Research Progress in Preparation of Graphene

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Abstract. Graphene have excellent physical and chemical properties, so the preparation of graphene is becoming the focus of material science research. The main preparation methods of graphene are reviewed, including mechanical stripping, chemical oxidation-reduction, chemical vapor deposition, SiC epitaxial growth, electrochemical and so on. At the same time, the advantages and disadvantages of these methods were discussed. And the development of graphene is prospected.

1. Introduction
Graphene is a new carbon nanomaterial after fullerene and carbon nanotubes and as a dazzling new star in the field of nanomaterials science it has rapidly become the research focus of material science. Graphene is a two-dimensional honeycomb structure formed by the close accumulation of carbon atoms, which can be regarded as a layer of stripped "graphite sheet", as shown in Figure 1. The ideal graphene is only the thickness of a single layer of carbon atoms, (0.34nm). With a thickness of only 1/10000 of the thickness of hair, graphene is the thinnest two-dimensional material in the world, but its strength is the highest of the known materials and 1/10000 times higher than the best steel. The force required to break a single layer of graphene with the same cross section is 200 times that of steel [1].

Figure 1. Typical conformation of graphene single-layer.

Graphene is widely used in biochemistry, electronics, energy storage and sensors because of its high strength, high hardness, light weight, good electrical conductivity and special optical properties.
How to produce high-quality, low-cost, large-scale graphene has become a difficult problem to be solved.

2. Preparation of graphene
There are two main ways to prepare graphene, one is the top-down method of stripping graphite by various physical and chemical methods, and the other is the bottom-up synthesis of graphene by small molecules.

2.1. Mechanical stripping method
Mechanical stripping method is a method to destroy the van der Waals force between the graphite layers of bulk materials by mechanical force or ultrasonic force, to peel off the nano-layer from the upper layer of the main body, and finally to obtain graphene. This is a very simple method and an effective way to get graphene in the first place [2]. In 2004, Novoselov et al [3] repeatedly torn and glued the highly oriented pyrolytic graphite (HOPG), fixed to the platform with transparent tape and transferred the obtained sheet to the Si sheet. Finally, through the characterization of atomic force microscope, it is found that by using this simple method, not only graphene with several atomic layer thicknesses can be obtained, but also monatomic layer graphene can be obtained. Although high quality graphene can be obtained by the above methods, the yield of graphene is low, which is only suitable for laboratory research and is not conducive to large-scale production. With the deepening of research, it has been found that the method of preparing graphene by ultrasonic-assisted liquid phase stripping is more suitable for large-scale production. Jan et al [4] added graphite sheets to polyvinyl alcohol (PVA) aqueous solution for 48 h, and finally obtained graphene with a size of about 1μm and a thickness of 6 to 8 atomic layers. Lin et al [5] successfully separated natural graphite into multi-layer graphene with intact structure in water by ozone-assisted ultrasound. This method does not involve any chemical reagents or organic solvents in the whole preparation process, so it is a green and environmentally friendly preparation technology. It is particularly important that the graphene prepared can exist stably in water for several months without reunion.

2.2. Chemical oxidation-reduction method
The chemical oxidation-reduction method first causes the graphite to react with the strong oxide to form graphite oxide, which weakens the van der Waals force between the graphite molecules, and then obtains graphene oxide by ultrasonic vibration and other techniques. Graphene was then prepared by adding reductant to remove the oxygen-containing functional groups on its surface. At present, the most important oxidation-reduction method is Hummers method [6]. Wang Bin [7] and others improved the use of Hummers method. He first pretreated graphite with K2S2O8 and P2O5, and then oxidized graphite by Hummers method, which significantly improved the oxidation effect. Zhang Dong et al [8] found that it has a great influence on the reduction of oxide particle size by increasing the dosage or reaction time. Ishulun [9] prepared graphene oxide at 70-90℃ by ultrasonic treatment. It was found that the dispersion of graphene oxide was very good. Graphene with different shapes were prepared by adjusting ultrasonic time and frequency. The oxidation-reduction method has some advantages such as simple test method, low cost and large-scale production. However, the oxidation reduction method also has shortcomings: first, the fabrication process will destroy the intrinsic structure of graphene, resulting in incomplete structure; second, the reductant is toxic; third, the purity of graphene is not high.

