Application of Graphene and Its Derivatives in Design of Functional Apparels

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Abstract: In order to meet the growing market demand for functional apparels, for the application of graphene in functional apparels, the methods of combining graphene and its derivatives with apparels are introduced in detail, and the thermal conductivity, antibacterial, hydrophobic and anti-UV properties of graphene are listed. The combination of graphene fiber and textile apparels at home and abroad in recent years in thermal conductivity, antibacterial, hydrophobic and anti-UV are summarized. The cutting-edge applications of graphene fiber combined with textile and apparel in recent years are summarized. The challenges of difficult preparation, high costs and single application of graphene in functional apparel are pointed out, and the prospects of the application of graphene and its derivatives in design of functional apparels are presented to provide new ideas and directions for the research of functional apparel.

Keywords: Graphene; functional apparel; application progress

1. Introduction

Functional textile materials, in addition to their basic functions, also have one or several other functions such as antibacterial, hydrophobic, flame retardant, mothproof, anti-ultraviolet, anti-virus and so on. The combination of graphene and apparels can enhance the performance of apparels, which can realize "multi-purpose" and enhance the value of apparels, and also open up new ways for the design and innovation of apparels.

Graphene and its derivatives have many excellent properties such as thermal conductivity, electrical conductivity, flame retardant, antibacterial, hydrophobic, etc., which have become a new textile material of great interest and are widely used in the apparel field.

The application of graphene and its derivatives in the textile field has been extensively described, but its application in the functional apparel field has not been reviewed. This paper presents an overview of the application of graphene and its derivatives, a new textile material, in the field of functional apparel in terms of thermal conductivity, antibacterial, hydrophobic, and UV resistance.

2. Preparation and properties of graphene and its derivatives

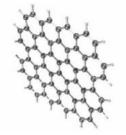


Figure 1: Graphene structure diagram.

As seen in Figure 1, the two-dimensional planar honeycomb-like graphene formed by carbon atoms in the SP2 hybridization mode is extremely thin^[1], linked by C=C covalent bonds, and has excellent mechanical properties; each carbon atom in graphene steps into the PZ orbital with an unbound electron,

while the excellent electrical conductivity of graphene stems from the fact that the PZ orbitals of adjacent atoms are perpendicular to the plane, forming π -bonds in a semi-filled state, and they are able to move freely in the Porbitals.

Graphene is ductile and bendable with high strength. Although it looks fragile, the functionalized graphene is made by oxidation, so the strength of the graphite paper is high. 2020, Lu Yang et al ^[2] conducted in situ tensile tests on large-area monolayer graphene and learned that monolayer graphene has good tensile strength and elastic strain rate, and these excellent mechanical properties make graphene more widely used in the field of functional apparel.

Due to the stable structure of graphene, its derivatives are relatively more active in chemical performance. Graphene can be oxidized to make its derivatives graphene oxide (GO), which has roughly the same structure as graphene, but the surface of GO contains oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH), and epoxy (-CH(O)CH-) ^[3], making it more chemically active and easy to react with other groups. such as reduced graphene oxide (rGO), carboxylated graphene oxide (GO-COOH), and nitroxylated graphene oxide (GO-NO₂). Expanded research on graphene derivatives is beneficial to the innovation and development of new functional apparel materials.

2.1. Graphene

Chao Gao's group made continuous, fine filamentary graphene fibers (GF) for the first time in 2011 by wet spinning graphene oxide (GO) liquid crystals (LCs) in the laboratory.

Zhang Hua et al ^[4] used wet spinning method to disperse and feed acetone solution of graphene and propionitrile-vinylidene copolymer with DMF mixture in the ratio of 1:1, composite graphene onto the fiber surface by coaxial-like spinning process, and then make nanofibers by non-solvent pore-forming method, and the data showed that the antibacterial rate was 83% against E. coli and 87% against Staphylococcus aureus. Yunyu Lai et al ^[5] prepared graphene by a modified Hummer method, added with polyacrylonitrile to a dimethylformamide solution to make a spinning solution, and obtained nanofibers by 16 kV voltage, which had a more pronounced antibacterial effect on E. coli after drying.

