Preparation and Force Sensitive Properties of ZnO/Graphene Composite Films

Jianming Wang, Zhaomin Luo, Feng Zheng, Qiaozhi Wang and Xingming Xu*
Shandong University of Science and Technology, Taian, China

*Corresponding author email: xxm1601@163.com

Abstract. In this paper, the preparation and force sensitivity of ErGo-ZnO composite films were studied. In order to improve the application value of graphene composite film in optical devices, sensors, photocatalysis, etc., ZnO is added. In this experiment, the ErGo-ZnO film was successfully prepared by vacuum filtration. At the same time, by adjusting the self-assembled layer of the composite film and the concentration of graphene oxide in the self-assembly growth process, the optimal design parameters are further optimized. The experimental results show that the self-assembled 6 layers have the best performance of the graphene oxide concentration of 0.5mg/ml. The crystallinity of the 0.05wt% graphene oxide ErGo-ZnO composite film is obviously improved. The amount of phase in the film after axial stretching is greatly increased (from 20% before stretching to 92%). In addition, comprehensive characterization and experimental results show that the excellent mechanical properties and specific surface area of graphene oxide and the excellent compatibility with ErGo-ZnO materials are the key factors to improve the interface stress transfer efficiency. This makes the crystallinity and mechanical properties of the composite film greatly improved, and the piezoelectric properties are further enhanced, which greatly improves the application value of the graphene composite film in optical devices, sensors, photocatalysis and the like.

1. Introduction
The basic structural unit of graphene is the most stable benzene six-membered ring in organic materials, and it is the most ideal two-dimensional nanomaterial. The ideal graphene structure is planar hexagonal lattice, which can be regarded as a layer of stripped graphite molecules. Each carbon atom is sp2 hybridized and contributed to the remaining electrons in the p orbital to form a large bond. The electrons can move freely, giving the graphene good electrical conductivity. The two-dimensional graphene structure can be seen as the basic building block for forming all sp2 hybrid carbonaceous materials.

The introduction of graphene into inorganic semiconductor materials can increase the surface area increase the charge transfer rate of electrons, compensate for the weak conductivity of metal oxides, and reduce the recombination of photogenera electron pairs by reducing the interaction of graphene-bonds. The photocurrent is increased, and the synergistic effect of graphene and ZnO makes the composite material have great application prospects in the field of optoelectronics. Graphene and ZnO composites have many synthetic routes such as thermal decomposition, electrochemical pathway, ultrasonic spray pyrolysis, electrokinetic atomization and solvent heat treatment.
At present, there are few researchers’ studied force-sensitive properties of graphene composite films. Based on the research of the existing literature, the forcesensitive- properties of graphene composites, while adjusting the self-assembled layers of composite films in self-assembly growth process, The concentration of graphene oxide is further optimized to screen out the best design parameters.

2. Basic theory and test method of flexible force sensor

2.1. Basic theory and test method of flexible strain sensor
Compared with the traditional strain gauges, the flexible strain sensor not only has the characteristics of the flexible folding of the traditional strain gauge, but also has the stretchable characteristics, which greatly expands its application field. In practical applications, the flexible strain sensor is closely attached or fixed to the object to be tested, and the slight deformation will cause the resistance or capacitance of the sensor to change, and the signal is visualized and recorded in real time by connecting a resistance or capacitance test device. Therefore, in the laboratory test, it is necessary to build a comprehensive test platform, which includes dynamic motion platform and real-time data monitoring and recording platform. The integrated test platform system is composed of a dynamic movable platform system and a real-time data monitoring and recording platform system. For flexible ductile strain sensors, the deformation is mainly divided into transverse tensile strain and longitudinal compression deformation. Therefore, according to different deformation modes, the test principle is slightly different.

2.2. Basic theory and test method of flexible piezoelectric sensor
The device is an electrical component based on the piezoelectric effect of a flexible material, which can convert the mechanical change amount applied to the object to be measured into a visible electrical signal through a certain law, thereby achieving the purpose of detection. The specific principle is shown in the Figure below.

The total system of this experiment mainly includes four units: a device starting unit, a charge amplifying circuit unit, a noise processing unit, and an output display unit. In the starting unit of the device, the amplitude and the magnification of the vibrator are controlled by an external signal input, so that the piezoelectric device generates periodic vibration, thereby generating a corresponding load form in the structure to obtain a voltage output signal generated by the sensor. Since the amount of charge generated is weak, it is necessary to amplify the output signal by the charge amplifying unit. The amplified signal contains the piezoelectric device output signal and the external noise signal, so the noise processing unit is required for noise reduction processing, and then the output electrical signal is collected by the oscilloscope in the display unit. Finally, the collected data is analyzed and processed.

