Research Article

Lu Zhang*, Minghua Wu, Qun Liu, and Haidong Wang

High-performance wearable flexible strain sensors based on an AgNWs/rGO/TPU electrospun nanofiber film for monitoring human activities

https://doi.org/10.1515/ntrev-2023-0119
received May 18, 2023; accepted August 20, 2023

Abstract: Wearable flexible strain sensors have attracted considerable attention in recent years, while it is still a significant challenge to fabricate wearable flexible strain sensors with high sensitivity and wide sensing range simultaneously. In this work, a high-performance wearable flexible strain sensor based on a thermoplastic polyurethane electrospun nanofibers (TPUNFs) film embedded with a silver nanowires/reduced graphene oxide (AgNWs/rGO) composite conductive material was fabricated via a simple drop-coating technique. The effect of the amount of AgNWs/rGO composite conductive material on the strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor was investigated, the strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor was compared with that of the AgNWs/TPUNFs and GO/TPUNFs film flexible strain sensor, and the strain sensing properties of the AgNWs/rGO/TPUNFs film flexible strain sensor were measured. The results showed that the AgNWs/rGO/TPUNFs film flexible strain sensor with high sensitivity and wide sensing range simultaneously was achieved by compounding AgNWs and the reduced graphene oxide (rGO) conductive material. The strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor could be improved by increasing the amount of the AgNWs/rGO composite conductive material, and it was obviously better than that of AgNWs/TPUNFs and the rGO/TPUNFs film flexible strain sensor. The obtained AgNWs/rGO/TPUNFs film flexible strain sensor possessed high sensitivity (the gauge factor could reach a maximum of 2513.23) as well as a wide sensing range (~187%). Furthermore, the obtained AgNWs/rGO/TPUNFs film flexible strain sensor had a fast response/recovery time (200 ms/300 ms) and good cycling stability (~3,000 cycles). Benefitting from the outstanding strain sensing performance, the AgNWs/rGO/TPUNFs film flexible strain sensor could detect large human motions such as finger, wrist, and knee bending as well as expression, which demonstrates great potential applications in wearable devices.

Keywords: silver nanowires, reduced graphene oxide, electrospun nanofibers, flexible strain sensor, human activities

1 Introduction

Wearable devices have promising applications in personal healthcare, human motion monitoring, disease diagnosis, human–machine interface, and virtual reality [1–7]. Among wearable devices, wearable strain sensors are recognized as one of the most indispensable sensors, as they can transduce mechanical strain into electrical signals and integrate into some smart devices to detect useful information about people [8–11]. However, conventional strain sensors were composed of semiconductor material or metal foil, the application range was seriously restricted due to their rigidity, low sensing range, and resolution [12,13]. To satisfy the requirements of wearable, numerous efforts have been devoted to fabricating wearable flexible strain sensors, while it is still a significant challenge to fabricate wearable
flexible strain sensors with excellent sensitivity and wide sensing range simultaneously [14,15].