Compared with traditional antibacterial materials, graphene has lower biotoxicity and is a good carrier of antibacterial active substances. Based on its more excellent antibacterial effect, the preparation of graphene composite antimicrobial fiber has become a hot spot that is heating up year by year. Therefore, graphene composite antibacterial fibers can be well applied to various textile industries such as home textiles and apparels, and their research should also be developed in the direction of more comprehensive functionality.

2.2. Graphene oxide (GO)

Prof. Chao Gao's team ^[6] produced a high concentration of GO by oxidizing graphite intercalation and diffusing it in water or organic solvents to obtain GO liquid crystal spinning solution, which was solidified and dried after capillary extrusion to form GO fibers.

GO shows good hydrophilicity due to the abundance of oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH), and epoxy (-CH(O)CH-) groups on the surface, while the middle part is composed of C=C and thus shows hydrophobicity, which makes GO a special hydrophobic finishing agent. Tissera et al. ^[9], on the other hand, impregnated cotton fabrics directly into GO dispersion to make graphene oxide/cotton fabrics with more excellent hydrophobicity. Kangkai Liu et al ^[10] used CVD method to prepare carbon nanofibers on the surface of GO films, and then coated fluoropolymers on the surface of these carbon nanofibers to obtain graphene nanoflakes with superhydrophobic properties. With the increasing demand for green environment in the industry, the prospect of hydrophobic textiles prepared from graphene for apparel application becomes more practical.

The GO modification also has good UV resistance properties. Ma Lin et al ^[11] used dopamine hydrochloride and graft copolymerization of aramid with graphene oxide by grafting method to make aramid/graphene oxide modified fibers with improved UV resistance. Kunning Yu et al ^[12] used a modified "sol-gel" method to prepare a hydro-alcoholic mixture of zinc oxide nanoparticles, and then used the conventional "impregnation-drying-baking" method to synthesize zinc oxide on the surface of cotton fabrics, and then used the low-temperature impregnation method to obtain graphene oxide/zinc oxide (GO/ZnO) finishes. GO/ZnO)-finished functional cotton fabric, and the UV resistance of the finished fabric is greatly improved. This provides more options for the development of outdoor functional clothing and special work clothing.

2.3. Reduced graphene oxide (rGO)

Oxygen functional groups on GO were removed by reducing graphene oxide to obtain graphene materials, which are called reduced graphene oxide (rGO). rGO with high reduction was prepared by Zhao Bong ^[13] in 2014 using ultrasound-assisted hydrazine reduction.

Yang Honglin et al ^[14] prepared polyester-based copper nanoparticles/reduced graphene oxide composites by loading copper nanoparticles emulsion and graphene oxide into fabrics by dip-rolling method, and then using chemical reduction of graphene oxide, and the obtained fabrics were tested to have better handfeel, significantly improved hydrophilicity, and good electromagnetic shielding properties. Hou Min ^[15] prepared rGO coating on polyester by combining rGO and MnFe2O4, and then composite molding with textile substrate, and the obtained functional fabric has electrical conductivity and better oleophobicity. Jing Fang et al ^[16] used the reduction group of graphene oxide on the surface of silk fiber to obtain rGO on fabric and improved its UV protection level by optimizing the preparation process of rGO/silk fabric N.R. Dhineshbabu et al ^[17] used a modified Hummer method to prepare rGO nanostructures and coated them on cotton fabric, and it was determined that rGO coated fabrics showed better thermal stability and moisture absorption.

By combining rGO with other two-dimensional materials and treating them with various chemicals to create new compounds, the properties of the compounds can be enhanced, thus making the prepared textile materials more relevant to the needs of functional apparels.

