Strain Sensing Properties of Graphene/Elastic Fabric

Bayazid Bustami Shaun1, Runxuan Cai3, Xiaojiang Sun1, Chaokun Huang1, Shuguang Bi1,2* and Jianhua Ran1*

1 Hubei Key Laboratory of Biomass Fibers & Eco-Dyeing & Finishing; Key Laboratory of Textile Fiber & Product (Wuhan Textile University), Ministry of Education, Wuhan Textile University, Wuhan 430200, China
2 State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China
3 Department of Biochemistry and Molecular Biology, University of Massachusetts Amherst, Amherst, 01003, USA
Email: SGBi@wtu.edu.cn; JHRan@wtu.edu.cn

Abstract. The smart fabric is a new material that began to develop in the 1990s, and on the basis of the nature and function of original material, it joined the features of intelligent perception. On the performance, intelligent fiber can sense the changes of heat, light, chemistry, mechanical, temperature, and electromagnetic, then react accordingly. For smart textiles, the sensor is the core part, now most commonly used micro/nano strain sensor are using silicon and zinc oxide and others inorganic as main material. But inorganic materials have limited deformation ability, once deformation occurs, the sensor will be strictly damaged. So, the development of flexible, high sensitivity, wide range of strain of the flexible intelligent fiber strain sensor has a very important application prospect. For the stretch-able sensor, the prepared conductive material must be placed on the substrate of the flexible polymer. In this paper, graphene is used as conductive material to construct an orderly conductive layer. Waterborne polyurethane was used as dispersant and adhesive, then strengthen the interface between the layer of conductive material and elastic fabric binding force, and finally prepare a kind of high sensitivity, wide strain range, stable performance and high elastic intelligent fibers.

Keywords. Graphene, waterborne polyurethane, strain sensor, smart fabric, composite.

1. Introduction

From nineteenth century, progressive changes have been happening at an extraordinary rate in numerous fields of science and innovation. The investigation of the historical backdrop of textile and clothing follows the advancement, use, and accessibility of fashion and textiles over mankind’s history [1, 2]. The advancement of smart materials gives another approach to functional textiles. For smart textiles, the sensor is the core part. The acknowledgement of the intellectual textile recognition work relies upon the sensor [3]. Smart materials can likewise be ordered relying upon their function and capability as passive smart, active smart or very smart [4]. Materials, for example, metallic, optical fibers and conductive polymers might be incorporated into the textile structure, in this manner providing electrical conductivity, sensing capacities and information transmission [5].

Carbon nanotube, also called, nanoscale hollow tubes made up of carbon atoms is known for genuine nanotechnology which can be controlled chemically as well as physically in fruitful ways [6, 7]. Graphene’s structure is flat honeycomb lattice. Construction of the structure is by a single layer of carbon atoms, that combined by a backbone of overlapping sp² hybrids bonds [8]. Researchers have
been driven to build the sensitivity utilizing various types of strategies since the first graphene-based strain sensor was invented [9]. There are numerous kinds of graphene. Genuine Graphene is just a single atomic layer thick (frequently known as monolayer) and exists ordinarily as a film yet it tends to float off the substrate and by redepositing onto another substrate or utilized in its isolated structure [10]. Preparation of graphene can be done by mechanical exfoliation method [11], Liquid Phase Stripping Method [12], Chemical Vapor Deposition [13], Oxidation-reduction method [14] and many other methods [15]. Flexible wearable electronic devices received considerable attention and enabled higher significant in the advancement of future applications such as energy harvesting, chemical, and physical sensors and actuators [16, 17].

Strain sensors have been intended for application territories in which it is applied to measure the deformation because of outer forces following up on effectively existing, passive components [18]. The use of strain sensing systems for the applications of personalized healthcare [19, 20], military and security [21], fashion and lifestyle purposes are gradually increasing. The innovation of this work is to design a high-elasticity intelligent fiber, fully exert the functionality and modification of graphene and the disperse ability and bonding of WPU, and explore the orderly arrangement and electron transfer of conductive sheets on the surface of elastic fibers. WPU is selected as the dispersant and binder of GO to prepare a composite coating of dispersed and stable GO nanosheet and WPU solution. The composite system can not only impart strong mechanical properties and thermal stability to the composite, but also able to give the material a good elasticity. The addition of graphene not only enhances the tensile strength of the smart fabric, but also imparts electrical conductivity.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Graphite powder (Graphite), Potassium permanganate (K$_2$MnO$_4$), 99% Hydrogen peroxide (H$_2$O$_2$) were from Sinopharm Chemical Reagent Co. Ltd. 98% Concentrated sulfuric acid (H$_2$SO$_4$), 36% Hydrochloric acid (HCl) were from Wuhan Operation Fine Chemical Co. Ltd. Chemically pure anionic waterborne polyurethane (WPU) was self-made in the laboratory. Self-made Deionized water was used throughout the experiments.

