Preparation and Application Prospect of Graphene Fiber

Mingjian Zhu

High School Affiliated to Nanjing Normal University, China

zhumingjian2019@hotmail.com

Abstract

Graphene has unique electrical and mechanical characteristics. The macro graphene fibers are assembled from nanoscale graphene, which integrates the outstanding properties of micro graphene Therefore, it not only has the flexibility of conventional fibers for textile, but also has the advantages of light weight, molding processing andeasy functionalization. The recent progress in graphene fiber research is summarized, including its controllable preparation technology, functionalization and applications in flexible fiber devices such as actuators, robots, photovoltaic cells and capacitors.

Keywords

Graphene fiber,Controllable preparation,Functional composition.

1. Introduction

Carbon fiber is widely used in life because of its light weight, high mechanical strength and stable performance. But it still has the disadvantages of high cost and high brittleness. Graphene is a new material with single-layer honeycomb structure composed of carbon atoms, which is the construction basis of other dimension carbon materials [1]. Graphene has many unique properties, such as high electron mobility [2], high thermal conductivity [3], good elasticity and stiffness [4]. Therefore, the assembly of graphene into macro functional structures such as fibers is an important way to realize the practical application of graphene.

Graphene has anano sheet structure, so graphene can easily get two-dimensional graphene film by solution filtration method or three-dimensional graphene block by hydrothermal method [5]. Because the size and shape of the chemically synthesized graphene is irregular,and the stack between layers is easy to loosen, it seems difficult to assemble micro nanoscale graphene sheets into macro graphene fibers.

The successful synthesis of graphene fibers in recent years and its important role in some special applications have aroused people's research interest. One-dimensional graphene fibers are not only a supplement to two-dimensional thin films and three-dimensional graphene blocks, but also play an important role in the development of textile functional materials and devices. This paper will give review and prospect on the research status and development of graphene fibers. This paper mainly discusses the controllable preparation, functional modification and application of graphene fibers in non-traditional devices(such as flexible fiber actuators, robots, motors, photovoltaic cells and supercapacitors).

2. Preparation of graphene fiber

2.1 Liquid crystal phase wet spinning method

It has been found that soluble graphene oxide films can form liquid crystal phase and present sheet arrangement or spiral structure, which makes it possible to prepare macro graphene fibers [6].].This liquid crystal structure enables graphene oxide to disperse at high enough concentration for efficient coagulation. Gao et al. [6] used a syringe to inject graphene dispersion into a sodium hydroxide/methanol solution with 5% mass fraction, and made even graphene oxide fibers. Then, the graphene fibers were obtained by chemical reduction of hydroiodized acid. Although the strength of the fiber obtained by this method needs to be improved, this wet spinning method has the potential to produce graphene fibers on a large scale. Yu et al. [7] later proved that graphene oxide suspension could be used as the raw material, and the graphene

fibers could be prepared by chemical reduction after fluid spinning, and the mechanism of the curly-folded structure of graphene oxide fiber was proposed. The wet spinning technology has promoted the development of multi-functionalization of graphene and other organic and inorganic composite fibers. The methods of wet spinning with graphene oxide are shown in reference [8] and [9].

The tensile strength of graphene oxide produced by wet spinning is relatively low, which is related to the internal arrangement of graphene oxide layers in the axial direction of the fibers. In order to solve this problem, the Tour research team used large sheets of graphene oxide (average diameter is 22 μm) as raw materials for wet spinning to synthesize fibers[10]. The results show that the tensile modulus of the fiber is an order of magnitude higher than that of the previous method. Fiber has a 100% high knot rate.

By improving the wet spinning process, Qu research team invented a "double capillary coaxial spinning method", which can continuously produce hollow graphene fibers with controllable morphology [11]. FIG. 1 shows the experimental device and preparation process. Because highly viscous graphene oxide suspension can directly bubble up, the morphology of graphene oxide fibers can be accurately adjusted. For example, instead of the liquid in the inner tube, compressed air can produce hollow graphene "necklace" fibers.

