

Theoretical Studies of Graphene, Superconductors and Metals as Plasmonic Systems

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Abstract

Graphene is a thin layer carbon material that has become a hot topic of research during this decade due to its excellent thermal conductivity, mechanical strength, current density, electron mobility and surface area. These extraordinary properties make graphene to be developed and applied in various fields. On this basis, researchers are interested to find out the methods to produce high quality graphene for industrial use. Various methods have been developed and reported to produce graphene. This paper was designed to summarize the development of graphene synthesis methods and the properties of graphene products that were obtained. The application of graphene in the various fields of environment, energy, biomedical, sensors, bio-sensors, and heat-sink was also summarized in this paper. In addition, the history, challenges, and prospects of graphene production for research and industrial purposes were also discussed.

Introduction

Graphene is a type of carbon allotrope that is very popular in the research and industry sector today.¹⁻³ This material has a single layer of carbon atoms and it is the basic structure of other carbon allotropes, such as charcoal, graphite, fullerene and carbon nanotubes.⁴⁻⁶ Graphene have better physical properties compared to other materials, such as high thermal conductivity ($5000 \text{ Wm}^{-1} \text{ K}^{-1}$),⁷ high electron mobility ($250,000 \text{ cm}^2\text{V}^{-1} \text{ s}^{-1}$),⁸ high Young modulus values (1.0 TPa),⁹ large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$),¹⁰ and better electrical conductivity and optical transmittance. On this basis, graphene can replace conventional materials in a variety of applications and industries.

In general, graphene can be synthesized using mechanical exfoliation, arc-discharge, and chemical vapor deposition or CVD. Other methods for graphene synthesis were also developed such as chemical reduction, sonochemicals, electrochemicals and laser ablation. All these methods were developing very rapidly with various types of modifications being made to produce high quality graphene. The conditions of synthesis and selection of precursor chemicals greatly affect the quality of graphene. This paper reports the progress of the latest methods and their modifications to obtain graphene with good quality. The general history of graphene production and application is explained in this paper. In addition, the challenges and prospects in the production of graphene for research and industrial purposes were also discussed.

Graphene for Research and Industry

Graphene has some excellent properties to make it extremely appealing for applications in many fields such as energy, environment, future material, biomedical, and sensor, bio-sensor and heat-sink (Fig. 1). Those wide application shows that graphene has a high commercial value. Taking this into account, the commercial impact of graphene is quite likely to increase in the future. Scientists have also found a way to transform graphene from a material ideal only for fundamental studies to an engineering material, which gives further alternative substantial solutions for industrial and consumer needs. In regard to their applications, research and industry are much related to each other and cannot be separated. Industries cannot develop without research, whereas the results of research will be meaningless if they cannot be utilized in industrially scale. In this section, each of the applications of graphene in several fields is reviewed.

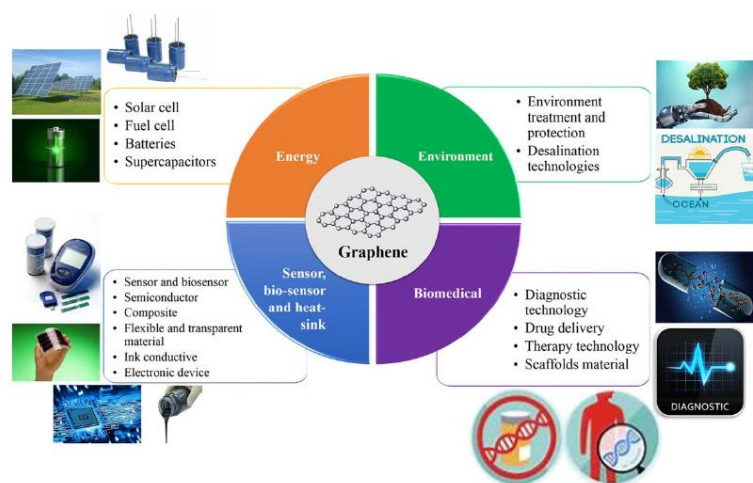


Figure 1. Graphene application in research and industry.

Energy fields.—One of the main concerns for today is the availability of renewable and clean energy. In response, scientists have made great efforts on seeking and designing materials that have the right properties for energy storage technology. Energy storage technology is found in solar cell, fuel cell, batteries, and supercapacitors. Useful properties of graphene such as high mechanical flexibility, high specific surface area, ultra-thinness, good electrical conductivity, and high theoretical capacitance can be used for energy storage technology. Graphene have been used and thoroughly researched for lithium ion batteries, flexible or micro-supercapacitors, lithium air batteries, lithium-sulfur batteries, electrode for fuel cell and solar cell. On this basis, ultra-high specific surface area of graphene is needed for large ion storage in electric double layer capacitors, whereas functionalized graphene is needed for anchoring other active species in batteries. Highly flexible and conductive graphene-based membranes may also be used as either interlayers or current collectors in lithium-sulfur batteries. Graphene with a macro porous structure is substantial for catalytic growth/decomposition and accommodation of lithium batteries.

