УДК 330:372.854
DOI: 10.26140/anie-2020-0904-0095

RESEARCH PROGRESS ON PREPARATION AND APPLICATION OF GRAPHENE

Qian Zhang, master
ITMO University
(191002, Russia, St. Petersburg, Lomonosov street, e-mail: zhangqian422198@yandex.ru)

Abstract. Graphene is a kind of honeycomb planar film formed by carbon atoms in sp2 hybridization, and it is a quasi-two-dimensional material with only one atomic layer thickness. As a new nanomaterial with the thinest, strongest and strongest conductivity, graphene is called "black gold" and is the "king of new materials". Scientists even predict that graphene will "completely change the 21st century" and is likely to set off a disruptive new technology and new industrial revolution sweeping the world. Many countries in the world have made strategic deployment of graphene, attached great importance to the development of graphene industry, and issued a series of relevant policies for systematic layout. Countries have provided large amounts of funds to support the graphene industry, hoping to seize the development plateau of the graphene industry in the new round of competition. The classification, biocompatibility, optical, electrical, thermal and mechanical properties of graphene and its derivatives are reviewed. The applications of graphene in various fields are discussed. The main preparation methods of graphene, REDOX method, mechanical stripping method, crystal epitaxial growth method and chemical vapor deposition were investigated. Finally, the prospect of graphene is prospected.

Keywords: Graphene; Structure; Performance; Application; Refining; graphene oxide; extract

ПРОГРЕСС ИССЛЕДОВАНИЙ ПО ПОЛУЧЕНИЮ И ПРИМЕНЕНИЮ ГРАФЕНА

Чжан Цянь, мастер
Университет ИТМО
(191002, Россия, Санкт-Петербург, ул. Ломоносова, e-mail: zhangqian422198@yandex.ru)

Аннотация. Графен представляет собой плоскую пленку в форме сот, образованную sp2-гибридизацией атомов углерода, и представляет собой квазидвумерный материал с толщиной всего в один атомный слой. Как новый тип наноматериала с самой тонкой, самой прочной и самой сильной электрической и теплопроводностью, обнаруженный до сих пор, графен называется «черным золотом» и является «королем новых материалов». Ученые даже предсказывают, что графен «полностью изменит 21 век». Многие страны мира применили графен на стратегическом уровне, придали большое значение развитию индустрии графена и выпустили ряд соответствующих политик для систематической компоновки. Страны предоставили много средств для поддержки индустрии графена, надеясь захватить высокие позиции для развития индустрии графена в новом раунде конкуренции. В этой статье рассматривается классификация графена и его производных, а также биосовместимость, оптические, электрические, термические и механические свойства. Обсуждали применение графена в различных областях. Исследованы основные методы получения графена: окислительно-восстановительный метод, метод механического расслоения, метод эпитаксиального роста кристаллов и химическое осаждение из газовой фазы. Наконец, открывается перспектива графена.

Ключевые слова: графен; структура; производительность; применение; нефтепереработка; оксид графена; экстракт

INTRODUCTION

Graphene materials since 2004 was found can make since in a simple way, ultrathin, super light, high strength, super conductivity, good thermal conductivity, large specific surface area, good pervious to light, stable structure features, can be widely used in new energy, electronic information, biological medicine, aerospace and other fields, has become the new star in the field of materials. Countries are starting to deploy at a strategic level, setting up research and development centers, and trying to commercialize graphene applications. For example, the European Commission has designated graphene as a "flagship emerging technology of the Future project" and will allocate 1 billion euros to develop graphene materials over the next 10 years. The UK government has established the National Graphene Institute, which is dedicated to the production and application of graphene. The Former Ministry of Knowledge Economy expects to provide a total of $250 million in graphene funding between 2012 and 2018. China, the United States and Japan have established graphene research institutes. Graphene materials are on the eve of large-scale industrialization, and the global graphene market will enter a period of rapid development in the next 5 to 10 years, aiming at the research and development and application of graphene functional devices. In 2015, the global graphene market was about us $4.53 million. It is estimated that the global graphene market will reach US $385 million in 2020 and US $2.103 billion in 2025.