3. Preparation and Force Sensing Properties of 3 ZnO/Graphene Composite Films

3.1. Preparation process of ErGo-ZnO nanocomposite film
In this experiment, the ErGo-ZnO film was successfully prepared by vacuum filtration. First, the EuGo nanosheets were prepared by chemical oxidation method by controlling the amount of strong oxidant added, and the zinc acetate dihydrate was used as raw material. The epoxy groups, hydroxyl groups and carboxyl groups on the Zn nanorod 9-1001ErGo nanosheets were prepared under solvothermal conditions as Celsius. The ZnO nanorods with abundant hydroxyl groups on the surface can pass
hydrogen bonding and electrostatic interaction. The effect is attached to the ErGo nanosheet, and the bonding of the layered ErGo nanosheet under vacuum pressure results in the embedding of the ZnO nanorod in the interlayer of the ErGo nanosheet. The unique advantages of ErGo nanosheets and ZnO nanorods will reasonably adjust the surface morphology and channel structure of the ErGo-ZnO film, so that the prepared ErGo-ZnO film can effectively separate the dye solution.

3.2. Composite film characteristics and analysis
Fourier transform infrared spectroscopy (FT-IR) analysis
During the preparation of the composite membrane, FT-IR was used to characterize the changes in functional groups at different stages. Figure 3 is an infrared spectrum of the sample ErGo nanosheet, ZnO nanorod and ZnO film, respectively. A curve from Figure 3 shows that the absorption peaks corresponding to 3350 cm\(^{-1}\), 1820 cm\(^{-1}\), 1640 cm\(^{-1}\), 1420 cm\(^{-1}\), and 1030 cm\(^{-1}\) are respectively water OH, carboxyl C=, aromatic carbon ring, C=C, CO in the carboxyl group and vibration of CO in the hydroxyl group, which is consistent with the characteristic peaks of the reported ErGo nanosheets, indicating that the ErGo nanosheets were successfully prepared. As can be seen from the b curve in Figure 3, a characteristic peak of ZnO appeared at 524 cm\(^{-1}\), indicating that the ZnO nanorods were successfully prepared. As can be seen from the c curve in Figure 3, the absorption peak at 1640 cm\(^{-1}\) is significantly weakened due to the electrostatic interaction between the ErGo nanosheet and the ZnO nanorod. In addition, the characteristic peaks in ErGo nanosheets and ZnO nanorods were successfully retained, indicating that the ErGo-ZnO film was successfully prepared.

![Figure 3](image)

**Figure 3.** Infrared spectrum of sample ErGO nanosheet (a), ZnO nanorod (b) and ErGO-ZnO film (c)

3.3. Study on the performance and sensitivity mechanism of flexible strain sensors

3.3.1. Study on compressive strain characteristics of flexible strain sensors
Compared with other composite film preparation methods, the layer-by-layer self-assembly technology constructs a multi-layer structure by alternating adsorption, which has the characteristics of simple operation and controllable film thickness. Therefore, the influence of the self-assembled layer of the composite film and the concentration of graphene oxide on the overall performance of the device must be considered during the experiment. Here we define a single-layer polyethyleneimine film and a single-layer graphene film as a composite film. In this experiment, a 1% w/v PEI solution and a graphene solution with a concentration of 0.5 mg/ml were used for layer-by-layer self-assembly.

Figure 3 Infrared spectrum of sample ErGO nanosheet (a), ZnO nanorod (b) and ErGO-ZnO film (c)

Four, six, eight and ten layers of ZnO-ErGo composite films were prepared by the process. The flexible composite film was packaged as strain sensor S (4L-GO/0.5mg/ml), strain sensor S (6L-GO/0.5mg/ml), strain sensor S (8L-GO/0.5mg/ml) and strain sensor S (10L-GO/0.5mg/ml).
In order to study the influence of the number of self-assembled layers on the device, we tested the initial resistance of these devices. The experimental results are shown in Figure 4. It can be concluded that as the number of self-assembled layers increases, the initial resistance of the device decreases. It shows that with the increase of the number of self-assembled layers, the conductive network in the composite film is gradually improved, and the initial resistance is drastically reduced.

