Analysis on the Conductivity of Graphene-based Composite Material

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Abstract. Electric energy is the main energy source in production and life. How to make efficient transmission and utilization of electric energy is a problem that requires long-term research. Graphene, as a material with a single-layer two-dimensional honeycomb lattice carbon chain structure, has good electrical conductivity. Its composite with conductive polymer or inorganic metal materials can effectively improve its electrical conductivity and obtain more outstanding electrochemical performance. In order to understand the application of graphene's electrical conductivity in life in more detail, this article first reviews the electrical properties of graphene, and then reviews and analyzes the research progress of graphene polymer electrical conductivity based on different composite materials and processing methods. The author also points out that the biggest problem facing graphene composites now is that the expensive price of graphene nanosheets and its unavailability in large-scale applications and industrial production, as well as proposes that the future of graphene composites is still through scientific research in a short period of time. Continuously improving its electrical conductivity is necessary, yet the long-term strategic goal should be reducing the cost of industrialized production of graphene products and find the preparation conditions of graphene composite materials that are more suitable for industrial production.

1. Introduction
Since the discovery of graphene in 2004, British scientists successfully exfoliated flakes composed of only one layer of carbon atoms from highly oriented pyrolytic graphite. Graphene has important application prospects in materials science, micro-nano processing, energy, biomedicine, and drug delivery due to its excellent optical, electrical and mechanical properties, and is considered to be a revolutionary material in the future [1], because pure graphene is difficult to manufacture and expensive to manufacture. Although graphene has good chemical properties, it has good toughness and is easy to bend. Therefore, it is difficult to apply graphene in production and life so scientists have determined the direction of its research and application.

In order to analyze how graphene plays a higher role in daily production in detail, which is based on the electrochemical properties of graphene as a starting point, this article reviews its electrochemical properties and summarizes the analysis history of the electrical conductivity of composite materials with graphene as the main raw material, according to different preparation methods and different substrates. This article briefly discusses the properties of each different composite material and focuses on the analysis of the current problems facing graphene composite materials and the future development direction.
2. The electrical properties of graphene

A carbon atom has four valence electrons so that each carbon atom contributes an unbonded π electron. These π electrons can form an orbital perpendicular to the plane. The π electrons can move freely in the crystal. Graphene is a kind of carbon atoms connected by sp2 hybridization that are closely packed into a single-layer two-dimensional honeycomb lattice structure. The theoretical specific surface area is as high as 2630m²/g. The large area of π–π conjugate determines its excellent electrochemical performance [2]. The carrier mobility of graphene at room temperature is about 15000cm²/(V⋅s), and the conduction rate of electrons in it can reach 1/300 of the speed of light. It is 10 times that of silicon material and more than twice that of indium antimonide (InSb), which is the substance with the highest carrier mobility currently known. The reason why graphene has local superconductivity and high carrier mobility is that the carriers in graphene follow a special quantum tunnelling effect, which does not produce backscatter when encountering impurities [3].

In addition, graphene has an energy band structure with a zero bandgap. The resistivity is 10⁻⁸Ω⋅m, which is lower than the resistivity of copper/silver. As shown in figure 1, graphene is a zero-distance semiconductor because its conduction and valence band meet at the Dirac point. The Brillouin division at the edge of the momentum space at the six positions of the Dirac point is divided into two sets of equivalent triplicates. In contrast, the main point of traditional semiconductors is usually Γ, with zero momentum [4].

![Figure 1 Brillouin band and band structure of graphene [4]](image)

3. Graphene composite

Graphene itself is thinner and lighter than paper, and its flexibility is twice as hard as diamond, but it is expensive to manufacture. Therefore, it cannot be widely used in production and life. For this reason, graphene composite materials have emerged, and graphene composite materials have various forms according to their composites with other materials. It can form a multi-phase material with metals, inorganic non-metal materials and organic polymer materials, which can not only have the good conductivity of graphene itself but also have the good properties of the matrix itself.

3.1. Graphene/polymer composite

3.1.1. Graphene filled composite

The composite of graphene and polymer is to break the van der Waals force between graphene molecules in a covalent manner. Through melt blending or in-situ polymerization to mix graphene with organic polymers can effectively improve the conductivity of the polymer itself.

