International Journal of Computer Applications (0975 – 8887)
Volume 186 – No.19, May 2024

Synthesis and Application of Graphene

Amandeep Kaur Rozi
Guru Nanak Dev University
Regional Campus, Jalandhar, Punjab, India

Harminder Singh
Guru Nanak Dev University
Amritsar, Punjab, India

Deepkamal Randhawa
Guru Nanak Dev University
Regional Campus, Jalandhar, Punjab, India

Anu Sheetal
Guru Nanak Dev University
Regional Campus, Gurdaspur,
Punjab, India

ABSTRACT
The discovery of graphene and graphene based polymer nanocomposites is an important addition in the area of nano-science, playing a vital role in modern technology and science. To overcome the shortcomings of carbon based nano-fillers such as a carbon nanotubes graphene is an important discovery. Carbon nanotubes have proven very good conductive fillers but the main drawback of carbon nanotubes is its high production cost. Graphene is modified with oxygen and nitrogen with functional groups. Thus, graphene is nothing else than a single layer of graphite. The main goal of the researchers is to develop graphene, very thin carbon sheet with hexagonal network and study the highly controlled growth method and synthesis of graphene by hummer method. This study describes the literature review of graphene, graphene oxide and synthesis by hummer method is comparatively better than other variant of graphene oxide.

Keywords
Graphene, Hummer Method, Flakes, Graphene oxide

1. INTRODUCTION
Graphene, a wondrous material, was accidentally observed in 1859, by Prof. B.C. Brodie at University of Oxford. He was attempting to find the molecular weight of graphite. During his attempt, he found that graphite has different properties than other allotropes of carbon i.e. diamond and charcoal. When he analysed graphite by doing its oxidation, he observed it to be a thin film of approximately one atom thick. But his method for preparing graphene was not satisfactorily useful. Its theoretical studies continued till 1948. In 1907, Acheson found that corrosion of a metal could be prevented by coating metal with deflocculated graphite. Main discovery by Acheson was silicon carbide (SiC) which he called carborundum. In 1958, hummer method was invented by William S. hummers and Richward. In 1962, Bohem founds that by using hydrazine it is possible to reduce graphite oxide. He was able to measure the thicknesses of these graphene layers using a combination of surface measurements. Then in 1970′s, it was first experimentally prepared by its epitaxial growth on electrically insulating surfaces e.g. SiO_2 on a small scale. In 1998 confirmed these results, but also indicated that the graphite layers were essentially decoupled from the substrate, causing them to conclude, that “layer by layer growth opens up the possibility of an isolated single graphene layer “floating” above the substrate” [1-8].

In 1999 Ruoff and coworkers recognized that graphene might be important for various reasons, and developed a mechanical method to exfoliate graphite. Their goal was to produce graphene sheets by this method. For its large scale production, Andre Geim and Kostya Novoselov discovered a micromechanical exfoliation method, also called Scotch Tape method and got Nobel prize in Physics in 2010 [9-12].

2. LITERATURE REVIEW
Geim A K et. al. [5] mainly introduces that how graphene is better than that of the silicon based devices and gives the complete detail of graphene structure its various thermal electrical and thermal properties. It gives the detail about graphene that it is a flat monolayer of carbon atoms tightly packed into a two dimensional honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. Basically it is a substance composed of pure carbon with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. It is very light, with a 1-square-meter sheet weight. From the conclusion it is obtained that due to its excellent properties it is used as filler in various polymers to increase the conductivity of the composites and to make it flexible and less costly.

Acheson [1] describes the history of graphene, and gives the information about the exfoliation methods which is also called deflocculation to produce colloidal suspensions of small graphitic flakes that he called “dags”. These colloidal graphite suspensions have been extensively used in the electronics industry as a conducting paint to produce conducting surfaces in vacuum tubes and this paper also gives the information that coating metals with deflocculated graphite prevented corrosion and also the detail of silicon carbide (SiC) that he called carborundum is given which is first used as an abrasive.

Novoselov et al. [3] gives the detail about the history of graphene and also describes the electric field effect in atomically thin films and it describes that mono-crystalline graphite films are stable under ambient conditions and of high quality. The graphene film is found to be a two dimensional with a small overlap between valence and conduction band and strong electric field effect such that electrons and holes concentration at room temperature mobility of 10000 square centimeters per volt second can be generated by applying gate voltage.

