Fabricate Graphenne-based Textile Sensors and Their Applications

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Abstract. Advanced material science, textile technology and electronic information technology have promoted the development of new functional textiles. Especially the emergence of wearable sensors in textile realizes the monitoring of human vital signs in daily life. Its combination with textile can undoubtedly help people to grasp the individual health situation and even the public health status in a timely, accurate and comprehensive manner. Graphene-based textile sensors and their applications were focused on in this paper. In addition, some technical problems on combining of wearable sensors and textile were summarized in the end.

1. Introduction
Introducing the concept of sustainable fashion from the source promotes the clothing industry is aimed at forming a new trinity orientation of science and technology, fashion and green ecology. From the raw materials of clothing to the garment making process and fashion designing should ensure environmental protection and adhere to the concept of sustainable development. Fashion manufactures and designers adopt using new eco-friendly materials and less harmful or harmless manufacturing methods to make clothing. The research and development of graphene-based intelligent wearable textile materials, on the one hand, is consistent with the concept of sustainable fashion. On the other hand, it also realizes the fusion and application of intelligent wear performance in textile materials through scientific and technological methods. Thus, clothing nowadays could detect human vital signs and has multiple functions of keeping warm, fashionable, environment friendly and healthy far beyond the inherent properties. Therefore, the development and application of graphene-based smart wearable textile materials play a significant role in the field of clothing.

2. The classification and application of wearable sensor
In recent years, wearable electronic devices have attracted numerous attention in the world because of their great application value and market space[1-8]. Sensors are the key component of the wearable electronic devices. Wearable sensors were used to detect human vital signals, recognize human behavior and realize human-computer interaction. According to their applications, there are flexible pressure sensor, flexible strain sensor, flexible temperature sensor, flexible humidity sensor, flexible magnetoresistance sensor and so on. Wearable sensors based on flexible substrates, which are divided into implantable[1,2], contact skin type[3-5], and wearable sensors[6-8], are effective carriers in the future wearable field.

The current requirements for flexible wearable sensors include flexibility, stretchability and air permeability, etc.[4,9,10], while smart textiles combine the softness of textiles and the rigidity of traditional sensors. In addition, the trend of wearable sensors move towards more sensitive,
miniaturized and integrated, so that makes it possible to combine the nanomaterials, yarn forming and modern weaving technology to produce advanced intelligent textile sensors with real-time capturing and recognizing ability in multi-dimensional positions. It’s of great significance to health data collection and bring new changes in clothing field.

Nowadays, wearable sensors based on the textile materials have been greatly developed and applied, especially in the fields of exercise monitoring, personalized medical treatment and rehabilitation training. But there are still many problems existed. For example, the materials of smart sensors need to be explored more deeply, the volume needs to be further reduced, the flexibility and sensitivity need to be further improved, and the diversification of functions needs to be further developed. The team of Fei Li[11] made a major breakthrough in the research of flexible fabric intelligent wearable sensors. The team adopted the noodles squeezing method, which was to fill the syringe with multi-walled carbon nanotubes (MWNTs) and polydimethylsiloxane (PDMS) mixture and squeeze through a sieve with micron aperture, to produce MWNTs/PDMS fiber material with adjustable conductivity and size and to develop functional chips that can recognize and transmit finger flexibility, gestures and temperature. Finally, the fiber sensor was woven into gloves and an electronic chip was integrated on the gloves. Gestures, temperature and other signals were output through the display screen, audio and Bluetooth and other carriers. This multifunctional intelligent glove would be used in the fields of rehabilitation training, temperature recognition and standardized teaching of sign language.

3. Research and application of graphene-based sensors

In 2004, Geim and Novoselov[12] produced single-layer graphene nanosheets for the first time using graphite as raw material and transparent tape as auxiliary micromechanical stripping tool, which set off a worldwide upsurge of research on graphene. The macroscopic assemblies of graphene mainly included one-dimensional (1D) graphene fibers, two-dimensional (2D) graphene films, and three-dimensional (3D) graphene framework structures. Especially, 2D graphene films showed outstanding advantages in electrical conductivity and mechanical properties and were widely developed and applied in materials science and other fields. The research and development of graphene has achieved the breakthrough of technology in materials and greatly promoted the development of intelligent wearable systems.

