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Graphene and its application in flexible electronics

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Abstract. With the rapid development of technology and the dramatic improvement of living quality in recent years, traditional electronic technology is increasingly difficult to meet people's needs, and more portable flexible electronic (FE) technology products also stand out. However, with the development of research and application in the field of FEs, people put forward higher requirements for FE products in terms of electronic performance, light transmission performance, and mechanical tensile performance. As a new carbon nanomaterial, graphene has great mechanical, thermal, electrical and optical properties and is an excellent raw material for preparing FE devices, which has broad application prospects. This paper introduces the development of graphene preparation and application and its application results in the field of FEs summarizes the current research progress of graphene in the field of FEs and focuses on discussing and comparing the technical characteristics and development potential of different methods in each application. This review is expected to provide theoretical and data support for the application and preparation of graphene, especially in the field of FEs and provide new ideas for the development of graphene applications in the field of FEs.

Keywords: Graphene, Flexible Electronics, Biomaterial, Polymer.

1. Introduction

1.1. Research background and significance

As one of the three pillars of the development of modern society, material technology plays an increasingly significant role in various fields. With the advancement of The Times, materials science is also developing vigorously. However, while various new materials with excellent properties are widely used, the field of materials is also facing new challenges. The demand for automation and intelligence of equipment in production and life, as well as the trend of miniaturization and portability of equipment under this demand, make electronic materials a clear development direction.

1.2. Graphene

Graphene is a new type of carbon nanomaterial. Because of its excellent mechanical, electrical, thermal and optical properties, graphene has been widely concerned since it was discovered in 2004 and had good application prospects and scientific research value. In particular, it plays an important role in energy, biomedicine, materials science, micro-nano processing and drug delivery. Therefore, it is considered a revolutionary material of the future.

1.3. Flexible electronics (FEs)
FEs technology is a fabrication technology of electronic devices made of inorganic or organic materials on flexible and ductile thin substrates (plastic or metal). It has a wide range of applications in energy, defense, medical, information and other fields due to its unique flexibility, malleability, and efficient and low-cost manufacturing processes.

2. Development of graphene
In 2004, Geim of the University of Manchester led his team to produce graphene with a maximum width of 10 microns by mechanical exfoliation and published a paper in Science. Because of its excellent mechanical, electrical, optical and thermal properties, graphene has aroused a great response in the scientific community, and its discoverer was awarded the 2010 Nobel Prize in Physics.

2.1. Properties of graphene
Graphene is a two-dimensional (2D) honeycomb structure material composed of carbon atoms arranged by sp^2 hybrid orbitals. Bonds connect neighboring carbon atoms in their lattice. Because of the strong bond interaction, graphene has extremely high strength and toughness. After testing, Young's modulus of graphene monolayer is 1.0 TPa. The tensile strength is 130 GPa [1]. Electrons in graphene can move freely in its 2D plane unbound, which plays an extremely important role in its electron transport and other properties. Graphene obtained by mechanical cleavage on top of an oxidized Si wafer usually exhibits 10,000 $cm^2V^{-1}s^{-1}$. Graphene can achieve ballistic transport at room temperature on the millimeter scale, with carrier mobility up to 100,000 $cm^2V^{-1}s^{-1}$. If the external scattering in graphene was eliminated, the mobility could reach 200,000 $cm^2V^{-1}s^{-1}$ due to weak electron-phonon interaction [2]. At a low temperature of 5 K, graphene exhibits carrier mobility as high as 230,000 $cm^2V^{-1}s^{-1}$ [3].

Graphene also has excellent thermal and optical properties. At room temperature, the thermal conductivity is as high as 5,300 $WM^{-1}K^{-1}$, while the visible light absorption rate of the monolayer is only 2.3%, which means graphene has excellent heat dissipation and transparency [4, 5]. Graphene is a carbon substance composed of a single atomic layer, and its basic structural unit is the benzene six-membered ring, the most stable structure of organic compounds, which makes its chemical properties extremely stable and thin, with only a theoretical value of 0.35 nm [6]. In addition, the carbon that makes up graphene is an abundant element on earth, and its raw materials are readily available. It also has special properties (e.g., room temperature quantum ferromagnetism and Hall effect), so its application prospect is wide.