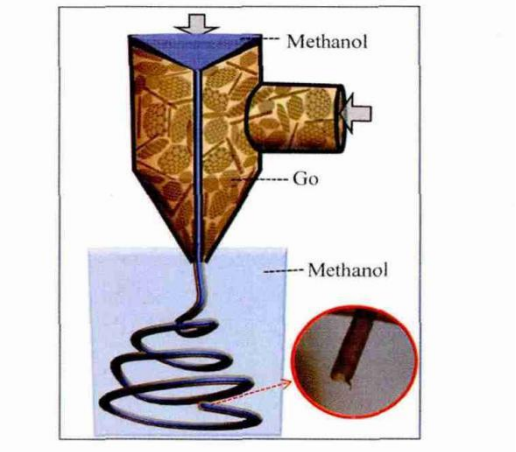

FIG. 1. Preparation of graphene tubes by double capillary coaxial spinning method

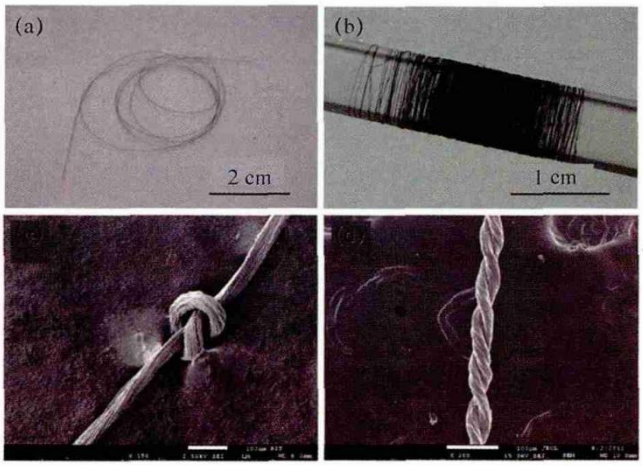

FIG. 2 graphene fibers (a), (b) and knotted (c) winding (d) structures prepared by confined hydrothermal method

2.2 Confined hydrothermal assembly method

As a result of strong π-π interaction between layers, hydrothermal graphene oxide will spontaneously form a network of graphene. The Qu research team has invented a confined hydrothermal assembly

method [12], which can be directly heated by graphene oxide solution in a tubular reactor to make graphene fibers.For example, an 8 mg/mL graphene oxide suspension is injected into the capillary glass tube as a reactor. After baking the sealed glass tube ends in 230 ℃ for 2 hours, it can obtain graphene fibers with morphology consistent with the glass tube. The diameter of the fiber is 5~200 μm which is adjustable, and the length is several meters (figure 2). Due to the strong interaction between graphene layers in the hydrothermal process, the strength of self-assembled graphene fibers is high, reaching 180 MPa.

On the basis of the hydrothermal assembly method, the "double confined assembly method" was developed to realize hollow graphene fibers with controllable diameter [13]. A removable linear template (such as copper wire, etc.) is used as the core, graphene is hydrothermal assembled in the capillary, and finally hollow graphene fibers are obtained by removing the template. Multichannel hollow graphene fibers can be obtained by changing the number of fiber templates.

2.3 Chemical vapor deposition (CVD) assisted synthesis

Zhu research team invented a "direct drawing" method for graphene fibers to be directly extracted by graphene films grown by chemical vapor deposition (CVD) [14]. The method first transfers graphene films from the growth substrate to organic solvents(such as ethanol), and then uses tweezer to extractgraphene with fiber structure from the solvent. In this process, the surface tension and evaporation rate of solvent have great influence on the structure of graphene fibers. The graphene fibers obtained by this method have a high conductivity, reaching about 1000 S/m, but are not suitable for large-scale production. The same team also used CVD method to grow graphene directly on the copper network [15], and then etched the copper network with ferric chloride hydrochloric acid solution to obtain reticular hollow graphene fibers, i.e., graphene fabric. The fabric can be transferred to a polydimethylsiloxane substrate to form a composite film and used in various devices.

2.4 Spontaneous reduction and assembly of graphene oxide

In addition to the above CVD method, hollow graphene fibers can be spontaneously synthesized on copper wires by substrate assisted reduction and assembly of graphene oxide [16]. The method is mild and effective. In this process, the active metal substrate loses electrons and is oxidized into metal ions, while the electrons are reduced from graphene oxide. This method does not need to add any reducing agent,and it can reduce the graphene oxide on any conductive substrate and make it accumulate in an orderly manner on the substrate, such as zinc, iron, copper, inert metal gold, silver, platinum, semiconductor silicon wafer, non-metallic carbon film, and conductive glass (ITO).

2.5 Carbon nanotube yarn

Based on the graphene nanoribbons formed by carbon nanotubes [17], Baughman et al. [18] used chemical drawing method to pull the graphene nanoribbon gauze from the highly arranged carbon nanotube film, and then dried and shrunk into yarn. The original multi-walled carbon nanotubes are placed layer by layer on the polytetrafluoroethylene framework and the graphene oxide nanoribbons are obtained by solution oxidation. Different reduction methods can be used to adjust the functional groups in order to improve the corresponding mechanical, electrical and electrochemical properties. In fact, the graphene oxide nanoribbons and the reduced graphene nanoribbons can be dispersed into high concentrations of chlorosulfonic acid to form anisotropic liquid crystal phase for wet spinning graphene fibers [19].