Graphene has become the most important new material for smart wearable systems attributed to the typical 2D lamellar structure, good transparency, strong thermal conductivity, and outstanding mechanical properties as well as excellent characteristics in terms of flexibility and conductivity. These features of graphene was applied to the development of intelligent wearable systems, such as pressure sensors[13-15], temperature sensors[16], biosensors[17], strain sensors[18], etc, and further in human vital signs feature monitoring, human action recognition, sweat analysis and other aspects.

3.1. Graphene-based pressure sensors

Due to the advantages in human-computer interaction, biomedical detection, human body action recognition and so on, flexible pressure sensors[13-15] has caused an upsurge in academic research. Generally speaking, flexible pressure sensors were divided into capacitive type, piezoresistive type and piezoelectric type according to different sensing mechanisms. Since graphene films did not have piezoelectric properties[14], they were mainly used as conductive layers of electrodes in pressure sensors and are rarely used directly in the study of pressure sensors. Graphene-based thin film pressure sensors improves the sensitivity, linear range and detection range. They were used for pulse signal collecting, sound signal recognition, plantar pressure detection and so on.

3.2. Graphene-based temperature sensors

Human body temperature is an important health indicator, which reflects a person's health to a large extent. The body temperature rises when the human body suffered from infection, while it falls down when the body function gets imbalanced or the blood circulation becomes worse. Timely detection of
body temperature can help people to detect physical problems in advance. The development and application of graphene-based temperature sensors help people to monitor body temperature through daily wearing. It’s reported that the graphene based temperature sensor\cite{16} was fabricated using graphene as a heat sensitive material, silver nanowires as a conductive electrode, and PDMS as stretchable substrate. This temperature sensor was able to work properly under 50% tensile strain and 360° distortion.

3.3. Graphene-based electrochemical biosensors

Nowadays, with the improvement of people's living level and the enhancement of medical prevention consciousness, especially the increase of medical cost and the problem of population aging, disease prediction and analysis and individualized medical treatment are urgently needed. Therefore, wearable biosensors of graphene-based films emerge to meet the universal need and developed rapidly. Instead of monitoring human vital signs by recording and detecting physical signals, biochemical sensor collected relevant information at the molecular level to study the state of human health, such as continuous and non-invasive molecular analysis of human sweat, tears, saliva, blood, respiration, and body fluids to detect human health. the graphene-based thin film biosensor mainly utilizes the large surface area and excellent electrical conductivity of graphene to improve the sensitivity, detecting limit, linear range and selectivity of the biochemical sensor by compounding with functional materials such as gold nanoparticles, gold platinum alloy, glucose oxidase and so on. The previously reported graphene-based biosensors\cite{17} were mainly used to detect glucose, lactic acid, ethanol, uric acid, and K⁺, Na⁺, Cl⁻, PH in body fluid. It is of great significance for the patients with diabetes, gout and other diseases in modern society.

3.4. Graphene-based strain sensors

The development of graphene-based thin film strain sensors is mainly based on the conductivity of graphene. When the graphene sheet is subjected to external forces, the electronic structure of graphene will change accordingly with the tensile stress, and then the conductivity of graphene will change. Compared with traditional metal-based strain sensors, graphene-based thin film strain sensors showed wider detection range and higher detection sensitivity. The research group of Shi\cite{18} has made outstanding contribution to the research and development of graphene strain sensors. The sensitivity of the strain sensors reached 150 and up to 82% of the human strain was detected, which realized the comprehensiveness and accuracy of the detection. The expansion of the detection range of graphene-based thin film strain sensors would help to realize the omnidirectional detection of human motion.

4. Research and development on graphene-based wearable textile sensors

The graphene-based textile wearable sensors exhibited great flexibility, stretchability, air permeability, biocompatibility/biodegradability, which enables it to be integrated with modern textile technology and textiles. At present, the published flexible textile sensors are mainly to embed electronic components into the fabric, weave conductive yarns into the fabric, or modify by attaching conductive films directly or indirectly to the fabric surface. The third one was one of the most preferred method to fabricate the flexible textile sensors.