2.2. Application of graphene
Graphene has good electrical conductivity, wide potential window and high electrocatalytic activity for a variety of redox reactions like common carbon materials but also has high electrocatalytic performance for some specific electrical pairs and substrates. Therefore, it can be widely used in electrochemical electrode modification materials, to cure biological macromolecules such as biological proteins or enzymes, and to manufacture specific bio-electrochemical sensors. In addition, graphene could be used as a gas sensor. On the one hand, graphene's unique layered structure gives it a vast specific surface area, which is necessary to make highly sensitive sensors; On the other hand, the unique electronic structure of graphene allows the adsorption of certain gas molecules to induce changes in the electronic structure of graphene, resulting in rapid and drastic changes in its electrical conductivity.

In heterogeneous catalysis, carbon materials are widely used as catalyst carriers. Since the structure of carbon support greatly influences the performance of the supported catalyst, graphene with a more regular 2D structure is an ideal template for the supported catalyst. The good biocompatibility and larger surface area of graphene enable it to obtain a higher drug load as a drug carrier and can be used for targeted transport and controlled release of drugs. Graphene combines the advantages of carbon materials and nanomaterials, and sp^2 hybridization gives it a special layered structure, which makes it have a small size effect, good catalytic activity and large specific surface area, which can greatly improve the specific capacity of batteries. It is an ideal substitute for carbon materials, frequently utilized as electrode materials for energy storage devices. It has broad application prospects in traditional lithium-ion batteries, fuel cells, and new green energy storage devices (secondary batteries and supercapacitors). Moreover, graphene also has a promising future in solar cells. Indium tin oxide (ITO) is widely used as the electrode material for solar cells, but the indium resource is very scarce. Graphene has high conductivity and light transmittance similar to ITO and easy access to raw materials, so it is a potential replacement material for ITO.

2.3. Preparation of graphene

Due to the excellent characteristics of graphene and its broad application value, with the strong demand for scientific research and the market for graphene in recent years, many researchers have conducted much research on graphene's production and preparation methods. At present, the main preparation methods of graphene include mechanical exfoliation, epitaxial growth, chemical vapor deposition (CVD), reduction of graphite oxide (redox method), etc.

Mechanical exfoliation is the method used when graphene was first discovered. Firstly, the grooves are etched on the surface of highly oriented pyrolytic graphite with oxygen and other ion beams, and then the grooves are pressed onto SiO_2/Si substrates with photoresist and roasted, and the excess graphite sheets are repeatedly peeled off with adhesive tape. The remaining sheets were then immersed in acetone, and the thicker sheets were removed by ultrasonic cleaning. The graphene sheets, which were only a few single atomic layers thick, were selected under AFM. This method can obtain graphene with a width of up to a micron with fewer defects. However, it is not easy to get independent single atomic layer thick graphene, and the yield is also very low, which is unsuitable for large-scale production and application.

In epitaxial growth, the surface of a 6H-SiC single crystal is pre-treated by oxidation or H_2 etching, heated to 1,000 ℃ under an ultra-high vacuum to remove the surface oxide, and the sample is reheated to 1,250-1,450 ℃ and constant temperature for 10-20 min after confirmation by Auger electron spectroscopy. This method can produce graphene with 1 or 2 carbon atom layers thick but obtaining graphene with a large area, and uniform thickness is not easy. The results obtained by this method show excellent characteristics such as high carrier mobility, but the quantum Hall effect is not observed [7]. Moreover, the material needs to have good resistance to high pressure, the environment and equipment requirements are high, the process is complex, and the cost is expensive.

CVD can effectively control the preparation of graphene without a granular catalyst. The planar substrate (metal film, single metal crystal, etc.) is placed in a high-temperature decomposing precursor (methane, ethylene, etc.) atmosphere, and the carbon atoms are deposited on the surface of the substrate to form graphene through high-temperature annealing. Finally, chemical etching is commonly used to remove metal substrates to obtain single-layer graphene. The growth of graphene (area, thickness, growth rate, etc.) may be regulated by growth temperature, selecting the type of substrate, the flow rate of precursor and other parameters. The greatest advantage of this method is that large graphene sheets can be prepared, and monolayer or multilayer graphene with an area of up to a square centimeter has been successfully prepared [8].

The redox method can prepare independent single-layer graphene sheets with high output and wide application. During oxidation, inorganic strong protic acid (such as concentrated sulfuric acid and fuming nitric acid) is used to treat raw graphite, and then strong oxidants ($KMnO_4$, $KClO_4$, etc.) are used to oxidize it. The chemical reduction can be used for reduction. Sodium borohydride, hydrazine and other reducing agents can effectively remove various oxygen-containing groups between carbon layers, but the obtained products are prone to defects, and the electrical conductivity cannot reach the theoretical value. There can also be an electrochemical reduction. This method involves placing the substrate coated with graphite oxide sheets in a phosphate buffer solution and contacting the working electrode directly with the graphite oxide sheet film. Alternatively, with the thermal reduction method, graphite oxide can be rapidly heat-treated under a nitrogen or argon atmosphere so that it expands and cracks rapidly and make part of the oxygen-containing group pyrolysis to generate CO_2 at the same time. In addition, there

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are two unique reduction methods: photocatalyst TiO_2 reduction under ultraviolet light irradiation and rapid flash photothermal reduction with a xenon lamp under an N_2 atmosphere [9].