2.6 Other assembly methods

The above method provides a variety of ways to synthesize various graphene fibers. There are other methods besides this. Kim et al. [20] prepared reduced graphene oxide nanoribbon fibers by electrophoresis assembly method. This method uses graphite needle as the positive electrode and inserts it into colloidal solution containing graphene nanoribbons. Graphene fibers are obtained by adding a constant voltage (1~ 2v) to the electrodes during graphitic needle drawing. This method is similar to the direct drawing method mentioned earlier, but the production rate is low and it is not suitable for large-scale production. Xu et al. [21] used solution self-assembly method to assemble graphene oxide

fibers at gas-liquid interface using graphene oxide solution. The method is dependent on electrostatic repulsion, Van der Waals force, and π-π accumulation. In the process of self-assembly and ultrasonic testing, the sample is gradually transformed from original graphite powder to graphene oxide sheet. It is then transferred to graphene oxide fiber and pure graphene oxide fiber film. Although the mechanism of this method needs to be further studied, its fiber diameter is small (1-2 μm) and its length is several hundred microns, which is a potential simple way for scale production of short graphene fibers.

The preparation methods of different types of graphene fibers are provided in various ways, which provides a material basis for further functionalization and application of graphene fibers.

3. Functional composition

3.1 Composition with functional components

The embedding of functional components in graphene fibers will help to realize its application in important devices such as sensors and electronic fabrics. Whether in situ composite or synthesis and embedding of functional components, graphene fibers provide a good adhesion platform for various unique functional materials. For example, adding ferric oxide (Fe O) nanoparticles in the primary position of graphene fibers can synthesize magnetic fibers [12]. The magnetic fiber has good mechanical flexibility and sensitive magnetic response.

The doping of titanium dioxide (TiO2) nanoparticles is a typical example of first synthesis and then functionalization [12]. The preliminarily synthesized graphene fibers are immersed in the TiO2 suspension and shaked until the TiO2 nanoparticles are embedded in the graphene sheet layer. After drying and annealing, graphene fibers with good photoelectric current response characteristics are obtained. It is shown that electron/hole pairs are generated between TiO2 nanoparticles and graphene sheet layer by light excitation, which proves the application of this material in photodetector, photocatalyst and photovoltaic cell.

To improve the electrical conductivity of graphene fibers, Gao et al. [22] made graphene/metal composite fibers by wet spinning. The specific method is to first mix graphene oxide liquid crystal and commercial silver nanowires, then conduct chemical reduction.

Silver doped graphene fibers have high conductivity (up to 9.3 x 104 S/m) and high current capacity (up to 7.1 x 103 A/cm2). Good mechanical strength and flexibility enable the doped graphene fibers to be used as stretchable wires in flexible circuits.

In addition to high electrical conductivity, the outstanding mechanical properties of graphene fibers are also expected. Generally speaking, the main influencing factors of mechanical properties are the aspect ratio of graphene structures inside the fiber and the alignment degree along the fiber axis. Studies have shown that the mechanical strength can be improved by introducing bivalent ions to form cross-linking between graphene sheet layers [23], and the tensile strength can reach the record value of 0.5 GPa. Further enhancing the strength of graphene fibers and combining graphene sheets with hyperbranched polyglycerol (HPG) adhesive will give them a "brick and mortar" structure [24]. The hydrogen bond network formed between graphene oxide and HPG is conducive to its super-strong properties [25]. The results show that the tensile strength of the biomimetic composite can reach 0.65 GPa and its rigidity can reach 18 MJ $\cdot m^{-3}$, which is the best among shellfish bionics. In addition, polymer grafted graphene oxide fibers have good chemical corrosion resistance, mainly because of their compact layered structure and strong interlayer interaction [26]. The covalent interaction between polymer chains on the surface of graphene oxide sheet and the neat and fixed tendencyavoid the occurrence of local phase separation. And strong interface interaction is also introduced. The polymer chain is then covalently bonded to the nanosheet by free radical in situ polymerization of vinyl monomer.