Verma et al. [6] demonstrate the fabrication and various properties of graphene-polymer nano-composites. It also describes that how graphene fillers are playing outstanding role in the nano composites by varying their different properties. Contemporary review clearly confirmed that graphene-polymer nano-composites are superb materials with applications ranging from transportation, biomedical systems, sensors, solar cells and electromagnetic interference. This review explains the different manufacturing method of graphene based composites and also assembles their electrical, mechanical and thermal properties.

Schedin, et al. [7] gives the information about various types of gas and bio sensors using graphene. This paper describes that operational principle of graphene based gas or bio electronic sensors is based on the change of graphene's electrical conductivity (σ) due to adsorption of molecules on graphene surface. The change in conductivity can be attributed to the change in carrier concentration of graphene due to the absorbed gas molecules acting as donors or acceptor and from this paper. It has been found that some interesting properties of graphene like higher conductivity aid to increase its sensitivity up to single atom or molecular level detection.

Won et al. [8] presents a description about various synthesis method of graphene like exfoliation and cleavage, thermal chemical vapour deposition techniques, processing routes, graphene properties and its various applications like sensors, transistors, field emission devices and in energy devices. This review paper describes the chemical vapour deposition method is the best method to generate graphene on centimeter scale substrate and successful transfer to other substrates like Si and glass.

William et al. [12] describes the synthesis method of graphene by hummer method and gives the complete detail of hummer graphite oxidation and reduction of graphite oxide process. This paper describes the how the fuel cells is being deferred due to the insufficiency and high expense of precious metal catalysts, which presently provide the most efficient oxygen reduction reaction (ORR).

William et al. [13] gives the reduction of graphene oxide by different reducing agents like H_2SO_4, H_2O and N_2H_4 and describes in detail that how hydrazine is better reducing agent if compared with other reducing agents. Graphene oxide (GO) films with two-dimensional structure were successfully synthesized via the Hummer method which is the best method because of its lower cost, high conductivity and simple chemicals are used for synthesis method. It is reveal that this method is an optimistic way to synthesize GO films on a large scale. Also explains that how conductivity is affected at different concentration of reducing agent. By using hydrazine as reducing agent diffusion occurs in large amount so we can use graphene in number of applications.

Kim et al. [19] gives the description that due to the extraordinary thermal, chemical and mechanical stability of graphene, combined with its high transparency and atomic layer thickness, makes it an ideal candidate for transparent conducting electrode applications. Kim et al. reported 80% transmittance when graphene is grown over a 300nm thick nickel layer, corresponding to 6 to 10 graphene layers. The transmittance was increased up to 91% by further reducing the growth time and nickel thickness, resulting in formation of thinner graphene film and it also gives detailed description of Raman spectroscopy technique which is used to examine the behavior of graphene.

Xuan et al. [20] describes that main aim to develop the graphene based dye sensitized solar cells to increase the conversion efficiency of the solar cell and graphene based dye sanitized solar cells which are better than that of the silicon based solar panels. Because in the graphene there is a zero band gap between the valance band and the conduction band so large number of electrons are excited from lower energy state to higher energy state therefore large conductivity and large conversion efficiency is obtained. And now we use mobilium disulphide on graphene to increase the conversion efficiency up to 60%.

Balamurugan et al. [14] proposed a physical significance of an inhomogeneous effect of particle size on electrons originating from various electronic levels of copper nitride nano-particles. X-ray photoelectrons and optical spectroscopy studies reveal that a direct modification of the valence band due to size effects explained by more appropriate surface bond contraction model results in a strong increase in the binding energy of valence band electrons as compared to core level electron.

Patsalas et al. [17] reported the study of spectroscopic ellipsometry which was employed to get insights on the optical, electronic and transport properties of nanocrystalline titanium nitride. The study of intra-band absorption has provided the conduction electron density with respect to ion energy and Td which promotes the densification of TiNx films due to different mechanisms. The optical and electrical properties of the graphene have been studied and the Arrhenius plots of electrical conductivity both for the as prepared anatase TiO_2 and the one subsequently reduced in hydrogen atmosphere at 673K show a distinct difference in the activation energy. Quantum confinement that manifests itself in widening of HOMO LUMO gap or the band-gap increase with decreasing crystalline size and its implications on the electronic structure and photo-physics of the crystallites has generated considerable interest.