Classification and properties of graphene. Graphene can be thought of as graphite with only one layer of carbon atoms. It is a hexagonal planar cellular atomic crystal formed by the compact arrangement of SP^2 hybridized carbon atoms. Monolayer graphene is a two-dimensional allotrope of carbon materials. Its structure can be considered as the compact accumulation of monolayer carbon atoms into a plane, showing the periodic arrangement and accumulation of the six-membed ring of the honeycomb in an ideal state.

Graphene and its derivatives are a huge family. According to the number of graphene layers, it can be divided into single-layer graphene, a few graphene layers (2-10 layers), and ultra-fine graphene (more than 10 layers, but less than 100 nm in thickness). According to different degrees of oxidation, it is further divided into graphene oxide (GO) and reduced graphene oxide (rGO). According to the different forms, it can be divided into graphene flakes, graphene nanoribbons and quantum dot graphene.

Graphene is biocompatible. Go can be effectively functionalized to deliver water-insoluble anticancer drugs [1]. Therefore, surface modification and functionalization of graphene materials can be used to improve the biocompatibility of materials and the drug load rate of carriers [2,3]. Studies have shown that polymer-modified graphene has good biocompatibility and high transfection efficiency [4,5]. When graphene interacts with cells, the Raman spectrometer detects that graphene charges rearrange to change the energy of atomic vibrations, a property that can be used to distinguish normal cells from active cancer cells [6]. The three-dimensional structure of graphene can promote the adhesion and proliferation of neural stem cells, as well as the differentiation of neural stem cells into neuron cells and astrocytes [7].

Graphene has electrical properties. Because the atoms of graphene are arranged in a very neat honeycomb structure, it has excellent natural conductivity. Electron transport measurements show that graphene has a very high electron mobility over 15,000 cm^2/vs at room temperature [8]. At temperatures between 10K and 100K, electron mobility is almost independent of temperature, which can be explained by the fact that the conductivity at this point is limited by the scattering caused by defects within graphene. The recombination rate of mobile electrons in graphene and trapped holes in the nanotube surface is enhanced due to the high mobility of electrons in graphene [9]. In addition, the two-dimensional structure of graphene is likely to generate the fraction of electric charges. This makes graphene an ideal material for making key sub-components of computers [10].

Graphene has thermal properties. In the monolayer carbon atom structure of graphene, due to the orderly arrangement of carbon atoms, phonons can conduct rapidly in graphene. At the same time, the structured structure of graphene enables the crystal vibration to propagate forward regularly and produce resonance, which is also an important reason for the good thermal conductivity of graphene. The simulated numerical value of graphene's thermal conductivity can reach 5500-6000W/(m•k), which is more than three times of the thermal conductivity of diamond [11].

Graphene has optical properties. According to optical theory, single-layer graphene should absorb 3.2% of white light. A single atomic layer of material should not have too much opacity due to the unique electronic properties of graphene. When infusing graphene quantum dots into epoxy, it was found that the graphene quantum dots that have the capability to improve the toughness of epoxy by 260%, increase the thermal conductivity by 144% [12].

Graphene has mechanical properties. The researchers found that the maximum pressure the graphene particles could withstand was about 2.9 micronewtons per 100 nanometers before they began to break. Lee's team at Columbia University used atomic force microscopy to actually measure the intrinsic elastic modulus and fracture strength of the monolayer graphene membranes. At the two-dimensional scale, defects have a very limited impact on intrinsic mechanical properties [13].

The future of graphene. Applications of graphene's electro-optical properties. Mullen and others by dip coating deposited by thermal annealing reduction of graphene, the characterization results show that the thin film resistor of 900 Ω, light transmittance was 70%. Using the material as a positive pole for a solar cell, the energy conversion efficiency of the solar cell can reach 0.26 percent. Thus, graphene could be used to make transparent electrodes, replacing indium tin oxide (ITO), which is expensive and highly toxic.

Applications of the thermal properties of graphene. Some scholars have added graphene to resin matrix and successfully prepared graphene and polymer composite materials. After testing, its conductivity and heat transfer performance have been significantly improved. The high thermal conductivity and strength of graphene make it possible for graphene to be used in the field of electronic aviation with high heat dissipation efficiency.