2.4. Functionalized Graphene Oxide

Graphene oxide is of great interest because of its more active chemical behavior compared to graphene, and thus functionalized graphene oxide. The Hong Kong Polytechnic University prepared a silk protein/poly(lactic acid-hydroxyacetic acid) copolymer/graphene oxide microfiber mat using electrostatic spinning method, and the microfiber mat had good protective properties. Shuangquan Lai et al ^[18] prepared carboxylated graphene oxide (GO-COOH) using bromoacetic acid (C2H3BrO2) and prepared GO-COOH modified polyacrylate leather finisher by co-blending method, and the dry and wet rub resistance, folding fastness and adhesion fastness of the coating became better and better with the increase of GO-COOH dosage after being used for leather finishing. Zahid Muhammad et al ^[19] used chloroacetic acid (c-GO) to functionalize GO and manufactured thermoplastic polyurethanes (TPU) films with different concentrations of c-GO by phase inversion technique, and the water permeability of the composite films was improved with increasing concentration of c-GO in the polymerized films.

3. Application of graphene and its derivatives in functional apparel

3.1. Graphene and its derivatives combined with apparel

3.1.1. Physical method

Han Mingyang ^[20] used graphene as a material for wearable electric heating apparel uniformly distributed in a specific carrier to provide additional heat by embedding a resistance wire in the garment and connecting it to a mobile power source for continuous heat generation.

By modifying the graphene aqueous dispersion and adjusting the material weaving process, Green Energy Jiaye Company made graphene flexible heating material and combined it with an intelligent circuit control system to make stable operation in this intelligent heating product under the condition of safe power supply.

Zhang Yichik et al ^[21] used graphene fiber filament and other fibers compound blended to form core yarn, and twisted and woven with each other with winding yarn to form graphene blended yarn, and the health performance and overall use performance of the fabric woven by this fiber were improved.

Bing-Hua Xi^[22] set a wear-resistant upper layer on the upper side of the graphene sandwich and a breathable bottom layer on the lower side, and sewed the graphene sandwich and the breathable bottom layer together, and the graphene-blended fabric had a soft texture and high strength, which greatly improved the use performance of the fabric.

The combination of graphene and its derivatives with clothing by physical method does not change the original good performance of graphene, but also can achieve the effect of making clothing with certain or some functions, while the cost is relatively low, which has certain advantages for the

marketization of functional clothing. In the future, the preparation method of graphene and its derivatives may be simplified by certain means, so as to achieve the purpose of large-scale production and cost reduction.

3.1.2. Chemical method

X. R. Shen^[23] provided a doped graphene coated fabric and its preparation method, which utilizes the excellent adsorption and outstanding electrical conductivity of graphene to coat the surface of the fabric with non-metal doped graphene, so that the fabric has excellent properties such as antistatic and antibacterial.

Haydale graphene conductive ink, which is a conductive carbon paste prepared by using Hdplas process to improve the performance of graphene specifically for heat generating products, has good heat resistance and can be applied to competitive sportswear and other applications.

Xian-Sheng Zhang et al ^[24] used wet spinning method to prepare graphene/regenerated cellulose composite fibers with different graphene content, and the results proved that the filament fibers prepared by this method have weaveability, flame retardancy, UV resistance and antistatic properties. Kai-Kai Sun et al ^[25] prepared graphene/polyurethane modified nylon fibers using surface coating method and demonstrated their sunlight resistance and anti-aging properties.

In addition, Tang et al ^[26] deposited graphene oxide nanosheets on the surface of cotton fabric using vacuum filtration precipitation method and dried them to obtain graphene oxide (GO) modified cotton fabric, which was placed in aniline monomer solution to make cotton fabric with graphene oxide/polyaniline (GO/PANI) functional film. The polyvinyl alcohol/graphene oxide composite cotton fabric with certain electrical conductivity and UV protection properties was produced by layer self-assembly method by Xili Hu^[25] et al.

Combining graphene and its derivatives with apparels using chemical methods can significantly improve the performance of apparels, and combining them with different chemicals can also produce different effects, giving them functions that graphene itself does not have, but because the preparation process requires the use of chemicals, environmental issues after disposal need to be considered in the future.

3.2. Application of graphene and its derivatives for functional clothing

3.2.1. Application of thermally conductive graphene clothing

The good performance of graphene in heat conduction is used in the award ceremonial clothing for the 2022 Beijing Winter Olympics. As seen in Figure 2, The second generation of graphene textile flexible heating material made of the liner can achieve rapid heating effect, when the body temperature is low, through the button hidden under the clothes, you can independently turn on the heating function, 30 seconds to a comfortable temperature. At the same time, the second generation of graphene textile flexible heating materials based on fabric and fiber muscle feel soft and delicate, excellent breathability at the same time, safety performance is also guaranteed.



