100% strain, but the GF of the strain sensor was still less than 7.1 [5]. Very recently, Park et al. reported a highly flexible wrinkled carbon nanotube thin film strain sensor which could be stretched to 700%. However, it exhibited a GF of only 0.65 in the strain range of 0–400%, limiting its applications in monitoring most deformations of a human body [6]. Moreover, the fabrication procedures of these strain sensors are complicated and unfit for large-scale production. Thus, it is necessary to develop a facile approach to fabricate polymer based strain sensors with high sensitivity and stretchability.

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In addition to high sensitivity and stretchability, the stability of the strain sensor is another essential factor as strain sensing applications often require stable electrical resistivity-strain behavior under long time cyclic strains. Instability is usually caused by the poor interaction between conductive nanomaterial fillers and the polymer matrix. For instance, Amjadi et al. reported highly flexible, stretchable sensitive strain sensors based on silver nanowires with PDMS that had a GF of 14 at 70% strain [7]. However, the PDMS based strain sensor exhibited poor stability due to the poor adhesion between the nanowires and PDMS. It was concluded that strong interfacial interaction between conductive fillers and polymer matrix would give better sensing performances [2]. Therefore, in order to fabricate high-performance strain sensor, the polymer substrates should have strong interfacial adhesion with the conductive fillers in addition to high stretchability and excellent processability.

Nanomaterials such as carbon materials (carbon black [8–10], carbon nanotubes [11–13], and graphene [14,15]), metal nanowires [16], and electrically conductive polymers are the most commonly used conductive fillers. Especially, graphene, a two-dimensional hexagonally structured material, consisting of sp^2-bonded carbon atoms, has been considered as a potential candidate for piezoresistive sensors owing to its extraordinary electrical and mechanical properties [17,18]. As polymer matrix, silicone-based elastomers (e.g., PDMS and Ecoflex) and rubbers (e.g., natural rubber and thermoplastic elastomers) have been widely studied. Among these, triblock copolymer poly(styrene-butadienestyrene) (SBS) has been used extensively for strain sensors due to its high stretchability, excellent elastic recovery, and good processability [19–21]. Furthermore, there is a strong interfacial interaction between graphene and SBS owing to the effective π–π interactions between the phenyl groups of SBS and graphene [22]. According to the above discussion, strain sensors based on SBS/FLG composite can be expected to attain high sensitivity and high stretchability simultaneously.

In this work, conductive SBS/FLG fibers (SGFs) were fabricated via a facile and scalable wet-spinning method and evaluated as piezoresistive strain sensors. The influence of FLG contents, applied strain and strain rate on the strain sensing behaviors were investigated by both uniaxial tensile and cyclic stretching-releasing tests. In particular, a modeling approach was used to further investigate the tunneling behavior of these SGFs under strain. Moreover, a schematic illustration of the conductive network evolution under stretching-releasing process was drawn for a better understanding of the strain sensing mechanism.

2. Experimental methods

2.1. Materials and reagents

1 to 5 layers graphene (G-100) was purchased from Shanghai Simbatt Energy Technology Co. Ltd, China. The total oxygen content was 7.0–7.5 wt%, and the conductivity was about 700–1500 S/m. The wrinkled and crumpled structure of graphene was observed (Fig. S1, Supporting information). SBS D1102K triblock copolymer with a butadiene/styrene weight ratio of 72/28 and a density of 0.94 g cm^{-3} was purchased from Kraton, USA. Tetrahydrofuran was purchased from Sinopharm Chemical Reagent Co. Ltd., China. All reagents were of analytical grade and used as received without further purification.

2.2. Spinning solution preparation and fiber spinning

The required amount of FLG was dispersed in 20 mL tetrahydrofuran (THF) and sonicated for 4 h at an output power of 45 W using a digital ultrasonic processor (S-450D-1/2, Branson) in water bath at 20 °C. Then, 3 g SBS was added to the FLG/THF suspension. The solution was agitated at room temperature for 24 h and finally sonicated for another 1 h. The SGFs fibers were fabricated through a facile and scalable wet-spinning process [23,24]. Briefly, the spinning solutions were injected into a rotating ethanol coagulation bath using a 10-mL syringe with a 23-gauge hollow needle (as spinneret). The resulting fibers, which are asymmetrically shaped with a dimension of ca. 60 times 250 μm (see insets in Fig. 1a–c), were drawn out vertically and wound onto a spool.

In this paper, samples are denoted SBS/xG for simplification, where x represents the content of FLG in weight percentage. For instance, SBS/3G represents the composite fiber containing 3 wt% FLG.

2.3. Morphological, mechanical and electrical characterization

The surface and cross-sectional (fractured in liquid nitrogen) morphology of fibers were characterized using a field emission scanning electron microscope JEOL JSM-4800LV. All the samples were sputter coated with platinum. Wide-angle X-ray diffraction (XRD) patterns were taken with 40 kV, 450 mA Cu Kα (the X-ray wave length is 1.54178A) radiation using DMAX/2550PC (Rigaku Denki Instrument). The detector moved step by step ($\Delta 2\theta = 0.02°$) in a scanning range from $2\theta = 5°$ to 60° at a speed of 6° min^{-1}.

Fiber conductivity was measured using the two-point probe method, in which probes were connected to a Keithley 6487 source meter. The electrical conductivity of the fiber was calculated using $\sigma = L/(R \times S)$, where σ (S/cm) is the electrical conductivity, R (Ω) is the electrical resistance, and L (cm) and A (cm^2) are the length and cross section area of the composite fiber, respectively.

The mechanical properties of the fibers were measured using a universal testing machine (Instron 5996). For tensile tests, samples were prepared by attaching the fibers to paper frames (10 mm in aperture), and fibers were stretched to failure at a strain rate of 20 mm min^{-1} (200% min^{-1}). Electromechanical tests were conducted by coupling a digital multimeter (Keithley 6487) to measure the electrical resistance of SGFs during cyclic straining. The sample preparation was similar to the mechanical property test. Copper tapes were attached tightly onto both ends of three fibers to allow for resistance measurements. Silver paste was used to ensure good contact between the copper tape and the fiber. The cyclic stretching-releasing test was performed to investigate the dynamic strain sensing behavior. Samples with a resistance above 1×10^{10} Ω are considered as nonconductive due to the limitation of experimental set-up. All these experiments were carried out at room temperature. The free length of the fibers was set to be 10 mm and the strain rate was 5 mm min^{-1} corresponding to 50% min^{-1}, if not mentioned otherwise.

3. Results and discussion

3.1. Morphology and structure of SGFs

SBS/FLG composite fibers (SGFs) were fabricated using a facile wet-spinning process. The fabrication schematic and photographs of obtained SGFs with different FLG loadings are shown in Fig. S2, Supporting Information. As mentioned earlier, the dispersion of the filler and interfacial interactions are critical to the sensing properties of the composites. To further investigate the FLG dispersion on the electrical and morphological properties of SGFs, the SEM micrographs of SGFs with different FLG loadings are shown in Fig. 1. It can be seen that the fracture surface of the SGFs appears porous, and the porosity increased with increasing FLG