2.2. Preparation of Graphene Oxide (GO)

In this experiment, the improved Hummers method was used to prepare graphene oxide. Graphite powder in to concentrated sulfuric acid with the addition of potassium permanganate to the reaction solution while keeping the temperature at 20 °C. Then transfer the reaction system to a definite temperature in an oil bath and heat and stir for half an hour. Deionized water was then added thereto and the temperature was raised and stirred for 15 min. Hydrogen peroxide solution (30%) was added to make the color of the solution change from black to yellow. The mixed solution was filtered and washed with a HCl solution to remove metal ions. The filtered solid is dried and added water to prepare a graphite oxide solution. Purification was done by dialysis membrane separation for one week to remove metal ions without washing residue. Finally, the dispersed GO solution was diluted, stirred overnight and sonicated to peel the GO into a single layer, and then centrifuged to remove non-monolayer GO.

2.3. Preparation of Reduced Graphene Oxide (rGO)

After determine the solid content of the GO solution, three dry film-formed GO films were taken out from the bottom of the small beaker, and the GO film was reduced by a thermo-pressure reduction method. Firstly, the hot press is preheated to 150 °C, and the prepared GO film is sandwiched between two high temperature resistant protective sheets of silicone paper, then placed on a heating table, and the pressure plate is pressed to fix the film, and the film is kept at a constant temperature of 150 °C. for 10 min. Then stopped heating, loosen the hot-pressed platen, wait for the temperature of the hot
press to drop to room temperature, remove the silicone paper, and carefully remove the obtained rGO film from the protective film of silicone paper. The remaining sample film is divided by the same method. The reduced graphene oxide film prepared by heating to 180 °C, heating for 10 min and heating to 200 °C, heating for 1 min, 5 min, 10 min was properly stored for subsequent characterization tests.

2.4. Preparation of GO/WPU Composite System

The prepared GO and WPU solution are mixed and dispersed according to the dry weight ratio of 5:5 by ultrasonic dispersion for 10 min.

2.5. Design and Preparation of Flexible Strain Sensor

Most commonly used micro-nano strain sensors use inorganic materials such as silicon and zinc oxide as the main materials [22]. This paper selects WPU as a flexible substrate, which has strong elastic and elastic deformation ability [23], and is made of a thin film with a flexible substrate. WPU is poured into a film-forming mold, placed in a 50 °C warm blast oven, and then completely dried to form an elastic film, and then taken out, and the GO/WPU mixed dispersion is uniformly sprayed to the prepared elastic film and naturally dried at room temperature, and after the mixed liquid is completely bonded to the elastic film, it is subjected to hot pressing to a different temperature by a hot press to obtain an elastic film attached to rGO/WPU, and then used four probes and a multimeter to test their electrical conductivity. The uppermost layer is an elastic film made of WPU. As a flexible substrate, the middle layer is a reduced material of rGO/WPU composite material with a conductive material interposed in the middle, and the lowermost layer is also a WPU elastic film. It is the “sandwich” model of flexible sensors, as shown as figure 1.

Figure 1. Schematic diagram of “sandwich” model of flexible sensors.

3. Characterization and Performance Testing of GO and rGO

Fourier transform IR (FTIR) is mainly used for the identification of functional groups on the surface of GO and rGO. The experiment uses the method of tableting to form a film of GO, rGO (hot pressed to reduce the film of different time and temperature). All membranes were prepared for scanning, and scanning tests were carried out under the conditions of a wave number range of 4000-600 cm⁻¹ and a resolution of 4 cm⁻¹. Thermogravimetric analysis (TGA) test was taken under a nitrogen atmosphere at a temperature increase rate of 10 °C/min from room temperature to 800 °C. X-ray diffractometer had scanning range 10-80°, test voltage 40 kV, test current 40 mA. The prepared GO/WPU and rGO/WPU elastic film were clamped on both ends of the elastic film with a holder at a clamping distance of 5 cm, and the predetermined elongation was 50%, 100%, and 150%. After stretching, it is stagnant for one minute, and then the resistance value of the elastic film with the initial distance of 1 cm is measured by a multimeter. After the measurement, the elastic mold is naturally restored to the original length, and then repeatedly stretched 3 times according to the above procedure, respectively.