2.3. Chemical vapor deposition method
Chemical vapor deposition (CVD) is a chemical reaction in which carbon-containing compounds are used as precursors under gaseous conditions and decomposed into carbon atoms, and then carbon atoms are deposit on the surface of substrate or catalyst to obtain graphene [10]. Zhang et al [11] Multi-layer graphene was prepared by CVD method, and Br2 was used to doping multi-layer graphene. The effect of chemical doping of Br2 on graphene band gap was studied. Lin Jun and others [12]
prepared double-layer graphene thin films on the surface of flattened Cu foil with CH$_4$ as carbon source by improved CVD method. The conditions and mechanism of double graphene growth were further studied by controlling the flow rate of CH$_4$ and reaction time. However, in this method, the cooling temperature, annealing temperature and the selection of substrate are difficult to control. Babichev et al [13] graphene with four atomic layer thicknesses was obtained by CVD method using CH$_4$ as carbon source and Si as substrate. Komissarov et al [14] using atmospheric pressure CVD technique (APCVD), with n-decane as precursor, N$_2$ and H$_2$ mixture as carrier gas and polycrystalline copper foil as substrate, graphene with 1 to 2 atomic layer thickness was obtained. The experimental process of CVD method has the characteristics of low cost and uniform particle size, and can prepare graphene with large size and few defects, which can meet the commercial demand of graphene products and is suitable for large-scale production. However, due to the complexity of the CVD process, which is greatly affected by the substrate, high reacting temperature, expensive equipment and other unfavorable factors and so on, its application is limited.

2.4. SiC epitaxial growth method
SiC epitaxial growth method, also known as silicon carbide pyrolysis, is single crystal SiC heated under the high temperature (1000-1500°C) and the silicon atoms on its surface are sublimated. With the increase of time, after the sublimation of silicon atoms, the remaining carbon atoms can be rearranged on the surface of single crystal SiC to form graphene. The quality of graphene is mainly related to the growth matrix, growth conditions (temperature, pressure, protective gas) and high temperature furnace [15].

CHOI et al [16] found that SiC epitaxial growth method can adjust the thickness of graphene lamellar by adjusting the temperature in the preparation process. High quality graphene can be obtained by this method, but the SiC substrate is expensive and takes a long time to prepare. In order to solve these problems, scientists have improved this method. AMJADIPOUR et al [17] found that hydrogen can saturate the Si atom at the top of the substrate by using core level photoelectron spectroscopy and low energy electron diffraction. After heating the sample at 850°C, the hydrogen can saturate the Si atom in the uppermost layer of the substrate. The intercalated hydrogen will be completely desorbed and the buffer layer will appear again, and its structure and properties are similar to those of the reported SiC substrate, which indicates that the Si coated with SiC film can replace the pure SiC substrate for graphene growth to a certain extent. This reduces the production cost compared with the direct growth of graphene on SiC. YANG et al [18] reported an internal and external carbon synergistic method for the growth of graphene on the Si surface of 6H-SiC. This method combines the advantages of SiC-based CVD method and traditional epitaxial growth method (EG). Graphene can be synthesized within 3 minutes by this method and the growth of graphene on 6H-SiC substrate is more than one order of magnitude faster than that of EG method. The growth temperature is 200°C lower than that of EG.

This method has the advantages of large growth area and good product quality, and has gradually become one of the best methods for the preparation of large area graphene, but it needs to be carried out in high temperature and vacuum.

2.5. Electrochemical method
The preparation of graphene by electrochemical method has developed rapidly in recent years. It has the advantages such as green environment friendly, speed high and preparation method simple and so on, so it has attracted the great attention of many researchers. The basic principle of electrochemical preparation of graphene is that the electrochemical reaction on the electrode produces the stripping of the graphite layered structure to obtain the graphene lamellar [19].

Zhu Longxiu [20] prepared graphene by electrochemical method and explored the electrical conductivity. In the experiment, a graphite rod with a distance between 3cm was used as the electrode. 0.6 M Na$_2$SO$_3$ solution was electrolyzed at a DC voltage of 10V for 5hours, during which the temperature was controlled by ice water at 35°C to 40°C. The upper electrolyte was treated by
ultrasonic treatment for 5min after electrolysis. Then the larger suspended particles were removed by centrifuge, and the impurity ions in the suspension were completely removed and dried to obtain graphene. It can be seen from TEM and Raman spectra that the structure of graphene prepared by electrochemical method is regular and uniform, and the conductivity of graphene obtained by electrochemical method is $10^4 S\cdot m^{-1}$, which is much higher than that of graphene prepared by chemical oxidation-reduction method. It should be noted that the graphene prepared by electrochemical method may have the problem of high degree of oxidation, and sometimes it is necessary to reduce the graphene after electrode stripping before using it.

3. Conclusion

Now, the preparation methods of graphene are becoming more and more diversification, after decades of research. Researchers are committed to finding more efficient, convenient and cheap methods to prepare graphene. It is also necessary to improve the quality of graphene while increasing the yield of graphene. However, due to the limitations of various preparation methods hindered the application of graphene research and industrial development, how to find a low-cost large-scale production method of high-quality graphene is still the focus of the current graphene research. In addition, accelerating the functionalization of graphene and the study of graphene composite materials can also broaden its application fields. With the deepening of graphene research by scientists, graphene and its composites will have broad application prospects in the fields of new energy materials, biomedicine, water purification, nanoelectronic devices and so on.

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