3.2 Full carbon composite

Graphene is a unique two-dimensional nanomaterial, while carbon nanotube is important one-dimensional material. Combining the two materials may have unexpected effects. Li et al. [27] prepared the mixed yarn of two-wall carbon nanotubes and graphene by after- drawing treatment using chemical vapor reaction. First of all, the thick rod carbon nanotubes are formed in horizontal reactors by chemical vapor deposition method, and graphene is also generated spontaneously in the process of carbon nanotubes. Then the mixed yarn of carbon nanotubes and graphene are then drawn from the polymer and twisted into a fiber. The mechanical measurement results show that the yarn strength obtained by this method can reach 300 MPa and the conductivity can reach 10^5 S - m^{-1}.

Another method is to grow carbon nanotubes directly on graphene fibers. Cheng et al. [28] first obtained graphene fibers doped with Fe3O4 nanoparticles by hydrothermal method, and then used chemical vapor deposition method to grow carbon nanotubes on graphene fibers. Although the mechanical strength of the hybrid fiber produced by this method is relatively low, it can be used to make the electrode of flexible super capacitor for flexible textile. Unlike graphene/carbon nanotube, the composite fiber, there is also a nuclear shell structure made entirely of graphene. This fiber is made by covering graphene fibers with three-dimensional reticulated graphene [29]. Three-dimensional graphene structures have many outstanding properties, such as high specific surface area, high conductivity and good chemical stability. The high conductivity of the graphene fiber as a "core" is well combined with the high specific surface area of the outer 3D graphene, so that the fiber can be used as a flexible electrode in the fiber device.

3.3 Polymer composite

Previous work has shown that carbon nanotubes enhance the strength of polymer fibers more strongly than known materials. Kim et al. [30] combined carbon nanotubes and reduced graphene oxide sheets, embedded textile polymer fibers, and obtained high strength composite fiber materials. They dispersed various proportions of reduced graphene and single-walled carbon nanotubes into a sodium dodecyl benzene sulfonate aqueous solution. They then injected the dispersion into a fluid of polyvinyl alcohol (PVA) with a mass fraction of 5 percent which coagulates to form the composite fiber.

Finally, the composite fiber based on PVA was obtained by methanol treatment to improve the crystallinity of PVA. Graphene sheets are connected to each other to form a network, makingmechanical properties of the fiber very good. Polymer composite fibers have a mass rigidity of 1000 J•g-1, far exceeding spider silk (165 $J•g^{-1}$) and Kevlar silk (78 $J•g^{-1}$). It was observed from the experiments that a partially ordered network of graphene sheets and carbon nanotubes was formed during solution spinning. This composite fiber has the characteristics of being able to weave, wear and deform into high modulus helical springs.

The study of graphene and polymer composites has been very common. Adding a small amount of graphene nanosheets into the polymer can significantly improve the mechanical strength and electrical properties of the material. The planar structure of graphene nanosheets has a large interface area, which is conducive to the interaction between graphene and polymers, so they can be well combined with polymers. In addition, carboxyl groups and hydroxyl functional groups at the scale and edge of graphene oxide nanosheets also play a role in linking graphene and polymer. For example, graphene nanoband/carbon composite fiber spinning can be obtained by electrostatic spinning with polyacrylonitrile (PAN) [31]. The directional shear force produced in the process of electrostatic spinning and the external electric field force interact with the flowing spinning solution. Adding a small amount of graphene nanoribbons can greatly improve the mechanical properties of composite fiber spinning. The production of graphene polymer fibers (including PVA[32], polyvinyl acetate (PVAc) [33] and polyacrylic acid (PAA) [34]) by electrostatic spinning has been widely reported.

4. Special application

4.1 New functional fiber

The flexibility of graphene fibers enables it to be woven into a variety of macro self-supporting textile fabrics (FIG. 3) [12] or blended into cotton fabrics with good electrical conductivity for use in electronic fabrics. At the same time, various special shape devices can be made according to the need, such as retractable spring, transparent, conductive composite film and so on. Because graphene fibers have good conductivity and high elasticity, they can be used on flexible wires. Gao et al. [22] proved that silver doped graphene fibers could stretch 150%. Even with electricity, the stretching process does not damage the fabric structure.

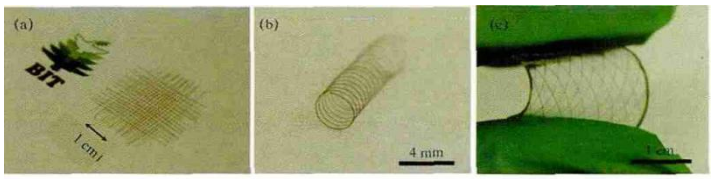

FIG. 3 graphene fiber textile fabrics (a), graphene fiber spring (b) and graphene fiber transparent conductive film(c)

4.2 Graphene fiber actuator

Intelligent materials, which can respond to environmental stimuli quickly and reversibly, and have shape control ability, are attracting increasing attention. Graphene-based materials show many properties suitable for actuators [35~37]. Compared with carbon fiber, graphene fiber is flexible, easy to weave, light in weight and easy to be modified. This makes graphene fibers have greater application advantages in non-traditional flexible devices. Recently, a two-layer graphene/polypyrrole (PPy) electrochemical fiber actuator has been made [38].