However, the sensitivity and strain sensing range of wearable flexible strain sensors are closely related to their compositions [12,16–18]. Generally, wearable flexible strain sensors are composed of elastomers and active sensing materials [19,20]. The elastomers are usually insulation materials including silicone rubber (SR), Ecoflex, styreneic block copolymer (SBC), poly(dimethylsiloxane) (PDMS), and thermoplastic polyurethane (TPU), etc. [14,21]. TPU exhibits relatively higher tensile properties and better stretchability compared to other elastomers, and it was widely used in the fabrication of wearable flexible strain sensors [22,23]. However, the active sensing materials are conductive materials including metal (e.g., silver, copper, zinc, etc.) nanoparticles/nanowires, carbon materials (e.g., carbon nanotube, graphene, carbon black, etc.), and conductive polymers (e.g., polyaniline, polythiophene, polyphenylenevinylene, polypyrrole, etc.) [24–26]. Among these conductive materials, silver nanowires (AgNWs) with outstanding conductivity, flexibility, and easy preparation were considered the most promising candidates for wearable flexible strain sensors [23,27,28], whereas they tended to entangle because of their high aspect ratio and one-dimensional structure, which would increase contact resistance of AgNWs and affect the sensitivity of wearable flexible strain sensor [29]. Through further research, it was found that constructing a susceptible conductive network that had a low initial resistance was profitable in increasing the sensitivity of wearable flexible strain sensors [28,30,31]. Graphene oxide (GO) is a two-dimensional conductive material, it has attracted considerable attention owing to its unique properties (such as mechanical properties, thermal and flexibility, etc.), and it was often composited with other conductive materials to fabricate wearable flexible strain sensors [32,33]. While the additive amount would increase when GO was used alone because of its poor electrical conductivity, then the mechanical property and sensitivity of wearable flexible strain sensor would be affected. Fortunately, AgNWs have good conductivity, and GO has many functional groups that could form hydrogen bond with carbonyl and acylamino on the surface of AgNWs [34–37], by compounding AgNWs and GO, the dispersibility of AgNWs and conductivity of AgNWsGO and AgNWs/rGO composite conductive materials could be improved. At the same time, it was found that the formation of the conductive network by AgNWs/rGO was more susceptible than that of AgNWs or rGO [28], and the AgNWs/rGO composite conductive material could exploit the properties of both AgNWs and rGO synergistically endowing good conductivity and better sensing performance for wearable flexible strain sensor [25,38]. Through further research, it was found that the interaction between elastomers and active sensing materials directly influenced the stability of wearable flexible strain sensors. Yin et al. [28] spay-coated AgNWs and GO on the surface of the TPU electrospun nanofibers mat to fabricate rGO/AgNWs/TPU flexible strain sensor, and the sensor showed good stability. Lu et al. [25] loaded rGO and AgNWs on high-elastic PBT meltblown non-woven fabric to fabricate rGO/AgNWs@PBT MB flexible strain sensor, which showed excellent stability in 1,200 stretching-releasing cycles. This may be because of that the PBT meltblown non-woven fabric and TPU electrospun nanofibers mat had rough surfaces. Through the interface mechanical interaction and strong physical interaction between the conductive active material and the rough surface, the interface stability between the active material and the substrate material would be increased, thus the obtained wearable flexible strain sensor had excellent stability.

Therefore, in order to fabricate a wearable flexible strain sensor with high sensitivity and wide sensing range simultaneously in this study, the hydrogen-bond interaction between AgNWs and graphene oxide was utilized to fabricate AgNWs/rGO composite conductive material, and the AgNWs/rGO composite conductive material dispersion liquid was drop-coated on the surface of TPU electrospun nanofibers (TPUNFs) film to fabricate AgNWs/rGO/TPUNFs film flexible strain sensor. Benefitted by the lower initial resistance of AgNWs/rGO composite conductive material and high extensibility of TPUNFs film, the AgNWs/rGO/TPUNFs film flexible strain sensor with high sensitivity and wide sensing range simultaneously was achieved. The strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor could be improved by increasing the amount of AgNWs/rGO composite conductive material. Through the compositing of AgNWs and GO, the strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor was broadened remarkably compared with that of AgNWs/TPUNFs and GO/TPUNFs film flexible strain sensor. The interface mechanical interaction and strong physical interaction between elastomers and active sensing materials endowed the flexible strain sensor with excellent stability. In addition, the AgNWs/rGO/TPUNFs film flexible strain sensor was successfully applied to detect large human motions such as finger, wrist, and knee bending as well as expression.

2 Experimental section

The experimental section is displayed in the Supplementary Information document.
3 Results and discussion