3. Applications of graphene in FEs

FEs mainly refer to the emerging electronic technology in which devices, circuits, substrates and functional systems have bendable, foldable and malleable characteristics. Compared with the traditional silicon-based electronic technology built on a hard substrate, the FE system can be seamlessly connected with the traditional silicon-based electronic system, although the device structure, composition materials and system function are quite different.

With the development of world informatization, production digitization, life intellectualization and health monitoring routinize, electronic products' humanization and personalization are becoming increasingly important. The new features of flexible display, sensing, storage, luminescence and detection align with the application object, bringing revolutionary changes to the electronic information industry. IDTechEx predicts that the FEs industry will reach $301 billion by 2028, making it one of the most promising information technologies in the world today [10].

3.1. Significance and mechanism of graphene applied in FEs

FEs require graphene. The original development goal of FEs is not to compete with traditional silicon-based electronics in high hardware performance, high processing speed and other fields but to achieve low-cost, large-scale production of new electronic devices and products with unique advantages such as flexibility and ductility. Under the concept of "fabricating high transistor with chip characteristics but smaller size performance with large flexible substrates at low cost", carbon nanochannel materials exhibit excellent performance in flexible thin film transistors (TFTs), making the flexible materials can meet or even exceed the performance requirements of traditional electronic devices, which greatly promotes the development of FE technology. FE products are enough to bring revolutionary changes in lifestyle, and today's market has a strong demand for them. It also simultaneously puts higher requirements, and graphene is the perfect solution.

Moreover, graphene is a wonderful material for flexible electrons. As a brand-new kind of carbon nanomaterial, graphene has excellent mechanical, thermal, electrical, and optical properties, which make graphene completely accords with the demand for flexible material: good support and bending to meet the needs of flexibility, high thermal conductivity to meet the needs of heat dissipation, good light transmittance to meet the needs of display. Graphene has greater advantages than traditional materials of FEs, which can greatly improve the performance of FEs and lead a new research direction, so it has great application value. Graphene can be a conductor, semiconductor, or dielectric material in FEs. Specific applications include the fabrication of TFT, electrodes or energy storage devices, flexible conductive film substrates instead of hard substrates and printed circuits.

3.2. Specific applications of graphene in FEs

Graphene is an important material for preparing FE products and has many precedents for its development. Based on the existing research results, the specific application methods and mechanism of graphene as a FE semiconductor material and conductor material are discussed, the characteristics of different preparation processes are compared, the problems faced are discussed, and the development direction prospects.

3.2.1. Graphene acts as a semiconductor material for flexible electrons. In theory, graphene is a semiconductor material with excellent electronic and heat dissipation properties. Its carrier mobility at room temperature is much higher than that of traditional semiconductor material silicon, even higher than that of new ideal semiconductor materials such as indium antimonide and carbon nanotubes. The resistivity is lower than copper and silver, and the room-temperature ballistic effect can be achieved with a large Fermi velocity and low contact resistance. Graphene also has excellent thermal conductivity, the most heat-dissipating of any known material, more than three times as much as a diamond.

However, some obstacles are difficult to ignore in practical application. Firstly, graphene is a special semiconductor with a zero bandgap, where the conduction band and valence band intersect in the Brillouin zone, making it difficult to open and close the band. Although bandgaps can be given to graphene, the on-off ratio can be improved by adsorbing or doping other substances, breaking the symmetry of bilayer graphene and making special structures using quantum confinement and edge effects. These modification methods may lead to unstable performance and loss of bandgap during use or reduce electrical conductivity and limit their availability [11]. Secondly, any carbon-mixed metal can easily cause short circuits, and graphene is difficult to build complex circuits. Due to the accuracy and success rate of preparation, process standards and production costs are too high to make it out of the laboratory for mass production and commercial use. Graphene has become one of the candidate materials to replace silicon in the post-Moore because of its unique advantages as a semiconductor material. However, long-term, in-depth research is needed to replace silicon as a mainstream microelectronics material in the future.