**Figure 4. Initial resistance of six flexible composite devices**

In order to further understand the influence of the number of self-assembled layers on the performance of the device, this paper studied the resistance change response of several devices under small pressure (1kPa-5kPa). Several devices have excellent response under small strain. At the same time, it can be found that the device has excellent linearity (R2>0.9) in a small compressive strain range, so the device has excellent performance and broad application prospects. According to the formula defined by the strain coefficient formula (1) and the sensitivity formula (2), the sensitivity coefficients of self-assembled 4-layer, 6-layer, 8-layer and 10-layer strain sensors can be calculated, and a self-assembled 6-layer strain sensor can be obtained. Has the largest response, the best linearity and the maximum sensitivity factor (S = 3.895). Therefore, the following conclusions can be drawn. After comprehensive testing of different layer-count strain devices prepared by the layer self-assembly process, it is found that the self-assembled 6 layers are the optimal self-assembled layer number design parameters.

\[ GF = \frac{\Delta R}{R_0} \left( \frac{L}{L_0} \right) = \frac{R/R_0 - 1}{\varepsilon} \]  \hspace{1cm} (1)

\[ S = \frac{\Delta R/R_0}{\Delta \varepsilon} \]  \hspace{1cm} (2)

In order to further study the effect of graphene oxide concentration on the performance of the device in the self-assembly process, this chapter based on the previous optimal layer design parameters (6
layers), using a layer-by-layer self-assembly process to prepare 6 layers of PEI based on 1% w/v. Solution and concentration of 0.25 mg/ml, 0.5 mg/ml and 1.0 mg/ml of graphene solution ZnO-ErGo composite film. The flexible composite film was packaged as strain sensor S (6L-GO/0.25mg/ml), strain sensor S (6L-GO/0.5mg/ml) and strain sensor S (6L-GO/1.0mg/ml). The test results are analyzed by using a self-made test system. The experimental results are shown in Figure 6. It can be seen that the three strain devices still have excellent response and linearity in a small pressure range. At the same time, it can be found that in three kinds of strain devices based on different graphene oxide concentrations, the self-assembled 6-layer graphene oxide concentration of 0.5mg/ml strain sensor has the maximum response value and sensitivity as well as the optimal linearity.

![Figure 6. Curves of different graphene concentration strain devices](image)

![Figure 7. Dynamic response of strain sensor S (6L-0.5mg/ml)](image)

Comprehensive above, this also is obvious that under the small compression pressure strain, the strain sensor S (6L-GO/0.5mg/ml) prepared by the layer self-assembly process has the best performance. Therefore, it can be concluded that the optimum layer number design parameters of the strain sensor prepared by the layer self-assembly process are 6 layers, and the optimal GO concentration parameter is 0.5 mg/ml. In order to further verify the other properties of the device, the stability test and repeatability test of the optimal design strain sensor S (6L-GO/0.5mg/ml) are shown in this experiment. It is obvious from Figure 7. that the strain sensor is under the small pressure range (1kPa-5kPa), the relative change of resistance remains stable, and the curve has no obvious delay or drift, which indicates that the device has excellent stability performance. In addition, it can be seen from the repeatability test result curve of the device that the relative change of the resistance of the device at different pressures is substantially maintained without a large increase or decrease, indicating that the device has excellent repeatability.
3.3.2. Study on Tensile Strain Characteristics of Flexible Strain Sensor. Similar to the test under compressive strain, firstly, in response to the influence of the number of layers and the concentration in the self-assembly process, several experiments of the devices prepared in the previous section were tested in the small strain range. Aiming at the influence of the number of layers in the self-assembly process, the tensile test system is used to test the relative resistance value of four different layer strain devices at 1%-5% strain. The dynamic test, the experimental test results are shown in Figure 8. It can be seen from the Figure that the resistance fluctuation curves of several devices at 2.5% tensile strain are stable, indicating that the devices have good stability under tensile strain. Combined with the strain response test results of several devices under different strains, the comprehensive analysis can clearly find that 4 The device has excellent linearity and sensitivity and ultra-high response in the small strain range. According to the strain coefficient (GF) formula, the maximum strain coefficient of the four devices (at 5% strain) is 105, 754, 326 and 79. Therefore, it can be concluded that the optimum number of layers of the strain sensor under compressive strain is designed. The self-assembled 6 layers are the optimal layer design parameters.

![Figure 8. Dynamic response curves of different self-assembled layer strain devices](image)

**Figure 8.** Dynamic response curves of different self-assembled layer strain devices

After determining the optimal layer number design parameters of the layer self-assembly process, in order to further study the influence of the graphene oxide concentration on the performance of the variable device, the dynamic test of the three strain devices is shown in Figure 10. It can be seen from the Figure that the curves of the relative resistance of the three devices under 2.5% tensile strain are undulating and there is no large increase or decrease, which indicates that the device has good stability under tensile strain. performance. Combined with the response curve of different tensile strains (Figure 11), it can be seen that the optimized graphene oxide concentration design parameter is 0.5 mg/ml.