3.1 Fabrication and characterization of AgNWs/rGO/TPUNFs film

In order to fabricate a wearable flexible strain sensor with high sensitivity and wide sensing range simultaneously, AgNWs/rGO/TPUNFs film was fabricated via a simple drop-coating technique, and it was used as an active sensing material to fabricate an AgNWs/rGO/TPUNFs film flexible strain sensor. The AgNWs that we used in this study were homemade, which were fabricated by the solvothermal method, are longer and uniform, the length of AgNWs is about 158 μm, the diameter is about 77 nm, and the details were presented in our previous study [39]. The morphology structures of GO and AgNWs/rGO composite conductive material are shown in Figure 1. The GO was fabricated by the modified Hummers method, it showed a two-dimensional lamellar structure with wrinkles on the surface of the lamellar structure, which was beneficial to composite with AgNWs (Figure 1a and d). The SEM and TEM images of AgNWs/rGO composite conductive material (Figure 1b, c, e, and f) revealed that AgNWs and rGO were compounded successfully, and the AgNWs were not only distributed on the surface of rGO but also inserted into the gap between rGO sheets forming uniform AgNWs/rGO composite conductive material, which was advantageous to the sensitivity and strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor.

In order to certify the successful fabrication of AgNWs/rGO composite conductive material, the XRD patterns and Raman spectra were used to characterize the structure of GO, rGO, and AgNWs/rGO, and the results are displayed in Figure 2. As shown in Figure 2a, the GO presented a distinct diffraction peak at 10.9°, which could correspond to the (001) plane of graphite [40]. While the diffraction peak located at 10.9° disappeared after the reduction reaction, a new wide diffraction peak appeared at about 24.5°, which could be assigned to the (002) crystal plane of graphite. For the AgNWs/rGO composite conductive material, the diffraction peak located at about 20.84° could belong to the characteristic peak of rGO, the diffraction peak located at 38.1°, 45.6°, 64.3°, and 77.6° could be ascribed to the (111), (200), (220), and (311) crystal plane of AgNWs, respectively. These characteristic peaks confirmed the combination of AgNWs and rGO [41,42]. Raman spectra of GO, rGO, and AgNWs/rGO are shown in Figure 2b, which exhibited two main dominant peaks (D and G peaks) that appeared at 1,350 and 1,590 cm$^{-1}$, respectively. The D band reflected the disorder between graphite sheets and indicated the presence of defects in the sample. The G band represented the structure of sp$^2$ carbon and reflected its symmetry and degree of crystallization [43]. The intensity ratio of $I_D/I_G$ of rGO (1.47) and AgNWs/rGO (1.44) increased compared to that of GO (1), indicating the successful reduction of GO.

Considering that the mass ratio of AgNWs to rGO has an important influence on the conductivity of AgNWs/rGO composite conductive material, and the conductivity of

Figure 1: SEM images of GO (a), AgNWs/rGO (b), and the amplifying SEM image of AgNWs/rGO (c), TEM images of GO (d), AgNWs/rGO (e) and HRTEM image of AgNWs/rGO (f).
AgNWs/rGO composite conductive material directly affects the sensitivity and strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor. Therefore, the effect of the mass ratio of AgNWs to GO on the conductivity of AgNWs/rGO composite conductive material was investigated. As shown in Figure S1, the resistivity of pure AgNWs was about 68 Ω cm, and the resistivity of pure GO was about 37 kΩ cm. As the amount of GO increases, the resistivity of AgNWs/rGO composite conductive material showed a downward trend, when the mass ratio of AgNWs to rGO was 1:1, the resistivity of AgNWs/rGO composite conductive material could reach 10.4 Ω cm. After that, the resistivity of AgNWs/rGO composite conductive material increased as the amount of GO increased. This may be because of that the conductivity of AgNWs had a significant role when a bit of GO was added into the AgNWs/rGO composite conductive material, a small amount of GO could decrease the contact resistance of AgNWs, thus the resistivity of AgNWs/rGO composite conductive material was reduced. When the amount of GO was excess, the amount of AgNWs was decreased obviously, the conductivity of rGO played an important role, thus the resistivity of AgNWs/rGO composite conductive material was increased. Hence, it was chosen that the mass ratio of AgNWs to rGO was 1:1 to fabricate the AgNWs/rGO composite conductive material.

