Research of Graphene in Wearable Sweat Sensors

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Abstract. Wearable sweat sensors have shown significant development prospects in the field of healthcare and health monitoring in the era of excellent health with their advantages of convenient, real-time and non-invasive measurements, with functions such as providing personalized health services for different users. This paper demonstrates the basic structure and preparation of graphene, a two-dimensional (2D) crystalline material, as well as the application of different graphenes in wearable sweat sensors, such as the combination of laser-induced graphene with flexible printed circuit boards in the sensors, which utilizes the material's strong mechanical flexibility and improves the monitoring performance of the sensors to enable them to perform the detection of the concentration of ions, such as Na+ and K+, in sweat with good stability and selectivity. The sweat sensor cycle work process ion selection sensor will produce a water layer, affecting the sensor function; at this time, the 3D gradient porous graphene and the sensor combination, the use of material structure of the hydrophobicity, can improve the efficiency of the ion conduction to the electron, shorten the diffusion distance of the ion, effectively alleviate the problem of the formation of the water layer, and improve the stability and sensitivity of the sensor. The use of graphene in conjunction with wearable sweat sensors is currently a hot field, and this paper selectively discusses the basic structure and preparation of graphene, as well as the research progress of laser-induced graphene-based and 3D gradient porous graphene-based wearable sweat sensors.

Keywords: Graphene, Sweat Sensor, Wearable.

1. Introduction

Wearable sweat sensors are a non-invasive way to monitor the user's health and athletic performance in daily life. For example, sweat is tested to determine the presence of electrolyte imbalances and excessive sodium loss in sweat, which can lead to heat cramps and low-sodium dehydration (associated with headaches, nausea, and muscle weakness) [1].

Wearable sweat sensors are generally worn on the user's body or closely combined with the user's skin. Through the real-time detection and analysis of the user's sweat, the user's health can be detected continuously, rigorously, and accurately, and in the event of abnormalities in the user's body, the user's health abnormalities can be reminded promptly through the cell phone software supporting the sensors, and the user's daily life, exercise and work can be basically unrestricted and unaffected during the whole process. In the whole process, it basically does not limit and affect the user's daily life, exercise and work behavior, thus alleviating to a certain extent the problems brought by the traditional health detection methods, such as the complexity of the detection process, long time-consuming, and relying on medium and large equipment. With the continuous progress of society and the continuous improvement of human living standards, most people pay more and more attention to their health, so the development prospect of wearable sweat sensor is extensive.

Two major requirements for wearable sweat sensors are mechanical flexibility and simple array patterning for multi-parameter analysis [2-4]. Currently, most reported such devices are fabricated by conventional micromachining and screen-printing methods, which usually require complex and expensive fabrication processes such as multi-step photolithography and etching, severely hindering their widespread use. Now, the wearable sweat sensor fabrication field needs a new solution with a simple process, low cost, and excellent usage [5].

In recent years, with the continuous development of graphene materials, more and more flexible wearable sweat sensors have begun to use graphene as a novel material, replacing some precious metals within the sensors with it to reduce the manufacturing cost of the sensors, and at the same time, relying on its excellent electrical, optical, and mechanical properties, to improve the sensors' indexes such as sensitivity, stability, and mechanical flexibility. This paper will introduce the structure and related preparation process of graphene, as well as the application of two kinds of graphene in wearable sweat sensors, in order to provide some theoretical help for the combination of graphene and sweat sensors.

2. Structure and Preparation of Graphene

Graphene, an allotrope of carbon, is formed by bonding carbon atoms on a hexagonal honeycomb lattice array of dots with sp^2 hybridization and has excellent electrical, optical, and mechanical properties. It is the world's thinnest two-dimensional (2D) crystalline material and exhibits excellent prospects for development in materials science, biomedicine, and drug delivery [6]. However, the physical structure of graphene is not strictly 2D. On the one hand, the high crystal mass in graphene seems to indicate the 2D nature of this material, propagating over sub-micrometer distances without scattering electrons [7]. On the other hand, the non-existence of perfect 2D crystals in the free state has been theoretically and experimentally confirmed. However, graphene can avoid this incompatibility because it is generally part of a larger three-dimensional structure, either contained in a three-dimensional matrix or supported by a vast substrate [8].

In recent years, with the development of theoretical research and related technology, the preparation of graphene methods continued to increase according to the different principles of preparation, which can be divided into two preparation methods: one is the graphite for external intervention and the other way is the chemical synthesis method involving chemical vapor deposition and other related methods. The advantages of preparing graphene by using physical methods are that the prepared graphene is structurally intact, and the electrical conductivity is much better. The disadvantages are that the yield is low in a single run, and some physical properties of the final prepared graphene, such as size, cannot be determined. Due to the above characteristics, this preparation method cannot be used for large-scale mass production, product quality and yield cannot be guaranteed, and can only be prepared in the laboratory to meet experimental needs. Another method to produce high-quality graphene is to prepare graphene over a large area chemically, the disadvantage of which is its high cost, cumbersome process, and the difficulty of transferring the graphene generated on the substrate surface.