It can be used to make tweezers and mesh actuators with multiple arms, and these actuators will have great application prospects in biological research and other fields.

The Qu research team made graphene/graphene oxide (G/GO) asymmetric fibers by laser localization and reduction of graphene oxide fibers [39].The G/GO fiber is very sensitive to humidity. Complex, controllable and predictable deformation is shown in moist environments. In turn, the G/GO fiber can be used to make a conceptual new type of fiber walking robot, which can move between two glass slides. In principle, the walking speed of this concept robot can be accelerated by adjusting the alternating period of relative humidity and the length of the device.

4.3 Graphene fiber motor

In conventional graphene fibers, graphene sheets are often arranged along the fiber direction. Spiral graphene fibers are obtained by rotating and processing the newly spun graphene oxide fiber hydrogel, as shown in FIG. 4 (a) [40]. Due to the existence of oxygen-containing functional groups, the adsorption and desorption of water molecules occur in graphene oxide under a certain humidity, causing the reversible expansion and contraction of graphene layers, which induces the rotation movement of fiber and becomes the graphene motor. Therefore, when the relative humidity changes alternately, the spiral graphene oxide fiber can undergo reversible rotation, as shown in FIG. 4 (b). The maximum rotation speed can reach 5190 $r \cdot min^{-1}$.This twisted graphene fiber (TGF) can be used as a new humidity switch. The humidity-sensitive property of TGF can also be used to make the generator triggered by humidity. That is, through the change of ambient humidity to achieve mechanical movement, and then into electric power. FIG. 4 (c) shows that when the ambient humidity changes, TGF drives the magnet to rotate and induces the current in the copper coil. Although no experimental conditions have been optimized, the generator can generate1 mV open-circuit voltage andshort-circuit current of 40 40 μA .

The self-driven micro motor has always been concerned by the scientific community. Functionalization of hollow graphene fibers can be used to make micro driving motors that move in water [13]. For example, metal platinum nanoparticles are modified on the inner wall of hollow fiber. Because platinum can catalyze the decomposition of hydrogen peroxide to produce a large amount of oxygen, when ejected from the open end, the thrust is produced to make it move rapidly. This graphene fiber concept motor will have important application space in liquid phase drive systems.

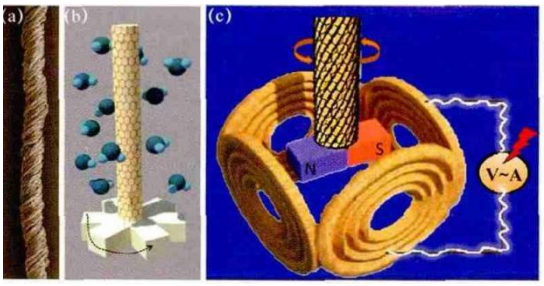

FIG. 4 spiral graphene fibers (a) drive magnets to rotate under changing humidity to generate electric power (b) and (c)

4.4 Linear dye-sensitized solar cell

The good mechanical and electrical properties of graphene fiber make it a new electrode material. Peng et al. [41] invented a new linear photovoltaic device, which uses graphene/platinum composite fiber as the opposite electrode and Ti wire doped with TiO_2 nanotubes as the working electrode. The high flexibility, high strength and good electrical conductivity of graphene fibers enable the maximum energy conversion efficiency of this device to reach 8.45%, far higher than other linear photovoltaic devices.

Using textile technology, these photovoltaic lines can be embedded in clothes, bags and other portable items as a new type of automatic power generation device.

4.5 Graphene fiber supercapacitor

Graphene is a good electrode material for electrochemical capacitors. Conventional supercapacitors are generally bulky, and efficient, miniaturized supercapacitors are important for the development of flexible wearable electronic devices. High conductivity graphene fibers are combined with high specific surface area 3D graphene to form a nuclear shell structure, which can be used as a new electrochemical fiber supercapacitor electrode [29].When coated with H_2SO_4-PVA gel electrolyte, two interwoven fibers are composed of all-solid fiber supercapacitors with good elasticity, which can be made into flexible spring supercapacitors, or embedded into textile fabrics for wearable electronic products (FIG. 5). Recently, Gao et al. [42] developed a coaxial wet spinning method to directly prepare the fiber structure of polymer electrolyte coated graphene/carbon nanotubes. Two strands of the fiber are directly wound to form a fiber capacitor with high electrical capacity and energy density.