4. Result and Discussion

4.1. GO/rGO Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Figures 2 and 3 are rGO infrared spectra of GO and different degrees of reduction. Where a is the spectral line of rGO with a reduction temperature of 200 °C and a reduction time of 10 minutes,
denoted as rGO-200 °C-10 min, the same b is rGO-200 °C-5 min, c is rGO-200 °C-1 min, d is rGO-180 °C-10 min, e is rGO-150 °C-10 min, f is the infrared spectrum of GO. In figure 2, the telescopic vibration wave at 1049 cm\(^{-1}\) can be clearly observed, and then the original image is enlarged to obtain a partial enlarged view of the range of 900-1200 cm\(^{-1}\) in figure 3, and the 1049 cm\(^{-1}\) can be clearly seen. The stretching vibration peak of the CO single bond, and as the reduction temperature increases from 150 °C to 200 °C and the reduction time increases from 1 min to 10 min, the CO stretching peak becomes weaker and weaker, indicating that the oxygen-containing functional groups are less and less, and the temperature is higher. The higher the degree of high reduction, the greater the oxygen-containing groups of GO are reduced.

4.2. GO/rGO Thermal Weight Loss (TGA) Analysis
The proportion of GO, rGO oxygen-containing groups can be known by thermogravimetric analysis. It can be seen from figure 4 that both GO and rGO will have different degrees of thermal weight loss. The higher the degree of reduction, the less the thermal weight loss. In the figure, a is GO, and it can be clearly seen that compared to rGO, GO produced by Hummers contains many oxygen-containing groups and is light in weight at high temperatures. There is only 10% weight loss before 150 °C, and the main weight loss stage of GO between 150 °C and 200 °C, the weight loss is about 50%, b is rGO, its inertia is stronger than GO, and the weight loss is less, in the main weight loss stage. Only 30% of the weight loss, wherein the f curve is rGO reduced at 200 °C for 10 min, the degree of reduction is the highest, so the thermal weight loss is the least, only weight loss 10%.

4.3. GO/rGO X-ray Diffraction (XRD) Analysis
Figure 5 shows the XRD patterns of GO and rGO. It can be seen from the figure that the rGO curves e and f with higher degree of reduction show sharper and higher intensity peaks around 25, which is the characteristic diffraction peak of graphite. The highly crystalline structure of graphite has a high degree of reduction at 200 °C. The characteristic peak of graphite oxide GO appears around 20, it can be seen that the characteristic peak of GO is not very sharp compared with rGO, and the peak intensity is not high, indicating that the originally highly ordered graphite crystal structure of GO prepared by Hummers method has been after destruction, the crystal structure was reconstructed after reduction, and the obtained rGO was close to the diffraction peak of graphite.
4.4. Flexible Strain Sensor Performance

4.4.1. Conductivity. The reduction degree of GO and rGO was compared by infrared spectroscopy, thermogravimetry and X-ray diffraction. It can be seen that the degree of reduction was the highest at 200 °C, and the best time was obtained when the reduction time was 10 min. Then test the sheet resistance of GO and rGO with four probes. The test results are as follows:

| Sample            | Resistance R□ | Test effect |
|-------------------|---------------|-------------|
| GO                | 737.5 kΩ/□    | Unstable    |
| rGO-150 °C-10 min | 560.4 kΩ/□   | Unstable    |
| rGO-180 °C-10 min | 434.9 kΩ/□   | Stable      |
| rGO-200 °C-1 min  | 553.7 kΩ/□   | Unstable    |
| rGO-200 °C-5 min  | 3.816 kΩ/□   | Stable      |
| rGO-200 °C-10 min | 228Ω/□       | Stable      |

It can be seen from table 1 that the temperature rises from 150 °C to 200 °C, and the resistance value of the reduced graphene oxide is decreasing. The decrease from 737.5 kΩ/□ to 228 Ω/□ indicates the conductivity of rGO. The better, the conductivity is the strongest at a temperature of 200 °C and a reduction time of 10 min.