With the continuous improvement and updating of the standard preparation methods of graphene, many new preparation methods have begun to appear on this basis. Chakrabarti and other scholars proposed the direct combustion method, which successfully obtained a small amount of graphene film, but the number of levels is relatively small [9]. Jiao and other scholars have successfully prepared carbon nanotubes, graphene nanoribbons, and other materials by utilizing the Ar plasma to cut the carbon bond [10]. However, the current method of preparing graphene still has many shortcomings that need to be more refined, such as low yield, relatively cumbersome preparation process, material preparation cost and other shortcomings, the preparation of graphene materials in future development should be more focused on updating and improving the preparation method, and constantly approaching to the direction of large-scale mass production, simplifying the preparation process, enhancing the quality of the material, and greening the environment.

3. Laser-induced graphene in sweat sensors

The process of graphene utilization has been iteratively updated in recent years; through the use of high-power laser pulses, the laser direct writing (LDM) technology can be transformed into a carbonaceous precursor of highly conductive porous graphene; this material with strong mechanical flexibility is known as the laser-induced graphene (LIG) [11,12]. Kong et al. have found that the electrical properties of LIG are not significantly damaged and remain relatively good after 5000 cycles of bending [13]. Today, the production of graphene has evolved to be very diverse, utilizing common materials such as food and paper. Due to the material's several high-quality properties mentioned above, as well as its corrosion resistance and stability, LIG has been widely used in the field of wearable electronic devices related to health monitoring.

The researchers fabricated the entire electrode array, which is miniaturized and flexible, using laser-directed engraving of a polyimide film. Having these features allows for the fabrication of wearable multiplexed sensors that can simultaneously monitor pH, Na+, and K+ levels in sweat and make wearable sweat sensors selective and stable.

Furthermore, in static cycling tests (Figure 1), graphene-based sensors were used in combination with flexible printed circuit boards to demonstrate their real-time sweat analysis capabilities. Moreover, due to the unique advantages of laser-induced graphene technology, such as mass production, simple fabrication, and versatility, graphene-based wearable sensors can be easily scaled up to more physiological signals (e.g., glucose and uric acid, etc.) to enable real-time monitoring of an individual's health status or clinical needs. Moreover, the sensor can also send relevant body data to a customized cell phone application via remote unlimited communication technology for user body condition analysis [5].

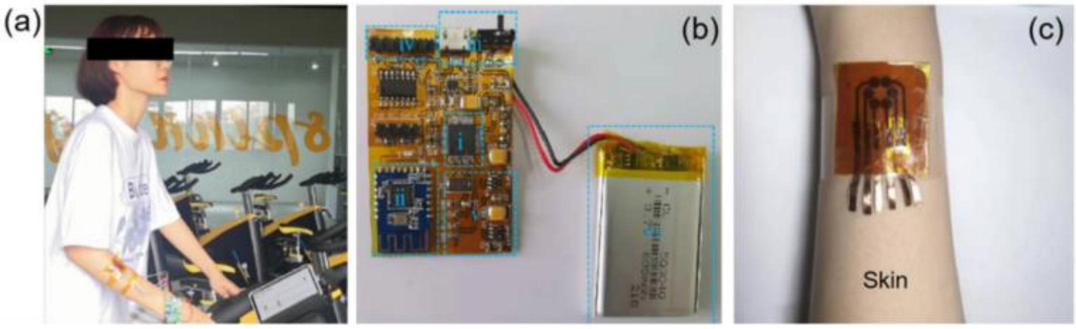

Figure 1. (a): static cycling experiment wearing LIG-based sweat sensor; (b): flexible printed circuit board (FPCB) appearance; (c) enlarged photo of the LIG-based sweat sensor [5].

So, LIG-based sweat sensors first, compared to ordinary sweat sensors, have many advantages, such as LIG material production is relatively simple, can be mass-produced at a lower cost, and LIG as the material used in the manufacture of sweat sensors, has excellent biocompatibility, stability, etc. However, there is also the problem of sensitivity not being high enough. It should be based on the user to develop a personalized measurement program in order to enable the sensors to be a better service for the user.