Zhang Haobin prepared PET graphene nanocomposites by using a 285°C melt blending method. In the experiment, they compared the conductivity of the filling rate of the graphite composite material with the conductivity of the filling rate of the graphene composite material and obtained the relational image shown in figure 2 [5].
As can be seen from the above figure, when the permeation threshold is determined to be 0.47%, when graphene is used instead of graphite to participate in the production of composite materials. The composite material can achieve an ultra-high conductivity of 2.11 S/m at a graphene content of 0.3 vol%.

3.1.2. Functionalized graphene polymer composite

Graphene and its derivatives can also be covalently or non-covalently functionalized by polymer modification to form functionalized graphene polymer composites. Non-covalent functionalization is to modify the surface of graphene without changing its chemical structure through van der Waals force, electrostatic interaction and π-π stacking. This method can improve the electrical properties of composite materials.

Yang Ying-Kui used NaBH4 as a reducing agent and successfully non-covalently functionalized graphene oxide with an imidazole ionic liquid (Imi-IL) with active vinyl benzyl under alkaline conditions. Afterwards, the uniform dispersion of the graphene sheets and the strong interface bonding with the poly (methyl methacrylate) (PMMA) matrix were successfully achieved, and the conductivity images of the composite materials containing different volume fractions of graphene were obtained as shown in figure 3 [6].
It can be seen from the above figure that when the low permeability threshold is 0.25 vol.%, the composite material achieves a high conductivity of 13.3S/m with a low content of 2.08vol.%. This proves that the functional composite can significantly improve the electrical properties of the material.

3.2. Graphene/inorganic composite material
Dispersing inorganic materials (metal nanomaterials, semiconductors and insulating nanomaterials) on the surface of the graphene nanolayer can synthesize graphene-based inorganic nanocomposites. Inorganic nanoparticles can reduce the interaction between graphene sheets, and the combination of graphene and specific nanoparticles makes this type of composite material have a wide range of applications in the fields of catalysts, electricity, etc.

3.2.1. Chemical reduction method
The reducing agent and organic solvent used in the chemical reduction method will reduce the activity of the graphene-nanoparticle binding interface, thereby reducing the performance of the composite material. The electrochemical deposition of inorganic nanomaterials directly on the graphene matrix is a green method for preparing graphene composite films. Environmentally friendly and efficient method.

Li Fenghua successfully used SnCl₂ to reduce graphene oxide to graphene flakes using sodium chloride and urea [7], and then combined SnO₂ particles with graphene flakes perfectly. Then he compared graphene/Sn composite (GS), graphite oxide (GO) and pure graphene (CCG) synthesized by the chemical method in sulfuric acid solution. Nyquist plots as shown in the figure 4 are obtained through the summary of the experiment.
Figure 4 Nyquist plots of GS, CCG and GO [7]

Figure 4a is the summary of the three composite materials, b, c, d are the data of the three composite materials themselves in a [7]. As can be seen from the above figure, compared with CCG and GO, the conductivity of graphene/Sn composites is much stronger than the former two. In addition, GS composite materials have broader application prospects in the fields of batteries, supercapacitors and sensors.
3.2.2. Electrochemical deposition
The hydrothermal method is a simple method that can generate high pressure at a high temperature and a fixed volume to prepare inorganic nanocomposites.

Wang Huanwen used a two-step method to prepare graphene-bismuth oxide composite materials [8]. First, the graphite oxide and Bi(NO$_3$)$_2$$\cdot$5H$_2$O are mixed ultrasonically and crushed, and then heated with high-pressure steam at 180°C for 12 hours. Next, the mixture is thoroughly mixed and reacted with hot air heated to 300°C for 4 hours to obtain a composite material. Finally, the resistance value of the composite material at different potentials was tested accordingly and the corresponding curve as shown in the figure 5 below was obtained.

![Figure 5 EIS analysis of graphene-Bi$_2$O$_3$ composite at the different potentials [8]](image)

As can be seen from the above figure, at low frequencies, the resistance of the graphene-bismuth oxide composite material tends to a vertical line, which indicates that the composite material has very good capacitance. This composite material has very good potential for supercapacitors [9].