Daniel et al. [18] gives the review of graphene oxide and chemical route of graphene oxide. From the study of this paper it is concluded that graphene is act as substrate with variety of chemical transformation when we use different type of reducing agent and easily modify its properties according to our requirements and can use in different applications. Hydrazine is used as reducing agent describes that graphene oxide has outstanding properties can easily use as miracle material by replacing silicon and polymer type materials in different applications.

3. HUMMER METHOD

Hummer method which is used for synthesis of Graphene generates the rGO which decrease the conductivity but we sacrifice conductivity because cost is less. Due to large thermal conductivity, graphene devices is more to suitable ultra large scale (ULSI) application and less pron to self-heating effect(SHE).

The major problem (during sonication) the bonds of graphene layer break and resultant graphene layer is break into crystals. So, hummer method is convenient to generate 3-4 layer of graphene. Before hummer method exfoliation method generates a very pure and perfect single field graphene with approximately ideal thermal, electrical and mechanical properties; it has one of the biggest disadvantages. That is in the exfoliation method resultant graphene which is generated the flakes of graphene are randomly scattered on a substrate. And in CVD method cost is very high and not economical. So, hummer method is the best and well proven method to generate the graphene oxide at large scale by using different reducing agents. Because when we use hydrazine as reducing agent then conductivity is high we can easily use it in different applications.

In the future research reduction of GO should basically target on two topics: (1) a full wide considerate of the reduction mechanism and (2) how to control the oxidation and reduction of graphite and graphite oxide (GO). This is because that a tractable functionalization that can change the properties of graphene which is fulfil specific requirements in applications is equally important to obtain a non-defective graphene. For example, to change the gapless semi-metallic graphene into a semiconductor with proper band gap. The previous research on GO and rGO has inspired a possible way to achieve such change that GO and rGO show obvious semiconductor-like properties. Research on the oxidation and reduction combined with a deep understanding of graphene structure may give us the key to realize good control of the attaching and elimination of functional groups to some specific locations on the carbon plane. Further research on the controllable oxidation and reduction of graphene may facilitate the applications of graphene as semiconductors used in transistor and photo-electronic devices. Future efforts for graphene and n-layer graphene such as achieving desired surface functionalization, and, e.g., the 'cutting' or preparation into desired shapes, could generate novel structures having many applications.

Table 1. Graphene oxide synthesis methods [1][12][15-18]

Method	Pros	Cons	Applicability
Exfoliation method	• Safe and simple process. • Few layer graphene can be easily obtained. • The chances of impurity on the graphene so obtained are less. • Sample preparation is simplified.	• Very scalable to large scale production. • Flakes are not single layered, multilayered. • Number of layers is hard to control. • Yield obtained may not meet the requirements.	This method is used for small scale production because large number of layer is generated which is not effective for various applications.
Epitaxial growth of graphene on SiC	• High quality graphene. • The layers of graphene can be controlled conveniently. • Higher temperature ensures reproducible, clean and ordered graphene. • Patterning of graphene is easier due to the use of insulating SiC.	• High temperature. • Difficulty in growing uniform multilayered graphene in UHV conditions. • Lattice constant mismatch and difference in coefficient of thermal expansion of SiC-C can lead to various defects.	SiC is a large band gap semiconductor already used in electronic applications but with graphene it enhances its properties.
Electrochemical exfoliation	• High yield. • Scalable to large scale production. • Few layered graphene easily obtained. • The graphene obtained can be functionalized depending upon electrolyte and can be more compatible with certain organic compounds.	• The impurities may be present in the form of unwashed salts in between the graphite layers. • This may affect the conductivity of the graphite. • The thickness control is not as promising as in hummer and CVD method.	• Optoelectronics • Corrosion protection.
Hummer method	• High yield. • Scalable to industrial level. • Hummer method which is used for synthesis of Graphene generates the rGO which decrease the conductivity but we sacrifice little amount of conductivity because cost is less. • Due to high electrical and thermal conductivity, graphene devices is more to suitable ultra large scale application. • Economical. • Simple chemicals are used and not costly equipments are needed like in CVD cost of equipments in lakhs.	• The major problem (during sonication) the bonds of graphene layer break and resultant graphene layer is break into crystals. • Band gap opening is the major problem in a single layer and few layer graphene because zero band gaps with Dirac fermions prevents the controlling conductivity of semiconductor material. • Difficulty in production of monolayer graphene. • Multilayered graphene is formed.	• Hummer method is point of interest in photocataysts. • After the formation that graphene oxide is reactive to many of the wavelengths of light found with sunlight. • Used in solar cells and various type gas and bio sensors.
Chemical vapour deposition method	• High quality, impervious and harder graphene is obtained. • Produce large of graphene is easy. High growth rate possible. • Good reproducibility.	• High temperature leads to wrinkled graphene due to difference of thermal expansion. • Complex and high cost process. • Production of corrosive and toxic gases. • Difficulty in controlling the thickness in some cases. • Difficulty in transferring the film on other surface. • Difficulty in achieving the uniform deposition of the carbon.	Graphene that is formed by CVD method is used in transparent electrodes, field effect transistors and lithium ion batteries.

