

RESEARCH ADVANCEMENTS IN THE AREA OF GRAPHENE AND TECHNIQUES FOR DISPERSING GRAPHENE OXIDE

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Abstract: Graphene has excellent application value in many fields due to its unique lamellar structure. However, its easy agglomeration problem has always restricted the further application of graphene. Therefore, the dispersion problem of graphene has become a hot research issue in recent years. This article reviews graphene oxide and graphene dispersion methods (physical and chemical modification), conducts key analysis based on the dispersion principle, and provides an outlook for future graphene dispersion research.

Keywords: Graphene oxide; Graphene; Dispersion preparation; Physical and chemical modification

1 PHYSICAL METHODS OF GRAPHENE DISPERSION

Graphene is a two-dimensional carbon atom crystal with a unique structure and excellent properties. Its uniform and stable particle material dispersion is crucial to the composite synthesis industry, especially when preparing nanoscale materials. This requirement is even greater. protrude. The structural stability and excellent performance of graphene make it a hot topic in research and application today [1]. Due to the localized characteristics of graphene, the localization of sp² carbon atoms and π electrons makes it chemically inert, and π - π stacking interactions easily form agglomerates. These factors hinder the development of graphene. development and application.

Graphene oxide (GO) has a large number of oxygen-containing functional groups (such as hydroxyl-OH, carboxyl-COOH and ether bond-COC) on its surface, which can be reduced to reduced graphene oxide (rGO) through a disproportionation reaction. Under the influence of oxygen functional groups, GO has good dispersion stability in water or other solvents. There are a large number of oxygen-containing functional groups on the edge of GO and it is extremely hydrophilic, while on the plane it is relatively hydrophobic, making it amphiphilic. However, in non-polar solutions similar to xylene, graphene oxide has extremely poor dispersion due to the strong π - π interaction and strong van der Waals forces between the sheets. The severe agglomeration between these lamellae greatly interferes with the good performance of graphene as a material. Therefore, in order to change these phenomena, surface repair work on graphene oxide is very necessary. At present, people have used various methods to deal with these phenomena in the laboratory, including chemically and physically destroying the interactions between the sheets, and bonding through special functional groups formed by graphene oxide on its surface. Various initiators, monomers and other reactive groups, etc., and on this basis, the edges and surfaces of graphene oxide are grafted with polymers in different ways.

Improving the stability and dispersion efficiency of GO dispersions through covalent or non-covalent methods has attracted more and more attention from researchers, and it also shows broad application prospects. This article starts from the current research status of graphene dispersion, reviews the research methods of chemical modification of graphene, and focuses on analyzing the reaction mechanism of covalent modification and non-covalent modification of graphene.

Among the methods for preparing dispersions, physical methods are relatively low-cost and fastest-acting methods. Through water bath ultrasonic treatment, high shear mixing method, jet cavitation or microfluidization, the graphene sheets are peeled off into single or oligo-layer graphene by physical means to achieve the purpose of dispersion.

(1) Preparation of graphene dispersion by water bath ultrasound. Among the current research methods, the water bath ultrasonic liquid phase exfoliation method is a relatively common method to prepare dispersions, which uses high energy to generate cavitation to stably disperse graphene sheets in the solvent. Chen Kui et al. [2] used ultrasonic liquid phase exfoliation to prepare graphene molybdenum disulfide (MoS₂). They used a mixture of 1, 4-butanediol (BDO) and water (alcohol-water mixture instead of alcohol). Molybdenum disulfide was added, the sample was sealed, and then centrifuged in a water bath for 40 hours at a power of 600 W for 30 minutes at a speed of 10, 000 r/min to prepare a dispersion. Although water bath ultrasonic treatment is low-cost and has low technical requirements, due to uneven energy during the peeling process, defects will be produced in the local groups of graphene due to high temperature and high pressure due to the cavitation effect, further affecting the graphite. Dispersion stability of ene. (2) Preparation of graphene dispersion liquid by high shear mixing method. The high-shear mixing method uses the joint influence of shear force, collision effect and jet cavitation to separate graphene sheets in its space through a high-shear mixer. In 2014, Paton et al. [3] demonstrated the use of high-speed shearing technology to process graphene dispersed in solvent. In 2019, Wang Chen et al. [4] used high-pressure homogeneous liquid phase exfoliation (HPH-LPE) to prepare an aqueous dispersion of graphene with a maximum lamella of 3.0 μm under the condition of PHAH=120MPa. In 2020, Miao Weijun et al. [5] used in-situ research on the effect of high shear rate on the epitaxial crystallization behavior of polyvinyl lactone (PCL)/reduced graphene oxide (RGO) and concluded that when the high shear rate is 75 s⁻¹, the viscosity of the material is decreasing and dispersed in the base material at temperatures of 65°C, 70°C and 75°C respectively. At the same time, the functional relationship can be

constructed through the graphene concentration C , rotor speed N , shearing time t , rotor diameter D and solvent volume V , and the graphene sheets were sheared and peeled under different solvent volumes. On the basis of this method, high-speed shearing suppresses van der Waals forces and stacking effects, and oligolayer or single-layer graphene stably exists in various solutions.