4.4.2. Strain Sensing. In the performance test of the previous experiment, the resistance values of GO/WPU and rGO/WPU elastic film stretched to different elongations were roughly tested with a multimeter, and then the resistance values under different elongation conditions were as follows:

It can be seen from figure 6 that the larger the elongation of GO/WPU or rGO/WPU, the larger the measured resistance value, indicating that the conductive network of the elastic film is destroyed and the resistance value is changed after being stretched by external force. Large, the conductivity is deteriorated, and the sensitivity is lowered. The rate of change of the resistive film of the reduced composite film is smaller than that of the unreduced film a, indicating that the reduced elastic film re-
constructs the conductive layer, and the resistance change rate is not very good despite the tensile external force. Large, the sensitivity range is wider.

Figure 6. Relationship between the change of elongation and resistance of GO/WPU and rGO/WPU.

5. Conclusion
The GO produced by the Hummers method can be stably dispersed in the WPU, but the conductivity is poor. As a flexible substrate for strain sensors, WPU has good elasticity and tensile strength at break, and its elongation can reach 150%. WPU can enhance the adhesion between conductive materials and elastic films, and also acts as a binder to make electricity. The layer is not easy to fall off. The spraying method is more convenient than the coating method to uniformly disperse the GO/WPU mixed solution on the surface of the elastic film. In order to obtain the conductivity of the composite material, the composite film is reduced to 200 °C by hot pressing reduction process, and the reduction effect is reduced for 10 min. It achieves the best and has the best electrical conductivity. After the reduction, the conductive layer is reconstructed on the stretched elastic film to obtain a highly elastic stretch sensing smart fabric with relatively high sensitivity and relatively wide strain range.

References
[1] Schumacher E F 2011 Small Is Beautiful: A Study of Economics as if People Mattered Random House
[2] Taylor L 2002 The Study of Dress History Manchester University Press
[3] Trung T Q, Lee N E 2016 Advanced Materials 28 (22) 4338-4372
[4] Rogers C A 1993 Intelligent material systems-the dawn of a new materials age Thousand Oaks CA SAGE Publications
[5] Alexandre M, Dubois P 2000 Materials Science and Engineering: R: Reports 28 (1-2) 1-63
[6] O’connell M J 2006 Carbon Nanotubes: Properties and Applications CRC Press
[7] Patzke G R, Krumefich F, Nesper R 2002 Angewandte Chemie International Edition 41 (14) 2446-2461
[8] Jose D, Datta A 2014 Accounts of Chemical Research 47 (2) 593-602
[9] Amjadi M, Kyung K U, and Park I, Sitti M 2016 Advanced Functional Materials 26 (11) 1678-1698
[10] Kozicki M N, Barnaby H J 2016 Semiconductor Science and Technology 31 (11) 113001
[11] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A 2004 Science 306 (5696) 666
[12] Tung T T, Yoo J, Alotaibi F K, Nine M J, Karunagaran R, Krebsz M, Nguyen G T, Tran D N H, Feller J F, Losic D 2016 ACS Applied Materials & Interfaces 8 (25) 16521-16532
[13] Zheng G, Chen Y, Huang H, Zhao C, Lu S, Chen S, Zhang H, Wen S 2013 ACS Applied Materials & Interfaces 5 (20) 10288-10293
[14] Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T, Ruoff R S 2007 Carbon 45 (7) 1558-1565
[15] Ren S, Rong P, Yu Q 2018 Ceramics International 44 (11) 11940-11955
[16] Park S H, Lee H B, Yeon S M, Park J, Lee N K 2016 ACS Applied Materials & Interfaces 8 (37) 24773-24781
[17] Pang C, Lee C, Suh K Y 2013 Journal of Applied Polymer Science 130 (3) 1429-1441
[18] Zheng Y, Ding X, Poon C C Y, Lo B P L, Zhang H, Zhou X, Yang G, Zhao N, Zhang Y 2014 IEEE Transactions on Biomedical Engineering 61 (5) 1538-1554
[19] Jovanov E, Milenkovic A, Otto C, de Groen P C 2005 Journal of NeuroEngineering and Rehabilitation 2 (1) 6
[20] Preston J, Edmans J 2016 Occupational Therapy and Neurological Conditions Wiley Online Library
[21] Brynjolfsson E, McAfee A 2014 The second machine age: Work, progress, and prosperity in a time of brilliant technologies WW Norton & Company
[22] Hu B, Chen W, Zhou J 2013 Sensors and Actuators B: Chemical 176 522-533
[23] Sengupta A 1998 Water-based polyurethane polymer, release coating, adhesive tape and process of preparation US Patent 5750630