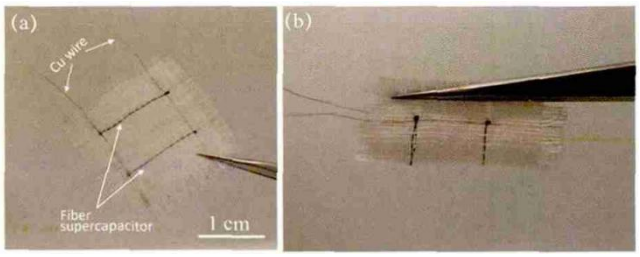

FIG.5Textile fabrics embedded in graphene fiber capacitor.

4.6 Solid phase microextraction adsorbent

Solid phase microextraction (SPME) is simple in operation and easy to be combined with gas chromatography (GC), liquid chromatography, capillary electrophoresis, ion chromatography and other separation technologies, so it is widely used in the analysis of trace organic pollutants. When used with chromatography, SPME can integrate sampling, separation, enrichment, and injection to make the analysis easier. Graphene can be used as a coating in SPME. Chen et al. [43] used it to separate and prepare pyrethroid pesticides from environmental water samples. Compared with commercial fiber products, graphene not only has high separation efficiency for target analytes, but also has great improvement in thermal stability and mechanical stability. Feng et al. [44] synthesized graphene fibers for SPME by hydrothermal method, and then analyzed 5 organochlorine pesticides by combination with gas chromatography/electron capture detector (GC/ECD). The results show that compared with conventional fibers, graphene fibers have better thermal stability and longer life for higher enrichment factors. Because of the interaction of π-π accumulation and hydrophobic effect, graphene fibers are used in capillary gas chromatography by direct immersion, which is more efficient than aromatics in the separation of n-alkanes [45]. In addition, graphene fibers exhibit excellent durability, can be reused more than 160 times, and the separation capacity has not significantly decreased.

5. Conclusion

In recent years, many interesting discoveries have been made through large amount of research on graphene fibers, and many breakthroughs have been made in the synthesis and application of graphene fibers. In particular, the assembly of graphene sheets into macro fibers has promoted the development of intelligent systems and devices. Typical applications include fiber actuators, robots, motors, photovoltaic cells and supercapacitors. So far, the large-scale production of graphene fibers has been mature, which has laid a foundation for the application of graphene fibers in future devices. Moreover, many functional methods of in-situ and post-treatment have given graphene fibers new functions and properties.

Compared with carbon fiber, which has been developed for a long time, the research of graphene fiber is still in its infancy. There is no systematic theory in this field, and there are still many problems to be solved. For example, the mechanical strength and conductivity of graphene fibers need to be improved. Currently, the strongest graphene fibers are bionic graphene fibers with the strength of only 0.65 GPa. As a new type of fiber, graphene fibers still have less mechanical and electrical properties than metal wires and carbon fibers, mainly because graphene sheets are stacked relatively loosely in fiber. As a light-weight conductor, graphene fiber has low conductivity, and adding metal nanowires to it may be a good way to solve this problem. In addition, graphene fibers are composed of graphene or graphene oxide nanosheets. The size, defect, shape and chemical composition of these materials are all uncertain, which greatly influence the properties of the final graphene fibers. For example, graphene fibers made from small sheets of graphene and large sheets of graphene have different mechanical properties. Most of the current studies have focused on new methods for the synthesis of graphene fibers. There is a lack of systematic study on the comprehensive factors affecting the fiber performance. In addition, although continuous production of graphene fibers can be realized through wet spinning, the actual production of high-quality graphene fibers still requires the joint efforts of researchers in various fields. In conclusion, the synthesis of macro graphene fibers from micro graphene provides new opportunities for the development of new materials and devices. With further understanding of the graphene assembly process, high-performance graphene fibers will emerge in the near future, and their new application will be more than just intelligent electronic textile.