4. CONCLUSION

From the present study it has been found that by dispersing a small amount of graphene in polymers, many properties of the composites such as tensile strength and elastic modulus, electrical and thermal conductivity can be significantly improved. All of these enhancements have a great potential that may be preferred over conventional nano-fillers for applications in structural or functional materials such as lightweight gasoline tanks, plastic containers, more fuel efficient aircraft and car parts, stronger wind turbines, medical implants, LED, coating for solar cells displays and sports equipment. Besides graphene, Hummer's method has recently become a point of interest in photo catalysts. After discovering that graphite oxide is reactive to many of the wavelengths of light found within sunlight, teams have been looking into methods of using it to bolster the speed of reaction in decomposition of water and organic matter. The most common method for producing the graphite oxide in these experiments has been Hummers' Method. Before the method was developed, the production of graphite oxide was slow and hazardous to make because of that is its cost is very less. Hummer method which is used for synthesis of Graphene generates the rGO which decrease the conductivity but we sacrifice conductivity because cost is less. Graphene is a material which has the capability to eliminate the current semiconductors such as silicon.

5. REFERENCES

[1] Acheson, E. Deflocculated graphite. Journal of the Franklin Institute (1970), 164, 0375-0382.

[2] Boehm, H., et al. Nomenclature and terminology of graphite intercalation compounds. Carbon (1986), 24, 241-245.

[3] Novoselov, K. S., Geim, A. K., et al. Electric field effect in atomically thin carbon films. Science Journal (2004), 306, 666.

[4] Suk, J. W., et al. Mechanical properties of monolayer graphene oxide. American Chemical Society of Nano (2010), 4, 6557.

[5] Geim, A. K. and Novoselov, K. S. The rise of graphene. Nature Materials (2007), 6, 183.

[6] Verma, D., et al. Mechanical-Thermal-Electrical and Morphological Properties of Graphene Reinforced Polymer Composites. Transactions of the Indian Institute of Metals (2014), 67, 813.

[7] Schedin, F., et al. Detection of individual gas molecules adsorbed on graphene. Nature Materials (2007), 6, 652.

[8] Wonbong, C., et al. Synthesis of graphene and its applications: A Review. Solid Sate and Material Science (2010), 35, 63.

[9] Kong, H. X., et al. Hybrids of carbon nanotubes and graphene/graphene oxide. Solid State Material Science (2013), 17, 31–37.

[10] Eigler, S. et al. Investigation of the thermal stability of the carbon framework of graphene oxide. Chemistry a European Journal (2014), 20, 984–989.

[11] Wang, X., et al. Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells. Nano Letters (2013), 17, 1, 31–37.

[12] William, S., et al. Preparation of Graphitic Oxide. Journal of the American Chemical Society (1958), 80, 1339.

[13] William, I. H. et al. Production of reduced graphene oxide via hydrothermal reduction in an aqueous sulphuric acid suspension and its electrochemical behavior. Journal of Solid State Electrochemistry (2015), 19, 361–380.

[14] Balamurugana, B., et al. Department of chemical Engineering, Graduate school of engineering, Kyoto university (2006), Kyoto 615-8510.

[15] Rao, K. S., et al. Role of peroxide ions in formation of graphene nanosheets by electrochemical exfoliation of graphite. Scientific Reports (2014), 4, article number: 4237.

[16] Hiroki, H., Hiroyuki, K., et al. Graphene growth on silicon carbide. NTT technical review.

[17] Patsalasa, P., et al., Department of physics, solid state physics section, Aristotle University of Thessaloniki, GR-54006 Thessaloniki, Greece-2001.

[18] Daniel, R., et al. The chemistry of graphene oxide. The Royal society of chemistry (2009), 39, 228-240.

[19] Kim, K. S., et al. Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature (2009), 457, 706-710.

[20] Xuan, W., et al. Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells. Nano Letters (2008), 8, 323–327.