At present, graphene has made some progress as a semiconductor material in the field of FEs, mainly applied to TFT. TFT is a field effect tube composed of a channel, dielectric layer, electrode and substrate material fabricated on the substrate in the form of a thin film. Source, drain and drain are generally composed of metallic materials; Dielectric materials include insulating materials with different dielectric constants, such as SiO_2, Al_2O_3 and polymer materials. Substrate materials include hard (such as glass and silicon wafers) and flexible (such as polymer plastics) substrates. Graphene TFT uses graphene film as channel material, which can meet the corresponding requirements of flexibility, light transmittance and mechanical stretchability according to the characteristics of FE devices. Usually, graphene is separated by a wet etching metal substrate. The process inevitably causes pollution and damage to graphene films, and the high transfer cost also limits the macro application of graphene. Gao et al. invented the electrochemical Bubbling transfer method to transfer graphene non-destructively from the platinum substrate to different substrates. The undamaged platinum substrate can be reused for graphene preparation, making a breakthrough in a large area and continuous transfer [12].

The next step is to build TFT, which can be classified as solid phase, liquid phase, and gas phase, according to the process. The solid-phase method uses a catalyst to grow graphene on a hard substrate and then transfer it to a plastic substrate to make TFT. However, the size of the fabricated flexible devices is limited by the hard substrate, which is unsuitable for the large-scale practical application of FE devices. Generally, the normally-on transistor cannot be completely cut off at zero gate voltage, which causes more energy loss than the normally-off transistor. In the gas-phase method, floating catalytic CVD synthesis is used first, and then the gas phase is directly collected through the filter film and transferred to the substrate to make transistors. It can effectively avoid the pollution and damage of carbon nanomaterials caused by the treatment process in the liquid-phase method. At the same time, it has the advantages of simple, fast, non-vacuum room temperature operation, good continuity, etc., which is an important direction of scientific research and application [13].

3.2.2. Graphene acts as a conductor of flexible electrons. The application of graphene as a conductor material in the field of FEs can be divided into two categories: one is the main body of FE products, which is actively explored to meet the needs of flexibility and transparency, such as flexible transparent conductive materials that replace traditional screens and substrates; The other is a passive material used as an add-on to FE products to cater to existing products, which is used to prepare supporting power supply equipment for deformable electronic equipment, such as electrodes and diaphragms of flexible lithium batteries.

The flexible transparent conductive material is a solution to meet the needs of portable, thin and miniaturized electronic equipment in modern production and life based on the transparent conductive material. As a flexible and transparent conductive material, graphene not only meets the market demand but also has obvious advantages over traditional electronic materials in applications such as displays, film switches, solar cells and so on. It plays a revolutionary role in promoting the development of electronic products. As an alternative to the raw materials of electronic screens, graphene can not only

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meet flexibility needs but also obtain superior performance. The touch screen has no strict requirements on the surface resistance and wettability of graphene transparent conductive film. Graphene has high conductivity, light transmittance, and adjustable work function for OLED screens. Therefore, graphene is considered an ideal material for making flexible screens. In solar cells, ITO is widely used as electrode material. However, due to the scarcity of indium resources and the ITO cannot be bent repeatedly, its application and development are limited. It is necessary to find a flexible alternative material with common raw materials. Graphene meets the requirements and has excellent photoelectric performance and a wide light absorption range. This makes it have great potential application value in transparent electrodes and electron acceptor materials of solar cells and has a good role in promoting the development of OPV.

With the emergence and development of deformable electronic devices, flexible lithium batteries have received extensive attention in recent years. With the continuous development of FE products that can bend and fold, in order to avoid dragging down their portability, it is inevitable to give a clear development direction to the supporting power supply equipment - it is difficult for the electrochemical devices that supply power to electronic products to achieve flexible bending. It is not easy to meet the needs of the future development of FE technology. To develop FE technology, it is necessary to develop new thin and flexible electrochemical energy storage devices that adapt to it. Graphene is an ideal raw material for preparing flexible lithium batteries because of its light mass, thin thickness and good mechanical and electrical properties. Specific applications can be divided into two categories.