References

[1] Geim A K, Novoselov K S. The rise of graphene [J]. Nature Materials, 2006, 6(3): 183-

191.
[2] Novoselov K S, Geim A K, Morozov S V, et al. Two-dimensional gas of massless dirac fermions in graphene[J]. Nature, 2005, 438(7065): 197- 200.
[3] Balandin A A, Ghosh S, Bao W Z, et al. Superior thermal conductivity of single-layer graphene[J]. Nano Letters, 2008, 8(3): 902-907.
[4] Lee C, Wei X D, Kysar J W, et al. Measurement of the elastic properties and intrinsic strength of monolayer graphene [J]. Science, 2008, 321 (5887): 385-388.
[5] Xu Y X, Sheng K X, Li C, et al. Self-assembled graphene hydrogel via a one-step hydrothermal process[J]. ACS Nano, 2010, 4(7): 4324-4330.
[6] Xu Z, Gao C. Graphene chiral liquid crystals and macroscopic assembled fibres[J]. Nature Communications, 2011, 2: 571.
[7] Cong H P, Ren X C, Wang P, et al. Wet-spinning assembly of continuous, neat, and macroscopic graphene fibers[J]. Scientific Reports, 2012, 2: 613.
[8] Jalili R, Aboutalebi S H, Esrafilzadeh D, et al. Scalable one-step wet- spinning of graphene fibers and yarns from liquid crystalline dispersions of graphene oxide: towards multifunctional textiles[J]. Advanced Functional Materials, 2013, 23(43): 5345-5354.
[9] Chen L, He Y L, Chai S G, et al. Toward high performance graphene fibers[J]. Nanoscale, 2013, 5(13): 5809-5815.
[10] Xiang C S, Young C C, Wang X, et al. Large flake graphene oxide fibers with unconventional 100% knot efficiency and highly aligned small flake graphene oxide fibers[J]. Advanced Materials, 2013, 25 (33): 4592-4597.
[11] Zhao Y, Jiang C C, Hu C G, et al. Large-scale spinning assembly of neat, morphology-defined, graphene- based hollow fibers[J]. ACS Nano, 2013, 7(3): 2406-2412.
[12] Dong Z L, Jiang C C, Cheng H H, et al. Facile fabrication of light, flexible and multifunctional graphene fibers[J]. Advanced Materials, 2012, 24(14): 1856-1861.
[13] Hu C G, Zhao Y, Cheng H H, et al. Graphene microtubings: Controlled fabrication and site- specific functionalization[J]. Nano Letters, 2012, 12(11): 5879-5884.
[14] Li X M, Zhao T S, Wang K L, et al. Directly drawing self-assembled, porous, and monolithic graphene fiber from chemical vapor deposition grown graphene film and its electrochemical properties[J]. The Langmuir, 2011, 27(19): 12164-12171.
[15] Li X, Sun P Z, Fan L L, et al. Multifunctional graphene woven fabrics [J]. Scientific Reports, 2012, 2: 395.
[16] Hu C G, Zhai X Q, Liu L L, et al. Spontaneous reduction and assembly of graphene oxide into three- dimensional graphene network on arbitrary conductive substrates[J]. Scientific Reports, 2013, 3: 2065.
[17] Kosynkin D V, Higginbotham A L, Sinitskii A, et al. Longitudinal unzipping of carbon nanotubes to form graphene[J]. Nature, 2009, 458 (7240): 872-876.
[18] Carretero- Gonzalez J, Castillo- Martinez E, Dias- Lima M, et al. Oriented graphene nanoribbon yarn and sheet from aligned multi- walled carbon nanotube sheets[J]. Advanced Materials, 2012, 24(42): 5695-5701.
[19] Xiang C S, Behabtu N, Liu Y D, et al. Graphene nanoribbons as an advanced precursor for making carbon fiber[J]. ACS Nano, 2013, 7(2): 1628-1637.
[20] Jang E Y, Carretero- Gonzalez J, Choi A, et al. Fibers of reduced graphene oxide nanoribbons [J]. Nanotechnology, 2012, 23(23): 235601.
[21] Tian Z S, Xu C X, Li J T, et al. Self- assembled free- standing graphene oxide fibers[J]. ACS Applied Materials and Interfaces, 2013, 5(4): 1489-1493.
[22] Xu Z, Liu Z, Sun H Y, et al. Highly electrically conductive ag-doped graphene fibers as stretchable conductors[J]. Advanced Materials, 2013, 25(23): 3249-3253.
[23] Xu Z, Sun H Y, Zhao X L, et al. Ultrastrong fibers assembled from giant graphene oxide sheets[J]. Advanced Materials, 2013, 25(2): 188-193.
[24] Hu X Z, Xu Z, Gao C. Multifunctional, supramolecular, continuous artificial nacre