Coating method\cite{19} repeated infiltration step to obtain a large amount overlaped graphene oxide anchored polymer fibers and then followed by a reduction step to get conductive graphene. Chemical vapor deposition (CVD) is a technology to grow large-area graphene films, which was reported to prepare polyacrylonitrile (PAN) nanofiber graphene (PAN/G) film by Zhang et al. \cite{20}, as shown in Figure 1. PAN nanofibers was elestrostatic spinned on the CVD prepared graphene film and then went through cyclization and a partial carbonization reaction during the annealing process. After being etched and washed, the a-PAN/G film was spread on ultrapure water without other supporting material. Compared with the monolayer graphene film, the PAN/G film can self-standing on water, suspended in air with high transparency and enhanced electrical and mechanical properties. The obtained pressure sensors using with flexible transparent a-PAN/G films as active materials showed
high sensitivity (44.5 kPa$^{-1}$ within 1.2 kPa), low voltage range (0.01–0.5 V), 5500 times loading and unloading cycles with good stability and promising application future in electronic products.

Figure 1. Schematic of the fabrication procedure for a-PAN/G film and its application on pulse detection.

Ding’s Group applied graphene/polyvinylidene fluoride/polyurethane DMF system to prepare polymer nanospheres modified graphene porous network fibers in aqueous phase separation process, which greatly improved the sensitivity of graphene-based fibers. The sensitivity factor is 51 at strain of 0-5% and 87 at strain of 5-8%[21]. Compared with synthetic polymer fibers, silk fibers have good biocompatibility, mechanical stability and large-scale sustainable production, which takes them as the preferred substrate materials for wearable electronic products. Flexible foldable graphene/silk composite paper[22] was developed through vacuum filtration of mixed suspension of graphene oxide and silk fiber, combining graphene oxide with silk fiber and further reduced. The graphene/silk composite paper was carried out as a substrate for glucose sensor. In addition, Zhang and co-authors[23] fed silkworm directly with mulberry leaves loaded with graphene or single walled carbon nanotubes (SWNT), so silkworm can directly spit out the composite fiber of graphene or carbon nanotubes combined with silk protein. These SWNT- or graphene-embedded silk sensors prepared by in vivo feeding had higher tensile strength and higher sensitivity, which captured the subtle changes of vital signs of human body.

Figure 2. (a) Schematic of degreasing cotton pieces soaked in GO solution. (b) conductive rGO cotton and pressure sensors.

Cotton is the most popular clothing material since its more abundance, lower-cost and more environmentally friendly properties. As shown in Figure 2, the conductive cotton fibers modified by reduced graphene oxide (rGO) was prepared, and applied to pressure sensor[24]. The highest sensitivity of the constructed pressure sensor was 0.21 kPa$^{-1}$, and the pressure range scaled up to 500 kPa, which demonstrated a combination of fine sensitivity and broader pressure range. The pressure sensor indicated great performance in real-time monitoring of human physiological signals like pulse, breath rate and speech recognition, boasting great application value in wearable electronics and smart clothing.

5. Limitations of graphene-based textile sensors
To date, a large number of research results also confirmed the high sensitivity of the graphene-based sensors. However, there are many technical problems for mass manufacture need to be solved. As typical clothing, the comfort, resistance to washing and low cost are still subject to further study. For wearable sensing clothing, future research should break through in weaving theory and electronics
assembly technology and combining the two products organically. Additionally, even higher sensitivity, repeatability and flexibility reserve more efforts.

6. Conclusion
In summary, sustainable fashion in the field of clothing has gone beyond the aesthetic point of view. The combination of intelligent wearable textile materials with technology and health is bound to promote the emergence of new fashion ideas. Smart wearable textile sensors are organic integration of smart wearable sensors and textile materials. To date, the research and development of smart wearable textile materials is still in its infancy, so both the research and development of sensors and the preparation of materials need to be further deepened. The research and development of graphene-based wearable textile materials is undoubtedly one of the most important breakthroughs, which will help us improve the quality of flexible wearable sensors and textile materials.

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