Applications of graphene sensing properties. The researchers found that graphene provides a two-dimensional environment for electron transport and rapid polyphase electron transfer at the edges, making it an ideal material for electrochemical biosensors. Graphene quantum dots can detect DNA based on their sensing properties [1].

Applications of mechanical properties of graphene. Graphene can be harder and stronger than diamond, making it an ideal material for future space instruments. In addition, graphene can also be of great help to industry and construction industry, such as wire rope for cranes.

METHODOLOGY

A method of extracting graphene. According to the application field and range of graphene materials, the preparation methods are also different. The preparation technology of graphene is developing rapidly. At present, the main methods to prepare graphene include REDOX [14,15], mechanical exfoliation [16], crystal epitaxial growth [17] and chemical vapor deposition (CVD) [18-20].

REDOX method is to oxidize natural graphite through the role of strong oxidant, and graphene oxide can be obtained. The reduction process USES chemicals with strong reducibility to reduce them. Brodie [21], Staudemnaier [22], Hummers [14] and other improved methods are the main REDOX methods. Brodie and Staudemnaier use a mixture of potassium chlorate and concentrated nitric acid to directly oxidize graphite, resulting in expansion of graphite and intercalation of water molecules, and at the same time, various oxygen-containing functional groups appear on the edge and surface of graphite. Hummers' method is to oxidize graphite in a mixed system of potassium permanganate and concentrated sulfuric acid. Modified Hummers [23] is the most commonly used chemical oxidation method. Based on Hummers method, this method improves the dosage and proportion of strong oxidants and adjusts the reaction time at various temperatures appropriately. REDOX is the most commonly used method to prepare graphene. Its advantages are low cost, high yield and large area of graphene preparation. The main disadvantages are low purity, large size distribution and large amount of impurity ions.

Mechanical stripping method USES ion beam to etch the material surface, which will form grooves on the material surface. Then, external forces can be applied to achieve the effect of material stripping, and high-quality, well-arranged graphene sheets can be prepared [24]. Graphene was first prepared in 2004 by Geim and Novoselov et al [25]. Of the University of Manchester in the United Kingdom through mechanical dissection. A 20 m-2mm platform was formed by etching a groove with a depth of about 5 m on the surface of high-orientation pyrolytic graphite using oxygen ion beam. The etched pyrolytic graphite is pressed on the photoresist to remove the graphite structure beyond the platform. The graphite platform is then repeatedly peeled off with cellophane until only very thin sheets of graphite remain. Atomic force microscopy (AFM) reveals graphene sheets that are several atoms thick, with a single layer of graphene visible between these sheets.

High quality graphene can be obtained by mechanical exfoliation with simple equipment, low cost and high purity. To a certain extent, it can meet the research needs of the laboratory and is widely used in the basic research of physical and chemical properties of graphene. The main disadvantages are low yield, difficulty in separation and serious agglomeration. Therefore, it is not suitable for mass production of graphene.

Crystal epitaxy growth methods include silicon carbide epitaxy growth method and metal catalytic epitaxy growth method. Sic epitaxial growth method is to separate silicon atoms from raw materials under high temperature and vacuum conditions to make Si or C rich surfaces, and then to regenerate graphene after graphitization [26]. In the process of preparing graphene, this method can control the number of graphene layers by controlling the temperature and time. However, after annealing treatment, the material is prone to generate some residual stresses, which may lead to the fracture of graphene. Therefore, it is difficult to prepare graphene with good overall morphology and high quality. In addition, due to the use of Sic as the base, the graphene prepared is difficult to separate from the base [27], so this method also has some limitations in the application and promotion. Metal catalytic epitaxial growth method is used to pass hydrocarbons into the surface of transition metal substrate in a high vacuum environment. These transition metals must have good catalytic performance, such as Pt (111) [28], Ir (111) [29], Ru (0001) [30], Ni (110) [31], etc. When the gas reaches the metal surface, under heating conditions, a catalytic dehydrogenation reaction takes place to prepare graphene. This method requires that the adhesion between the metal substrate and graphene be as low as possible, so that graphene can be easily separated from the substrate, which is beneficial to the subsequent experiment and operation of graphene.