4. Gradient porous graphene in sweat sensors

Sweat sensors are an essential component of biosensors, and in recent years, wearable sweat detection devices have become a popular area in healthcare and social health. This is because such sweat detection devices are generally small, easy to wear, and can provide more accurate and rich sweat detection. However, there is a limitation of this kind of detection, and some related studies have found that the ion-selective sensors in the detection devices form a water layer during the cycling process, which has a more significant impact on the regular operation of the sweat sensors, resulting in unstable sensor operation and reduced sensitivity [14]. In order to solve the above problems, minimize the formation of the water layer and make the ion conduction to electrons more efficient, a solid contact transducer layer can be embedded between the ion-selective membrane (ISM) and the electron conduction liner.

Kan and other researchers have developed a wearable sweat sensor based on three-dimensional (3D) graphene by using chemical vapor deposition (CVD) gradient porous graphene as a solid connecting layer and utilizing the hydrophobicity of the structure of this material to improve the efficiency of ionic conduction to the electrons, which results in a shorter distance of ionic diffusion, and not only provides the prospect of enhancing the interfacial ECSA but at the same time greatly reducing the formation of the water layer on the ion-selective sensor, improving the working stability and sensitivity of the sensor. As shown in Figure 2, at present, 2D solid contact layers such as screen-printed carbon inks are generally used as materials for solid contact selective electrodes (ISE), which is a more advanced use of the material. How its ECSA forward is limited and the distance of the ion diffusion is larger, compared to the later, graphene materials with 3D gradient porous structure play an enhancement role in the ECSA, and shorten the distance of the ion diffusion [15].

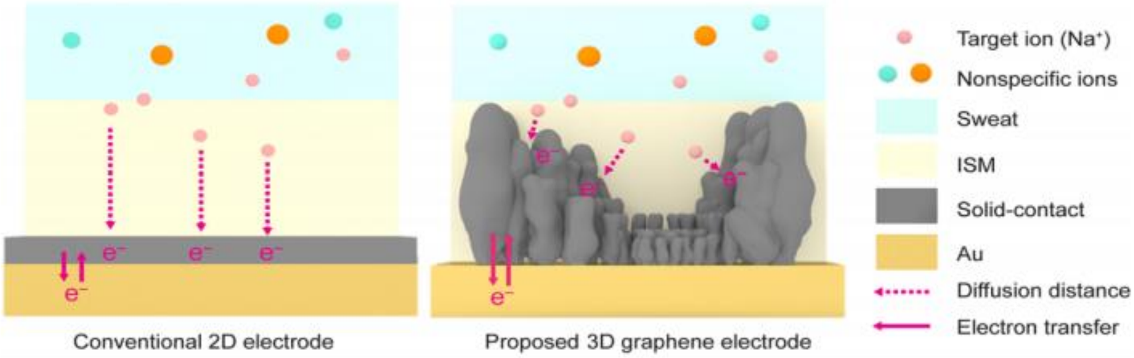

Figure 2. Compared to planar 2D electrodes, the combination of 3D graphene with sweat sensors enhances ECSA and shortens ion diffusion distances [15].

This sweat sensor based on 3D gradient porous graphene material dramatically reduces the water layer formed on the ion-selective sensor compared to ordinary sensors, improves the stability and sensitivity of the sensor itself, enables the sweat samples collected during wearing to be measured accurately and in real-time, and can be altered by changing some of the physical characteristics of the graphene so that the sensor obtains the desired different effects. These sensor characteristics provide technical support for a real-time health detection and analysis system based on wearable sweat sensors.

The above are two typical cases of graphene application in flexible wearable sweat sensors, which effectively alleviate the problems of low sensitivity and poor stability in sweat sensors by utilizing their excellent physical and chemical properties. At present, the theory and experiment of the sweat sensor, a non-invasive biosensor that outputs chemical signals, are still immature. The overall development of the field is still in its infancy. There are still many deficiencies in real-time and continuous health monitoring for users, such as the sensor not being sensitive to the concentration of low-target analytes in the analysis of sweat, resulting in inaccurate measurements or even the inability to measure the situation. As well as, the mechanical elasticity and biocompatibility of the sensor still need to be improved. Therefore, the author believes that the combination of graphene, a novel material, with flexible wearable sweat sensors, has a very great application prospect. The future flexible wearable sweat sensors should be developed in the direction of the low-cost, simplified manufacturing process, high flexibility and high sensitivity. The excellent physicochemical properties of graphene help sweat sensors to be continuously refined in this direction. With the continuous exploration of the relevant theoretical basis and the continuous updating of experimental techniques while insisting on the in-depth study of preparation methods and practical applications, the combination of graphene and sweat sensors will have a broad space for progress and development prospects.