One is a non-conductive flexible matrix, which uses polymer, paper and textile cloth as the flexible framework. Although the process technology and production cost are relatively low, due to no contribution to the electrode's capacity, the device's overall energy density is reduced, and there is also a risk of reaction with the electrolyte. Moreover, the flexible framework generally has poor conductivity, which is not conducive to improving the fast-charging performance of flexible batteries. Graphene is used here as an electrode reinforcing phase to improve the conductivity of flexible electrode sheets. The non-conductive flexible framework is used to meet the demand for flexibility and composite into a conductive matrix to support active substances. The other is a conductive flexible matrix. Active substances attach to their structural units to form flexible electrodes, making them the basic element for constructing the conductive network and the support skeleton of the entire electrode. As a cathode material, its function is similar to its application in the non-conductive flexible matrix. Common cathode materials such as $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ are poor electronic conductors. In order to make full use of the cathode material in the charge-discharge process and improve the magnification performance of lithium batteries, conductive agents should be added to the cathode material. Therefore, graphene, with very high electronic conductivity, is an ideal material for a positive conducting agent. However, there are also the following problems: because of its large specific surface area and rich functional vacancies and groups, the electrolyte will break down on the graphene surface during the cycle, forming a solid electrochemical interface film, causing partial capacity loss, so the first-coulomb efficiency is significantly lower than that of the graphite anode; At the initial stage, the capacity decays rapidly, and it is generally stabilized after more than ten cycles; Except for the 0.7V voltage plateau because of the formation of solid electrochemical interface film in the first charge-discharge process of graphene anode materials, there is no obvious voltage plateau; The discharge specific capacity is linear with the voltage, and the charge-discharge curve is not completely coincident, that is, there is voltage lag. Although graphene film is difficult to be directly used as the negative electrode of flexible lithium-ion secondary battery due to the above reasons, if the 2D flexible structure and surface functional groups of graphene can be fully utilized to composite with other materials, defects can be improved to play its unique and excellent performance [14].

In addition, graphene can also be used as a membrane material for flexible lithium batteries. It is mainly compounded with conventional diaphragm materials to improve its mechanical properties and reduce its loss and has good liquid absorption and retention properties of conventional materials. It increases the contact area between the diaphragm and electrolyte, provides electron transfer and ion transfer paths, and speeds up the transmission rate of ions and electrons.

4. Conclusions

It has been 18 years since graphene was first discovered, and significant research progress has been made in many fields. With the input of large-scale production, the related industries have gradually matured. Due to the excellent characteristics of graphene, it will be a hot spot of scientific research for a long time. The key lies in how to meet the low-cost, large-scale and controllable synthesis of graphene. Mechanical exfoliation obviously cannot meet the needs of future industrialization; The redox method's crystal integrity and electronic structure are seriously harmed by powerful oxidants, which limits its application in microelectronic devices. For epitaxial growth and CVD, the production environment, equipment accuracy and other factors seriously limit their large-scale production and application effects. It can be said that any production method is difficult to satisfy people, and technological innovation is urgently needed. One is to explore the properties of graphene and develop entirely new ways of preparing it. The other is to study further and improve traditional methods with potential. Even secondary research on existing results can advance the development of graphene. For example, the redox method has been considered unsatisfactory, but graphene oxide, an intermediate product, is now considered an excellent material for applications such as battery membranes and desalination filters. In order to give full play to graphene's excellent properties and further expand its application fields, new functionalization methods need to be developed and improved, such as methods to control the number of functionalized groups, sites and functional groups, and methods to remove unnecessary functional groups from devices and restore the properties and structure of graphene. At present, graphene is in an awkward situation with strong theoretical performance but unable to achieve the expected practical application, and it is not easy to make technical breakthroughs in some fields in a short period. In addition, most of the major achievements come from the laboratory; subject to production costs, preparation success rate and other factors, commercial mass production is far away. However, once these key problems are solved, the application prospect of graphene is undoubtedly very broad.

FEs technology has the potential to lead to a new revolution in electronic technology, bringing many changes to human production and life. Graphene has become an ideal material in the field of FEs due to its excellent properties and has unlimited possibilities in the direction of semiconductor and conductor materials. However, although graphene material has higher carrier mobility and better chemical stability than organic semiconductors and other materials, its nature as a zero-bandgap material is difficult to find practical applications in digital integrated circuits. Due to the lack of simple, effective, controllable processes and relatively low-cost preparation methods, there is a big gap between graphene and traditional electronic products from the perspective of industrial production alone. However, it is foreseeable that graphene will be combined with printing electronics and other technologies, with the advancement of The Times and technological progress, to play its theoretical advantages and promote the development of social information and intelligence. Applying graphene as a conductor material in FEs is more practical. In recent years, it has been seen to replace traditional electronic devices such as OLED and solar acceptor materials, and flexible transparent conductive materials will become a hot application in this field. Flexible lithium batteries, compatible with FE products, will continue to develop. Based on the enhanced mechanical properties of flexible graphene electrodes, their high deformability will be further developed to adapt to a variety of complex force applications, become the mainstream electrode and diaphragm materials, and eventually achieve fast charging.

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