fibres[J]. Scientific Reports, 2012, 2: 767.
[25] Hu X Z, Xu Z, Liu Z, et al. Liquid crystal self-templating approach to ultrastrong and tough biomimic composites[J]. Scientific Reports, 2013, 3: 2374.
[26] Zhao X L, Xu Z, Zheng B N, et al. Macroscopic assembled, ultrastrong and H2SO4-resistant fibres of polymer- grafted graphene oxide[J]. Scientific Reports, 2013, 3: 3164.
[27] Zhong X H, Wang R, Wen Y Y, et al. Carbon nanotube and graphene multiple-thread yarns [J]. Nanoscale, 2013, 5(3): 1183-1187.
[28] Cheng H H, Dong Z L, Hu C G, et al. Textile electrodes woven by carbon nanotube-graphene hybrid fibers for flexible electrochemical capacitors[J]. Nanoscale, 2013, 5(8): 3428-3434.
[29] Meng Y N, Zhao Y, Hu C G, et al. All- graphene core- sheath microfibers for all- solid-state, stretchable fibriform supercapacitors and wearable electronic textiles[J]. Advanced Materials, 2013, 25(16): 2326-2331.
[30] Shin M K, Lee B, Kim S H, et al. Synergistic toughening of composite fibres by self-alignment of reduced graphene oxide and carbon nanotubes[J]. Nature Communications, 2012, 3: 650.
[31] Matsumoto H, Imaizumi S, Konosu Y, et al. Electrospun composite nanofiber yarns containing oriented graphene nanoribbons[J]. ACS Applied Materials and Interfaces, 2013, 5(13): 6225-6231.
[32] Wang C, Li Y D, Ding G Q, et al. Preparation and characterization of graphene oxide/poly (vinyl alcohol) composite nanofibers via electrospinning[J]. Journal of Applied Polymer Science, 2013, 127(4): 3026-3032.
[33] Bao Q L, Zhang H, Yang J X, et al. Graphene- polymer nanofiber membrane for ultrafast photonics[J]. Advanced Functional Materials, 2010, 20(5): 782-791.
[34] Jiang Z X, Li Q, Chen M L, et al. Mechanical reinforcement fibers produced by gel – spinning of poly- acrylic acid (PAA) and graphene oxide (GO) composites[J]. Nanoscale, 2013, 5(14): 6265-6269.
[35] Zhang J, Zhao F, Zhang Z P, et al. Dimension- tailored functional graphene structures for energy conversion and storage[J]. Nanoscale, 2013, 5(8): 3112-3126.
[36] Lu L H, Liu J H, Hu Y, et al. Graphene-stabilized silver nanoparticle electrochemical electrode for actuator design[J]. Advanced Materials, 2013, 25(9): 1270-1274.
[37] Liang J J, Huang L, Li N, et al. Electromechanical actuator with controllable motion, fast response rate, and high-frequency resonance based on graphene and polydiacetylene[J]. ACS Nano, 2012, 6(5): 450-4509.
[38] Wang Y H, Bian K, Hu C G, et al. Flexible and wearable graphene/ polypyrrole fibers towards multifunctional actuator applications[J]. Electrochemical Communications, 2013, 35: 49-52.
[39] Cheng H H, Liu J, Zhao Y, et al. Graphene fibers with predetermined deformation as moisture-triggered actuators and robots[J]. Angewandte Chemie International Edition, 2013, 52(40): 10482-10486.
[40] Cheng H H, Hu Y, Zhao F, et al. Moisture- activated torsional graphene- fiber motor[J]. Advanced Materials, 2014, 26(18): 2909- 2913.
[41] Yang Z B, Sun H, Chen T, et al. Photovoltaic wire derived from a graphene composite fiber achieving an 8.45% energy conversion efficiency[J]. Angewandte Chemie International Edition, 2013, 52(29): 7545-7548.
[42] Kou L, Huang T, Zheng B, et al. Coaxial wet- spun yarn supercapacitors for high-energy density and safe wearable electronics [J]. Nature Communications, 2014, 5: 3754.
[43] Chen J M, Zou J, Zeng J B, et al. Preparation and evaluation of graphene- coated solid-phase microextraction fiber[J]. Analytica Chimica Acta, 2010, 678(1): 44-49.
[44] Luo Y B, Yuan B F, Yu Q W, et al. Substrateless graphene fiber: A sorbent for solid- phase microextraction[J]. Journal of Chromatography A, 2012, 1268: 9-15.

[45] Fan J, Dong Z L, Qi M L, et al. Monolithic graphene fibers for solid- phase microextraction [J]. Journal of Chromatography A, 2013, 1320: 27-32.