After that, the TPUNFs film was prepared by electrospinning process, and AgNWs/rGO composite conductive material dispersion liquid was drop-coated on the surface of TPUNFs film to fabricate AgNWs/rGO/TPUNFs film active sensing material. The surface morphology structure of pure TPUNFs and AgNWs/rGO/TPUNFs film is shown in Figure 3. As shown in Figure 3a, the pure TPUNF film revealed a network structure, and the diameter of the TPUNF film is about 0.5–1 μm (Figure 3b). After drop-coating AgNWs/rGO composite conductive material dispersion liquid on the surface of TPUNFs film, the network structure of TPUNFs film disappeared and a denser covering layer was formed on the surface of TPUNFs film (Figure 3c). By further magnifying the SEM image of the denser covering layer, it could be seen that the AgNWs were dispersed uniformly in the denser covering layer, which was beneficial to improving the conductivity of AgNWs/rGO/TPUNFs film (Figure 3d), thus the sensitivity and strain sensing range of the flexible strain sensor would be improved. In order to test the strain responsiveness of the AgNWs/rGO/TPUNFs film, the film was inserted into a circuit as part of the traverse (Figure S2). The circuit was able to light an LED lamp indicating that the resistivity of the AgNWs/rGO/TPUNFs film was small. The LED lamp showed different brightness levels while being stretched after the AgNWs/rGO/TPUNFs film was inserted into the circuit. This demonstrates that the AgNWs/rGO/TPUNFs film had great potential for preparing wearable flexible strain sensors.

3.2 Strain sensing performance of AgNWs/rGO/TPUNFs film flexible strain sensor

Except for the mass ratio of AgNWs to GO, the drop-coating amount of AgNWs/rGO composite conductive material on the surface of TPUNFs film has a great impact on the sensitivity and strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor. When the drop-coating amount of AgNWs/rGO composite conductive material was fewer, the strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor may be narrower, and the AgNWs/rGO composite conductive material would peel off the TPUNFs film when the AgNWs/rGO composite conductive material was excess. Therefore, the effect of the drop-
coating amount of AgNWs/rGO composite conductive material on the strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor was investigated. From Figure S3, it could be seen that the strain sensing range increased gradually with the increase in the drop-coating amount of AgNWs/rGO composite conductive material, the strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor was less than 60% with AgNWs/rGO-1mL composite conductive material, when the drop-coating amount of AgNWs/rGO composite conductive materials was 5 mL, the strain sensing range of AgNWs/rGO/TPUNFs film flexible strain sensor could reach 187%, which could be due to the fact that the interaction of AgNWs and GO enlarged the strain sensing range (as shown in Figures 1 and 2 the successful fabrication of AgNWs/rGO composite conductive material). Therefore the AgNWs/rGO/TPUNFs film active sensing material with AgNWs/rGO-5mL composite conductive material was used to fabricate the AgNWs/rGO/TPUNFs film flexible strain sensor.

To further measure the sensitivity of the AgNWs/rGO/TPUNFs film flexible strain sensor, it could be found that the relative resistance change ($\Delta R/R_0$) increased with the increasing applied strain (as shown in Figure 4a). The strain sensing range of the flexible strain sensor could reach 187%, and the gauge factor (GF) could reach a maximum of 2513.23, demonstrating that the AgNWs/rGO/TPUNFs film flexible strain sensor had high sensitivity and wide strain sensing range simultaneously, which benefitted from the high extensibility of the TPUNF film and the low initial resistance and structure of the AgNWs/rGO/TPUNFs composite conductive material. After that, the stress–strain properties of the AgNWs/rGO/TPUNFs active sensing material and the strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor were compared with that of AgNWs/TPUNFs and GO/TPUNFs film flexible strain sensors. As shown in Figure S4a, it had little effect on the stress–strain properties by drop-coating AgNWs, GO, and AgNWs/rGO on the surface of the TPUNF film. Apparently, the strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor was broader than that of AgNWs/TPUNFs and the GO/TPUNFs film flexible strain sensor (as shown in Figure S4b), indicating that the combination of AgNWs and rGO could produce synergistic effect during being stretched; therefore, the strain sensing range of the AgNWs/rGO/TPUNFs film flexible strain sensor was broadened. Compared with similar sensors reported in the literature (as shown in Figure 4b), our obtained flexible strain sensor had higher sensitivity and wider sensing range, indicating that the AgNWs/rGO/TPUNFs film flexible strain sensor had excellent properties, which benefitted from the high extensibility of the TPUNF film and the low initial