Chemical vapor deposition (CVD) is a method for large-scale preparation of semiconductor thin film materials. Carbon nanotubes have been successfully prepared by this method. First, the hydrocarbons are passed to the surface of the high-temperature heated metal substrate, and the gas flow rate and temperature are controlled. After the reaction lasts for a certain time, the substrate is cooled. Layers or monolayers of graphene form on the surface of the substrate. This process involves the dissolution of carbon atoms on the substrate and the diffusion of carbon atoms in the substrate. CVD method can react to form films at relatively low temperatures, which reduces energy consumption and is easy to separate from the substrate [32,33]. In the process of preparing graphene by CVD method, Miyata [34] obtained more monolayer graphene by means of rapid cooling. This experiment shows that the growth of graphene does not occur at the stage of carbon deposition, but depends on the diffusion of carbon on the surface of the substrate. A large cooling rate can effectively inhibit the dissolution of carbon, so that most of the carbon can be deposited on the surface of the substrate, and finally graphene is formed through the diffusion of atoms. Zhou [35] also demonstrated that a large cooling rate enables carbon atoms to quickly reach a supersaturated state on the substrate to form a single layer of graphene with uniform thickness. Therefore, when using CVD method to prepare graphene, more monolayer graphene can be obtained by accelerating the cooling rate of the substrate. The graphene prepared by CVD method has the highest purity and the size is easy to be controlled, but the carbon atom utilization rate is low and the thickness of graphene is difficult to be controlled.

CONCLUSIONS

Above all, chemical vapor deposition (CVD) method is the preparation of high quality, large areas of graphene, the structure of small defects and the outstanding performance, control, material shape can be obtained more and more attention and application. The application of graphene materials has been constantly innovated, and various excellent properties have been developed for commercial use. However, there are still many challenges, for how to prepare graphene on a large scale with high quality, the unique properties of graphene and new applications need to be developed continuously. Graphene has been developed. They act as potential candidates for photo - catalysts, sensors, photo - current switching, photo detectors, dentistry and other optical applications. [36,37]. However, the cross-application of graphene with other disciplines still needs to be explored. Researchers are studying the combination of organic chemistry and material chemistry in the hope of developing better preparation methods. As a promising alternative material, graphene still needs further development and research.

REFERENCES:

1. Jie G T, Zhou Q, Jie G F. Graphene quantum dots-base electrochemiluminescence detection of DNA using multiple cycling amplification strategy. Volume 194, March 2019. P. 658-63. – URL: https://www.sciencedirect.com/science/article/abs/pii/S0039914018311469

2. Brodie B C. On the Atomic weight of graphite. Philos Trans R Soc London, 1859, 149: 249-59. – URL: http://rspl.royalsocietypublishing.org/cgi/doi/10.1098/rspl.1859.0007

3. Staudenmaier L. Verfahren zur darstellung der graphitsäure. Ber Deutsch Chem Ges, 1898, 31: 1481-7. – URL: https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/cber.18980310237

4. Hummers W S, Offeman R E. Preparation of graphitic oxide. J Am Chem Soc, 1958, 80: 1339. – URL: https://pubs.acs.org/doi/abs/10.1021/ja01539a017

5. Yang X Y, Zhang X Y, Liu Z F, et al. High-efficiency loading and controlled release of doxorubicin hydrochloride on graphene oxide. Journal of Physical Chemistry C, 2008, 112(45): 17554-8. – URL: https://pubs.acs.org/doi/10.1021/jp806751k

6. Keisham B, Cole A, et al. Cancer Cell Hyperactivity and Membrane Dipolarity Monitoring via Raman Mapping of Interfaced Graphene: Toward Non-Invasive Cancer Diagnostics. ACS Appl. Mater. Interfaces 2016, 8, 48, 32717-32722. –URL: https://pubs.acs.org/doi/abs/10.1021/acsami.6b12307

7. [7] Lu X K, Yu M F, Huang H, et al. Tailoring graphite with the goal of achieving single sheets. Nanotechnology, 1999, 10: 269-72. – URL: https://iopscience.iop.org/article/10.1088/0957-4484/10/3/308

8. Wang X, Sone Y, Kuwajima S. ha situ investigation of the volume change in Li-ion cell with charging and discharging • satellite power applications. J. Eleetrochem. Soc. 2004, 151: A 273-80. – URL: https://scholar.cnki.net/Detail/index/WWMERGEJ01/SIPD052B50C1B0B28FD37C74AE2E39B48340