![Figure 9. Pressure-response curves of four strain devices](image)

**Figure 9.** Pressure-response curves of four strain devices
Figure 10. Dynamic response curve of different graphene concentration strain devices

Figure 11. Pressure response curves of three kinds of strain devices

In order to further analyze other performance parameters of strain sensor S (6L-GO/0.5mg/ml), the ohmic behavior, repeatability, tensile mechanical properties, minimum detection limit, response time and practical application of the device were analyzed. Figure 12 shows the real-time resistance value of the strain sensor S (6L-GO/0.5mg/ml) under 1%-5% tensile strain. The device can have excellent dynamic resistance response. At the same time, it has excellent stability under different strains. In order to further study the repeatability of the device, this paper uses the dynamic test platform to repeat the test at 2.5% tensile strain for 500 times. The experimental results are shown in Figure 13. The black part of the Figure is the change curve of the relative change value of the resistance of 500 cycles. The two embedded pictures below the Figure are the initial change curve and the change curve of 500 cycles. It can be clearly seen that after 500 cycles of testing, the overall response value change is almost negligible, and there is no significant change in response value and stability before and after the test. A comprehensive analysis can conclude that the flexible strain sensor S (6L-GO/0.5mg/ml) has excellent repeatability.
According to the characteristics of transverse tensile strain, the relationship between tensile strain and tensile force of flexible devices is one of the important performance parameters of the device, because it can not only reflect the flexibility of the flexible device, but also reflect the strain and tension of the flexible device. The linear relationship between tensile strain and tensile force is the foundation of the practical application. The excellent linearity can not only calculate the tensile strain size through the response value, but also calculate the tensile force. As one of the most important performance evaluation parameters of the sensor, the detection limit largely determines the application range and application value of the sensor. The flexible strain sensor detection limit is defined as the ability to detect the minimum strain change of the object under test, significantly different from the background signal. Through the test and analysis of the prepared strain sensor, it is found that the device still has good responsivity and excellent stability under 0.1% minimum strain. In addition, as one of the most important performance evaluation parameters of the sensor, the response time of the strain sensor is usually defined as the time required for the sensor to reach the maximum value after the test amount changes by one step. It can be clearly seen from Figure 14 that the response time of the flexible strain sensor is less than 0.6s. This result further indicates that such devices not only have great sensitivity, but also can quickly detect small strains. In order to further verify the practical application value of this kind of device, the flexible strain sensor prepared in this paper is closely attached to the joints of human fingers, and the dynamic response of the device under the minimal strain of the finger is measured. The test results are shown in Figure 15. It can be seen from the Figure that during the bending of the finger, since the flexible device is closely attached to the joint of the finger, the device undergoes a slight deformation as the finger joint is bent, resulting in an increase in the resistance value of the device. By analyzing the measured resistance response data, it is found that the resistance response of the device is almost unchanged and has excellent repeatability. These results are a good proof of the composite film strain sensor prepared by the layer-by-layer self-assembly process. Has a unique advantage and use value.
4. Conclusion
In this paper, five kinds of samples were prepared by adjusting the mass percentage of graphene oxide doping (0wt%, 0.02w%, 0.05wt%, 0.08wt%, 0.1wt%). To show the effect of graphene oxide doping on PDF-HFP film, four kinds of composite films were tested by Fourier transform infrared spectroscopy (FT-IR). The results show that with the increase of the mass percentage of graphene oxide doping, the content of $\beta$ crystal phase in the composite film increases first. The trend of reduction.

The test results show that as the number of self-assembled layers increases, the conductive network in the region becomes more complete. In order to further study the self-assembled layer number and the optimal design parameters of graphene oxide concentration, four kinds of composite films were packaged to prepare flexible strain sensors. For the different strain formation methods, compressive strain test and tensile strain test were performed on all devices. The comprehensive test results showed that the self-assembled 6 layers and the concentration of graphene oxide were 0.5 mg/ml as the optimal parameters. The device exhibits an excellent linearity in the 1%–5% strain range with a minimum detection limit of 0.1% strain, a response time of less than 0.6 s, and a maximum strain factor (GF) of 754. The device has excellent stability and repeatability. Sex, 500 cycles test still has good stability, so it can be used to detect human finger bending in real time. Based on the comprehensive characterization test results and strain test results, the response mechanism of the graphene-based flexible strain sensor is preliminarily explored.

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