![Figure 3](image-url)
resistance and the structure of the AgNWs/rGO/TPUNFs composite conductive material [15, 40, 44–46]. Subsequently, the relative resistance changes in the AgNWs/rGO/TPUNFs film flexible strain sensor during cyclic stretching–releasing to different strains (20, 25, 30, 35, and 40%) were investigated, and the results are shown in Figure 4c. It could be seen that $\Delta R/R_0$ increased with the increase in stretching strain, and it showed negligible change for the same stretching strain during cyclic stretching–releasing, indicating that the AgNWs/rGO/TPUNFs film flexible strain sensor had excellent repeatability and stability. The relative resistance change in the flexible strain sensor under different working frequencies is shown in Figure 4d, in which the invariable amplitude of the curves demonstrated that the resistance of the AgNWs/rGO/TPUNFs film flexible strain sensor was not affected by the stretching rate. As shown in Figure 4e and f, the AgNWs/rGO/TPUNFs film flexible strain sensor exhibited excellent stability and durability, which benefitted from the interface’s mechanical interaction and strong physical interaction between the conductive active material and the rough surface.

The response/recovery time is another important parameter of the flexible strain sensor for the real-time detection of human motions. As shown in Figure 5, the AgNWs/rGO/TPUNFs film flexible strain sensor was stretched to 25% and then recovered to its original state, and the
AgNWs/rGO/TPUNFs film flexible strain sensor showed rapid response with negligible hysteresis. The response/recovery time was about 200 and 300 ms, respectively.

### 3.3 Stretching mechanism of the AgNWs/rGO/TPUNFs film flexible strain sensor

Based on the structure and performance detection of the AgNWs/rGO/TPUNFs film flexible strain sensor, the flexible strain sensor had higher sensitivity and wider detection range compared to similar flexible strain sensors reported in the literature (Figure 4b), which benefitted from the composite conductive material design of two-dimensional GO and one-dimensional AgNWs, the high extensibility of TPUNF film, and the interface mechanical interaction and strong physical interaction between the AgNWs/rGO composite conductive material and the rough surface of the TPUNF film (Figure 6). Using the composite of two-dimensional GO and one-dimensional AgNWs, the AgNWs were not only distributed on the surface of rGO but also inserted into the gap between rGO sheets (Figure 1b and c), which could significantly improve the conductivity of AgNWs, expand the conductive path of the conductive material, reduce the initial resistance of the AgNW-based wearable flexible strain sensor, and improve the sensitivity of the flexible strain sensor. The high extensibility of the TPUNF film could endow the AgNWs/rGO/TPUNFs film flexible strain sensor wide detection range. The AgNWs/rGO dispersion was drop-coated on the surface of the TPUNF film forming a staggered interface structure between AgNWs/rGO and the TPUNF film, which could increase the interaction force between the interfaces. In addition, the amide group of the PVP pyrrolidone ring on the surface of AgNWs and the carbonyl and hydroxyl groups of rGO could form hydrogen bonding with the carbamate group of TPU. The interface mechanical interaction and strong physical interaction between AgNWs/rGO conductive materials and the rough surface of the TPUNF film.
film could prevent the AgNWs/rGO conductive materials from peeling from the surface of the TPUNF film while being stretched, which could endow the AgNWs/rGO/TPUNF film flexible strain sensor with excellent stability. In normal application stretching, the interface structure between AgNWs/rGO conductive materials and the TPUNF film was not damaged, and the number of conductive paths of the AgNWs/rGO/TPUNF film flexible strain sensor changed with the change in stretching strain indicating that the flexible strain sensor had high sensitivity. However, when the stretching strain was too large beyond the scope of normal application stretching, the AgNWs/rGO conductive material would be irretrievably separated and broken destroying the conductive path of the AgNWs/rGO/TPUNFs film flexible strain sensor, and the failure of the sensor.