Figure 2: Winter Olympics ceremonial clothing.

In 2018, with the theme of "Aurora's Dawn", the 19th China International Silk Fair was held in Hangzhou. The highlight was the first chapter of AURORA's large-scale fashion silk scarf show with the theme "Wings of Star Dreams". As seen in Figure 3, The graphene eye mask with the same pattern as the silk scarf was launched at the same time. The eye mask is equipped with graphene heating film, which can heat up quickly and evenly in 3 seconds and release far infrared at the same time, resonating with the body's far infrared to activate cells by penetrating deep into the subcutaneous tissue.

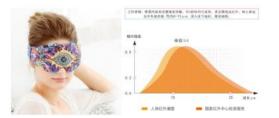


Figure 3: Aurora Graphene Eye Mask

In the Prada Line Rossa Fall/Winter 2018 release, the new thermobonded technology fabric is used for the first time in women's wear and is paired with the LineaRossa red label. The fabric is made of nylon as the main material, with graphene and recycled polyester, making a new padding material capable of achieving the effect of keeping the body at a constant temperature. As seen in Figure 4,This makes the collection more advanced in performance and more innovative in design.



Figure 4: Prada Linea Rossa graphene new clothing

3.2.3. Application of antibacterial graphene clothing

As show in Figure 5, In well-known designer Zhang Bo's WANMAY2022 spring/summer collection launch, new apparels and accessories designed by techniques such as I-fold clashing color splicing and face-bile separation are designed to clash with long lines of large structures with processes and technologies such as self-generating heat devices and fabric recycling, press pleating and 3D fabrics, while contrasting heavy materials with light fabrics. Among them, new graphene fabrics with excellent antibacterial properties, natural materials such as cotton and linen, silk and other antibacterial materials, as well as biodegradable protein fiber blend fabrics are used, which can reflect the brand's environmentally sustainable design concept.



Figure 5: WANMAY graphene new clothing



Figure 6: Peking University Medical and Nursing Costume Exhibition

As in Figure 6,In the 2021 medical apparel show, Beijing Institute of Fashion presented medical apparel made of graphene fiber and other new material fibers, which are softer to the touch and have good moisture absorption, quick drying and moisture wicking, as well as excellent antibacterial and antistatic properties.

3.2.4. Application of hydrophobic graphene clothing

The graphene reversible hydrophobic jacket from Dutch clothing brand Vollebak is designed with heat sealing technology, in which graphene/polyurethane modified fibers and nylon blends are able to conduct and store the body's own heat, and evenly transfer that heat around the human body. As in Figure 7, The jacket has good hydrophobic properties, excellent perspiration and repels bacteria to provide some protection for the body.



Figure 7: Vollebak Graphene Hydrophobic Jacket

3.2.5. Application of UV resistant graphene clothing

As seen in Figure 8, Changzhou Henglibao Nano New Material Technology Co., Ltd. Has improved the method of graphene in-situ polymerization of nylon and developed a nylon fabric containing graphene, which has excellent anti-UV effect.



Figure 8: Changzhou Hengli Bao Nano New Material Technology Co.

4. Conclusion

The prospect of graphene as a new textile material has attracted the attention of many functional apparel researchers, and the excellent properties of graphene and its derivatives are conducive to the diversification and functionalization of apparel materials. Nowadays, graphene and its composites can also degrade the residual printing and dyeing dyes in wastewater for the purpose of optimizing wastewater treatment, as the concept of sustainable development is promoted. However, at the same time, graphene and its derivatives are not easily adsorbed on modified fabrics, and the high cost of graphene preparation still prevents mass production. Despite some problems, the research and application of graphene textile materials in the field of functional apparel is still showing a growing trend, and there is still more room for research on its excellent properties, such as thermal conductivity, antibacterial, hydrophobic, flame retardant, anti-UV, etc., which are worthy of further exploration by the researchers.

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