4. Discussion
Although graphene composite materials have developed a large number of new and improved materials through continuous research, 80% of graphene composite materials are now used in scientific research. Only a small part will be used in actual production and manufacturing because all the improvements mentioned in the previous article are done in the laboratory. Although the performance has been significantly improved, it does not conform to the principle of low cost in industrial production. According to table 1, which shows the global price of graphite products in 2018, provided by China Foresight Industry Research Institute, the price of graphene nanomaterials far exceeds that of graphite products of the same level.

| Material                                | Market price(USD/kg) |
|-----------------------------------------|----------------------|
| Natural graphite                        | 0.5                  |
| Graphite product (+50mesh)              | 3-10                 |
| Graphene nanosheets (2-10nm)            | 3000-30000           |
| Graphene nanosheets (1-2nm)             | 500000               |
| Single wall carbon nanotube             | 300000               |
| Multi-walled carbon nanotubes           | 300000               |
| Silicon/carbon composite materia        | 15000                |

Table 1 Carbon product material price (2018)
In industrial production, there are far more problems that need to be solved than in laboratory environments. For example, hydrothermal processing methods are very expensive in industrial environments. Simultaneously, industrial production also needs to ensure the controllability of the product. That is, the structure of the graphene composite material can be controlled relatively easily, which is still a problem to be solved today.

5. Conclusion

Since the birth of graphene, it has been a research hotspot because of its excellent properties. Although there are many preparation methods, it is still difficult to prepare high-quality graphene in large quantities and at a low cost. Therefore, graphene composite materials are still the focus of current research. At present, the application of graphene composite materials in electricity is mainly concentrated in electronic materials, thin-film materials, energy storage materials and liquid crystal materials. However, there are relatively few studies on bulk graphene metal matrix composites. The excellent reinforcement effect of graphene and its unique interface with the metal matrix will make this type of composite material a research hotspot for graphene composites in the future. Moreover, large-scale synthesis and industrial applications still face a large number of problems and challenges. The short-term goal should still be to explore the new properties of graphene conductive polymer functionalized composites so as to continue to broaden the new fields of composite applications. However, the long-term strategic goal should be to reduce graphene production costs and environmental requirements for production.

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References

[1] A. K. Geim, “Graphene : Status and Prospects,” vol. 324, no. June, pp. 1530–1535, 2009.
[2] H. Chen, M. B. Müller, K. J. Gilmore, G. G. Wallace, and D. Li, “Mechanically strong, electrically conductive, and biocompatible graphene paper,” Adv. Mater., vol. 20, no. 18, pp. 3557–3561, 2008, doi: 10.1002/adma.200800757.
[3] K. S. Novoselov et al., “Two-dimensional gas of massless Dirac fermions in graphene,” vol. 438, no. November, pp. 197–200, 2005, doi: 10.1038/nature04233.
[4] D. R. Cooper et al., “Experimental Review of Graphene,” vol. 2012, 2012, doi: 10.5402/2012/501686.
[5] H. Zhang et al., “Electrically conductive polyethylene terephthalate / graphene nanocomposites prepared by melt compounding,” Polymer (Guildf.), vol. 51, no. 5, pp. 1191–1196, 2010, doi: 10.1016/j.polymer.2010.01.027.
[6] Y. K. Yang et al., “Non-covalently modified graphene sheets by imidazolium ionic liquids for multifunctional polymer nanocomposites,” J. Mater. Chem., vol. 22, no. 12, pp. 5666–5675, 2012, doi: 10.1039/c2jm16006d.
[7] F. Li et al., “One-step synthesis of graphene/SnO2 nanocomposites and its application in electrochemical supercapacitors,” Nanotechnology, vol. 20, no. 45, 2009, doi: 10.1088/0957-4484/20/45/455602.
[8] H. W. Wang et al., “Facile solvothermal synthesis of a graphene nanosheet-bismuth oxide composite and its electrochemical characteristics,” Electrochim. Acta, vol. 55, no. 28, pp. 8974–8980, 2010, doi: 10.1016/j.electacta.2010.08.048.
[9] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, “Graphene-Based Ultracapacitors,” pp. 6–10, 2008.