9. Tri Tuan Nguyen, Tran Thanh Tung, et al. Electromigration with enhanced green emission in the titanium dioxide nanotube/graphene composite. Volume19. Issue10. October 2019. P. 1082-7. – URL: https://www.sciencedirect.com/science/article/abs/pii/S1567173919301762

10. Stoller M D, Park S, Zhu Y, et al. Graphene-based ultracapacitors. Nano Lett. 2008. 8: 3498-3502. – URL: https://pubs.acs.org/doi/10.1021/nl802558y

11. Dimitrakakis G K, Tylianakis E, Froudakis G E. Pillared graphene: A new 3-D network nanostructure for enhanced hydrogen storage. Nano Letters, 2008, 8: 3166-70. – URL: https://pubs.acs.org/doi/10.1021/nl801417w

12. Joel R. S, Ozgur Keles, et al. Infusion of graphene quantum dots modulate thermal conductivity and dynamic mechanical properties of polymers Polymer, Volume 185, 17 December 2019, P. 121988. – URL: https://www.sciencedirect.com/science/article/abs/pii/S0032386119309954

13. Schniepp H C, Li J, Mc Allister M J, Functionalized single graphene sheets derived from splitting graphite oxide. Joumal of Physical Chemistry B, 2006, 110 (11): 8535-9. – URL: https://scholar.cnki.net/Detail/index/SJPD_02/SJPD12102300246608

14. Hummer W S, Offeman R E, et al. Preparation of Graphitic Oxide. Journal of the American Chemical Society, 1958, 80(6). – URL: https://www.scienceopen.com/document?vid=5e0f30ad-2577-4f6b-9eb1-3

15. Geng Y, Wang S J, Kim J K. Preparation of graphite nanoplatelets and graphene sheets. Journal of Colloid & Interface Science, 2009, 336(2): 592-8. – URL: https://www.sciencedirect.com/science/article/abs/pii/S0021979709004147?via%3Dihub

16. Mao H Y, Laurent S, Chen W, et al. Graphene: promises, facts, opportunities, and challenges in nanomedicine. Chemical Reviews, 2013, 113(5): 3407-24. – URL: https://pubs.acs.org/doi/10.1021/cr300335p

17. Chen H Q, Mueller M B, Gilmore K J, et al. Mechanically Strong, Electrically Conductive, and Biocompatible Graphene Paper. Advanced Materials, 2013, 20(18): 3557-61. – URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.200800757

18. Cote LJ, Cruz-Silva R, Huang J. Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite. Journal of the American Chemical Society, 2009, 131(31): 11027-32. – URL: https://pubs.acs.org/doi/10.1021/ja902348k

19. Compton O C, Dikin D A, Putz K W, Brinson L C, Nguyen S T. Electrically conductive "alkylated" graphene paper via chemical reduction of amine-functionalized graphene oxide paper. Advanced Materials, 2010, 22(8): 892-6. – URL: https://onlinelibrary.wiley.com/doi/full/10.1002/adma.200902069

20. Ning G Q, Xu C G, Cao Y M, et al. Chemical vapor deposition derived flexible graphene paper and its application as high-performance anodes for lithium rechargeable batteries. Journal of Materials Chemistry A, 2013, 1(2): 408-14. – URL: https://www.researchgate.net/publication/237836875_Chemical_vapor_deposition_derived_flexible_graphene_paper_and_its_application_as_high_performance_anodes_for_lithium_rechargeable_batteries

21. Reddy K M, Gledhill A D, Chen C H, et al. High quality, transferrable graphene grown on single crystal Cu (111) thin films on basal-plane sapphire. Applied Physics Letters, 2011, 98(11): 113117-3. – URL: https://aip.scitation.org/doi/10.1063/1.3569143

22. Coleman J N, Lotya M, O'neill A, et al. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. Science, 2011, 331(6017): 568-71. – URL: http://med.wanfangdata.com.cn/Paper/Detail/PeriodicalPaper_PM21292974