2 CHEMICAL PREPARATION METHOD OF GRAPHENE DISPERSION

Due to the large specific surface area and hydrophobic properties of graphene's surface functional groups, it is not easily dispersed in different solvents, thus hindering the application prospects of graphene materials. In order to solve the problem of difficulty in dispersion, chemical modification is one of the more common methods. Chemical modifications are mainly divided into two categories: covalent modification and non-covalent modification.

2.1 Covalent Modification to Prepare Graphene Dispersion

The main way to modify the dispersion by covalent method is to use covalent bonding to graft to the boundary or defect site between graphene and graphene oxide, and then pass through the active points existing therein, and through this activity At this point, the required substances can be directly grafted to GO to achieve the experimental purpose. Modified polymer materials are usually differentiated by the size of their molecular weight.

2.1.1 Modification of small organic molecules

In the coupling agent, organic small molecules such as organic amines and isocyanates are grafted to the surface of graphene oxide, which can regulate the interface structure with the base material and the compatibility of the material, thus changing the properties of graphene oxide. KH550 is a common amino-containing silane coupling agent. The primary amino group in KH550 is used to undergo a nucleophilic substitution reaction with the epoxy functional group in the GO sheet, and KH550 is grafted to the surface of the GO sheet. At the same time, the primary amino group in KH550 and the carboxyl group (-COOH) on the edge of graphene oxide can proceed. Amidation reaction[6]. Su Tian et al. [7] prepared GO (KH550-GO)/PSS dispersion in the ratio of GO:PSS:KH550=1:1:1.7. Wang Xinhui et al. [8] modified graphene oxide with organosilane in a one-step method, and the resulting graphene sheets had clear color and stretched structure, thus proving that after one-step organosilane modification, the obtained graphene oxide layer had a van der Waals forces are reduced and the risk of chemical stacking is reduced. In addition, -OH and -COOH on the surface of graphene oxide can also react with -NCO groups in isocyanate. Stankovivh et al. [9] first reported the use of isocyanates to graft-modify GO. They used different isocyanates to graft a series of different side chains on the surface of GO. The results show that compared with the original GO, the water solvent of GO connected with -NCO group is reduced, but after a short period of time in DMF, dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), etc. After ultrasonic treatment, a uniform dispersion system can be formed, and the system has good suspension stability. In covalent modification, some researchers use aminosilane coupling agents to modify GO and apply it to polymers. The results showed that the mechanical properties of the modified polymer materials were improved. Polyethylene glycol (PEG) can also be used for covalent modification of GO, which is an amphoteric GO with both hydrophilic and lipophilic properties.

In the modification of organic small molecules, functionalized graphene and GO not only improve the dispersion in solvents, but also improve their amphiphilicity and mechanical properties. At the same time, the modified GO prepared can be used in the biological field, broadening the application scope of graphene.

2.1.2 Modification of organic macromolecules

When organic polymers such as polyaniline, polyvinylpyrrolidone and polyethylene are used to modify GO, the steric hindrance caused by expanding the distance between graphene sheets can prevent agglomeration and improve dispersion. Esterification reaction is a commonly used chemical reaction for the modification of macromolecules. Cheng HK[10] used polyvinyl alcohol (PVA) to graft onto the surface of GO sheets, and proposed a method to create advanced polymer nanocomposites from polyvinyl alcohol (PVA) by incorporating PVA-grafted graphene oxide. new method. It was found that by adding PVA-g-GO, the mechanical properties of PVA greatly improved adhesion. The strong interfacial adhesion between PVA-g-GO and PVA matrix is attributed to the good compatibility between PVA-g-GO and matrix PVA as well as the hydrogen bonding interaction between them. At the same time, NAndi AK et al. [11] produced related modified silicone products by grafting polyvinylpyrrolidone acid (PVP) from GO, and modified PVP onto the GO layer to obtain The dispersion rate of GO sheets in different solutions, among which Hansen solubility values range from 6.3 to 5.8. Modified products of PVP and related silicones will not only improve the dispersion of GO in different solvents but also broaden the application space of GO and graphene.