Environmental fields.—Environmental protection has also become another major issue during this decade. Environmental issues should receive more attention in order to maintain the sustainability of the planet Earth. Strategies for pollution treatments have received more interest to be researched. Zhao et al., (2012) reported that graphene is a good sorbent, as well as being able to be recycled.³⁸ It was proven that graphene can adsorb liquids up to 600 times heavier than its own weight. Graphene can also perform exceptionally well when adsorbing gasoline until it reaches an adsorption of $2.77 \times 10^2 \text{ gg}^{-1}$. Other substances that graphene could adsorb include ethanol, olive oil, nitrobenzene, acetone, and dimethyl sulfoxide. Graphene was also investigated for desalination technology. It should be noted that an essential property of graphene when it comes to environmental treatment and technology is its surface area.

Biomedical fields.—Academicians and scientists have been investigating the feasibility of implementing graphene in biomedical industry. It was reported that several outstanding properties of graphene, such as its high opacity, high chemical reaction, and unparalleled thermal conductivity, are suitable for biomedical purposes. The great functional groups of graphene, such as graphene oxide and N-graphene, are being preferred for biomedical application. These functional groups produce high and effective results. As presented in Fig. 1, graphene is already used in several biomedical applications, such as diagnostic technology, drug delivery, therapy technology, and scaffolding materials.

A strong reason for using graphene in biomedical purposes is due to its consistency and its ability to develop a uniform structure. The suitability of graphene when it comes to biomedical application depends on its shape, size, morphology, thickness and degree of oxidation. Another suitable property of graphene is its low toxicity, proven by its ability to remain stable for a period of long time in metabolic pathways and during cellular intake. However, further observations are needed on the in vivo process with graphene, especially for drug delivery application. For commercialization purposes, biomedical industries should give more attention towards the aforementioned points. Hence for this reason, prior to commercialization, research is needed to be executed which may latterly be used as a basis and evidence to show the benefits of graphene towards major biomedical industries.

Sensor, bio-sensor, and heat-sink application.—Graphene is widely used as materials engineering due to its highly appealing properties since its first appearance in 2004. This material can be used as one of active material for Li-ion battery (LIB) anode and electrochemical double-layer capacitor (EDLC) electrode due to its presents a Li^+ storage capacity of 744 mAh.g^{-1} and electric double-layer capacitance of 550 F.g^{-1} . Han et al. in 2020 also reported the polymer composite with vertically graphene architecture. This material is a promising candidate for thermal interface materials due to its thermal conductivity reached $2.18 \text{ W.m}^{-1}.\text{K}^{-1}$.

Graphene and its derivatives also can be used as sensor and bio-sensor materials. Bai et al. made a new sensor using reduced graphene oxide (rGO) with combination by polyoxometalates-doped Au nanoparticles for sensing uric acid in urine. The sensor has a low detection limit for uric acid determination, i.e. $8.0 \times 10^{-8} \text{ M}$. Graphene-based bio-sensor also developed for early detection of Zika virus infection. The bio-sensor response for Zika virus is excellent in buffer condition at concentrations as low as 450 pM. Potential diagnostic applications were applied by

measuring the Zika virus in a human serum. Another sensor based on graphene also fabricated by Khalifa et al. in 2020. They made a smart paper from graphene coated cellulose for high-performance humidity and piezo-resistive force sensor. The sensor has high piezoresistive response i.e. between 125%–250%. They stated that cellulose paper with low cost, lightweight and biocompatibility combined with graphene could be a promising material for smart, wearable electronic devices. In the other side, graphene is also good material for semiconductor and electronic device. Graphene also can be formed as flexible and transparent materials for various application. The material easy to change become an ink with high conductivity for injecting printing purposes. Based on described examples, the presence of graphene in the recent times could serve as a future material for various fields especially as sensor, bio-sensor, and heat-sink.

General Synthesis Methods to Produce Graphene

Several methods for producing graphene have been reported. In general, graphene production can be done by two types of methods, which are top-down and bottom-up. More information about all methods are discussed as follow:

Properties	Details
Optical transparency	97.7%
Electron mobility	$200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Thermal conductivity	$5000 \text{ W m}^{-1} \text{ K}^{-1}$
Specific surface area	$2630 \text{ m}^2 \text{ g}^{-1}$
Breaking Strength	42 N m^{-1}
Young's modulus	0.25–1.0 TPa

Top-Down Method

The principle of the top-down method is to exfoliate graphite that is used as starting material. Mechanical exfoliation, chemical/ electrochemical exfoliation and chemical/electrochemical fabrications are classified in the top-down methods. The top-down technique is very easy to apply for large-scale graphene production. However, conventional top-down methods, such as Hummer graphite oxidation, requires a controlled reaction and always provide abundant structural defects that cause low electrical conductivity. Below are some of the top-down techniques that are usually used by researchers to synthesize graphene:

Exfoliation method.—Exfoliation is a simple and common technique that can be used for graphene synthesis from graphite or other carbon sources. There are several types of exfoliation such as mechanical

exfoliation, chemical exfoliation and/or electrochemical exfoliation. Mechanical exfoliation or more commonly known as the Scotch tape method, is a traditional method that has been applied for decades. This method is made famous by K. Novoselov and Andre Geim since they both won the Nobel Prize in Physics due to the results obtained by implementing this method. Mechanical exfoliation is the first method to obtain one layer of graphene. Examples of mechanical peels are micromechanical peels as shown. Dasari et al. in 2017 showed a representation of micromechanical stripping of graphene sheets using Scotch tape method. Graphite was placed on the substrate and repeatedly peeled using adhesive tape until a monolayer sheet is obtained. Although this process is simple but the main challenges with this method is that the product that obtained is small and contains some structural defects.

Kim et al. in 2016 reported a controllable and scalable aqueous arc discharge process that produces high quality bi- and trilayers of graphene. However, they still found by products when using this method, hence a separation method needs to be developed. Development of the arc discharge method to produce graphene was also studied by Cheng et al. in 2018, where they combined a vacuum arc discharge by using CVD method. Graphene was synthesized in a copper foil by using a furnace at a high temperature embedded in a vacuum arc discharge. This merging method can produce a single layer graphene at a high temperature.

Wu et al. explained the mechanism of the arc discharge method to obtain graphene sheets in different atmospheres for large-scale graphene production. Graphene sheets were synthesized using activated carbon as an anode and cathode by arc discharge method under a mixed gases conditions where in this case, nitrogen (N_2) and hydrogen (H_2) gases were used. The alternating current in the process causes both electrodes to react and evaporate simultaneously, thus eliminating the formation of deposits at the cathode. This process increases the temperature, which is needed to increase the diffusion rate of carbon atoms and clusters. The increasing of diffusion rate allows all carbon species and gas molecules to collide between each other. Graphene product can easily be obtained only if hydrogen gas is used since hydrogen gas has a very high cooling rate. To obtain such conditions, Wu et al. combined the hydrogen gas with inert gas such as N_2 , which has low thermal conductivity, in order to generate a graphene product with satisfactory quality.

According to the explanation above, the advantages and disadvantages of all methods mentioned above (top-down and bottom-up) are summarized.

Conclusion:

The advancements in the production strategies have been described, whilst the literatures have been analyzed extensively in evaluating the reinforcement efficiency of each graphene type in a range of matrices by involving different synthesis routes. It should be stated that there are still several challenges to overcome before industries can proceed with the mass production of graphene. An example of the challenges faced is the scale up of the production of high-quality graphene, as this is still a major issue which is always going to be reflected on the ultimate properties of the materials. Based on the findings presented earlier, the best quality graphene to be used in research and industry is the material with the largest aspect ratio with a thickness of few layers. In order for a graphene to be successfully produced graphene, all the parameters should be considered and controlled according to the method or route selected. The product of graphene still needs some characterization, which is compatible to industry scale. The important characterization technique to obtain graphene is Raman spectroscopy, XRD, XPS and other additional characterization for special application such as electrical or surface area parameters.

References:

1. A. K. Geim and K. S. Novoselov, Nat. Mater., 6, 183 (2007).
2. W. Ren and H.-M. Cheng, Nat. Nanotechnol., 9, 726 (2014).
3. A. Arshad, M. Jabbal, Y. Yan, and D. Reay, J. Mol. Liq., 279, 444 (2019), <http://sciencedirect.com/science/article/pii/S0167732218350207>.
4. J.-H. Choi, C. Lee, S. Cho, G. D. Moon, B. Kim, H. Chang, and H. D. Jang, Carbon, 132, 16 (2018).
5. D. A. C. Brownson and C. E. Banks, Analyst, 135, 2768 (2010).
6. K. E. Whitener and P. E. Sheehan, Diam. Relat. Mater., 46, 25 (2014).
7. E. B. Bahadır and M. K. Sezgentürk, TrAC, Trends Anal. Chem., 76, 1 (2016).
8. S. Sarma, S. C. Ray, and A. M. Strydom, Diam. Relat. Mater., 79, 1 (2017).
9. D. G. Papageorgiou, I. A. Kinloch, and R. J. Young, Prog. Mater. Sci., 90, 75 (2017).
10. Y. Zhong, Z. Zhen, and H. Zhu, FlatChem, 4, 20 (2017).
11. S. Schöche, N. Hong, M. Khorasaninejad, A. Ambrosio, E. Orabona, P. Maddalena, and F. Capasso, Appl. Surf. Sci., 421, 778 (2017).