23. Smith R J, King P J, Mustafa L, et al. Large-scale exfoliation of inorganic layered compounds in aqueous surfactant solutions. Advanced Materials, 2011, 23(34): 3944-8. – URL: https://onlinelibrary.wiley.com/doi/pdf/10.1002/adma.201102584

24. Marcano D C, Kosynkin D V, Berlin J M, et al. Improved synthesis of graphene oxide. Acs Nano, 2010, 4(8): 4806-14. – URL: https://pubmed.ncbi.nlm.nih.gov/20731455/

25. Meyer J C, Geim A K, et al. On the roughness of single-and bi-layer graphene membranes. Solid State Communications, 2007, 143(1-2): 101-9. – URL: https://www.sciencedirect.com/science/article/abs/pii/S003810980700316X

26. Deng B, Wang Y N, Zhao Y, et al. Scalable and ultrafast epitaxial growth of single-crystal graphene wafers for electrically tunable liquid-crystal microlens arrays, Science Bulletin, Volume 64, Issue 10, 30 May 2019, Pages 659-68. – URL: https://www.sciencedirect.com/science/article/abs/pii/S209592731930252X

27. Ouerghi A, Kahouli A, et al. Epitaxial graphene on cubic Sic (111)/Si (111) substrate. Applied Physics Letters, 2010, 96(19): 191910-3. – URL: https://pubmed.ncbi.nlm.nih.gov/20531979/

28. Gao M, Pan Y, Huang L, et al. Epitaxial growth and structural property of graphene on Pt (111). Applied Physics Letters, 2011, 98(3): 033101-3. – URL: https://aip.scitation.org/doi/10.1063/1.3543624

29. Busse C. Epitaxial graphene on metal surfaces; proceedings of the Nanotechnology, 2009 IEEE-NANO 2009 9th IEEE Conference on, F, 2009. – URL: https://www.researchgate.net/publication/224106287_Epitaxial_graphene_on_metal_surfaces

30. Sutter P W, Albrecht P M, Sutter E A. Graphene growth on epitaxial Ru thin films on sapphire. Applied Physics Letters, 2010, 97(97): 213101-3. – URL: https://www.researchgate.net/publication/235001233_Graphene_growth_on_epitaxial_Ru_thin_films_on_sapphire

31. Guo H X, Gao J H, et al. Growth of quadrilateral graphene flakes with a sulfur atomic template on the surface of Ni (110). Volume 153, November 2019, P. 116-9. – URL:https://www.sciencedirect.com/science/article/abs/pii/S0008622319306785

32. Wu W, Liu Z, Jauregui L A, et al. Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing.

Sensors & Actuators B Chemical, 2010, 150(1): 296-300. – URL: https://scholar.cnki.net/Detail/DOI/SJES_02/SJES3FA22BCA0B36C29142C7F7BA6E2D68D9

33. Kulkarni A, Kim H, Zang H, Choi J B, Hong B H, Kim TS. Graphene as Ion Sensitive Film for Ionic Liquids. Sensors, 2010, 362-4. – URL: https://ieeexplore.ieee.org/document/5690240

34. Miyata Y, Kamon K, Ohashi K, et al. A simple alcohol-chemical vapor deposition synthesis of single-layer graphenes using flash cooling. Applied Physics Letters, 2010, 96(26): 263105-3. – URL: https://aip.scitation.org/doi/10.1063/1.3458797

35. Zhou Q, Lin L W. Synthesis of graphene using Micro Chemical Vapor Deposition; proceedings of the IEEE International Conference on Micro Electro Mechanical Systems, F, 2010. – URL: https://www.researchgate.net/publication/224129257_Synthesis_of_graphene_using_Micro_Chemical_Vapor_Deposition

36. Chi H, Murali K, Li T D, et al. Recent advances in graphene based photoresponsive materials. Volume 29, Issue 6 December 2019, P. 603-611. – URL: https://www.sciencedirect.com/science/article/pii/S1002007119306136

37. M. Tahriri, M. Del Monico, R. Torres, et al. Graphene and its derivatives: Opportunities and challenges in dentistry. Volume 102, September 2019, P. 171-185. – URL: https://www.sciencedirect.com/science/article/abs/pii/S0928493119302097

Статья поступила в редакцию 13.08.2020
Статья принята к публикации 27.11.2020