5. Conclusion

This paper demonstrates the basic structure of graphene and related preparation methods and also introduces two typical cases of functional graphene combined with wearable sweat sensors. As an important part of biosensors, sweat sensors have become a hot field in health monitoring and the medical industry in recent years, attracting many researchers with their convenience and non-invasive detection. Although the development of this sensor is promising, at present, due to the relative lack of theoretical research, the relevant technology has not been broken through, resulting in the stability, sensitivity, and mechanical ductility of wearable sweat sensors have not yet reached the mass production standard, and cannot fully meet the user's needs. This paper introduces the application of graphene in wearable sweat sensors. Graphene, by its characteristics such as structural diversity and conductivity in terms of physical properties and stability in terms of chemical properties, can largely solve the two important needs of wearable sweat sensors in terms of mechanical flexibility and simple array patterning for multiparameter analysis. However, the matching technology between graphene sensors and conventional micromachining techniques remains difficult. The interface between graphene devices and back-end circuits needs to be improved for better signal quality and a more comfortable wearing experience, while the preparation process of graphene still needs to be simplified and efficient. There is still a long way before graphene manufacturing technology can be fully applied to real life.

In summary, the excellent performance of the graphene-based wearable sweat sensor in the relevant experimental tests can prove that it can successfully detect more kinds of signals and improve the signal quality compared with the traditional sensors. In addition, it is believed that with the continuous refinement of the relevant theoretical research and experimental technology, the graphene-based wearable sweat sensor will continue to develop in the direction of real-time, fast, accurate, and versatile functions and can be developed through the development of relevant supporting software, so that the sensor can be combined with the machine learning and big data technology to meet the needs of the users and the medical industry.

References

[1] E. Eichner, “Genetic and other determinants of sweat sodium,” Curr Sports Med Rep, pp. S36 − S40, July 2008.

[2] A. Yang, F. Yan, “Flexible Electrochemical Biosensors for Health Monitoring,” ACS Appl. Electron. Mater., pp. 53 - 67, March 2021.

[3] F. Criscuolo, I. N. Hanitra, S. Aiassa, I. Taurino, N. Oliva, S. Carrara, and G. de Micheli, “Wearable multifunctional sweat-sensing system for efficient healthcare monitoring,” Sens. Actuators B Chem., vol. 129017, pp. 328, 2021.

[4] R. Ghaffari, J. A. Rogers, Ray, and T. R, “Recent progress, challenges, and opportunities for wearable biochemical sensors for sweat analysis,” Sens. Actuators B Chem., vol. 129447, pp. 332, 2021.

[5] J. J. Liao, and et al, "Laser-induced graphene-based wearable epidermal ion-selective sensors for noninvasive multiplexed sweat analysis," Biosensors, pp. 397, December 2022.

[6] J. Z. Ding, A. L. Feng, X. D. Li, and et al, “Functionalized graphene composites and their applications in biosensors,” Funct. Mater., pp. 9056 - 9065, 2020.

[7] J. C. Meyer, A. K. Geim, M. I. Katsnelson, and et al, “The structure of suspended graphene sheets,” Nature, pp. 60, 2007.

[8] K. S. Novoselov, D. Jiang, F. Schedin, and et al, “Two-dimensional atomic crystals [J],” PNAS, pp. 10451 - 10453, January 2005.

[9] A. Chakrabarti, J. Lu, C. Jennifer, and et al, “Conversion of carbon dioxideto few-layer graphene,” J. Mater. Chem., pp. 9491 - 9493, 2011.

[10] L. Y. Jiao, L. Zhang, X. R. Wang, and et al, “Narrow graphene nanoribbons from carbon nanotubes,” Nature, vol. 458, pp. 877 - 880, 2009.

[11] R. Ye, D. K. James, J. M. Tour, “Laser-Induced Graphene: From Discovery to Translation,” Adv. Mater., vol. 1803621, pp. 31, 2019.

[12] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, “Laser-Induced porous graphene films from commercial polymers,” Nat. Commun., pp. 5714, May 2014.

[13] D. Kong, M. Kang, K. Y. Kim, J. Jang, J. Cho, J. B. In, and H. Lee, “Hierarchically Structured Laser-Induced Graphene for Enhanced Boiling on Flexible Substrates,” ACS APPL MATER INTER, pp. 37784 - 37792, December 2020.

[14] Y. Lin, M. Bariya, H. Y. Y. Nyein, L. Kivimäki, S. Uusitalo, E. Jansson, W. Ji, Z. Yuan, T. Happonen, C. Liedert, J. Hiltunen, Z. Fan, and A. Javey, “Porous Enzymatic Membrane for Nanotextured Glucose Sweat Sensors with High Stability toward Reliable Noninvasive Health Monitoring,” Adv. Funct. Mater., vol. 1902521, pp. 29 - 33, 2019.

[15] Yeung, Kan, and et al. "Utilizing gradient porous graphene substrate as the solid-contact layer to enhance wearable electrochemical sweat sensor sensitivity," Nano Lett., pp. 6647 - 6654, 2022.