3.4 Application performance of the AgNWs/rGO/TPUNFs film flexible strain sensor

Due to the excellent mechanical properties, high sensitivity, and wide sensing range, the AgNWs/rGO/TPUNFs film flexible strain sensor was attached to the surface of the human body for the real-time detection of human activities. In order to detect the response of the AgNWs/rGO/TPUNFs film flexible strain sensor to subtle motion, the AgNWs/rGO/TPUNFs film flexible strain sensor was attached above the eyebrow (Figure 7a), and the motion of frown could be distinguished indicating that the AgNWs/rGO/TPUNFs film flexible strain sensor could be used to detect facial expressions. As shown in Figure 7b, when the AgNWs/rGO/TPUNFs

---

Figure 7: Application of the AgNWs/rGO/TPUNFs film flexible strain sensor for real-time detection of human activities by adhering it onto the surface of skin: (a) eyebrow, (b) index finger, (c, d) knee, and (e) wrist. The insets show photographs of the AgNWs/rGO/TPUNFs film flexible strain sensor attaching to the skin at different bending degrees.
film flexible strain sensor was fixed on the finger, the relative resistance increased promptly with the change in the bending degree of the finger. At each bending cycle, it was found that the variation in the relative resistance was repeatable and reliable during the cyclic bending process of the finger. Also, the bending of the wrist could be distinguished by the AgNWs/rGO/TPUNF's film flexible strain sensor (as shown in Figure 7e), and the differences between the pattern of wrist bending and the pattern of finger bending indicated that the AgNWs/rGO/TPUNF's film flexible strain sensor had great potential in the application of gesture recognition. Additionally, the AgNWs/rGO/TPUNF's film flexible strain sensor could be used to detect the motions such as walking and running (Figure 7c and d), when it was attached to the knee of a volunteer. Walking, running in place, and running forward showed different relative resistance values, which could be due to the different stretching degrees of leg muscles caused by inconsistent steps, indicating the high sensitivity of the AgNWs/rGO/TPUNF's film flexible strain sensor. These results showed that the AgNWs/rGO/TPUNF's film flexible strain sensor has great potential in the application of full-range human activities.

4 Conclusions

In summary, a highly sensitive and wide-sensing range flexible strain sensor based on the TPUNF film embedded with the AgNWs/rGO composite conductive material was fabricated via a simple drop-coating technique. Through compounding AgNWs and GO, the AgNWs/rGO/TPUNF's film flexible strain sensor with high sensitivity and wide sensing range simultaneously was achieved. The strain sensing range of the AgNWs/rGO/TPUNF's film flexible strain sensor was broadened remarkably compared with those of AgNWs/TPUNFs and the GO/TPUNF's film flexible strain sensor. Benefitted from the high extensibility of TPUNFs and the low initial resistance and structure of the AgNWs/rGO/TPUNF's film, the obtained AgNWs/rGO/TPUNF's film flexible strain sensor possessed high sensitivity (the GF could reach a maximum of 2513.23) as well as wide sensing range (~18%). The GF and strain sensing range of the obtained AgNWs/rGO/TPUNF's film flexible strain sensor were higher than the similar sensors reported in the literature. Benefitted from the interface mechanical interaction and strong physical interaction between the AgNWs/rGO conductive film and the rough surface of the TPUNF film, the obtained AgNWs/rGO/TPUNF's film flexible strain sensor had good cycling stability (~3,000 cycles). Furthermore, the obtained AgNWs/rGO/TPUNF's film flexible strain sensor had a fast response/recovery time (200 ms/300 ms), and it could be used to detect large human motions such as finger, wrist, knee bending as well as expression. These results demonstrated the excellent potential of the AgNWs/rGO/TPUNF film flexible strain sensor for applications in wearable devices.

Acknowledgments: The authors would like to thank the anonymous reviewers for their valuable comments.

Funding information: This study was supported by the foundation of Jilin Institute of Chemical Technology (No. 222012212012) and Development Plan Project of Jilin Province Science and Technology Department (YDZJ202201ZYTS623).

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Conflict of interest: The authors state no conflict of interest.

References