The modified graphene/GO not only improves the dispersion in different solvents, but also improves the solubility during the blending process. However, in the modification of organic macromolecules, the continuity of the original structure of GO is destroyed during the reaction between the molecules and the groups on the surface of GO, thus inhibiting the development of its conductivity and optical properties.

2.2 Preparation of Graphene Dispersion by Non-Covalent Modification

The non-covalent bonding method is used to functionalize the graphene surface, and the interaction force between specific functional macromolecules and GO sheets is used to hybridize to obtain GO hybrid particles with corresponding functions.

The non-covalent method is another effective technology for using polymers to modify the surface of graphene oxide. Compared with the covalent bonding method, it has a particularly good feature, that is, the conjugated metal system on the surface of graphene oxide is not damaged during the polymer chain modification, and it can also improve the thermal dispersion performance of graphene oxide. Kim BJ's research group [12] used a similar method to prepare pH-responsive polymer-stabilized fluorescent quantum dot functionalized GO with pyrene end groups, and obtained quantum dot-GO hybrid nanomaterials with better performance within a certain range. Dispersion. Yang Yongfang et al. [13] used the ATRP (atom transfer radical) method to prepare pyrene-terminated poly-2-dimethylaminoethyl methacrylate (PDMAEMA), and grafted it to pyrene-terminated poly(PDMAEMA) based on π - π stacking. Electrostatic interactions coat the surface of graphene oxide on the surface of polystyrene microspheres to form a hydrophilic polymer brush-like structure. Then polystyrene microspheres were dissolved in THF to obtain amphiphilic polymer brush-modified Janus structure GO nanosheets. Based on the amphiphilic principle of polymer brushes, the obtained Janus structure nanomaterial sheets also have an excellent effect on stabilizing emulsions. The use of π - π stacking can achieve a stable effect by overcoming the van der Waals forces between the sheets through electrostatic interaction. Compared with this method, it is simpler, but the corresponding cost also increases.

In addition, the in-situ polymerization of polystyrene microspheres can solve the dispersion problem of graphene oxide solution in oily solution. The use of dispersions to prepare liquid crystals has extremely high requirements on the stability of high-concentration colloids composed of anisotropic colloidal particles. Because of its negative charge (highly oxidized graphene fragments), GO solution can achieve very good colloidal stability in water. As one of the most important non-covalent binding substances, the π - π effect widely appears in nature. It has a great impact on the work of supramolecular preparation and material identification. In the experiment of Professor Yan Haichen [14], it was proved that GO composite microspheres were successfully prepared through in-situ polymerization reaction, and it was proved that an ethanol-water mixture with an alcohol-to-water mass ratio of 4:1 was used as the dispersion medium. , after prepolymerization for 2 hours and then adding the GO diffusion solution, GO composite microspheres with ultra-high composite solution rate can be obtained. The particle size of composite microspheres is 0.78~1.15 μ m, and the standard deviation is less than 0.1 μ m. It is also proven that there is a strong π - π stacking effect between GO and PS, and this stacking effect is used to load the nanoparticles on the surface of GO and graphene sheets so that they can be stably dispersed in non-polar solvents for a long time.

GO has good physical and chemical properties and its unique two-dimensional layered planar structure with large specific surface area, which provides good conditions for the loading of inorganic nanoparticles. By loading GO on inorganic nanocomposites, inorganic hybrid functionalization of GO can be achieved. Through inorganic hybrid functionalization, many properties that GO does not have can be realized. At the same time, loading inorganic nanoparticles on the surface of GO can also effectively prevent its own damage. Reunion.

3 CONCLUSION

This review summarizes the preparation of polymer-functionalized graphene/graphene oxide surfaces by covalent and non-covalent methods of physical modification as well as chemical modification. Graphene oxide is currently relatively cheap to produce, and its dispersibility in a variety of solvents, including water, coupled with its tunable surface chemistry, make graphene oxide a versatile material. At present, there are still some challenges in graphene oxide and graphene dispersion technology, such as dispersion performance under high concentration, high temperature, high pressure and other conditions, impact on graphene properties, large-scale production and other issues. Therefore, further research on the mechanism and optimization methods of graphene dispersion is needed in the future to improve the stability and controllability of graphene dispersion and lay a more solid foundation for its widespread application.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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